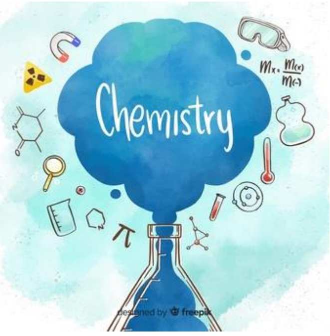
STUDENT SUPPORT MATERIAL

(CAPSULES AND CASE-STUDY BASED QUESTIONS)



CLASS-XII

CHEMISTRY

SESSION-2020-21

KENDRIYA VIDYALAYA SANGATHAN
REGIONAL OFFICE
LUCKNOW

STUDENT SUPPORT MATERIAL

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CHEMISTRY
Class-XII
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SYLLABUS
CHEMISTRY
CLASS-XII

Unit I: Solid State 8 Periods

Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects.

Unit II: Solutions 8 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 vapor pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties.

Unit III: Electrochemistry 7 Periods

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

Unit IV: Chemical Kinetics 5 Periods

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

Unit V: Surface Chemistry 5 Periods

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

Unit VII:p-Block Elements 7 Periods

Group -15 Elements: General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; Nitrogen preparation properties and uses; compounds of Nitrogen: preparation and properties of Ammonia and Nitric Acid.

Group 16 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties, dioxygen: preparation, properties and uses, classification of Oxides, Ozone, Sulphur -allotropic forms; compounds of Sulphur: preparation properties and uses of Sulphur-dioxide, Sulphuric Acid: properties and uses; Oxoacids of Sulphur (Structures only).

Group 17 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens, Preparation, properties and uses of Chlorine and Hydrochloric acid, interhalogen compounds, Oxoacids of halogens (structures only).Group 18 Elements: General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.

Unit VIII: d and f Block Elements 7 Periods
General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, color, catalytic property, magnetic properties, interstitial compounds, alloy formation.
Lanthanoids - Electronic configuration, oxidation states and lanthanoid contraction and its consequences.

Unit IX: Coordination Compounds 8 Periods
Coordination compounds - Introduction, ligands, coordination number, color, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT.
Unit X: Haloalkanes and Haloarenes. 9 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).

Unit XI: Alcohols, Phenols and Ethers 9 Periods
Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration.
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 10 Periods
Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical
and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.
Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

Unit XIII: Amines 7 Periods
Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Unit XIV: Biomolecules 8 Periods
Carbohydrates - Classification (aldoses and ketoses), monosaccharides (glucose and fructose), D-L
configuration
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.
Nucleic Acids: DNA and RNA.

CLASS XII - CHEMISTRY

DETAILS OF REVISED SYLLABUS 2020-21

CHEMISTRY SYLLABUS IN NCERT TEXT BOOK	DELETED PORTIONS	CHEMISTRY REVISED / REDUCED SYLLABUS 2020-21
UNIT – 1 SOLID STATE Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three-dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties. Band theory of metals, conductors, semiconductors and insulators and n and p type semiconductors.	1. Electrical and magnetic properties. 2. Band theory of metals, conductors, semiconductors and insulators and 3. n and p type semiconductors.	**1. Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea).** **2. Unit cell in two dimensional and three-dimensional lattices.** **3. Calculation of density of unit cell.** **4. Packing in solids, packing efficiency.** **5. Voids, number of atoms per unit cell in a cubic unit cell, point defect s.**
UNIT – 2 SOLUTIONS Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.	1. Abnormal molecular mass 2. 2.van't Hoff factor	**1. Types of solutions** **2. Expression of concentration of solutions of solids in liquids** **3. Solubility of gases in liquids, solid solutions, Raoult's law.** **4. Colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of masses using colligative properties.**
UNIT–3 ELECTROCHEMISTRY Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.	1. Lead accumulator, fuel cells. 2. Corrosion. 3. law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells	**1. Redox reactions, EMF of a cell, standard electrode potential.** **2. Nernst equation and its application to chemical cells.** **3. Relation between Gibbs energy change and EMF of a cell.** **4. Conductance in electrolytic solutions.** **5. Specific and molar conductivity, variations of conductivity with concentration.** **6. Kohlrausch's Law.** **7. electrolysis.**

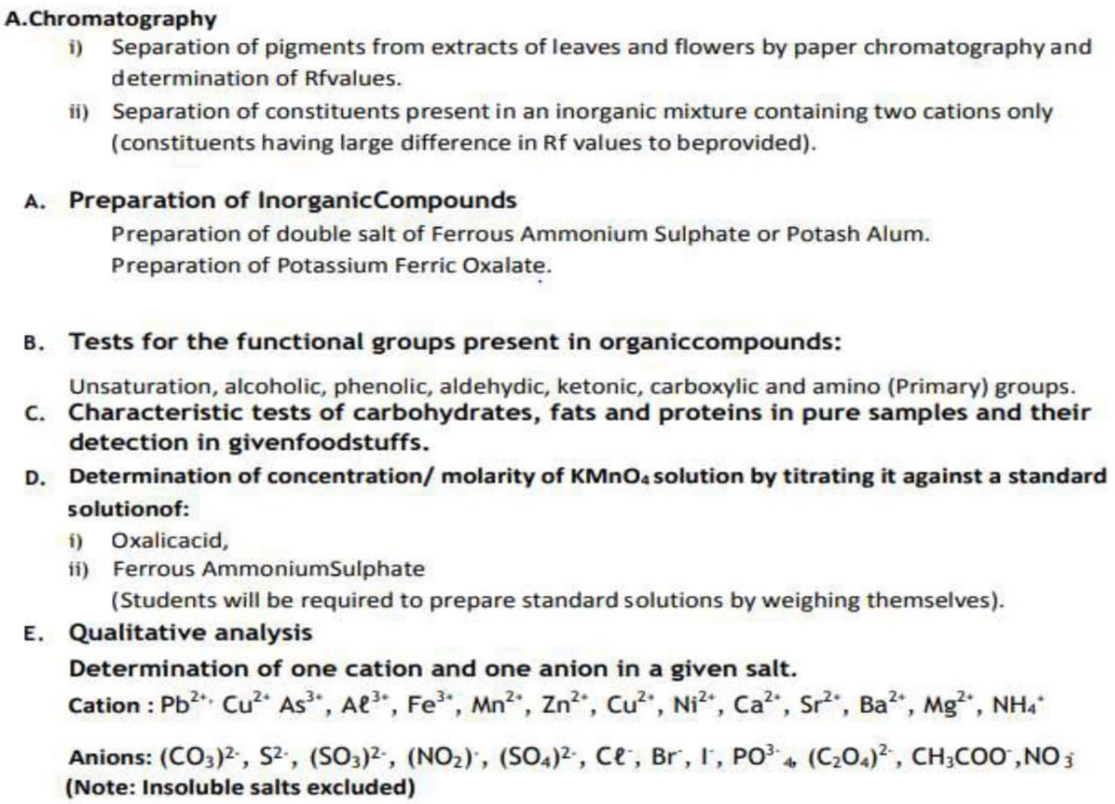
UNIT–4 CHEMICAL KINETICS Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.	1. Concept of collision theory (elementary idea, no mathematical treatment). 2. activation energy, Arrhenius equation.	1. **Rate of a reaction (Average and instantaneous)** 2. **Factors affecting rate of reaction: concentration, temperature, catalyst.** 3. **Order and molecularity of a reaction.** 4. **Rate law and specific rate constant.** 5. **Integrated rate equations and half-life (only for zero and first order reactions)**
Unit 5 - Surface Chemistry Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, catalysis: homogenous and heterogenous, activity and selectivity of solid catalysts; enzyme catalysis, colloidal state: distinction between true solutions, colloids and suspension; lyophilic, lyophobic, multi-molecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion - types of emulsions.	(1) emulsion - types of emulsions. (2) catalysis: homogenous and heterogeneous. (3) activity and selectivity of solid catalysts; (4) enzyme catalysis,	**1. Adsorption - physisorption and chemisorption.** **2. Factors affecting adsorption of gases on solids.** **3. Colloidal state: distinction between true solutions, colloids and suspension.** **4. Lyophilic, lyophobic, multi-molecular and macromolecular colloids.** 5. **Properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation.**
UNIT 6 : GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS	**ENTIRE UNIT – DELETED**	
Unit 7 :p-Block Elements Group -15 Elements: General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; Nitrogen preparation properties and uses; compounds of Nitrogen: preparation and properties of Ammonia and Nitric Acid, Oxides of Nitrogen (Structure only); Phosphorus - allotropic forms, compounds of Phosphorus: Preparation and properties of Phosphine, Halides and Oxoacids (elementary idea only). Group 16 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties, dioxygen: preparation, properties and uses, classification of Oxides, Ozone, Sulphur -allotropic forms; compounds of Sulphur:	1. Preparation and properties of Phosphine. 2. Sulphuric Acid: industrial process of manufacture, 3. Oxides of Nitrogen (Structure only); 4. Phosphorus - allotropic forms, compounds of Phosphorus: 5. Preparation and properties of Halides and Oxo acids (elementary idea only)	**GROUP -15 ELEMENTS:** **1. General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties;** **2. Nitrogen preparation properties and uses; compounds of Nitrogen:** **3. Preparation and properties of Ammonia and Nitric Acid.** **GROUP 16 ELEMENTS:** **4. General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties.** **5. Dioxygen: preparation, properties and uses.** **6. Classification of Oxides, Ozone,** **7. Sulphur -allotropic forms;** **Compounds of Sulphur:** **8. Preparation properties and uses of Sulphur-dioxide.**

preparation properties and uses of Sulphur-dioxide, Sulphuric Acid: industrial process of manufacture, properties and uses; Oxoacids of Sulphur (Structures only). Group 17 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens, Preparation, properties and uses of Chlorine and Hydrochloric acid, interhalogen compounds, Oxoacids of halogens (structures only). Group 18 Elements: General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.		**9. Sulphuric Acid: properties and uses; Oxoacids of Sulphur (Structures only).** **GROUP 17 ELEMENTS:** **10. General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties;** **Compounds of halogens.** **11. Preparation, properties and uses of Chlorine and Hydrochloric acid.** **12. interhalogen compounds, Oxoacids of halogens (structures only).** **GROUP 18 ELEMENTS:** **13. General introduction, electronic configuration, occurrence, trends in physical and chemical properties, uses.**
Unit 8: d and f Block Elements General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of K2Cr2O7 and KMnO4. Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences. Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids	1. Chemical reactivity of lanthanoids, Actinoids 2. -Electronic configuration, oxidation states and comparison with lanthanoids. 3. Preparation and properties of KMnO4 and $K_2Cr_2O_7$	**1. General introduction, electronic configuration, occurrence and characteristics of transition metals.** **2. 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.** **3. Lanthanoids - Electronic configuration, oxidation states and lanthanoid contraction and its consequences**
Unit 9: Coordination Compounds Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).	1. Structure and stereoisomerism, 2. importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).	**1. Coordination compounds - Introduction, ligands, coordination number, colour.** **2. Magnetic properties and shapes.** **3. IUPAC nomenclature of mononuclear coordination compounds.** 4. **Bonding, Werner's theory, VBT, and CFT.**

Unit 10: Haloalkanes and Haloarenes Haloalkanes: Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions. Haloarenes: Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.	1. Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.	**Haloalkanes:** **1. Nomenclature, nature of C–X bond.** **2. Physical and chemical properties.** **3. Optical rotation mechanism of substitution reactions.** **Haloarenes:** **4. Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only).**
Unit 11: Alcohols, Phenols and Ethers Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol. Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols. Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses	1. uses with special reference to methanol and ethanol.	**Alcohols:** **1. Nomenclature, methods of preparation.** **2. Physical and chemical properties (of primary alcohols only).** **3. Identification of primary, secondary and tertiary alcohols.** **4. Mechanism of dehydration.** **Phenols:** **5. Nomenclature, methods of preparation.** **6. Physical and chemical properties.** **7. Acidic nature of phenol.** **8. Electrophillic substitution reactions.** **9. uses of phenols.** **Ethers:** **10. Nomenclature, methods of preparation, physical and chemical properties, uses**
Unit 12 : Aldehydes, Ketones and Carboxylic Acids Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses. Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.		**Aldehydes and Ketones**: **1. Nomenclature, nature of carbonyl group.** **2. Methods of preparation.** **3. Physical and chemical properties.** **4. Mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.** **Carboxylic Acids:** **5. Nomenclature, acidic nature,** **6. Methods of preparation,** 7. **Physical and chemical properties; uses**.
Unit 13 : Amines 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	1. Diazonium salts: Preparation, chemical reactions and importance in synthetic	**Amines:** **1. Nomenclature.** **2. Classification.** **3. Structure, methods of preparation.** **4. Physical and chemical properties, uses.** 5. **Identification of primary, secondary and tertiary amines.**

importance in synthetic organic chemistry	organic chemistry.	
Unit 14 - : Biomolecules Carbohydrates - Classification (aldoses and ketoses), monosaccahrides (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	1. Oligosaccharides (sucrose, lactose, maltose). 2. polysaccharides (starch, cellulose, glycogen), 3. importance of carbohydrates. 4. Vitamins– classification and functions. Enzymes. 5. Hormones - Elementary idea excluding structure.	**Carbohydrates -** **1. Classification (aldoses and ketoses), monosaccahrides (glucose and fructose).** **PROTEINS** **2. D-L configuration Proteins -Elementary idea of - amino acids, peptide bond, polypeptides.** **3. Proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only).** **4. Denaturation of proteins.** 5. **Nucleic Acids: DNA and RNA.**
Unit 15- Polymers	**ENTIRE UNIT – DELETED**	
Unit 16 - Chemistry in Everyday life	**ENTIRE UNIT – DELETED**	

CLASS XII – CHEMISTRY PRACTICALS



A.Chromatography

i) Separation of pigments from extracts of leaves and flowers by paper chromatography and determination of Rfvalues.

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

A. Preparation of InorganicCompounds

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

B. Tests for the functional groups present in organiccompounds:

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

C. Characteristic tests of carbohydrates, fats and proteins in pure samples and their detection in givenfoodstuffs.

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

i) Oxalicacid,

ii) Ferrous AmmoniumSulphate

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

E. Qualitative analysis

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

Cation : Pb^{2+} Cu^{2+} As^{3+}, $A\ell^{3+}$, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cu^{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^{3-}_4, $(C_2O_4)^{2-}$, CH_3COO^-, NO_3^-

(Note: Insoluble salts excluded)

Investigatory Project -

CHEMISTRY THEORY – (043) - MAX MARKS – 70

CLASS XII (2020-21)
(THEORY)

Total Periods (Theory 98 + Practical 36)

Time :3Hours **70Marks**

Unit No.	Title	No. of Periods	Marks
Unit I	Solid State	8	23
Unit II	Solutions	8	
Unit III	Electrochemistry	7	
Unit IV	Chemical Kinetics	5	
Unit V	Surface Chemistry	5	
Unit VII	p -Block Elements	7	19
Unit VIII	d -and f -Block Elements	7	
Unit IX	Coordination Compounds	8	
Unit X	Haloalkanes and Haloarenes	9	28
Unit XI	Alcohols, Phenols and Ethers	9	
Unit XII	Aldehydes, Ketones and Carboxylic Acids	10	
Unit XIII	Amines	7	
Unit XIV	Biomolecules	8	
	Total	**98**	**70**

CHEMISTRY PRACTICALS – (043) - MAX MARKS – 30

PRACTICALS

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**

SOLID STATE
UNIT -1

TERMS	EXPLANATIONS
Amorphous and Crystalline Solids	Amorphous- short range order, Irregular shape eg-glass Crystalline Solids- long range order, regular shape eg : NaCl
Molecular solids	Ar, CCl_4, H_2O (ice)
Covalent or Network solid	SiO_2 diamond
No of lattice points per unit cell	Simple cubic -4, BCC- 9, FCC - 14 , End-Centred- 10
No of atoms per unit cell (z)	Simple cubic -1, BCC- 2, FCC - 4 , End-Centred- 2
Coordination Number	FCC- 6:6 BCC- 8:8
Calculation of number of voids	Let the number of close packed spheres be N, then: The number of octahedral voids generated = N The number of tetrahedral voids generated = 2N
Relation between r and a	Simple Cubic→ $a = 2r$, BCC→ $4r = a\sqrt{3}$ FCC→ $4r = a\sqrt{2}$
Packing Efficiency	Simple Cubic→52.4% , BCC→ 68% , FCC→ 74%
Calculations Involving Unit Cell Dimensions	$\boxed{d = \frac{zM}{a^3 N_A}}$ M=molar mass (g/mol) a = edge length in cm , $N_A = 6.023\times 10^{23}$
Frenkel Defect:	Ccation is dislocated to an interstitial site. It does not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.
Schottky Defect	A vacancy defect. The number of missing cations and anions are equal. Density decreases. For example, NaCl, KCl, CsCl and AgBr.
Metal excess defect due to anionic vacancies (F-centres)	When NaCl heated in an atmosphere of Na vapour, the Na atoms deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. The released electrons diffuse into the crystal and occupy anionic sites The anionic sites occupied by unpaired electrons are called F^-centres They impart yellow colour to the crystals of NaCl. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

Unit 1 The Solid State

Very Short Answer Type Questions (1mark)

1. How may the conductivity of an intrinsic semiconductor be increased ?
Ans. By increasing its temperature conductivity can be increased.

2. Which stoichiometric defect increases the density of a solid ?
Ans. Schottky defect in a crystal lowers its density.

3. What are n-type semiconductors ?
Ans. Doping of silicon or germanium with electron rich impurities like P, As, Sb results in formation of n-type semiconductors

4. What type of semiconductor is obtained when Si is doped with As
Ans. n-type semiconductors
5. Which point defect decreases the density of a solid
Ans. Schottky defect
6. What is the No. of atoms in a unit cell of fcc crystal ?
Ans. 4
7. Define forbidden zone of an insulator ?
Ans. The energy gap between conduction band and valence band is called forbidden zone.

8. What is the No. of atoms in a unit cell of simple cubic crystal?
Ans. 1
9. State a feature to distinguish a metallic solid from an ionic solid .
Ans. Metallic solids are conductors in solid as well as in molten state but ionic solids are electric conductor only in molten state

10. "Crystalline solids are anisotropic in nature ." What does this statement mean ?
Ans.These solids are **anisotropic**, i.e. their physical properties such as electrical conductivity, refractive index, thermal expansion etc. have different values in different directions.

11. Which point in crystal does not change the density of a solid ?
Ans. Frankel defect does not change the density of the crystal.

12. What type of interaction hold the molecule together in a polar molecule ?
Ans. Dipole dipole attraction force

13. Wrire a distinguishing feature of metallic solid .
Ans. Metallic solids are conductors in solid as well as in molten state, hard,malleable.
14. What is meant by intrinsic semiconductor ?

Short Answer Type Questions (2 Marks)

1. Silver crystallises in fcc structure . Each side of the unit cell has a length of 409 pm .What is the radius of Ag atom?

Ans.Given, a= 409 pm

For fcc, $a = 2\sqrt{2} \times r$

$r = a/2\sqrt{2}$

$= 409/ 2 \times 1.41$

$= 145.03$ pm

2. Calculate the packing efficiency of a metal crystal for simple cubic lattice.

Ans.

For simple cubic $a = 2r$ Rank (Z) = 1

So volume occupied by one sphere in the unit cell = $\frac{4}{3} r^3$

Volume of the unit cell = $(2r)^3 = 8r^3$

Hence, packing efficiency = $\dfrac{\frac{4}{3} r^3}{8r^3} \times 100 = 52.36\ \%$

3. Define the following terms w.r.t. crystalline solid – (a) Unit cell (b) Coordination No.

Give example in each case.

Ans. (a) Unit cell- An unit cell is the smallest portion of the crystal lattice. When it is moved repeatedly a distance equal to its own dimension along each direction, a three dimensional crystal lattice is generated.

(b)Coordination No. -It is the number of atoms or spheres that surrounds the single sphere / atom in a crystal.

C.Nof tetragonal arrangement = 3

C.Nof tetrahedral arrangement = 4

C.Nof octahedral arrangement = 6

C.Nof body centered cubic arrangement = 8

Any close (tight) packing having C.N = 12 i.e. hcp and ccp i.e. fcc having C.N = 12

4. Aluminiumcrystallises in an fcc structure. Atomic radius of the metal is 125 pm. What is the length of the side of the unit cell of the metal?

Ans.

For an *fcc* unit cell, $r - \dfrac{a}{2\sqrt{2}}$

$a = 2\sqrt{2}r = 2 \times 1.414 \times 125 = \mathbf{353.5\ pm}$.

Short Answer Type Questions (3 Marks)

1. Copper crystallises with fcc unit cell .if the radius of Copper atom is 127.8 pm , calculate the density of copper metal . (Atomic Mass of Cu = 63.55 &Avagadro No. = 6.02x 10^{23} mol^{-1})

Ans.

For *fcc*, $a = 2\sqrt{2}r$

$\therefore$ $a = 2\sqrt{2} \times 127.8 \text{ pm} = 361.4 \text{ pm} = 361.4 \times 10^{-10} \text{ cm}$

Here, $z = 4$; $M = 63.55 \text{ g mol}^{-1}$; $a = 3.614 \times 10^{-8}$ cm; $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

Substituting the values in the expression,

$$d = \frac{z \times M}{a^3 \times N_A}, \text{ we get}$$

$$d = \frac{4 \times 63.55 \text{ g mol}^{-1}}{(3.614 \times 10^{-8} \text{ cm})^3 \times 6.02 \times 10^{23} \text{ mol}^{-1}} = 8.95 \text{ g cm}^{-3}$$

2. Iron has a bcc unit cell with the cell dimension of 286.65 pm . Density of iron is 7.87 g/cc .use this information to calculate &Avagadro’s No. (At. Mass of Fe = 56) .

Ans.

$a = 286.65 \text{ pm} = 286.65 \times 10^{-10}$ cm; $M = 55.845 \text{ g mol}^{-1}$; $d = 7.874 \text{ g cm}^{-3}$

For *bcc* unit cell, $z = 2$

Substituting the values in the expression, $N_A = \frac{z \times M}{a^3 \times d}$, we get

$$N_A = \frac{2 \times 55.845 \text{ g mol}^{-1}}{(286.65 \times 10^{-10} \text{ cm})^3 \times 7.874 \text{ g cm}^{-3}}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

3. The density of copper metal is 8.95 g/cc, if the radius of Cu atom is 127.8 pm , is the Cu unit cell simple Cubic, bcc or fcc ?

Ans.

Given, Radius (r) = 127.8 pm

For fcc $a - 2\sqrt{2}r$

$\therefore$ $a^3 = (2\sqrt{2}r)^3 = 4.723 \times 10^{-23} \text{ cm}^3$

Atomic mass of Cu = 63.54 g mol^{-1}

$N_A = 6.022 \times 1023 \text{ mol}^{-1}$

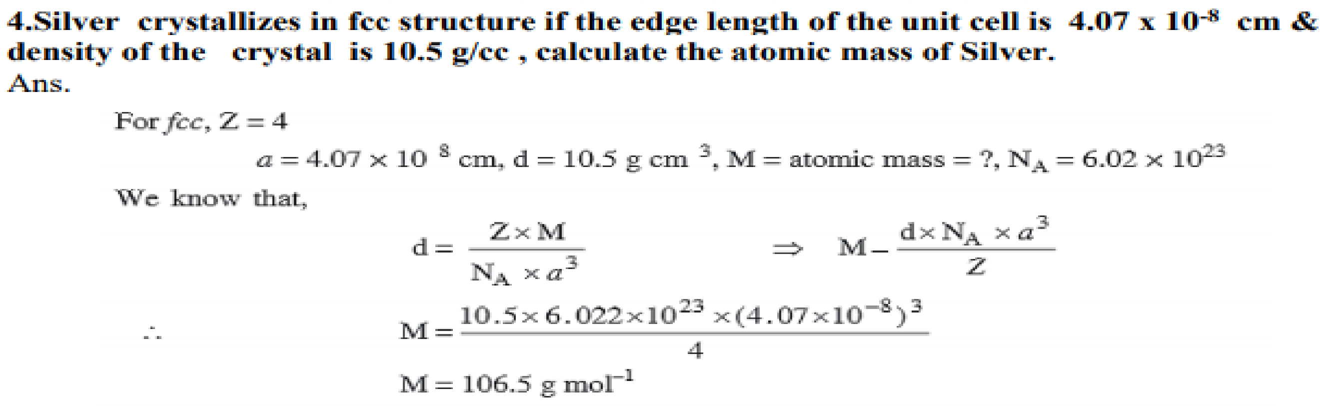
Density = 8.95 g cm^{-3}

$$d - \frac{Z \times M}{N_A \times a^3}$$

$$\Rightarrow \quad 8.95 = \frac{Z \times 63.54}{6.023 \times 10^{23} \times 4.723 \times 10^{-23}}$$

$$\therefore \quad Z - \frac{8.95 \times 6.022 \times 4.723}{63.54} \quad \Rightarrow \quad Z = 4.00$$

Thus copper has fcc structure.



4.Silver crystallizes in fcc structure if the edge length of the unit cell is 4.07 x 10^{-8} cm & density of the crystal is 10.5 g/cc , calculate the atomic mass of Silver.

Ans.

For *fcc*, Z = 4

$a = 4.07 \times 10^{\ 8}$ cm, d = 10.5 g $cm^{\ 3}$, M = atomic mass = ?, $N_A = 6.02 \times 10^{23}$

We know that,

$$d = \frac{Z \times M}{N_A \times a^3} \qquad \Rightarrow \qquad M - \frac{d \times N_A \times a^3}{Z}$$

$$\therefore \qquad M = \frac{10.5 \times 6.022 \times 10^{23} \times (4.07 \times 10^{-8})^3}{4}$$

$$M = 106.5 \text{ g mol}^{-1}$$

5. **Copper crystallises into a fcc lattice with edge length 3.61 × 10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3} 9atomic mass of Cu = 63.5 g molAns.** For face-centered cubic structure, no. of atoms per unit cell z =4

Density, *d* = z.M/a^3 .N_A

=4 x 63.5 g mol^{-1} /(3.61 × 10^{-8} cm$)^3$ x 6.02x10^{23} mol^{-1}

=8.97 g cm^{-3} , which is close to the measured value of 8.92 g cm^{-3}

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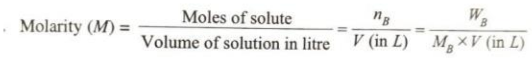
SOLUTION

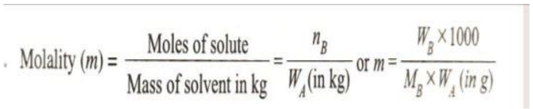
Key Concept

Molarity (M):- Number of moles of solute dissolved in one litre of solution.



$$\text{Molarity } (M) = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}} = \frac{n_B}{V \text{ (in } L)} = \frac{W_B}{M_B \times V \text{ (in } L)}$$

Molality (m):- Number of moles of solute per kg of solvent.



$$\text{Molality } (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{n_B}{W_A (\text{in kg})} \text{ or } m = \frac{W_B \times 1000}{M_B \times W_A \ (in\ g)}$$

Note:- Molality is independent of temperature whereas molarity is a function of temperature because volume depends on temperature and mass does not.

Mole fraction (x):- it is the ratio of number of moles of one component to the total number of moles of all the components present in the solution.

$$\text{Mole fraction of } A,\ x_A = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of } B,\ x_B = \frac{n_B}{n_A + n_B}$$

$$x_A + x_B = 1$$

HENRY'S LAW:- it is stated that at a constant temperature the amount of gas in liquid is directly proportional to the pressure of the gas above the surface of the liquid.

$$p_{\text{gas}} = K_{\text{H}} \times x_{\text{gas}}$$

APPLICATION OF HENRY'S LAW

1.to increase the solubility of carbon dioxide in soda water and soft drink the bottle is sealed under high pressure.

2. To avoid bends toxic effect of high concentration of nitrogen in the blood the tanks used by the scuba divers are filled with air diluted with He.

RAOULT'S LAW

1.for a solution of volatile liquid the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

2.for solution containing non volatile solute the vapour pressure of the solution is directly proportional to the mole fraction of the solvent.

IDEAL SOLUTION

The solution which obeys Raoult's law over the entire range of concentration when enthalpy of mixing and volume of mixing of pure component to form solution is zero.

Conditions

I. $P_A = P^0_A X_A$ $\quad P_B = P^0_B X_B$

II. $\Delta H_{mix} = 0$

III. $\Delta V_{mix} = 0$

This is only possible if A-B interaction is nearly equal to those between A -A and B-B interaction example:-solution of n-hexane and n-heptane.

NON-IDEAL SOLUTION

The solution which do not obey Raoult's law over the entire range of concentrations Conditions.

I. $P_A \neq P^0_A X_A$ $\quad$ $P_B \neq P^0_B X_B$

II. $\Delta H_{mix} \neq 0$

III $\Delta V_{mix} \neq 0$

i) Positive deviation:- A-B interaction are weaker than those between A-A and B-B

(Vapour Pressure is higher)

Ex. Mixture of ethanol and acetone

$P_A > P^0_A X_A$; $P_B > P^0_B X_B$

$\Delta H_{mix} =$ Positive $\Delta V_{mix} =$ Positive

ii) Negative deviation:- A-B interaction are stronger than those between A-A and B-B

(Vapour Pressure is lower)

Ex. Mixture of Chloroform

$P_A < P^0_A X_A$; $P_B < P^0_B X_B$

$\Delta H_{mix} =$ negative $\Delta V_{mix} =$ negative

AZEOTROPE

Mixture of liquid having the same composition in liquid and vapour phase and boil at constant temperature.
Azeotrope are of two types

i) **Minimum boiling azeotrope:-** The solution which shows a large positive deviation from Raoult's law.
example:- ethanol- water mixture

ii) **Maximum boiling azeotrope:-** The solution which shows large negative deviation from Raoult's law
example:- Nitric acid - water mixture

COLLIGATIVE PROPERTIES

Properties of Ideal solution which depends upon number of particles of solute but independent of the nature of the particles are called colligative properties.

a) RELATIVE LOWERING OF VAPOUR PRESSURE

$$\frac{p^o_A - p}{p^o_A} = x_B = \frac{n_B}{n_A + n_B}$$

b) ELEVATION OF BOILING POINT

$$\Delta T_b \propto m \text{ or } \quad \Delta T_b = K_b m \qquad \Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$$

c) DEPRESSION IN FREEZING POINT

$$\Delta T_f \propto m \text{ or } \Delta T_f = K_f m$$

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

d) OSMOTIC PRESSURE

$$\pi = CRT$$

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

$$M_B = \frac{W_B \times R \times T}{\pi \times V}$$

ISOTONIC SOLUTION

Two solutions having same osmotic pressure and same concentration 0.91% of sodium chloride is isotonic with fluid present inside blood cell

hypotonic solution have higher osmotic pressure and hypertonic solution have lower osmotic pressure then the other solution.

Q1. How does the molarity of a solution changes with temperature?

Ans. Molarity decreases with increase in temperature as volume of solution increases with increase in temperature

Q2. What is the similarity between Raoult's law and Henry law.

Ans. The partial vapour pressure of the volatile components or gas is directly proportional to its mole fraction in the solution.

Q3.out of two 0.1 molal solutions of glucose and of potassium chloride, which one will have a higher boiling point and why?

Ans. 0.1 M KCl solution will have higher boiling point as KCl is dissociate in the solution.

Q4. Under what condition do non ideal solution show negative deviation.

Ans.When the new forces of interaction between the components are stronger than those in the pure components , then non-ideal solution show negative deviation.

Q5. What do you mean by 10% aqueous solution of sodium carbonate.

Ans.it means that 10 gram of Na2CO3 is present in hundred gram of solution.

Q6. What type of liquids form ideal solutions?
Ans. Liquids that have similar structures and polarities form ideal solutions.

Q7. What are maximum boiling azeotropes ? give one example.
Ans. Maximum boiling azeotropes are those which boil at higher temperature than boiling point of each component in pure state 68% nitric acid and 32% water by mass

Q8. Define molal elevation constant or ebullioscopy constant.
Ans. it is defined as the elevation in boiling point when one mole of non-volatile solute is added to 1 kilogram of solvent.

Q9. What is reverse osmosis?
Ans. if the pressure applied on the solution is greater then the osmotic pressure than the solvent molecules start to move from solution into solvent through a semipermeable membrane this process called the reverse osmosis.

10. Why is glycol and water mixture used in car radiators in cold countries?
Ans. Ethylene glycol lowers the freezing point of water due to these coolant in radiators will not freeze otherwise radiators will burst due to the freezing of coolant.

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Unit-3 Electrochemistry

Important Concepts

***Reactivity α 1/ Reduction potential**
Oxidising power $\propto$ Reduction potential
Reducing power $\propto$ 1/ Reduction potential
Q. Can you store copper sulphate solution in zinc pot ?
A. No ,Reduction potential of zinc is less than copper and it is more reactive so it will displace copper .
***Nernst equation**
$Ecell = E^\circ cell - RT/nF \log [anode]/[cathode]$
$E^\circ cell = E^\circ cathode - E^\circ anode$
***Relationship between electrode potential and equilibrium constant**
$E^\circ cell = 2.303RT/nF \ \log Kc$
***Relationship between Electrode potential and Gibbs free energy change**
$\Delta G = -nFEcell$
$\Delta G^\circ = -nFE^\circ cell$ {n= number of electrons lost or gained ; F=96500 C/mol}
***Molar conductivity** : Conductivity of a solution having 1 mole of electrolyte dissolved in it .
Unit - Scm^2mol^{-1}
***Relationship between conductivity and molar conductivity:**
Molar conductivity = Conductivity x1000/ conc(molarity)
***Cell constant**- $G^* = l/a$ or κ xR
Unit- m^{-1} or cm^{-1}
***Limiting Molar Conductivity** : Molar conductivity of a solution at infinite dilution or zero concentration.
***Kohlrausch Law** : Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

Applications: 1. To find out limiting molar conductivity of weak electrolyte.
2. to calculate degree of dissociation of weak electrolyte.

***Faraday's first law of electrolysis** : Amount of substance deposited at any electrode is directly proportional to supplied charge.

W=ZQ

Charge on one mole of electron is 1Faraday or 96500 C

Q Amount of electricity required for following changes:

a)1mol Al → Al^{3+} (3F)

b)1mol H_2O →O_2 (2F)

***Products of electrolysis**

When electrode and electrolyte's are of same metal ,then at cathode metal will be deposited and at anode metal electrode will dissolve.

For eg : products of aq $AgNO_3$ with Ag electrodes

Cathode $Ag^+ + e^- \rightarrow Ag$

Anode $Ag \rightarrow Ag^+ + e^-$

***Faraday's second law of electrolysis** : when the same amount of current is passed through different electrolytes/elements connected in series, the mass of the substance liberated/deposited at the electrodes in g is directly proportional to their chemical equivalent.

$W \alpha E$

More Questions

1.What is effect of dilution on conductivity ?

A. Conductivity depends on number of ions per unit volume so it decreases with dilution.

2.What is effect of dilution on molar conductivity?

A . Molar conductivity depends on number of ions .so it increases with dilution.

3.What is role of Salt bridge ?

A. 1. It completes internal circuit of cell.
   2. It maintains electrical neutrality.

4. What is standard Hydrogen Electrode ?

A. It is reference electrode in which a piece of platinum coated with platinum black is dipped in 1 M HCl solution and hydrogen gas is passed at 1 atm .

5. Write cell representation of following cell ?

Zn(s)+2Ag+(aq) →Zn2+(aq)+2Ag(s)

A. $Zn(s)|Zn(aq)2+||Ag(aq)+|Ag(s)$

6.The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm–1. Calculate its molar conductivity?

A.Given, $\kappa = 0.0248 \text{ S cm}^{-1}$

c = 0.20 M

molar conductivity = conductivity x1000/molarity

$= 124 \text{ Scm}^2\text{mol}^{-1}$

7. Limiting molar conductivity for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 Scm2mol–1 respectively, calculate limiting molar conductivity for Acetic acid ?

Ans. 390.5 Scm^2/mol

8. **Calculate the emf of the cell in which the following reaction takes place: $Ni_{(s)} + 2Ag^+$ (0.002 M) → Ni^{2+} (0.160 M) + $2Ag_{(s)}$. Given that $E^{ø}_{cell}$ = 1.05 V.**

Solution:
By using Nernst equation

$$E^{-}_{Cell} - \frac{0.059}{2}\log\frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$$

$$= 1.05 - \frac{0.059}{2}\log\frac{[0.160]}{[0.002]^{2}}$$

$$= 1.05 - 0.02955\log\frac{0.160}{0.000004}$$

$= 1.05 - 0.02955 \log 4 \times 10^4$
$= 1.05 - 0.02955 (\log 10000 + \log 4)$

$= 1.05 - 0.02955 (4 + 0.6021)$

= 0.914 V

9.The standard emf of Daniell cell is 1.1 V . Calculate the standard Gibbs energy for the cell reaction ?

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

Ans.

$\Delta G^\circ = -nFE^\circ cell =$ 2x 96500 x1.1 = -212300 J/mole =-212.3 KJ/mole

10. What is unit of Molar conductivity ?

A. scm^2mol^{-1}

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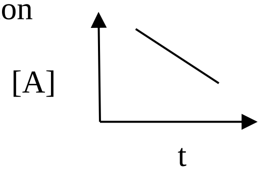
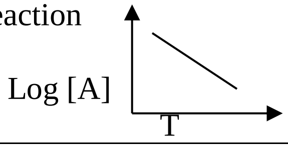
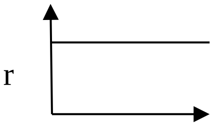
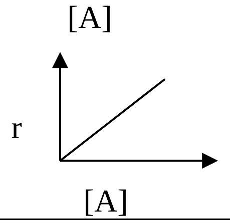
CHEMICAL KINETICS

(A) REVISED / REDUCED SYLLABUS (ONLY FOR 2020-21)

-Rate of a reaction (Average and instantaneous)
-Factors affecting rate of reaction (concentration, temp & 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)

(B)

S.No.	CONCEPT	THEORY AND FORMULA
1	Rateof reacton(r)	Change in concentration of reactant or product per unit time $A \longrightarrow B$, r = decreace in concentration of A / time = increace in concentration of B / time unit of r = mol L^{-1} sec^{-1}
2	General expression for rate of reaction	$N_2 + 3H_2 \longrightarrow 2NH_3$ $r = - [\Delta N_2] / \Delta t = - (1/3) [\Delta H_2] / \Delta t = + (1/2) [\Delta NH_3] / \Delta t$
3	Factors affecting rate of reaction	Rate of reaction increases with increase in concentration and temp. In presence of catalyst, rate of reaction generally increases and equilibrium state is attained quickly in reversible reaction.
4	Rate law	$aA + bB \longrightarrow$ Products $r = k [A]^m [B]^n$ k is rate constant
5	Order and molecularity of reaction	Order of reaction = m+n, experimental quantity , can be zero or even fraction Molecularity of reaction = a+b , theoretical quantity , can not be zero or a non integer
6	Zero order reaction	eq^n $A \longrightarrow B$, [$r = -d[A] / dt = k [A]^0 = k$ t=0 a 0 t a-x x [unit of k =unit of r = mol L^{-1} sec^{-1} $k = [A]_0 - [A] / t = a-(a-x) / t = x / t$ $t_{1/2} = [A]_0 / 2k$
7	First order reaction	eq^n $A \longrightarrow B$, [$r = -d[A] / dt = k [A]^1 = k [A]$ t=0 a 0 t a-x x [unit of k =unit of r / unit of [A] = sec^{-1} $k = (2.303 / t) \log ([A]_0 / [A])$ or $(2.303/t) \log (a/a-x)$ $t_{½} = 0.693 / k$
8	Half life period ($t_{1/2}$)	Time in which the concentration of a reactant is reduced to one half of its initial concentration (a or $[A]_0$)
9	Graph between [A] and t	For zero order reaction  slope = -k For first order reaction  slope = - k /2.303
10	Graph between r and [A]	For zero order reaction 

		For first order reaction 
11	Pseudo first order reaction	A bimolecular reaction ,in which one reactant is present in large excess and rate of reaction is independent of its concentration . Such a reaction is called Pseudo first order reaction. e.g $CH_3COOC_2H_5 + H_2O \dashrightarrow CH_3COOH + C_2H_5OH$ Molecularity =2 and order of reaction =1

(C) ONE MARK QUESTIONS

Q.1	What is the order of reaction whose rate constant has the same unit as the rate of reaction? **Ans**. Zero order
Q.2	Calculate overall order of reaction which has the rate rxpression $r = k [A]^{3/2} [B]^{-1}$ **Ans**. Order = 3/2+(-1) =1/2
Q.3	What is the unit of rate constant for a pseudo first order reaction ? **Ans.** Sec^{-1}
Q.4	A reaction is 50% complete in 4 hrs and 75% completes in 8 hrs . What is the order of reaction ? **Ans**. Since half life remains constant so it is a first order reaction.
Q.5	A reaction is first order in A. How is the rate affected if the concentration of A is reduced to half? **Ans.** $r = k [A]^1$ **now** $\mathbf{r_1 = k [1/2 A] = 1/2 r}$

(D) TWO MARKS QUESTIONS

Q.1	For the reaction R ---> P , the concentration of a reactant changes fron .05M to .02M in 30 sec. Calculate average rate of reaction . **Ans**. $r = -\frac{\Delta[R]}{\Delta t}$ = - (.02M - .05M) /30 sec =.03M /30 sec = .001M / sec $= 10^{-3}$ mole L^{-1} sec^{-1}
Q.2	The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value. **Ans:-** $t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$ $t = \frac{2.303}{60} \log \frac{1}{1/10}$

	$t = \frac{2.303}{60} \log 10$ $t = \frac{2.303}{60} = 3.83 \times 10^{-2}$ sec
Q.3	A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-12}\ \text{sec}^{-1}$. Find the half life of the reaction. **Ans**. Half life for a first order reaction is $t_{1/2} = \frac{0.693}{k} = 0.693 / 5.5 \times 10^{-12}\ \text{sec}^{-1}$ $= 1.26 \times 10^{+11}$ sec
Q.4	A first order reaction has a rate constant $1.15 \times 10^{-3}\ \text{sec}^{-1}$.How long will 5 gm of this reactant take to reduce to 3 gm ? **Ans.** **t** =(2.303/k) **log(** a/a-x) = $(2.303/ 1.15 \times 10^{-3})$ log (5/3) =2000 log 1.667 =2000 x 0.2219 = 443.8 sec

(E) ASSERTION-REASON TYPE QUESTIONS

A statement of assertion is followed by a statement of a 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 and reason is true.

Q.1	Assertion : Order of reaction with respect to any reactant or product can be zero, positive ,negative and fractional. Reason: Rate of a reaction cannot decrease with increase in concentration of a reactant or product.	Ans. (c)
Q.2	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.	Ans. (a)
Q.3	Assertion: In a zero order reaction , if concentration of the reactant is doubled, half life period is also doubled. Reason: The total time taken for a zero order reaction to complete is double of the half life period.	Ans. (b)
Q.4	Assertion: 50% of a reaction is completed in 50 sec, 75% of the reaction will	Ans.

	be completed in 75 sec. Reason: The rate constant of a zero-order reaction depends upon time.	(c)
Q.5	Assertion: With increase in temperature the rate of reaction decreases. Reason: For every 10 ^{0}C rise in temperature , the rate of the reaction doubles for most of the reaction.	Ans. (d)

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SURFACE CHEMISTRY

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

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

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

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

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

   (I)Physical adsorption/physisorption: - When weak Vander Waal interaction involve between adsorbate and adsorbent.

   (ii) Chemical adsorption/chemisorption: -When chemical bonds form between adsorbate and adsorbent.
5. Adsorption isotherm: - The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.
6. Application of adsorption: -

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

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

   (I)Surface area: - Adsorption increases with increases of surface area of adsorbent.

   (ii)Nature of adsorbate: -Easily liquefiable gases are readily adsorbed.

   (iii)Temperature: -Low temperature is favorable for physical adsorption and High temperature for chemisorption.

   (iv)Pressure: -Pressure increases, adsorption increases.

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

10. TYPES OF COLLOIDS

(1) On the basis of nature of interaction between dispersed phase and dispersion medium.

(a) Lyophobic colloid - solvent, hating colloid, these colloids cannot be prepared by simply mixing of dispersed phase into dispersion medium. e.g. metallic sols.
(b) Lyoph colloid-solvent loving these colloids can be prepared by simply mixing of dispersion phase into dispersion medium e.g. Starch sol.

(2) On the basis of types of particles of the dispersed phase

(a) Multimolecular colloid- on dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in colloidal range. The species thus, formed are called Multimolecular colloids e.g. Sulphur sol.
(b) Macromolecular colloids -macromolecules are suitable solvent from solution in which size of the particles are in range of colloidal range. e.g. starch sol.
(c) Associated colloids (micelles)- some substances in law concentration behaves as normal strong electrolyte but at higher concentration exhibit colloidal behavior due to formation of aggregates. The aggregated particles are called micelles and also known as associated colloids.
(3) Kraft temperature- Temp. above which formation of micelles takes places.

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

11. PREPERATION OF COLLOIDS

(a) Chemical methods- By double decomposition, oxidation reaction or hydrolysis
OXIDATION
e.g. $SO_2 + 2H_2S \rightarrow 3S\ (SOL) + 2H_2O$
HYDROLYSIS
e.g. $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$
(b) Bredig's arc method- For preparation of metallic sol. It involves dispersion as well as condensation.
(c) Peptization- Process of converting a precipitate into colloidal sol.by shaking it with dispersion medium in the presence of a small amount of electrolyte.

12. PURIFICATION OF COLLIODAL SOLUTION: -

(a) Dialysis-it is a process of removing a dissolved substance from a colloidal solution by membrane.
(a) Electro dialysis-when dialysis is carried out with an electric field applied around the membrane.

13. PROPERTIES OF COLLOIDAL SOLUTION: -

(1) They show colligative properties.

(2) Colloidal particles move in zig-zag motion called Brownian movement.

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

(4) Colloidal particles which carry on electric charge and nature of charge is same on all particles.

14. Electrophoresis - Movement of Colloidal particles towards opposite electrode in presence of external electric field.

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

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

E.g. $Na^{+} < Ca^{2+} < Al^{3+}$ for negatively charged sol.

$Cl^{-} < CO_3^{2-} < PO_4^{3-} < [Fe(CN)6]^{4-}$ for positive sol.

Important points

1. Blood is a positive colloid
2. Collodion is cellulose nitrate in alcohol
3. Coagulation leds to Delta formation, Blood clotting, Artificial raining.
4. All lyophobic colloids contain charge and the equal and opposite charge is present on dispersion medium.
5. If lyophobic sols are heated, shaked or an electrolyte is added to it then it gets coagulated.
6. A potential developed due to presence of charge on the particles and the medium is called Zeta potential.

(a) Multiple Choice questions

Questions carrying 1 mark

1.Colloidion is 4% solution of which one of the following in alcohol-ether mixture.

(a) Nitroglycerin (b) Cellulose acetate

(c) Glycol dinitrate (d) Nitrocellulose

Ans: d

2. When a small amount of $FeCl_3$ is added to a freshly precipitated $Fe(OH)_3$ a reddish-brown colloidal solution is obtained. This phenomenon is known as

(a) dialysis (b) peptization

(c) protection (d) dissolution

Ans: b

3. The stability of lyophobic sols is due to

(a) adsorption of covalent molecules on the colloid (b) the size of the particles

(c) the charge on particles (d) Tyndall effect.

Ans: c

4. The term ‘sorption’ stands for ___________ .

(a) absorption (b) adsorption

(c) both absorption and adsorption (d) desorption

Ans: c

5. Which is favorable for physical adsorption?

(a) High T and high P (b) High T and low P

(c) Low T and high P (d) T and P do not affect

Ans: c

VERY SHORT ANSWER TYPE QUESTION

Questions carrying 1 mark

1. What is protective colloid?
2. Define Electrophoresis.
3. What is peptization?
4. Why is it necessary to remove CO when ammonia is obtained from Haber's process?
5. Which one of this will be better reagent to coagulate blood a) $FeCl_3$b) NaCl c) $CaCl_2$?
6. Which will adsorb more gas, a lump of charcoal or its powder and why?
7. Name the type of colloid of cheese.
8. Define Brownian movement.

Answer key

1. lyophilic colloid that protect any colloid from coagulation.
2. The movement of colloidal particles under the influence of an electric field.
3. Conversion of a freshly prepared precipitate into colloidal sol by the addition of electrolyte.
4. Because CO act as poison.
5. $FeCl_3$because of greater valence of iron according to Hardy Schulz rule
6. Powdered form of charcoal, because of greater surface area.
7. Gel
8. It involves the motion of colloidal particles in zigzag path.

Questions carrying 2 marks

1. Differentiate between lyophilic and lyophobic colloids.
2. Why is adsorption always exothermic in nature?
3. What is demulsification? Name two demulsifying agent.
4. Why is it essential to wash the precipitate with water before estimating it quantitatively?
5. Comment on the statement that "colloid is not a substance but state of a substance."
6. Why is the ester hydrolysis slow in the beginning and becomes faster after some time?

Answer Key

1. a) Lyophilic sols are easily prepared by directly mixing with the liquid dispersion medium but lyophobic sols cannot be prepared directly by mixing with liquid.
lyophilic sols are stable and are not easily coagulated but lyophobic sols can be easily precipitated by the addition of suitable electrolyte.

2. When a gas is adsorbed on the surface of a solid, its entropy decreases and S becomes negative. Now G = H- TΔ S and for the process to be spontaneous, free energy change must be negative. As TΔ S is negative i.e. -TΔ S is positive and for free energy change to be negative enthalpy change should be negative hence reaction should be exothermic always.
3. The process of separation of constituent liquid of an emulsion is called demulsification. It can be done by either centrifuging or boiling.
4. Some amount of the electrolytes mixed to form the precipitate remains adsorbed on the

surface of the particles of the precipitate. Hence, it is essential to wash the precipitate with water to remove the sticking electrolytes or any other impurity before estimating it quantitatively.

5. The given statement is true. This is because the same substance may exist as colloid under certain conditions and as a crystalloid under certain conditions for e.g. NaCl in water behave as crystalloid but in benzene as a colloid. It is the size of solute particle which matters i.e. the state in which the substance exists. If it lies in the range of 1nm to 1000nm its a colloid.

6. RCOOR' + H_2O ---------------------→RCOOH + R'OH
The acid produced in above reaction act as auto catalyst for the reaction. Hence the reaction becomes faster after some time.

Questions carrying 3 marks

1. What is the difference between multimolecular and macromolecular colloids? Give one example of each.
2. Explain the terms coagulation, dialysis and Tyndall effect.
3. Explain the following terms alcosol, aerosol and hydrosol.
4. Give specific term to show the effect of the following process.
   a) Ferric hydroxide is mixed with arsenic sulphide sol
   b) Ferric chloride solution is mixed with freshly prepared precipitate of ferric hydroxide.
   c) H_2S is passed through arsenic oxide solution.

Answer key

1. Multimolecular colloids are formed by the aggregation of large number of molecules (for e.g. S_8). Macromolecular colloids are due to large size of molecule themselves (e.g. starch) so large that their size lies in the colloidal range. 2. Coagulation is the process of aggregation of colloidal particles so as to change them into large sized particles which ultimately settles as precipitate.
Dialysis is the process of separating the particles of colloids from those of crystalloids by diffusion of the mixture through parchment membrane.
Scattering of light through colloidal solution by the colloid particles is called Tyndall effect
3. Alcosol is colloidal dispersion having alcohol as dispersion medium e.g. collodion. Aerosol is colloidal dispersion of a liquid in gas for e.g. fog. Hydrosol is colloidal dispersion of a solid in liquid e.g. starch sol or egg albumin sol.
4. a) Coagulation b) Peptization c) Double decomposition

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p-block Elements

Group-15

1 Mark Questions-

1. Nitrogen does not form pentahalides. Why?
Ans. Nitrogen has no d-orbital. Therefore, it does not form pentahalides.
2. The stability of +5 oxidation state decreases down the Group-15. Why?
Ans. The stability of +5 oxidation state decreases due to inert pair effect.
3. What is inert pair effect?
Ans. Due to poor shielding effect of fully filled, d and f-orbitals, the ns electrons of the heavier elements of p-block become passive towards bonding. This is called inert pair effect.

4.Why is Nitrogen a gas while Phosphorous is a solid?
Ans. Nitrogen has unique ability to form p∏-p∏ interaction(weak interaction), Nitrogen is a gas. Phosphorous on the other hand, has the ability to form d∏-d∏ interaction(strong interaction) so, Phosphorous is a solid.
5. Bismuth is strong oxidizing agent in its pentavalent state. Why?
Ans. Due to Inert pair effect, +5 oxidation state is less stable so, in +5 state, it easily accepts 2 electrons to reduce itself to Bismuth +3.
6. PH_3 has lower boiling point than NH_3. Why?
Ans. Unlike NH_3, PH_3 cannot form Hydrogen bond, so its boiling point is less than NH_3.
7. Why are pentahalides of Group-15 elements, more covalent than their trihalides?
Ans. In +5 oxidation state, elements have more polarizing power than in +3 oxidation state, so the covalent character of bond is more in pentahalides.
8. The stability of -3 oxidation state, decreases down the group for group 15.
Ans. It is due to increase in size and metallic character or decrease in electronegativity down the group.
9. Why is BiH_3 the strongest reducing agent amongst all the Hydrides of Group-15 elements.
Ans. Down the group, the size of element increases and so the length of E----H bond decreases. Thus Bi-----H bond is weakest and easily evolves H_2 gas, which is a reducing agent.
10. What happens when Sodium Azide is heated?
Ans. It gives off Dinitrogen gas. $2NaN_3$ --------------> $2Na + 3N_2$
11. Why is Dinitrogen inert at room temperature?
Ans. Due to presence of Triple bond between the Nitrogen atoms, its bond dissociation enthalpy is very high, making it inert at room temperature.
12. Why Ammonia is basic in nature?
Ans. It is because, the Nitrogen atom of Ammonia has a lone pair of electrons which it can donate and act as a Lewis base.
13. Mention the conditions required for the preparation of Ammonia.
Ans. 200 atm. Pressure & 700 K Temperature.
14. Name the catalyst and promoter, used in Haber's Process, for preparation of Ammonia.
Ans. Catalyst- Iron oxide Promoter- Mo
15. How does Ammonia react with a solution of Cu^{2+}?
Ans. $Cu^{2+}(aq)+4NH_3$-------> $[Cu(NH_3)4]^{2+}$(Deep blue)
16. What is the Covalency of Nitrogen in N_2O_5?
Ans. 4
17. Why does NO_2 dimerise?
Ans. NO_2 contains odd number of valence electrons. It is converted to stable N_2O4 molecule on dimerization.

2 marks questions-

1. Name the industrial method of preparation of nitric acid and give the reactions involved in it.
Ans. Ostwald process.
Reactions-
$4NH_3 + 5O_2$---Pt/Pd--------> $4NO + 6H_2O$
$2NO + O_2$----------------> $2NO_2$
$3NO_2 + H_2O$--------------> $2HNO_3 + NO$
2. Give the reaction of dilute Nitric acid with Copper and Zinc.
Ans. $3Cu + 8HNO_3$ (dil) --------------->$3Cu(NO_3)_2 + 2NO + 4H_2O$
$4Zn + 10HNO_3$ (dil) -------------------->$4Zn(NO_3)_2 + N2O + 5H_2O$

3. Arrange the following in increasing order of the properties indicated within the brackets.
a. AsH_3, BiH_3, NH_3, SbH_3, PH_3 (Basic Strength)
b. AsH_3, NH_3, PH_3, BiH_3, SbH_3 (Thermal stability)
Ans.
a. $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$
b. $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

Group-16

1 Mark Questions-

1. Group-16 elements have low 1st Ionization enthalpy as compared to Group-15 elements. Why?
Ans. Group-15 elements have $ns^2 np^3$ configuration, which is stable, half filled configuration as compared to Group-16 elements which have $ns^2 np^4$ configuration. So Group-16 elements have lower 1st Ionization enthalpy.

2. List the important sources of Sulphur.
Ans. Epsom salt($MgSO_4.7H_2O$), Gypsum($CaSO_4.2H_2O$),Baryte($BaSO_4$)

3. H_2S is less acidic than H_2Te. Why?
Ans. Due to decrease in E---H bond dissociation enthalpy, down the group, acidic character increases.

4. Why is H_2O a liquid and H_2S a gas?
Ans. Due to Hydrogen bonding in H_2O.

5. Write the order of thermal stability of Hydrides of Group-16 elements.
Ans. $H_2Te < H_2Se < H_2S < H_2O$ (Increasing order)

6. Why does O_3 act as a powerful oxidizing agent?
Ans. It decomposes to give O_2 and nascent Oxygen, so it is a strong oxidizing agent.

7. Why is O_2 paramagnetic in nature?
Ans. It is because it has 2 unpaired electrons in its antibonding orbital.

8. Write down a reaction of Ozone layer depletion.
Ans. $NO + O_3 \text{------------->} NO_2 + O_2$

9. Which form of Sulphur shows paramagnetic behavior?
Ans. S_2. As it has 2 unpaired electrons in its antibonding orbital.

10. What happens when SO_2 is passed through a solution of Fe^{3+} salt?
Ans. $2Fe^{3+} + SO_2 + 2H_2O \text{------------>} 2Fe^{2+} + SO_4^{2-} + 4H^+$

11. Are the 2 S---O bonds in SO_2 equal?
Ans. Yes, they are equal.

12. How is the presence of SO_2 detected?
Ans. SO_2 decolorizes pink color of $KMnO_4$.

13. What happens when conc.H_2SO_4 is added to Calcium Fluoride?
Ans. It forms Calcium Sulphate and Hydrogen Fluoride.
$CaF_2 + H_2SO_4$----------------> $CaSO_4 + 2HF$

14. What happens when Sulphur Trioxide is passed through water?
Ans. Hydrogen Sulphate is formed.
$SO_3 + H_2O$--------------------> H_2SO_4

15. Mention 3 uses of H_2SO_4.
Ans. a. As a laboratory reagent.
b. In manufacturing dyes, paints, etc.
c. In manufacturing fertilizers.

16. Why SF_4 can be hydrolyzed but SF_6 cannot?
Ans. It is because SF_6 has a stable octahedral structure and steric effect due to which it cannot be hydrolyzed.

2 Marks questions-

1. How Ozone is estimated?
Ans. When Ozone reacts with an excess of potassium iodide solution, with a borate buffer (pH=9.2), Iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is used for estimation of Ozone.

2. Compare the bleaching action of SO_2 and Cl_2.
Ans. SO_2 does temporary bleaching, while Cl_2 does permanent bleaching.
SO_2 bleaches via reduction and Cl_2 bleaches via oxidation.

3. What happens when (a) Sulphuric acid reacts with sugar?
Ans. It forms Carbon black (dehydration of sugar).
(b) SO_2 reacts with Chlorine.
Ans. It forms Sulphuryl Chloride.
$SO_2 + Cl_2$------------> SO_2Cl_2.

Group-17

1 Mark questions-

1. Why Halogens have maximum negative electron gain enthalpy in their respective periods of periodic table?
Ans. It is due to the smallest size and highest effective nuclear charge of the Halogens, the readily accept one electron to acquire Nobel gas configuration.
2. Why are Halogens colored?

Ans. It is because Halogens absorb radiation in visible region which results in excitation of outer shell electrons to higher energy level so, they display different colors.
3. Why Fluorine has less negative electron gain enthalpy than Chlorine?
Ans. It is because of the smaller size of Fluorine, it cannot readily accept an electron to form an anion due to interelectronic repulsion.

4. Why Fluorine exhibits only -1 oxidation state, whereas other Halogens exhibit +1,+3,+5,+7.
Ans. Fluorine is the most electronegative element and cannot exhibit and positive oxidation state. Other Halogens have d-orbital and hence can expand their octet to show higher oxidation state.

5. Give two examples to show anomalous behavior of Fluorine.
Ans. It shows only -1 Oxidation state (Except HOF).
Its Hydrogen Halide, HF exists in liquid state.

6. Sea is the greatest source of Halogen. Comment.
Ans. Sea water contains Chlorides, Bromides and Iodides of Sodium, Potassium, Magnesium and Calcium. Mainly it contains 2.5% NaCl by mass. Thus, sea is the greatest source of Halogens.

7. Name 2 poisonous gases that can be prepared by Chlorine.
Ans. Mustard gas, Phosgene.

8. Give reason for the bleaching action of chlorine.
Ans. In aqueous solution Cl_2 liberates Nascent Oxygen. This Nascent Oxygen brings about oxygen to bleach the colored substances.

9. Why I---Cl is more reactive than I_2.
Ans. I----Cl bond is weaker than I-----I bond. Consequently, I-----Cl bond breaks easily. Hence it is more reactive.

10. Why HF is liquid and HCl is a gas.
Ans. It is due to the presence of Hydrogen bond in HF.

11. Which oxide of Iodine is used in estimation of Carbon Monoxide?
Ans. I_2O_5

12. What happens when Fluorine reacts with water?
Ans. It oxidizes water to Oxygen.

13. Arrange the following in increasing order of their acidic strength.
$HOCl$, $HClO_4$, $HClO_2$, $HClO_3$
Ans. $HOCl<HClO_2<HClO_3<HClO_4$

2 Marks questions-

1. Arrange the following in increasing order of the properties indicated within the brackets.
a. HF, HCl, HI, HBr (Acidic strength)

b. HOCl, HOF, HOI, HOBr (Acidic strength)
Ans.
a. HF<HCl<HBr<HI
b. HOI<HOBr<HOCl<HOF

2. Arrange the following in increasing order of bond dissociation enthalpy.
a. Cl_2, I_2, Br_2, F_2
b. HF, HCl, HI, HBr
Ans.
a. $I_2<F_2<Br_2<Cl_2$
b. HI<HBr<HCl<HF

3. What happens when-
a. Chlorine reacts with cold and dilute NaOH.
b. Chlorine reacts with hot and concentrated NaOH.
Ans.
a. Cl_2 +2NaOH(dil.)---------------> NaCl + NaOCl+ H_2O
b. $3Cl_2$ + 6NaOH(conc.)--------------> 5NaCl + $NaClO_3$ + $3H_2O$

Group-18
1 Mark questions-

1. Why are the elements of Group-18, known as noble gases?
Ans. As they have stable, fully filled configuration, they react with very few elements so, they are known as noble gases.

2. Nobel gases have very low boiling point. Why?
Ans. Nobel gases being monoatomic, they do not have any intermolecular forces of attraction, except weak Dispersion/ London forces. So, they liquefy as well as boil at a very low temperature.

3. Why Helium is used in scuba divers apparatus?
Ans. It is because it is less soluble in blood/ has very low solubility in blood.

4. Why is it difficult to study the chemistry of Radon?
Ans. It is because, Radon is Radioactive in nature.

5. Give the equations for the Hydrolysis of-
a. XeF_2
b. XeF_4
c. XeF_6
Ans.
a. $2XeF_2$ + $2H_2O$ --------------> 2Xe + 4HF + O_2
b.$6XeF_4$ + $12H_2O$ ----------------> 4Xe + $2XeO_3$ + 24HF + $3O_2$
c. XeF_6 + $3H_2O$ --------------------> XeO_3 + 6HF

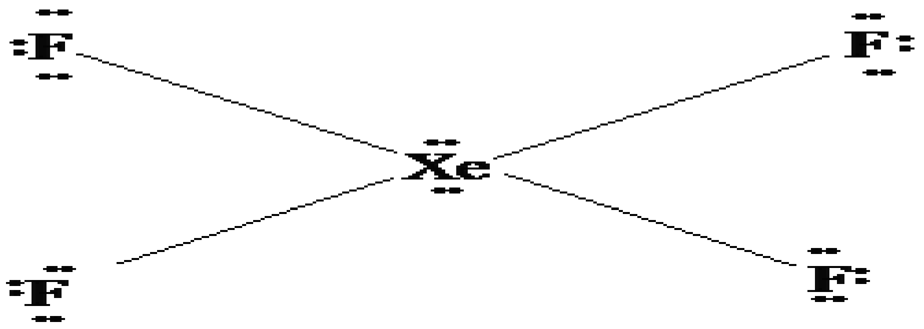
6. Give the equations for partial hydrolysis of XeO6.

Ans.

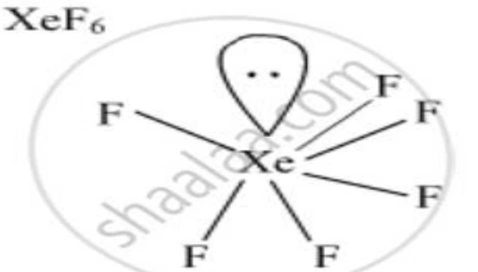
$XeF_6 + H_2O$ ----------------> $XeOF_4 + 2HF$

$XeF_6 + 2H_2O$ ---------------> $XeO2F_2 + 4HF$

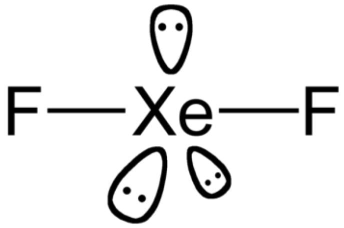
SOME IMPORTANT STRUCTURES

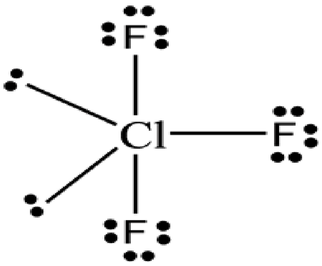


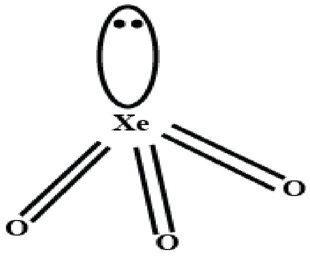
XeF_4



Distorted octahedral







XeO3

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The d – and f- block Elements

KEY CONCEPTS

- The d- block of the periodic table contains the elements of group 3-12 in which last electron enter into d subshell or d- orbital .
- Their general configuration is –
- (n-1) d^{1-10} ns^{1-2}
- Those elements which have incompletely filled d orbital in its ground state or in any one of the oxidation state are called Transition elements .
- Zinc, cadmium and mercury of group 12 have fully filled d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals .
- **Atomic size -** As we move from left to right in the series atomic size first decreases , then becomes constant and again increases .
- **Enthalpy of atomisation :-** The transition elements exhibit higher value of enthalpy of atomisation because due to presence of large no. of unpaired e^- s in their atom they have stronger inter atomic interaction and hence stronger bonding between atoms .
- **Melting and Boiling point :-** High melting and boiling points is due to the closed packed structures. In these structures transition metal atom are held together by strong metallic bonds which have considerable covalent character.
- **Oxidation states -**Transition element exhibits a large number of oxidation state in their compounds. This is due to participation of inner (n-1) d e^- s in addition to outer ns e^- in bonding due to less energy difference of ns and (n-1) d orbital .

  *The transition element which exhibit a single O.S. is Sc (+3).

  * The elements which show the greatest number of oxidation states occur in or near the middle of series due to presence of maximum no. of unpaired e^- .

  * The compounds of metals with oxygen and fluorine exhibit highest oxidation state as F and O are most electronegative element .

  *The stability of oxygen to stabilize the highest oxidation state exceeds that of fluorine. This is due to ability of oxygen to form multiple bonds .

  *Oxidation state of p block element differ by +2 because their variable oxidation state can be explained by exciting e^-s from ns and np to (n-1)d orbitals whereas in transition elements it differ by one due to loss of e^- by s as well as d- orbitals .
- **Catalytic properties -**The catalytic activity is due to

  i) Their ability to adopt multiple oxidation state .

  ii) In no. of cases transition metal provide large surface area with free valencies on which reactants are adsorbed.
- **Magnetic properties -** Most of the transition metals are paramagnetic in nature due to the presence of unpaired electrons in d-subshell .

  magnetic moment $(u) = \sqrt{n(n+2)}$

where n is the number of unpaired electrons .

- **Formation of complex compounds** - It is due to :-
- a) Small size.

  b) High nuclear charge.

  c) Availability of vacant d-orbitals of suitable energy to accept lone pair of electrons donated by ligands.
- **Formation of coloured ions -** The colour of transition metal compound is due to the presence of unpaired electrons which undergoes d-d transition by absorption of light in visible region.
- **Alloy Formation -** Transition metals form a large number of alloys. It is due to their similar atomic sizes .Due to this, atoms of one metal can easily take up the position in the crystal lattice of the other .
- **Interstitial compounds** – Transition metals forms a large number of interstitial compounds in which small atoms like hydrogen, carbon , boron and nitrogen occupy the interstitial sites in their lattice.These are non –stoichiometric compounds .
- **Electrode potential –**

  For M^{2+}/M :

  There is irregular variation in electrode potential due to irregular variation in ionisation enthalpy (IE_1+IE_2),sublimation energy and hydration enthalpy .
- **f –block elements -** Those elements in which differentiating electron enters into (n-2) f subshell are called inner transition element or f block elements .
  Their general electronic configuration is –

  $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$
- f- block consists of two series –
  1) Lanthanoids

  2) Actinoids
- **Lanthanoids -** The 14 elements which follow $_{57}La$ from $_{58}Ce$ to $_{71}Lu$ in the periodic table are called lanthanoids and in these filling of electrons occur in 4f subshell .
  Their general electronic configuration is –

  $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$
- **Lanthanoid Contraction -** The regular decrease in the atomic and ionic radii of lanthanoids with increasing atomic number is known as lanthanoid contraction .
  Cause – This is due to the addition of electron in 4f subshell which has poor shielding effect .
- **Consequences of Lanthanoid contraction –** 1) Similarity in size of elements belonging to same group of second and third transition series .
  2) Decrease in basic strength from $La(OH)_3$ to $Lu(OH)_3$.

  3) Difficulty in separation of lanthanoids .
- **Oxidation state -**Most common O.S. for lanthanoid is +3 .
  +2 and +4 is also exhibited by some elements which by losing 2 or 4 electrons acquire a stable configuration .

  *Ce and Tb exhibit +4 O.S. by losing 4 e^-s .

$_{58}$ Ce – [Xe] $6s^2\ 4f^1\ 5d^1$ Ce^{4+} – [Xe] $6s^0\ 4f^0\ 5d^0$

$_{65}$Tb – [Xe] $6s^2\ 4f^9$ Tb^{4+} – [Xe] $4f^7$

* Eu and Yb exhibit +2 O.S.by losing 2e$^-$.

$_{63}$ Eu – [Xe] $6s^2\ 4f^7$ Eu^{2+} – [Xe] $4f^7$

$_{70}$Yb – [Xe] $6s^2\ 4f^{14}$ Yb^{2+} – [Xe] $4f^{14}$

* La ,Gd and Lu exhibit only +3 O.S .

- **Colour -** Most of the trivalent metal ions are coloured .The colour is due to absorption of light in the visible region resulting in the f –f transition .

  * La^{3+} and Lu^{3+} ions are colourless because of having f^0 and f^{14} configuration respectively and hence no f-f transition is possible .
- **Magnetic property** -Among lanthanoids La^{3+} and Lu^{3+} which have 4f^0 and 4f^{14} configuration are diamagnetic and all other trivalent lanthanoids are paramagnetic because they have unpaired electrons .
- **Uses** - 1) Lanthanoids are used in the production of an alloy **misch metal** which consists of a lanthanoid metal (95%) , iron (5%)and traces of S , C, Ca and Al . It is used in Mg based alloy to produce bullets , shells and lighter flints.

  2) Mixed oxides of lanthanoids are used as catalyst in petroleum cracking .

Frequently asked questions –

Q-1 What are transition elements ?

Ans –Incompletely filled d –orbital in ground state or in any one of their oxidation state.

Q-2 Why Zn ,Cd and Hg are not regarded as transition elements ?

Ans – Do not have partly fiiled d –orbital in ground state or in any one of their oxidation state.

Q-3 Why do transition elements exhibit higher enthalpy of atomization ?

Ans –Due to stronger interatomic interaction .

Q-4 Transition elements have high melting and boiling points ?

Ans – Due to strond metallic bond .

Q-5 Why Zn ,Cd and Hg are soft and have low melting and boiling points ?

Ans – Due to weak metallic bonds present in them as all the electrons in d-subshell are paired .

Q-6 Why do transition elements shows variable oxidation states ?

Ans –Due to participation of (n-1)d and ns electron in bond formation .

Q-7 Name a transition element which does not exhibit variable oxidation states .

Ans- Scandium .

Q-8 Which of the 3d series of the transition metals exhibits the largest number of oxidation states and why ?

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

Q-9Which metal in the first transition series exhibits +1 oxidation state most frequently and why ?

Ans –Cu has the electronic configuration $3d^{10}$ $4s^1$ .It can easily lose $4s^1$ electron to give the stable $3d^{10}$configuration .

Q-10 Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only ?

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

Q-11 Cu^+ is not stable in aqueous solution .Why ?

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

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

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

Q-12 Transition elements form colored compounds . Why ?

Ans- Due to d-d transition .

Q-13 Why is Cu^{2+} ion colored while Zn^{2+} ion is colorless in aqueous solution ?

Ans –Presence of unpaired e- showing d-d transition in Cu^{2+} while in Zn^{2+} there is no unpaired electron .

Q-14 Transition elements form alloys .Why ?

Ans – Due to similar metallic radii .

Q-15 Most of the transition elements are paramagnetic .Why ?

Ans – Due to presence of unpaired electron in (n-1) d subshell.

Q-16 Which is the stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Ans – Cr^{2+} is the stronger reducing agent because in case of Cr^{2+} to Cr^{3+} change in configuration is from d^4 to d^3 and in Fe^{2+} to Fe^{3+} the change is from d^6 to d^5. In medium like water d^3 is more stable as compared to d^5 due to half filled t_2g configuration.

Q-17 Why do transition metals and their compounds show catalytic activity ?

Ans- Because of multiple oxidation state / ability to form complex / having large surface area .

Q-18 Why transition metals form large number of interstitial compounds ?

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

Q-19 The 4d and 5d series of transition metals have more frequent metal –metal bonding in their compounds than 3d series .Explain .

Ans –In the same group of d-block elements ,the 4d and 5d transition elements have larger size than that of 3d element .Thus the valence electrons are less tightly held and hence can form metal metal bond more frequently .

Q-20 The E^0 (M^{2+}/M) value for copper is positive (+0.34 v) .What is possible reason for this ?

Ans- Due to high enthalpy of atomization and low enthalpy of hydration .

Q-21 $Co^{2+}$is stable in aqueous solution but in the presence of complexing agent ,it is easily oxidised .Why ?

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

Q- 22 E^0 for Mn^{3+}/Mn^{2+} is more positive than for Fe^{3+}/Fe^{2+} . Why ?

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

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

Q-23 Zr and Hf have almost identical radii?

Ans - Due to filling of 4f orbitals which have poor shielding effect / lanthanoid contraction.

Q-24 $La(OH)_3$ is a stronger base than $Lu(OH)_3$?

Ans – As the size of lanthanoid elements decreases from La^{3+} to Lu^{3+} covalent character of hydroxide increases hence basic strength decreases .

Q-25 The d^1 configuration is very unstable in ions. Why ?

Ans – The ions with d^1configuration have the tendency to lose the only electron present in d-subshell to acquire stable d^0 configuration .

Practice Questions –

Q-1 On what ground can you say that scandium (Z=21) is a transition element but Zinc (Z=30) is not ?

Q-2 Calculate the spin only magnetic moment of M^{2+}ion (Z=27)

Q-3 Why transition elements have a strong tendency to form complexes?

Q-4 Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured . Why ?

Q-5 Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4) Mn^{2+} is an oxidising agent. Explain .

Q-6 Mn^{2+} is much more resistant than Fe^{2+} towards oxidation .Why ?

Q-7 What is lanthanoid contraction ? Write two main consequences of Lanthanoid contraction .

Q-8 Why the metallic radii of the third(5d) series of transition metals are virtually the same as those of the corresponding group members of the second (4d) series ?

Q-9 Name a member of lanthanoid series which is well known to exhibit +2 oxidation state.

Q-10 Name a member of lanthanoid series which is well known to exhibit +4 oxidation state.

Q-11 Ce^{4+} is a good oxidising agent and Eu^{2+} is a good reducing agent. Why ?

Q-12 Which is the most common oxidation state of Lanthanoids ?

Q-13 Give an example of disproportionation reaction .

Q-14 Which divalent metal ion has maximum paramagnetic character among the first transition metal. Why?

Q -15 Iron has higher enthalpy of atomisation than that of copper. Assign reason .

Q- 16 E^0 for Mn^{3+}/Mn^{2+} is more positive than for Cr^{3+}/ Cr^{2+}. Why?

Q-17 The third ionisation enthalpy of Manganese (Z=25) is exceptionally high. Why ?

Q-18 The highest oxidation state is exhibited in oxo-anions of a transition metal. Suggest a reason.

Q-19 Why is the separation of Lanthanoids difficult?

Q-20 Name an important alloy, which contains some of the lanthanoid metals. Mention its uses .

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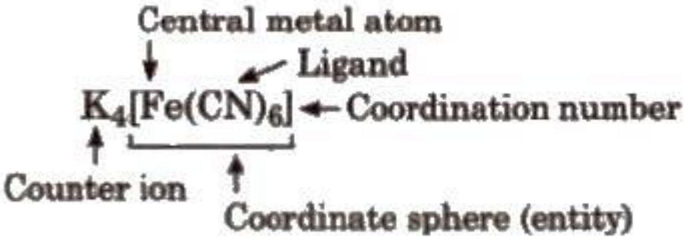
COORDINATION COMPOUNDS

Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds. the central metal atom or ion is linked by ions or molecules with coordinate bonds. e.g., Potassium ferrocyanide, K_4 [21 N)$_6$].

$$K_4[Fe(CN)_6] \overset{aq}{\rightleftharpoons} 4K^+ + [Fe(CN)_6]^{4-}$$



- **Double Salts:** These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr'S salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ get dissociated into Fe^{2+}, NH^+_4 and SO^{2-}_4 ions.

Terms Related to Coordination Compounds

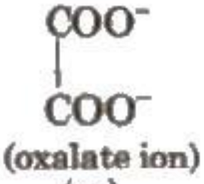
1. **Complex ion or Coordination Entity :** It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

(i) **Cationic complex entity** It is the complex ion which carries positive charge. e.g., $[Pt(NH_3)_4]^{2+}$

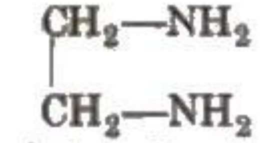
(ii) **Anionic complex entity** It is the complex ion which carries negative charge. e.g., $[Fe(CN)_6]^{4-}$

2. **Central Atom or Ion :** The atom or ion to which a fixed number of ions or groups are bound . It is also referred as Lewis acid. e.g., in $[NiCl_2(H_2O)_4]$. Ni is central metal atom.

3. **Ligands :** Ligands is electron donating species (ions or molecules) bound to the Central atom in the coordination entity.These may be charged or neutral. Ligands are of the following types: (i) **Unidentate** It is a ligand, which has one donor site, i.e., the ligand bound to a metal ion through a single donor site. e.g., H_2O, NH_3, etc.(ii) **Didentate** It is the ligand. which have two donor sites.



(oxalate ion)
(ox)



(ethylene diammine)
(en)

(iii) **Polydentate** It is the ligand, which have several donor sites. e.g., $[EDTA]^{4-}$ is hexadentate ligand.

(iv) **Ambidentate ligands** These are the monodentate ligands which can ligate through two different sites, e.g., NO^-_2, SCN^-, etc.

(v) **Chelating ligands** Di or polydentate ligands cause cyclisation around the metal atom which are known as chelates ,such ligands Uses two or more donor atoms to bind a single metal ion and are known as chelating ligands.

More the number of chelate rings, more is the stability of complex.

The stabilisation of coordination compounds due to chelation is known as **chelate effect**.

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

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

IUPAC Naming of Complex Compounds

1. Name of the compound is written in two parts (i) name of cation, and (ii) name of anion.
2. The cation is named first
3. The dissimilar ligands are named in alphabetical order before the name of central metal atom.
4. For more then one similar ligands. the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.
5. If the complex part is anion, the name of the central metal ends with suffix ‘ate’.
6. Names of the anionic ligands end in ‘0’, names of positive ligands end with ‘ium’ and names of neutral ligands remains as such. But exception are there as we use aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO.
7. Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses.
8. The name of the complex part is written as one word.
9. If the complex ion is a cation, the metal is named same as the element.
10. The neutral complex molecule is named similar to that of the complex cation. eg.

(i) $[Cr(NH_3)_3(H_2O)_3]Cl_3$	triamminetriaquachromium (III) chloride
(ii) $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris (ethane-l,2-diamine) cobalt (III) sulphate
(iii) $[Ag(NH_3)_2]$ $[Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I)
(iv) K_4 $[Fe(CN)_6]$	potassium hexacyanoferrate (II)
(v) $[Pt(NH_3)_2CI(NO_2)]$.	diamminechloridonitrito – N- platinum(II)
(vi) K_3 $[Cr(C_2O_4)_3]$	potassium trioxalatochromate (III)
(vii) $[CoCI_2(en)_2]CI$	dichloridobis(ethane1, 2diammine)cobalt(III) chloride

Bonding in Coordination Compounds

Werner’s Theory-Metals exhibit two types of valencies in the formation of complexes.

These are primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.

2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

Valence Bond Theory.(i) The suitable number of atomic orbitals of central metal ion (s, p, d) hybridise to provide empty hybrid orbitals.

(ii) These hybrid orbitals accept lone pair of electrons from the ligands and are directed towards the ligand positions according to the geometry of the complex.

(iii) When inner d-orbitals i.e. (*n*-1) d orbitals are used in hybridization, the complex is called – ***inner orbital*** complex., they are formed due to strong field ligands or low spin ligands and hybridisation is d^2sp^3. eg $[Fe(CN)_6]^{3-}$

(iv) **outer orbital complexes** When outer n d-orbital are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation is sp^3d^2. They have octahedral shape. $[CoF_6]^{3-}$.

Tetrahedral complex: A complex in which central atom/cation involves sp^3 hybridisation.

Square planar complex: A complex which has a flat structure and central atom/ion has dsp^2 hybridisation.

(v) There are two types of ligands namely strong field and weak field ligands. A strong field ligand is capable of forcing the electrons of the metal atom/ion to pair up (if required). Pairing is done only to the extent which is required to cause the hybridization possible for that Co-ordination number. A weak field ligand is incapable of making the electrons of the metal atom/ ion to pair up.

Strong field ligands : CN^-, CO, en, NH_3,H_2O, NO^-, Py.

Weak field ligands : I^-, Br^-, Cl^-, F^-, NO_3^-, OH^-, $C_2O_4^{2-}$, H_2O

Magnetic Properties A substance which do not contain any unpaired electron is not attracted by magnet. It is said to be diamagnetic. On the other hand, a substance which contains one or more unpaired e- in the electrons in the d-orbitals, is attracted by a magnetic field. It is said to be paramagnetic. Paramagnetism can be calculated by the expression, $\mu_s = \sqrt{n(n+2)}$ where μ = magnetic moment. *S* = spin only value and *n*= number of unpaired electrons.

Hence, if n = 1, $\mu_s = \sqrt{1(1+2)} = 1.73$ B.M, if n = 3 $\mu_s = \sqrt{3(3+2)} = 3.87$ B.M and so on

Geometry (shape) **and magnetic nature of some of the complexes** (Application of valence bond theory)

Crystal Field Theory (CFT): In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules. Due to approach of ligands, the five-degenerate d-orbitals split in two set of orbital t_{2g} and e_g,splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between t_{2g} and e_g level is designated by Δ and is called **crystal field splitting energy.**]

Spectrochemical series

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^-$$

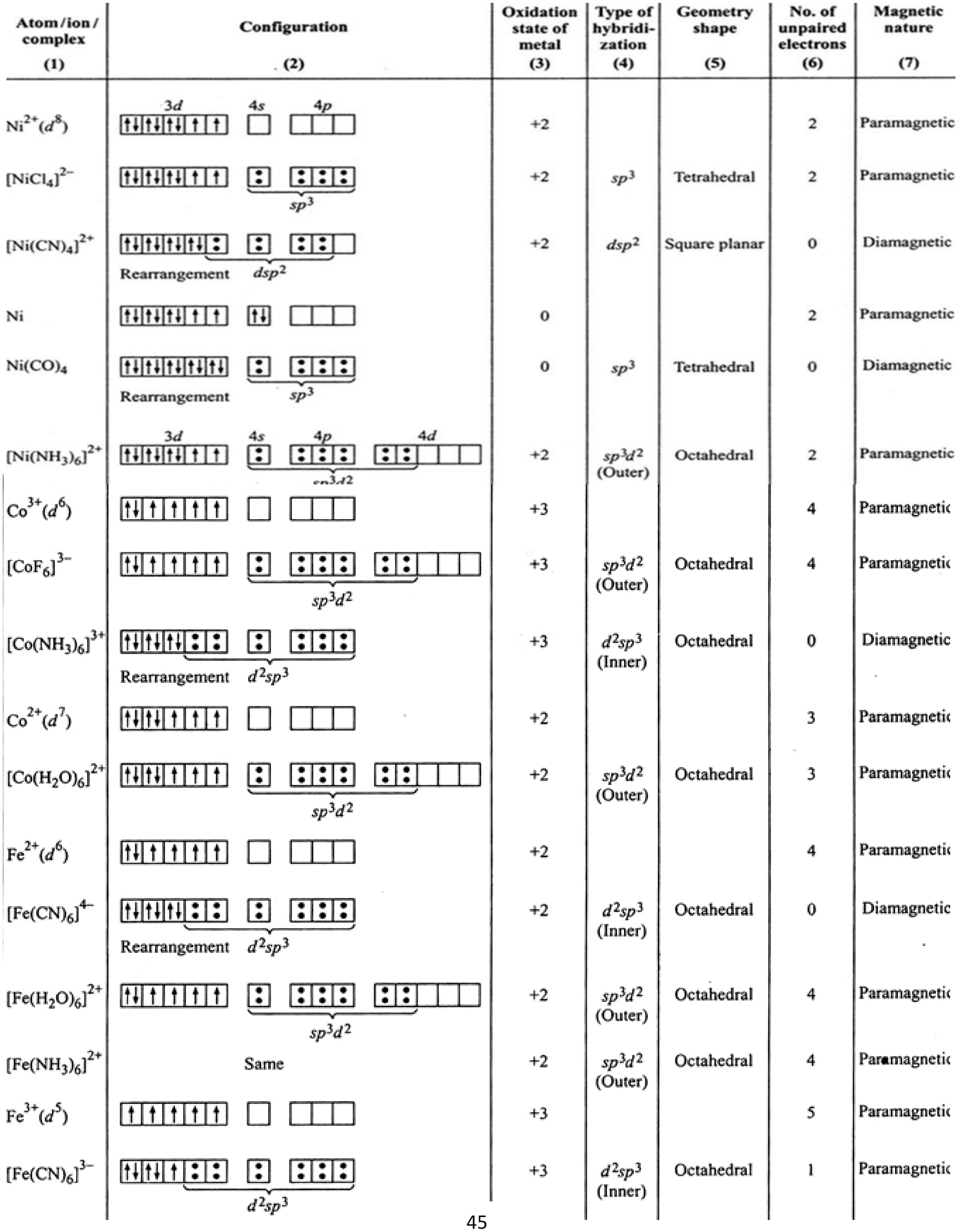
$$< C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO.$$

Crystal field splitting in octahedral complexes energy separation is denoted by Δ_o .In octahedral complexes, the six-ligands approach the central metal ion along the axis of $d_{x^2-y^2}$ and d_{z^2} orbitals.

Energy of e_g set of orbitals > energy of t_{2g} set of orbitals.

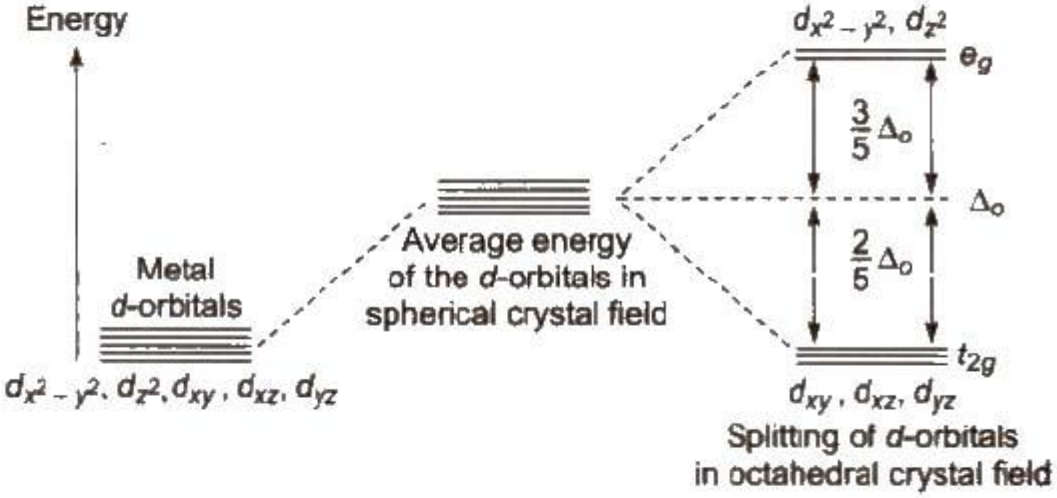
The energy of e_g orbitals will increase by (3/5) Δ_o and t_{2g} will decrease by (2/5) Δ_o.

If Δ_o < P, the fourth electron enters one of the e_g orbitals giving the **configuration t_{2g}^3 e_g^1.**



Atom/ion/ complex (1)	Configuration (2)	Oxidation state of metal (3)	Type of hybridi-zation (4)	Geometry shape (5)	No. of unpaired electrons (6)	Magnetic nature (7)
$Ni^{2+}(d^8)$	3d ↑↓ ↑↓ ↑↓ ↑ ↑ 4s ☐ 4p ☐ ☐ ☐	+2			2	Paramagnetic
$[NiCl_4]^{2-}$	↑↓ ↑↓ ↑↓ ↑ ↑ •• •• •• •• sp^3	+2	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2+}$	↑↓ ↑↓ ↑↓ ↑↓ •• •• •• •• ☐ Rearrangement dsp^2	+2	dsp^2	Square planar	0	Diamagnetic
Ni	↑↓ ↑↓ ↑↓ ↑ ↑ ↑↓ ☐ ☐ ☐	0			2	Paramagnetic
$Ni(CO)_4$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ •• •• •• •• Rearrangement sp^3	0	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(NH_3)_6]^{2+}$	3d ↑↓ ↑↓ ↑↓ ↑ ↑ 4s •• 4p •• •• •• 4d •• •• ☐ ☐ ☐ sp^3d^2	+2	sp^3d^2 (Outer)	Octahedral	2	Paramagnetic
$Co^{3+}(d^6)$	↑↓ ↑ ↑ ↑ ↑ ☐ ☐ ☐ ☐	+3			4	Paramagnetic
$[CoF_6]^{3-}$	↑↓ ↑ ↑ ↑ ↑ •• •• •• •• •• •• ☐ ☐ ☐ sp^3d^2	+3	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$	↑↓ ↑↓ ↑↓ •• •• •• •• •• •• Rearrangement d^2sp^3	+3	d^2sp^3 (Inner)	Octahedral	0	Diamagnetic
$Co^{2+}(d^7)$	↑↓ ↑↓ ↑ ↑ ↑ ☐ ☐ ☐ ☐	+2			3	Paramagnetic
$[Co(H_2O)_6]^{2+}$	↑↓ ↑↓ ↑ ↑ ↑ •• •• •• •• •• •• ☐ ☐ ☐ sp^3d^2	+2	sp^3d^2 (Outer)	Octahedral	3	Paramagnetic
$Fe^{2+}(d^6)$	↑↓ ↑ ↑ ↑ ↑ ☐ ☐ ☐ ☐	+2			4	Paramagnetic
$[Fe(CN)_6]^{4-}$	↑↓ ↑↓ ↑↓ •• •• •• •• •• •• Rearrangement d^2sp^3	+2	d^2sp^3 (Inner)	Octahedral	0	Diamagnetic
$[Fe(H_2O)_6]^{2+}$	↑↓ ↑ ↑ ↑ ↑ •• •• •• •• •• •• ☐ ☐ ☐ sp^3d^2	+2	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
$[Fe(NH_3)_6]^{2+}$	Same	+2	sp^3d^2 (Outer)	Octahedral	4	Paramagnetic
$Fe^{3+}(d^5)$	↑ ↑ ↑ ↑ ↑ ☐ ☐ ☐ ☐	+3			5	Paramagnetic
$[Fe(CN)_6]^{3-}$	↑↓ ↑↓ ↑ •• •• •• •• •• •• d^2sp^3	+3	d^2sp^3 (Inner)	Octahedral	1	Paramagnetic

If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with **configuration $t^4_{2g}\ e^0_g$.** (where, P = energy required for e^- pairing in an orbital). Ligands which produce this effect are known as strong field ligands and form low spin complexes.



Crystal field splitting in tetrahedral complexes , four ligands may be imagined to occupy the alternate comers of the cube and the metal ion at the center of the cube.

Energy of t_{2g} set of orbitals > Energy of e_g set of orbitals. In such complexes d – orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Colour in Coordination Compounds

The crystal field theory attributes the colour of the coordination compounds due to d-d transition of the electron, i.e., electron jump from t_{2g} level to higher e_g level.

Assertion and Reason Type Questions

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) 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 (A): Toxic metal ions are removed by the chelating ligands.**
2. **Reason (R): Chelate complexes tend to be more stable.**
3. **Ans:** (a) When a solution of chelating ligand is added to solution containing toxic metals ligands chelates the metal ions by formation of stable complex.

2. Assertion (A): $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature.

Reason (R): Unpaired electrons are present in their d-orbitals.

Ans: (b) In the complexes, Co exists as Co^{2+} and Fe as Fe^{2+}. Both of the complexes become stable by oxidation of metal ion to Co^{3+} and Fe^{3+}.

3. Assertion (A): Linkage isomerism arises in coordination compounds containing ambidentate ligand.

Reason (R): Ambidentate ligand has two different donor atoms.

Ans: (a) Linkage isomerism arises due to two different donor atoms in ambidentate ligand.

4. Assertion (A): $(Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

Reason (R): Because it has d^2sp^3 type hybridisation.

Ans: (d) $(Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.

5. Assertion(A) : $[Co(NH_3)Br]SO_4$ gives white precipitate with barium chloride.

Reason(R) : The complex dissociates in the solution to give Br^- and SO_4^{2-} . (Ans - c)

6. Assertion(A) : According to crystal field theory during complex formation, the d – orbitals split and form two sets of orbitals t_{2g} and e_g.

Reason(R) : Splitting of d - orbitals occurs only in case of strong field ligands. (Ans - c)

7. Assertion(A) : $[Fe(H_2O)_6]^{2+}$ is sp^3d^2 hybridised and paramagnetic complex ion.

Reason(R) : It has four unpaired electrons. (Ans - a)

8. Assertion(A) : Low spin tetrahedral complexes are not formed.

Reason(R) : For tetrahedral complexes, CFSE is lower than pairing energy. (Ans - a)

9. Assertion(A) : $[FeF_6]^{3-}$ is paramagnetic.

Reason (R): F^- is a weak field ligand, hence does not cause pairing of electrons. (Ans - a)

MCQ

1. Which of the following is a complex of metal other than transition metal?

(a) Haemoglobin (b) Chlorophyll (c) Ferrocene (d) Vitamin B12

2. Which of the following is not a double salt but a coordinate compound?

(a) $KCl.MgCl_2.6H_2O$ (b) $FeSO_4.(NH_4)_2SO_4.6H_2O$

(c) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ (d) $4KCN.Fe(CN)_2$

3. The donor atoms in ethylenediaminetetraacetate ion is

(a) two N and two O (b) two N and four O (c) four N and two O (d) three N and three O

4. The complex ion $[Cu(NH_3)_4]^{+2}$ is

(a) tetrahedral and paramagnetic (b) tetrahedral and diamagnetic

(c) square planar and paramagnetic (d) square planar and diamagnetic

5. The hybrid state of Co in high spin complex, $K_3[CoF_6]$ is

(a) sp^3d^2 (b) sp^3 (c) d^2sp^3 (d) sp^3d

6. In an octahedral crystal field, the t_{2g} orbital are

(a) raised in energy by 0.4 Δo (b) lowered in energy by 0.4 Δo

(c) raised in energy by 0.6 Δo (d) lowered in energy by 0.6 Δo

7. If $\Delta o < P$, then the correct electronic configuration for d^4 system will be

(a) $t_{2g}{}^4\ eg^0$ (b) $t_{2g}{}^3\ eg^1$ (c) $t_{2g}{}^0\ eg^4$ (d) $t_{2g}{}^2\ eg^2$

8. The tetrahedral complexes are generally high spin. This is because

(a) $\Delta_t < P$ (b) $\Delta_t > P$ (c) $\Delta_t = P$ (d) none of these

9.The primary and secondary valency of copper in the complex $[Cu(NH_3)_4]SO_4$ are

(a) 2, 4 (b) 4, 2 (c) 0, 4 (d) 1, 4

10. The hybridization state of the Cu in the compound [Cu(NH3)4]SO4 is

(a) sp^3 (b) $sp^2\ d$ (c) $sp^3\ d^2$ (d) dsp^2

11. Which of the following statement is correct?

(a) $[Cu(NH_3)_4]^{2+}$ is diamagnetic while $[Fe(CN)_6]^{4-}$ is paramagnetic

(b) $[Cu(NH_3)_4]^{2+}$ is paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic

(c) both are paramagnetic (d) both are diamagnetic

Answer key: 1 b , 2 d , 3 b , 4 c , 5 a , 6 b , 7 b , 8 a , 9 a , 10 d , 11 b .

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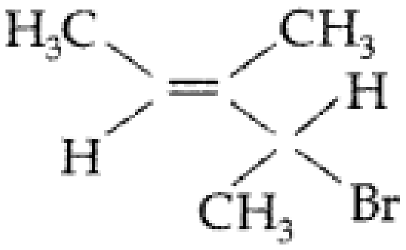
ORGANIC CHEMISTRY

Nomenclature of Organic Compound

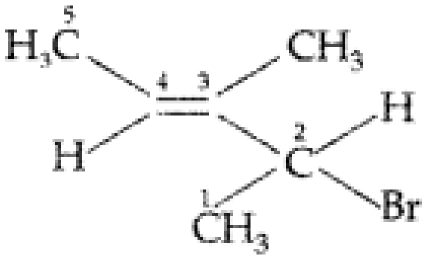
PREVIOUSLY ASKED QUESTIONS (IN AISSCE) ON IUPAC NOMENCLATURE OF ORGANIC COMPOUNDS & STRUCTURE

(1) Haloalkanes & Haloarenes

1. Give the IUPAC name of the following compound : (All India 2010)

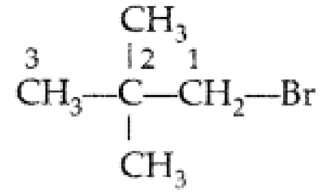


Answer:



IUPAC name : *2-Bromo-3-methylpent-3-ene*

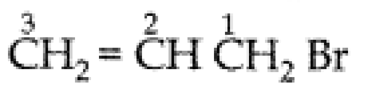
2. Write the IUPAC name of the following compound : $(CH_3)_3\,CCH_2Br$ (Delhi 2010)
   Answer:



$$\overset{3}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_2}-Br$$

   IUPAC name : 1-bromo-2, 2-dimethyl propane

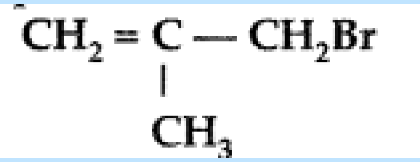
3. Write the IUPAC name of the following compound : $CH_2 = CHCH_2Br$ (All India 2010)
   Answer:



$$\overset{3}{C}H_2=\overset{2}{C}H\,\overset{1}{C}H_2\,Br$$

   IUPAC name : l-Bromo-prop-2-ene

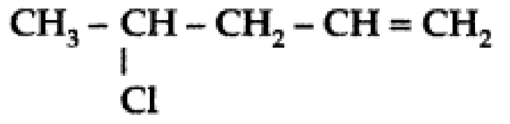
4. Give the IUPAC name of the following compound. (Delhi 2012)



$$CH_2=\underset{CH_3}{C}-CH_2Br$$

   Answer: IUPAC name : 3-bromo-2-methyl propene

5. Write the IUPAC name of

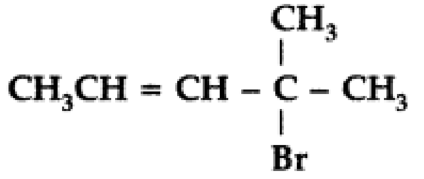


$$CH_3-\underset{Cl}{CH}-CH_2-CH=CH_2$$

(Delhi 2013)

Answer: IUPAC name : 4-chloropent-1-ene

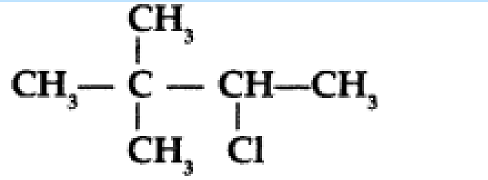
6. Write the IUPAC name of (Delhi 2013)



$$CH_3CH=CH-\underset{Br}{\overset{CH_3}{C}}-CH_3$$

Answer: IUPAC name : 4-bromo-4-methylpent-2-ene

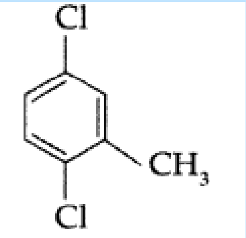
7. Write the IUPAC name of the following compound: (All India 2013)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Cl}{CH}-CH_3$$

   Answer: IUPAC name : 2-Chloro-3, 3-dimethylbutane.

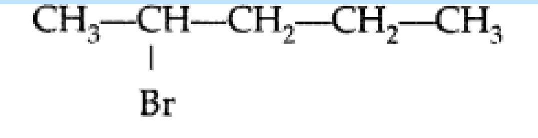
8. Write the IUPAC name of the following compound : (All India 2013)



Answer: IUPAC name : 2, 5-dichlorotoluene

9. Draw the structure of 2-bromopentane. (Comptt. Delhi 2014)

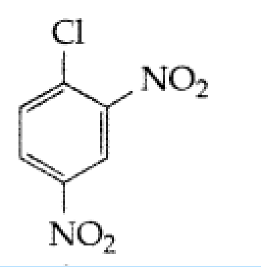
Answer:



$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_2-CH_3$$

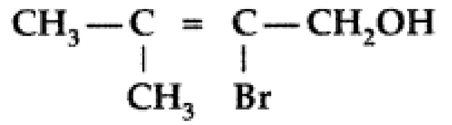
10. Write the structure of 2, 4-dinitrochlorobenzene. (Delhi 2017)

Answer:



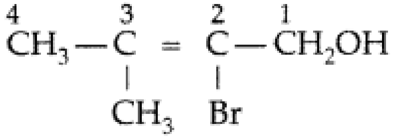
(2) alcohols, Phenols & Ethers

1. Give the IUPAC name of the following compound : (Delhi 2009)



$$CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{Br}{|}}{C}-CH_2OH$$

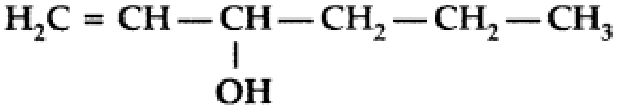
Answer:



$$\overset{4}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{3}{C}}=\underset{\underset{Br}{|}}{\overset{2}{C}}-\overset{1}{C}H_2OH$$

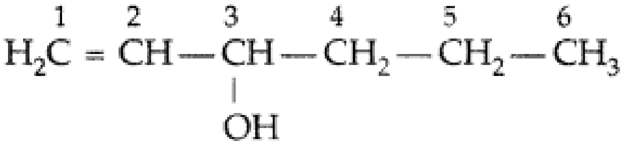
IUPAC name : 2-Bromo-3-methyl-but-2-ene-1-ol

2. Give the IUPAC name of the following (All India 2009)



$$H_2C = CH - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_2 - CH_3$$

Answer:

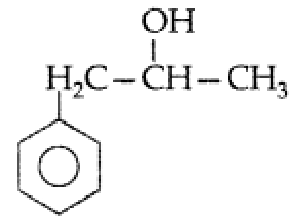


$$\overset{1}{H_2C} = \overset{2}{CH} - \underset{\displaystyle OH}{\underset{|}{\overset{3}{CH}}} - \overset{4}{CH_2} - \overset{5}{CH_2} - \overset{6}{CH_3}$$

IUPAC name: Hex-1-en-2-ol or 3-Hexenol

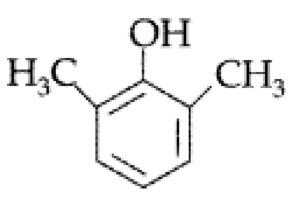
3. Write the structure of the molecule of a compound whose IUPAC name is 1-phenylpropan-2-ol. (All India 2010)

Answer: 1-phenylpropan-2-ol



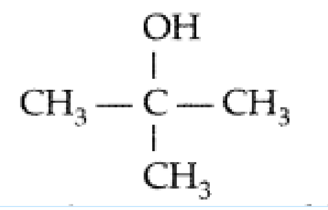
4. Draw the structure of 2, 6-Dimethylphenol. (All India 2011)

Answer:



5. Draw the structural formula of 2-methylpropan- 2-ol molecule. (Delhi 2012)

Answer:

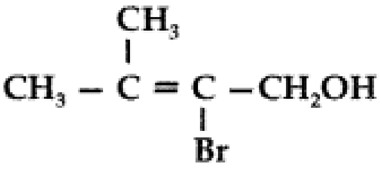


$$CH_3 - \overset{\displaystyle OH}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}} - CH_3$$

6. Draw the structure of hex-l-en-3-ol compound. (Delhi 2012)

Answer: $CH_2 = CH - CH(OH) - CH_2 - CH_2 - CH_3$

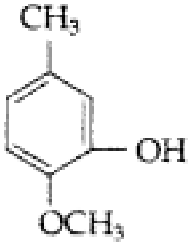
7. Write the IUPAC name of the following : (Comptt. All India 2012)



$CH_3-\overset{CH_3}{\overset{|}{C}}=\underset{Br}{\underset{|}{C}}-CH_2OH$

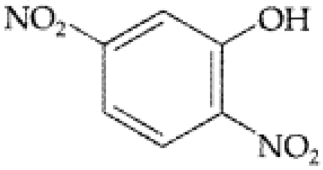
   Answer: IUPAC name : 2-Bromo-3-methyl but-2-en-l-ol.

8. Write IUPAC name of the following (Comptt. All India 2013)



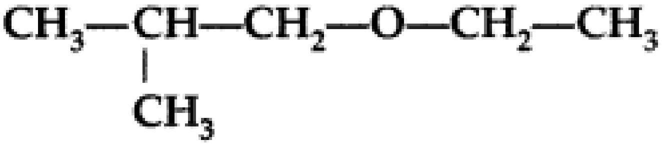
   Answer: IUPAC name : 2-Methoxy-5-methyl phenol

9. Write the IUPAC name of the given compound (Delhi 2015)



   Answer: 2, 5-dinitrophenol.

10. Write the IUPAC name of given compound: (All India 2015)

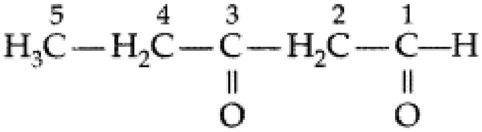


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-CH_3$

   Answer: IUPAC name : 1-Ethoxy-2-methylpropane

(3) Aldehydes, Ketones & Carboxylic acids

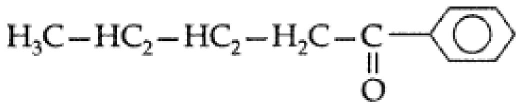
1. Write the structure of 3-oxopentanal. (Delhi 2009)
   Answer:



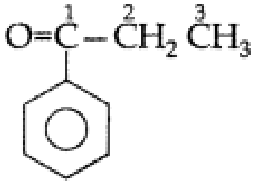
$\overset{5}{H_3C}-\overset{4}{H_2C}-\underset{O}{\underset{\|}{\overset{3}{C}}}-\overset{2}{H_2C}-\underset{O}{\underset{\|}{\overset{1}{C}}}-H$

3-oxopentanal

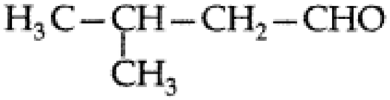
2. Write the structural formula of 1-phenylpentan- 1-one. (All India 2009)
   Answer:1-Phenylpentan-1-one



3. Draw the structural formula of 1-phenyl propan- 1-one molecule. (Delhi 2010)
Answer: 1-phenyl propan-1-one

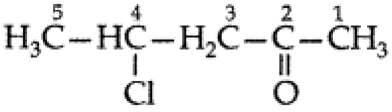


4. Draw the structure of 3-methylbutanal. (Delhi 2011)
Answer:



$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CHO$$

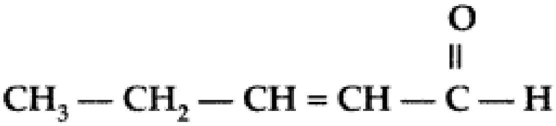
5. Draw the structure of 4-chloropentan-2-one. (All India 2011)
Answer:



$$H_3\overset{5}{C}-H\underset{\displaystyle Cl}{\underset{|}{\overset{4}{C}}}-H_2\overset{3}{C}-\underset{\displaystyle O}{\underset{\|}{\overset{2}{C}}}-\overset{1}{C}H_3$$

4-chloropentane-2-one

6. Write the IUPAC name of the following : (All India 2012)

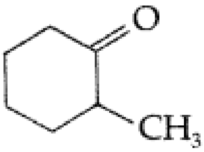


$$CH_3-CH_2-CH=CH-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

Answer: IUPAC name : Pent-2-enal

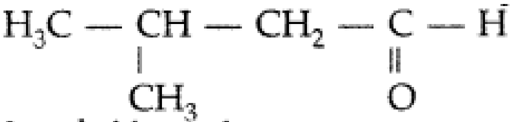
7. Write the IUPAC name of Ph – CH = CH – CHO. (All India 2012)
Answer: IUPAC name : 3-phenylprop-2-enal

8. Write the IUPAC name of the following : (Comptt. All India 2012)



Answer: IUPAC name : 2-methylcyclohexanone

9. Write the structure of 3-methyl butanal. (Delhi 2013)
Answer:



$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-H$$

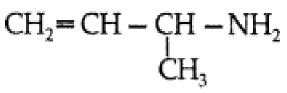
3-methyl butanal

10. Write the IUPAC name of the following: (Comptt. All India 2015)
CH_3— CH_2 — CHO
Answer: IUPAC name : Propan-1-al

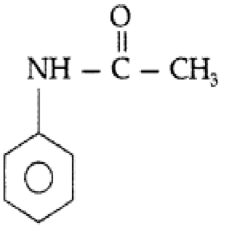
(4)Organic compounds containing nitrogen (Amines)

1. Give the IUPAC name of H2N — CH2—CH2—CH = CH2. (Delhi 2010)
   Answer: IUPAC name : But-3-ene-1-amine

2. Give IUPAC names of the following compounds : (Comptt. Delhi 2012)

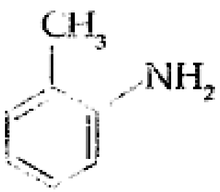
(a) 

$CH_2=CH-\underset{CH_3}{CH}-NH_2$

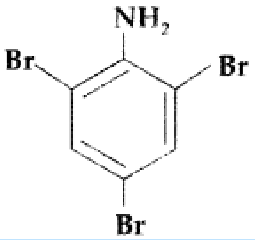
(b) 

Answer: (a) IUPAC name : Methylprop-2-en-1-amine
(b) IUPAC name : N-Phenyl acetamide.

3. Write the structure of 2-aminotoluene. (All India 2013)
   Answer:

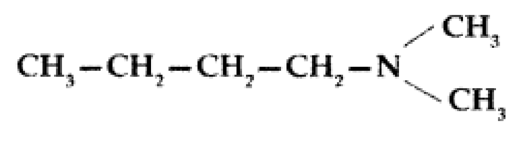


4. Write the structure of N-methylethanamine. (All India 2013)
   Answer: Structure of N-methylethanamine : $H_3C—H_2C—NH—CH_3$
5. Write the structure of prop-2-en-1-amine. (All India 2013)
   Answer: $H_2C=CH—H_2C—NH_2$
6. Write the IUPAC name of the given compound: (Delhi 2016)



   Answer: 2, 4, 6-Tribromoaniline
7. Write IUPAC name of the following compound: $(CH_3CH_2)_2NCH_3$ (Delhi 2017)
   Answer: N-Ethyl-N-methylethanamine
8. Write the IUPAC name of the following compound: (Comptt. All India 2017)
   $CH_3NHCH(CH_3)_2$
   Answer: IUPAC name: N-Methylpropan-2-amine

9. Write IUPAC name of the following compound : (Comptt. All India 2017)



$CH_3-CH_2-CH_2-CH_2-N(CH_3)_2$

Answer: IUPAC name : N,N-Dimethylbutanamine.

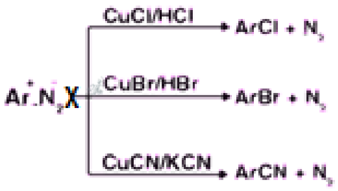
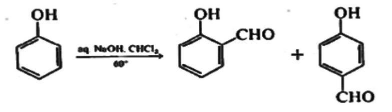
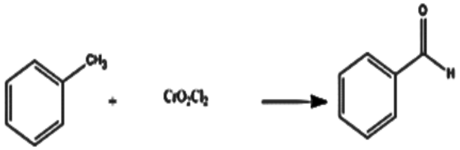
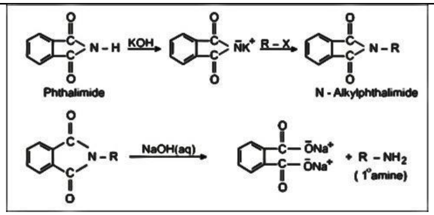
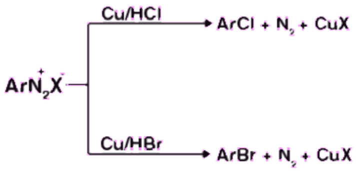
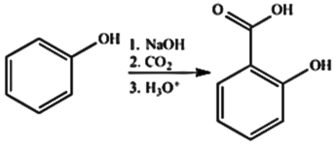
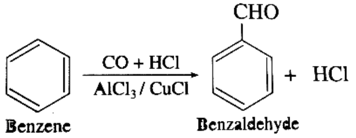
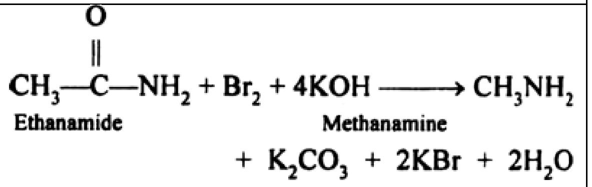
10. Write the IUPAC name of the following compound: (Delhi 2017)

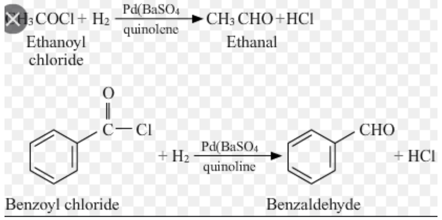
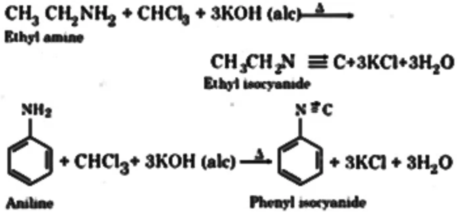
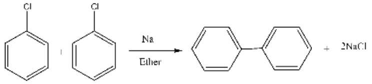
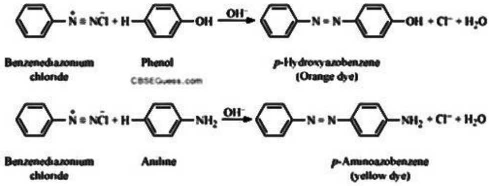
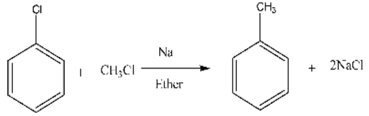
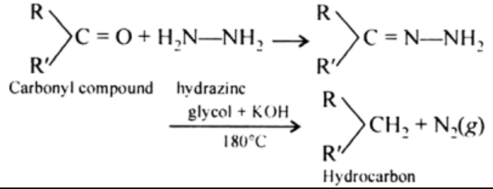
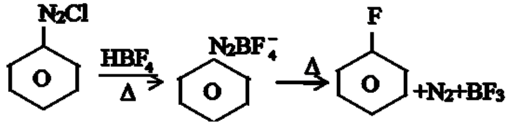
$(CH_3)_2N\text{-}CH_2CH_3$

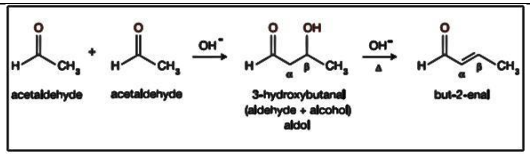
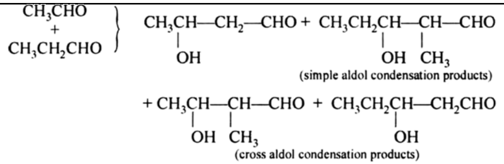
Answer: IUPAC name: N,N-Dimethylethanamine

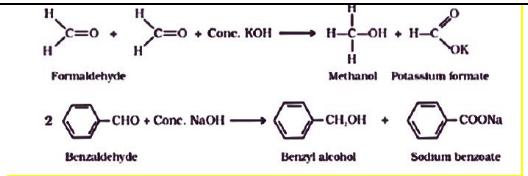
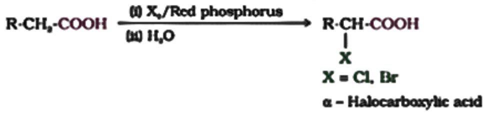
****

Named Reaction

Haloalkane & Haloarenes	**Alcohols, Phenols and Ethers**	**Aldehydes, ketones and Carboxylic acids**	**Nitrogen Compounds**
Sandmeyer Reaction: Preparation of Haloarenes: Aryl diazonium salts are converted to aryl halides in presence of halo acid and copper halide.	Reimer-Tiemann Reaction: Properties of Phenols: Phenol is converted to Salicylaldehyde when treated with chloroform in the presence of sodium hydroxide.	Etard reaction: Preparation of Aromatic aldehyde: Toluene is converted to benzaldehyde when oxidized with chromyl chloride gas.	Gabriel phthalimide synthesis: Preparation of 1°amines. Phthalimide is converted to 1 amines when treated with ethanolic KOH which produces potassium salt of phthalimide when heated with alkyl halide followed by alkaline hydrolysis.
			
Gattermann Reaction: Preparation of Haloarenes: Aryl diazonium salts are converted to aryl halides in presence of halo acid and copper powder.	Kolbe's Reaction: Properties of Phenols: Phenol is converted to salicylic acid when treated with CO_2 /NaOH in the presence of acidic medium.	Gatterman – Koch reaction: Preparation of Aromatic aldehyde: Benzene is converted to benzaldehyde when treated with CO and HCl in the presence of anhydrous aluminum chloride.	Hoffmann bromamide degradation reaction: Preparation of 1°amines. Amide is converted to 1 amine with one carbon less when treated with Br_2 and KOH
			 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$
Wurtz Reaction: Properties of haloalkane: When Alkyl halides react with sodium with dry ether; hydrocarbons are formed that include the double number of carbon atoms present in the halide.	Williamson Synthesis: Preparation of Ether: is an SN2 reaction in which an alkoxide ion is a nucleophile that displaces a halide ion from an alkyl halide to give ether.	Rosenmund Reduction: Preparation of Aldehyde: When Acyl chloride is hydrogenated to an aldehyde over a catalyst, known as Rosenmund catalyst which is either palladium or barium sulfate in presence of quinoline.	Carbylamine reaction: Properties of 1 amines: It is used for detection of primary amines. When 1 amine is heated with alc KOH and chloroform, the isocyanide (carbylamine) is formed which are foul smelling substances.

$R-X + 2Na + X-R' \xrightarrow{\text{dry ether}} R-R + 2NaX$ Alkan Eg : $C_2H_5-Cl + 2Na + Cl-C_2H_5 \xrightarrow{\text{dry ether}} C_4H_{10}$ n-Butane	$R—X + R'ONa \longrightarrow R—O—R' + NaX$ Alkyl halide Sod. alkoxide Ether $CH_3I + CH_3CH_2ONa \longrightarrow CH_3—O—CH_2CH_3 + NaI$ Methyl iodide Sod. ethoxide Ethyl methyl ether		
Fittig Reaction: Properties of Haloarenes: Aryl halides react with sodium in dry ether to give analogous compounds where two aryl groups joined.		Clemmensen Reduction: Carbonyl group is reduced to methylene group with zinc amalgam (Zn/Hg alloy) in concentrated HCl.	Coupling Reactions: Properties of Diazonium salts: The electrophilic aromatic substitution reaction of a diazonium cation with another aromatic ring to form a diazo compound.
		$RCOR \xrightarrow[\text{HCl}]{\text{Zn-Hg}} RCH_2R + H_2O$ $CH_3CHO + 4[H] \xrightarrow[\text{HCl}]{\text{Zn-Hg}} CH_3—CH_3 + H_2O$ Ethane $CH_3COCH_3 + 4[H] \xrightarrow[\text{HCl}]{\text{Zn-Hg}} CH_3CH_2CH_3 + H_2O$ Propane	
Wurtz-Fittig Reaction: When a mixture of alkyl halide and aryl halide gets treated with sodium in dry ether, we get an alkyl arene.		Wolff Kishner Reduction: It is the reduction of carbonyl compounds to hydrocarbons by heating them with hydrazine hydrate and a base. In this process the carbonyl group (>C=O) gets converted to methylene groups (>CH2) group via >C=N. NH2 and nitrogen gas evolves out.	Balz-Schiemann Reaction: Primary aromatic amine is transformed to an aryl fluoride via a diazonium tetrafluoroborate intermediate
			
Finkelstein Reaction: Alkyl iodides are prepared easily by the reaction of alkyl chlorides with NaI in dry acetone.		Stephen reaction: This reaction involves the preparation of aldehydes (R-CHO) from nitriles (R-CN) using SnCl₂ & HCl and quenching the resulting iminium salt with	

		water (H_2O)	
 $\underset{(X=Cl, Br)}{CH_3CHXCH_3} + \underset{\text{Soluble in acetone}}{NaI} \xrightarrow{\text{acetone}} CH_3CHICH_3 + \underset{\text{Insoluble in acetone}}{NaX\downarrow}$		$RCN + SnCl_2 + HCl \longrightarrow RCH=NH \xrightarrow{H_3O^+} RCHO$	
Swarts Reaction: When alkyl chloride is heated in the presence of a metallic fluoride like AgF, Hg2F2, SbF3 or CoF2, we get alkyl fluorides.		Aldol condensation: Properties of carbonyl compounds with at least one α H: an enolate ion reacts with a carbonyl compound in the presence of acid/base catalyst to form a β-hydroxy aldehyde or β-hydroxy ketone, followed by dehydration to give a conjugated enone.	
$H_3C{-}Br + AgF \longrightarrow H_3C{-}F + AgBr$			
		Cross aldol condensation: Properties of Carbonyl compounds: When aldol condensation is carried out between two different aldehydes, or two different ketones, or an aldehyde and a ketone, then the reaction is called a cross-aldol condensation.	
		 $\left.\begin{matrix}CH_3CHO\\+\\CH_3CH_2CHO\end{matrix}\right\} \underset{OH}{CH_3CH}{-}CH_2{-}CHO + CH_3CH_2\underset{OH}{CH}{-}\underset{CH_3}{CH}{-}CHO$ (simple aldol condensation products) $+ CH_3\underset{OH}{CH}{-}\underset{CH_3}{CH}{-}CHO + CH_3CH_2\underset{OH}{CH}{-}CH_2CHO$ (cross aldol condensation products)	
		Cannizzaro reaction: Properties of Aldehydes: Aldehydes without α-hydrogen atom undergo self-oxidation and reduction reaction to give an alcohol and salt of carboxylic acid when treated with concentrated alkali (KOH).	

			
		Hell-Volhard-Zelinsky (HVZ)reaction: Properties of Carboxylic Acids: converts the carboxylic acid into an acyl halide	
		$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red phosphorus}} R\text{-}\underset{X}{CH}\text{-}COOH$ $X = Cl, Br$ α – Halocarboxylic acid	

****

CHEMICAL DISTINCTION TEST FOR ORGANIC COMPOUND

1. Distinction test for carboxylic acid - (Sodium bicarbonate test)

   R-COOH ------NaHCO3------------→ Brisk effervescence of CO2

   Phenol --------NaHCO3 -----------→No brisk effervescence

   Alcohol -------NaHCO3 -----------→ No brisk effervescence

2. Phenol
   Phenol ---------Neutral FeCl3----→ Violet colour

   RCOOH ---------Neutral FeCl3--→ No colour

   Alcohol ----------Neutral FeCl3 -→ No colour

3. Formic acid (Methanoic acid)
   Exceptionally give the test of aldehyde besides NaHCO3.

   Formic acid ----------Tollens reagent ----→ Silver Mirror

   Formic acid ----------Fehling solution ----→ Red Brown ppt of Cu2O

4. Distinction test for Aldehyde and Ketone

   Aldehyde ----------Tollens reagent-----→ Silver Mirror
   Ketone -------------Tollens reagent-----→ No colour
   Aldehyde ----------Fehling solution ---→ Red brown ppt of Cu2O
   Ketone -------------Fehling solution ---→ No colour

5. For Aliphatic and Aromatic Aldehyde
   Aliphatic aldehyde ------Fehling solution ---→ Red Brown ppt of Cu2O

   Aromatic aldehyde -----Fehling solution ---→ no colour obtained

6. Iodoform Test –
   O.C. -------I2 + NaOH -------→ CHI3 (Yellow ppt)

   Condition – (i) Any aldehyde or ketone having (CH3-CO -)- group gives this test.

   (ii) Alcohol having (CH3-CHOH-)- gives iodoform test.

   (CH3CO-)- ------- I2 + NaOH -----→ CHI3 Yellow PPT

   (CH3CHOH-)- ------- I2 + NaOH -----→ CHI3 Yellow PPT

   That is it can be used to distinguish to

   (i) Two Aldehyde
   (ii) Two Ketones
   (iii) Aldehyde and Ketones
   (iv) Two alcohol

7. Primary, secondry and tertiary alcohol – (Lucas test)
   Lucas reagent Anhyd. ZnCl2 and con. HCl

   Tertiary alcohol gives turbidity immediately while secondry alcohol gives turbidity after 5 minute while tertiary alcohol gives no turbidity at room temperature.

8. Amines - primary secondry and tertiary amines

(i) Carbyl amine test

To distinguish primary amine from secondry and tertiary amine.

Primary amine -------CHCl3 + NaOH-----→ R-NC (Foul smell)

Secondry amine -------CHCl3 + NaOH-----→ no smell

Tertiary amine -------CHCl3 + NaOH-----→ no smell

(ii) HNO2 Test –

Primary amine -----HNO2/ HCl ------→ N2(g)

Secondry amine -----HNO2/ HCl ------→ N2(g)

Tertiary amine -----HNO2/ HCl ------→ N2(g)

NOTE- Pimary Aliphatic amine and primary aromatic amine can distinguish by this test only.

Primary aliphatic amine -----HNO2/ HCl ------→ N2(g)

Primary aromatic amine -----HNO2/ HCl ------→ Coloured azo dyes after coupling reaction.

(iii) Hinsberg test – Benzene sulphonyl chloride

Primary amine -----benzene sulphonyl chloride ------→ product ----→ soluble in alkali

Secondry amine --- benzene sulphonyl chloride ----→Product -→ not soluble in alkali

Tertiary amine ----- benzene sulphonyl chloride ------→ No reaction

Practice Questions-

1. Acetic acid and ethyl alcohol
Hint:- By NaHCO3 or Iodoform

2. Phenol and Propanol
Hint:- Neutral FeCl3

3. Benzoic acid and phenol
Hint:- By NaHCO3 or by neutral FeCl3

4. Formic acid and acetic acid
Hint:- either by T.R. or F.S.

5. Formaldehyde and formic acid
Hint:- By NaHCO3 test

6. Propanal and propanone
Hint:- either by T.R. or F.S.

7. Ethanal and propanal
Hint:- Iodoform test

8. Acetophenone and benzophenone
Hint:- Iodoform test

9. 1-butanol and 2- butanol
Hint:- Iodoform test

10. Ethanol and ethyl ethanoate
Hint:- Iodoform test

11. Benzaldehyde and propanaldehyde
Hint:- By F.S. test

12. Benzaldehyde and acetaldehyde
Hint:- By F.S. test and iodoform test

13. Ethyl amine and N-methyl ethyl amine
Hint:- By carbyl amine test

14. Methanamine and Aniline
Hint:- By HNO2 test

15. N,N-demethyl amine and N-methyl amine
Hint:- By HNO2 test or by Hinsberg test

****

SPECIFIC TEST

1) Phenol Test

(a) organic compound(O.C.) + Neutral Fecl$_3$ → Violet or Green color solution

(b) organic compound(O.C.) + Benzene diazonium chloride(B.D.C.)+ ice → Orange color dye

2) Carboxylic acid test

(a)O.C. + $NaHCO_3$(sol.) → Brisk effervescence is evolved → COOH is present

(b) O.C. + ethanol + few drops of conc. H_2SO_4 → Fruity smell of ester is formed – COOH is present

3**) Test of 1^0, 2^0, 3^0 alcohol (Lucas Test)**

Organic Compound + Lucas Reagent(conc. HCL + $ZnCl_2$) →

(a) If turbudity is formed at once = 1^0 alcohol
(b) If turbudity is formed within 5 minutes = 2^0 alcohol
(c) If no turbudity is formed at room temperature = 3^0 alcohol

4) 1^0 alcohol test (esterification test)

(a) O.C. + carboxylic acid + conc.H2SO4 → fruity smell of ester is formed   (1^0 alcohol is present)

5) Test of aldehyde

(a) O.C. Tollen's reagent + Heat→ Silvermiror is formed → Aldehyde is confirmed

(b) O.C. + Fehling solution + heat → Reddish brown precipitate is formed → Aldehyde is confirmed

6) Test of Formic Acid (HCOOH)(Methanoic Acid)

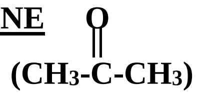
Formic acid + Tollen's Reagent $\xrightarrow{\text{placed (in water)}}$ A silver minor is formed after few minutes

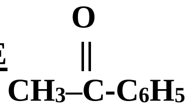
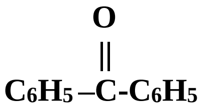
7) Difference between 1^0, 2^0 and 3^0 Amines (Hinsberg test)

$C_6H_5SO_2Cl$ is known as Hinsberg Reagent (Benzene Sulphonyl Chloride)

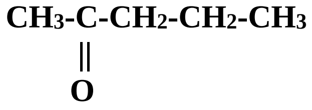
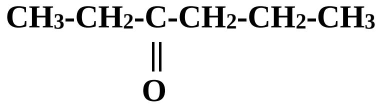
O.C. Containing amines + Hinsberg Reagent

O.C. Containing Amines		
1^0 amine is present	**2^0 amine is present**	**3^0 amine is present**
A white precipitate is formed which is soluble in aq. KOH.	A white precipitate is formed which is insoluble in aq. KOH.	No precipitate is formed.

PROPANAL **(CH_3CH_2CHO)**	**PROPANONE**  $(CH_3-\overset{O}{\overset{\|}{C}}-CH_3)$
(a) It gives silver mirror with Tollen's reagent. (b) It gives reddish brown precipitate of Cu_2O when react with fehling solution (A and B). (c) It does not give this test.	(a) It does not give this test. (b) It does not give this test. (c) It gives yellow precipitate of idoform and NaOH (idoform test).

ACETOPHENONE  $CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5$	**BENZOPHENONE**  $C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$
It gives yellow precipitate of Idoform with I_2 and NaOH. (Idoform Test)	It does not give this test.

PHENOL	**BENZOIC ACID**
(a) It gives violet or green colour with $FeCl_3$ solution. (b) It does not give this test.	(a) It does not give this test. (b) It gives brisk effervescence of CO_2 with $NaHCO_3$.

Pentan-2-one	**Pentan-3-one**
 $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$ It gives yellow precipitate idoform with I_2 and NaOH (Idoform test).	 $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$ It does not give this test.

BENZALDEHYDE	**ACETOPHENONE**
(a) It does not give this test. (b)It gives silver mirror with Tollen's reagent.	(a) It gives yellow precipitate of idoform with I_2 and NaOH. (Idoform Test).

	(b)It does not give this test.

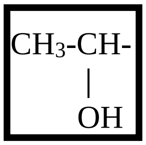
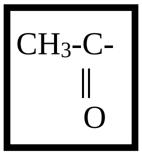
BENZOIC ACID	**ETHYL BENZOATE**
(a) It gives brisk effervescence of CO_2 with $NaHCO_3$ solution.	(a) It does not give this test.

FORMALDEHYDE	**ACETALDEHYDE**
(a) It does not give this test.	(a) It gives yellow precipitate of idoform with I_2 and NaOH. (Idoform Test).

Methanol (CH_3OH)	**Ethanol (CH_3CH_2OH)**
(a) It does not give this test.	(a) It gives yellow precipitate of idoform with I_2 and NaOH. (Idoform Test).

Ethyl amine	**Dimethylamine**
(a) It gives offensive smell of Isocyamide when react with chloroform and alc.(KOH) (Carbylamine test).	(a) It does not give this test.

8) Idoform Test (M.Imp)

Compound containing  $\boxed{\begin{array}{l}CH_3\text{-}CH\text{-}\\ \qquad\;\; | \\ \qquad\; OH\end{array}}$ group and  $\boxed{\begin{array}{l}CH_3\text{-}C\text{-}\\ \qquad \| \\ \qquad O\end{array}}$ group

gives yellow precipitate of Idoform (CHI_3) when react with I_2 and NaOH.

Such as Ethanol, Ethanal, Propanone, Butanone, propan-2-ol, butan-2-ol, acetone, pentan-2-one, Acetophenone.

9) All Primary amines gives Carbylamine test

1^0 amine + chloroform ($CHCL_3$) + KOH ➔ An offensive smell of Isocyanide is evolved.

10) Test of aniline and phenol (Azodye test)

Aniline + Benzene diazonium chloride ➔ Yellow coloured dye is formed (Azodye)

Phenol + B.D.C. (Benzenedicarboxylate)➔ Orange colour dye is formed (Azodye)

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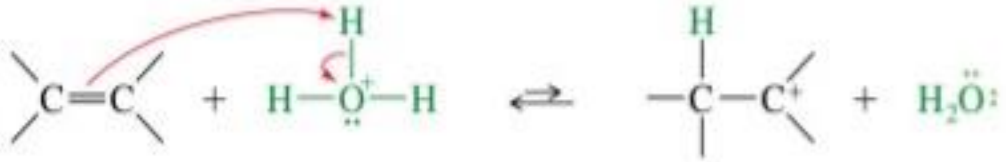
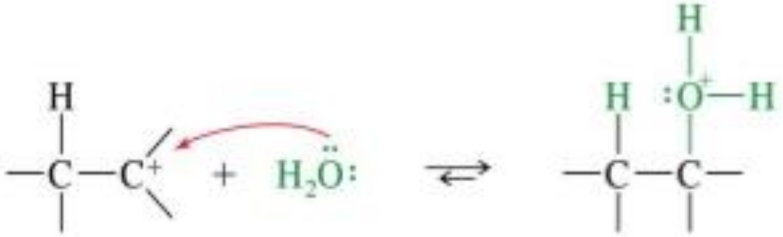
Mechanism for Hydration

Step 1: Protonation of the double bond forms a carbocation.



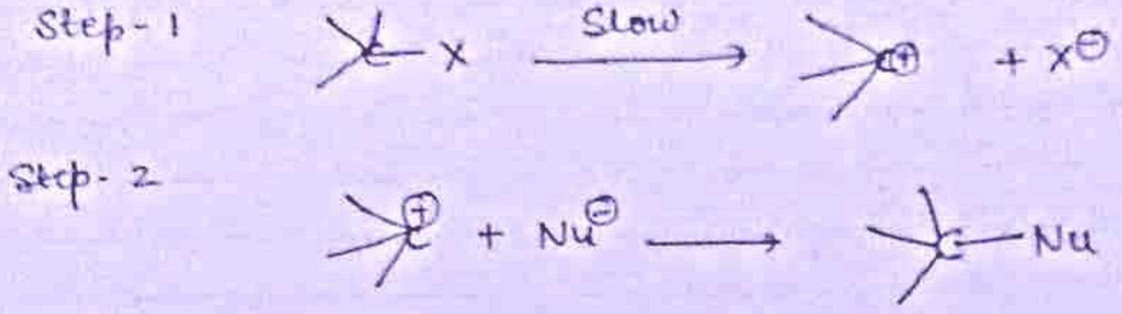
Step 2: Nucleophilic attack by water.



Step 3: Deprotonation to the alcohol.

SN, Mechanism (2 step, 1st order reaction)

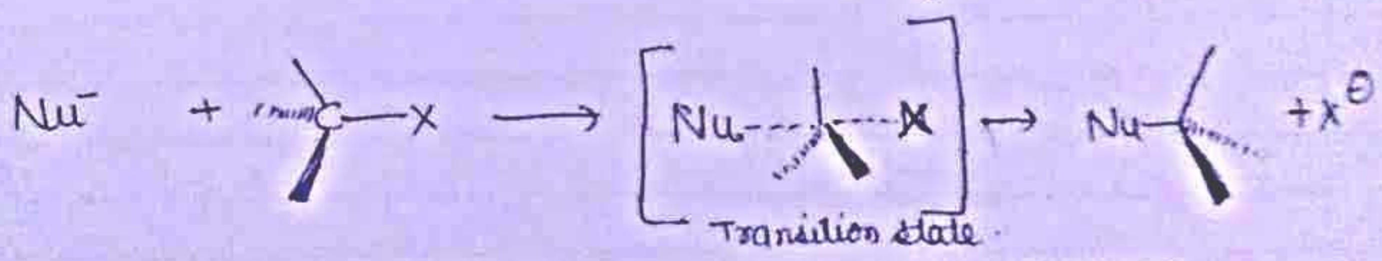
Racemization takes place



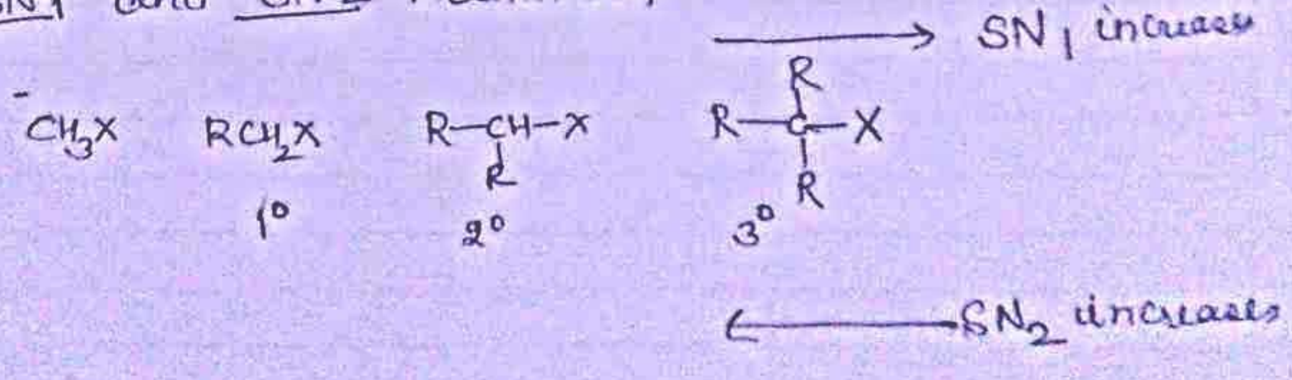
→

SN 2 Mechanism (one step, second order, Transition state)

Inversion of configuration takes place



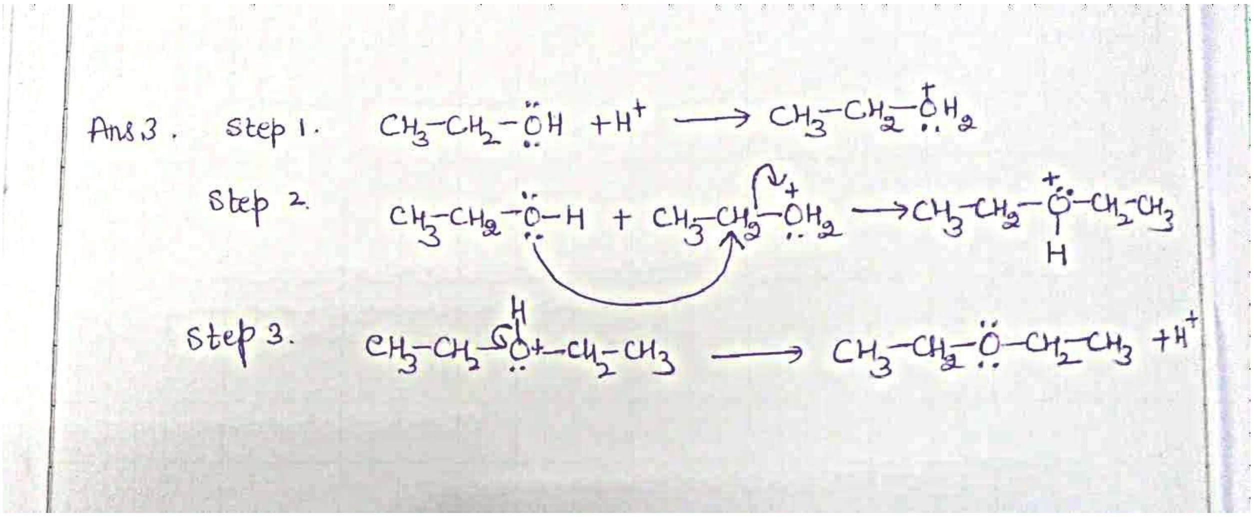
ORDER OF REACTIVITY OF AlKYL HALIDES TOWARDS SN1 and SN 2 MECHANISM



Q1 Write the mechanism of the following acid catalysed reaction at 413K.

$2CH_3CH_2OH.$ ————> $CH_3CH_2OCH_2CH_3$

Ans

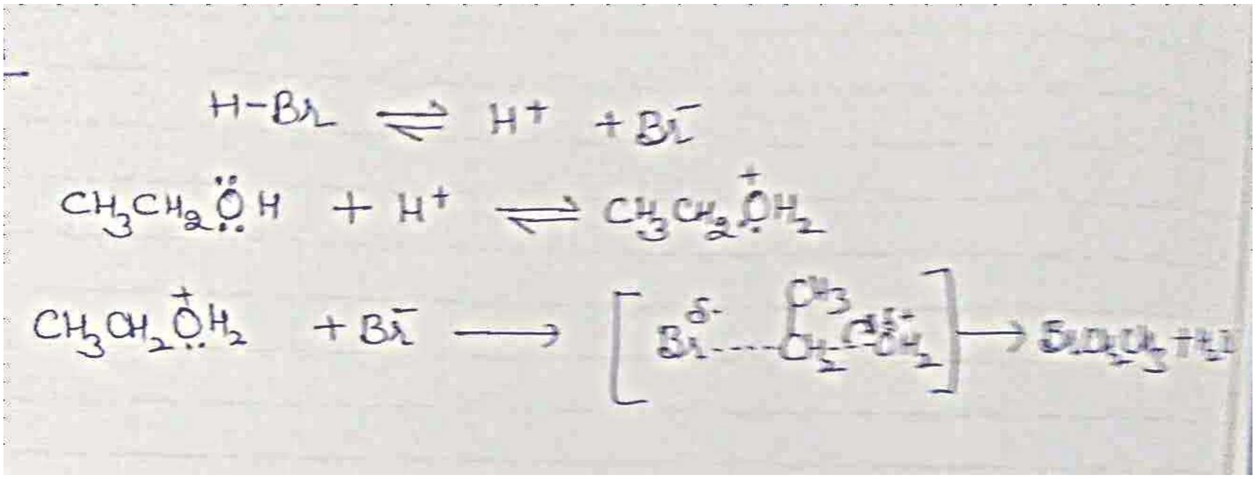


Ans 3. Step 1. $CH_3-CH_2-\ddot{O}H + H^+ \longrightarrow CH_3-CH_2-\overset{+}{\ddot{O}}H_2$

Step 2. $CH_3-CH_2-\ddot{O}-H + CH_3-CH_2-\overset{+}{\ddot{O}}H_2 \longrightarrow CH_3-CH_2-\underset{H}{\overset{+}{\ddot{O}}}-CH_2-CH_3$

Step 3. $CH_3-CH_2-\overset{H}{\overset{+}{\ddot{O}}}-CH_2-CH_3 \longrightarrow CH_3-CH_2-\ddot{O}-CH_2-CH_3 + H^+$

Q2 Write the mechanism for the conversion of ethanol to bromoethane

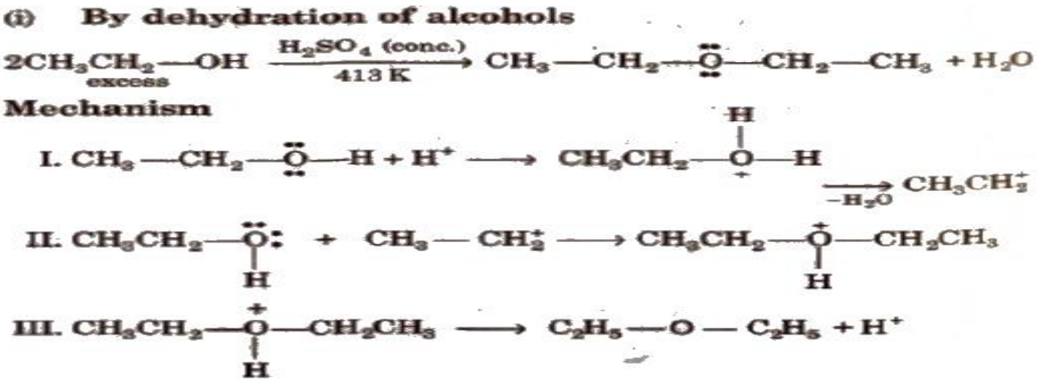


$H-Br \rightleftharpoons H^+ + Br^-$

$CH_3CH_2\ddot{O}H + H^+ \rightleftharpoons CH_3CH_2\overset{+}{\ddot{O}}H_2$

$CH_3CH_2\overset{+}{\ddot{O}}H_2 + Br^- \longrightarrow \left[\overset{\delta-}{Br}\cdots\overset{CH_3}{CH_2}\cdots\overset{\delta+}{O}H_2\right] \longrightarrow BrCH_2CH_3$ + [illegible]

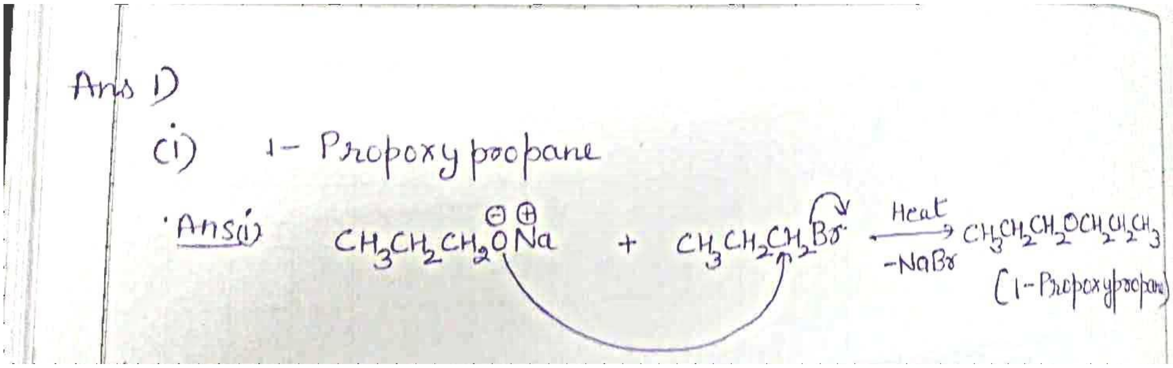
MECHANISM OF ETHER FORMATION FROM ALCOHOL



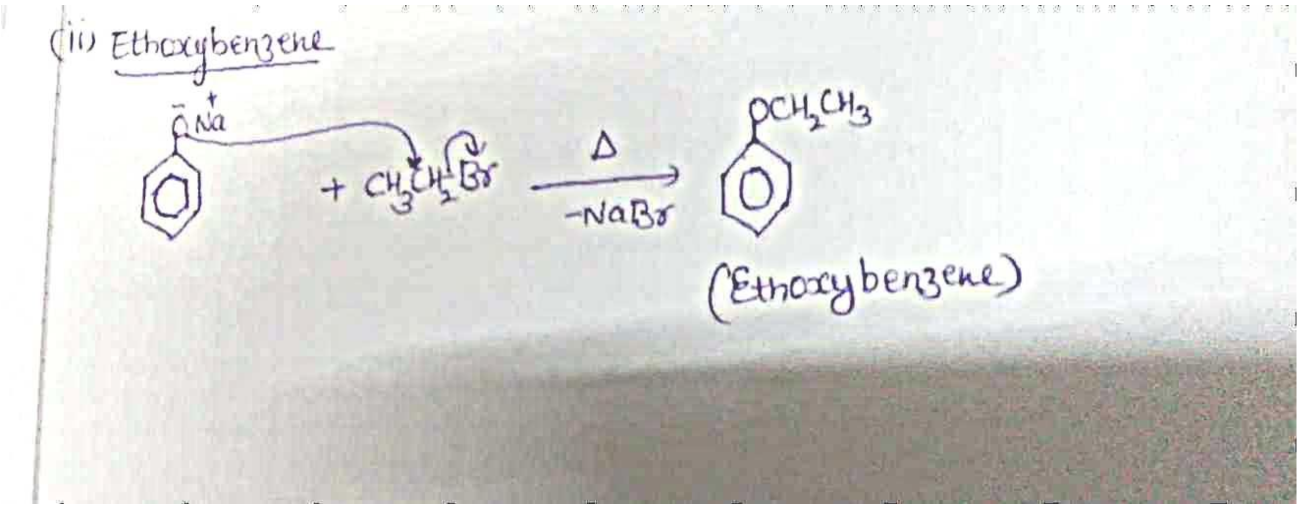
Q3 Write the equations for the preparation of the following ethers from Williamson's synthesis

1-Propoxypropane
2- Ethoxybenzene
3- 2methyl,2methoxypropane

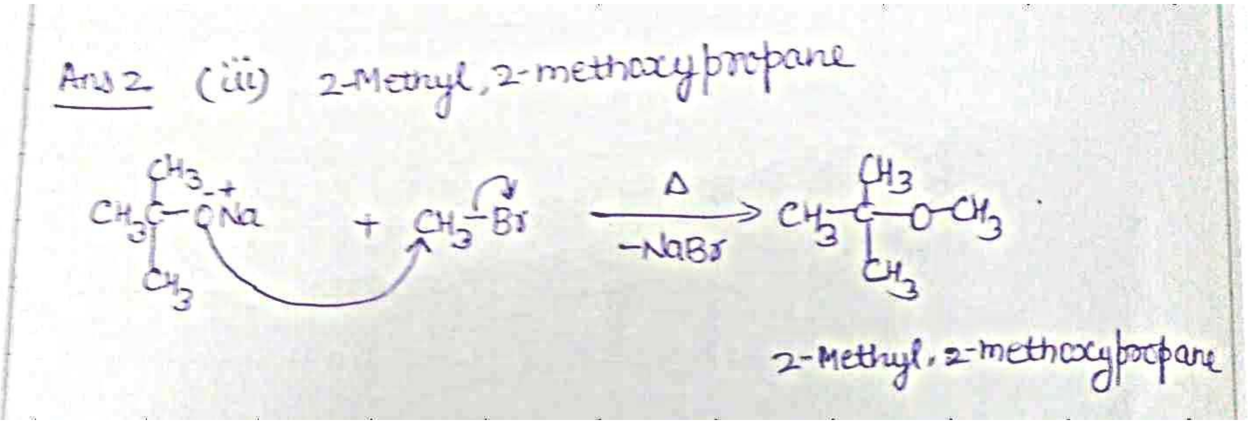
Ans (1) 1- propoxypropane



(ii) Ethoxybenzene



iii) 2 methyl, 2 methxypropane

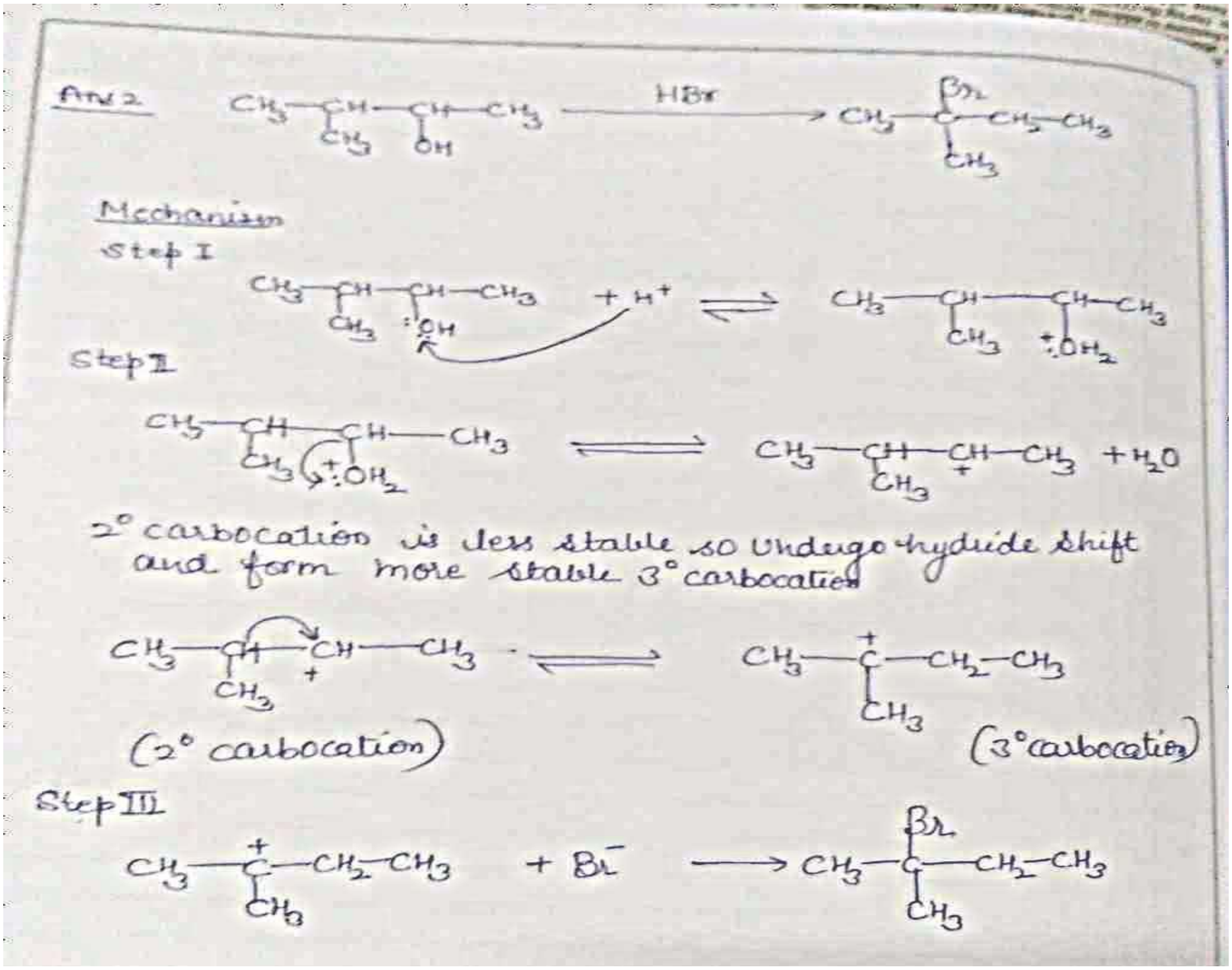


Ans 2 (iii) 2-Methyl, 2-methoxypropane

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{-\ +}{O}Na + CH_3-Br \xrightarrow[-NaBr]{\Delta} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3$$

2-Methyl, 2-methoxypropane

Q4 When 3methyl butan-2-ol is treated with HBr the product formed is 2-bromo,2 methyl. Butane. Give mechanism for this reaction Ans-1



Ans 2

$$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{HBr} CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3$$

Mechanism

Step I

$$CH_3-\underset{CH_3}{CH}-\underset{:\ddot{O}H}{CH}-CH_3 + H^+ \rightleftharpoons CH_3-\underset{CH_3}{CH}-\underset{\overset{+}{:}OH_2}{CH}-CH_3$$

Step II

$$CH_3-\underset{CH_3}{CH}-\underset{\overset{+}{:}OH_2}{CH}-CH_3 \rightleftharpoons CH_3-\underset{CH_3}{CH}-\overset{}{\underset{+}{CH}}-CH_3 + H_2O$$

2° carbocation is less stable so Undergo hydride shift and form more stable 3° carbocation

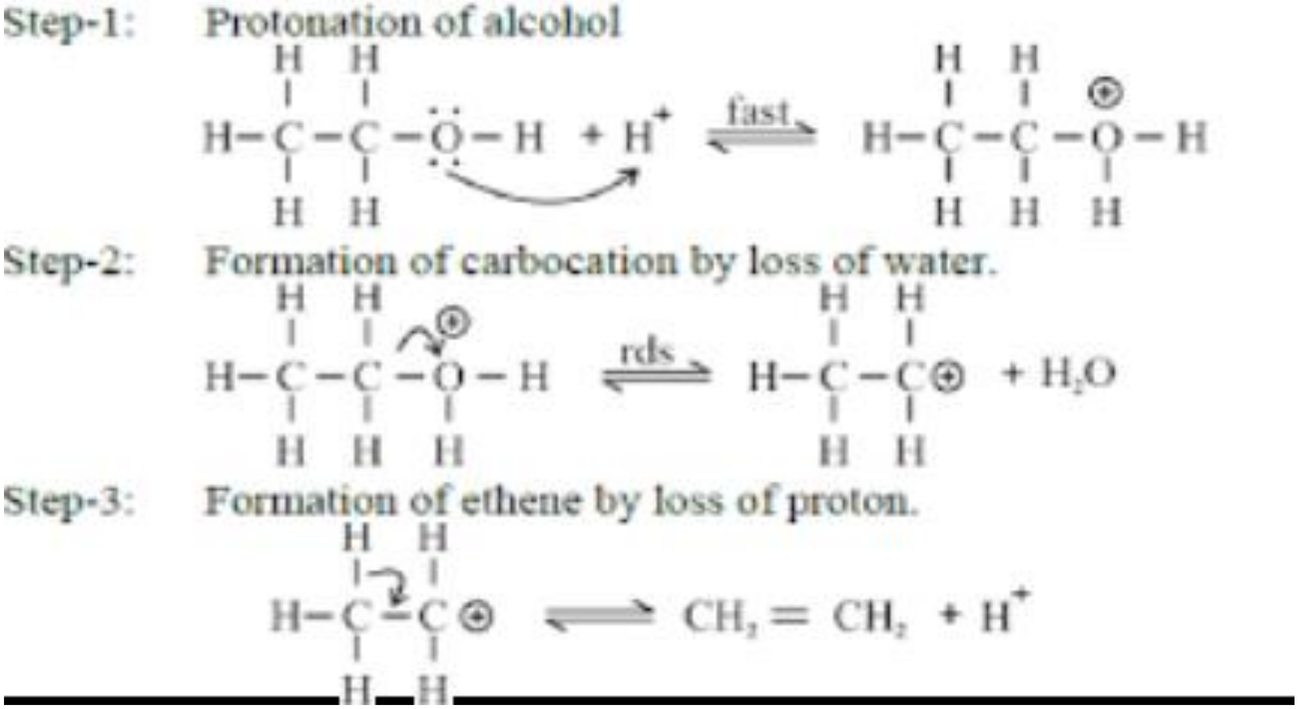
$$CH_3-\underset{CH_3}{CH}-\underset{+}{CH}-CH_3 \rightleftharpoons CH_3-\underset{CH_3}{\overset{+}{C}}-CH_2-CH_3$$

(2° carbocation) (3° carbocation)

Step III

$$CH_3-\underset{CH_3}{\overset{+}{C}}-CH_2-CH_3 + Br^- \longrightarrow CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3$$

DEHYDRATION MECHANISM OF ALCOHOLS



Step-1: Protonation of alcohol

Step-2: Formation of carbocation by loss of water.

Step-3: Formation of ethene by loss of proton.

* * *

Reasoning Based Question and Answer in Organic Chemistry

Based on : Melting Point, Boiling Point, Nucleophilic – substitution and Electrophilic substitution Reaction, Reactivity, solubility, Dipole moment etc.

M.P. of organic compounds depends on the following factors-

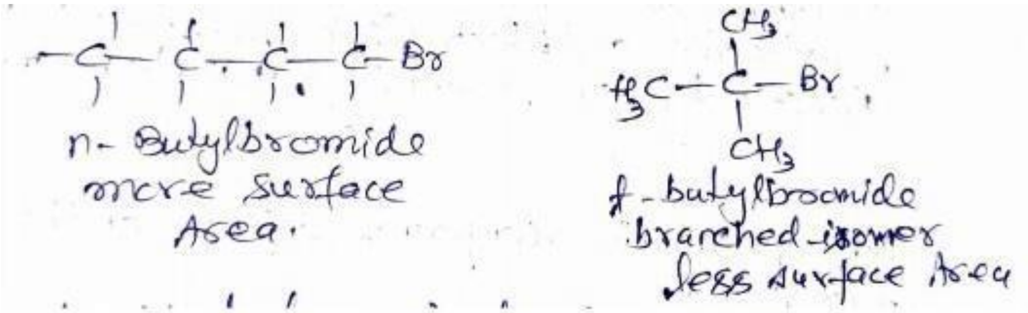
1. Lattice structure of compound .
2. Shape of molecule.
3. Dipole-dipole interaction between molecules.
4. Surface area of molecules.
   (Branched chain isomers have lesser surface area hence low m.p. than straight chain isomers with larger surface area.)
5. Vander Waal forces between molecule.
6. H-bonding between molecules if applicable.

Ques 1) B.P. of bromoethane is higher than that of chloroethane. Why?

Ans : Due to larger size and more mass of Br than that of Cl, the molecules of bromoethane have greater magnitude of vander Waal forces of attraction than that in chloroethane. Hence B.P. of bromoethane is higher than the B.P. of chloroethane.

Ques 2) n-Butybromide has higher B.P. than t-tubylbromide. Why?

Ans : n-Butylbromide has a straight chain hence larger surface area than t-butybromide that has a branched structure.



Vander Waal forces of attraction is more when surface area is more. Hence n-Butyl bromide will have higher B.P. than t-butyl bromide.

Ques 3) Alkyl halides, though polar, are immiscible with water. Why?

Ans: As alkyl halides are polar molecules they are held together by dipole-dipole attraction. The molecules of water are held together by strong ‘H’ bonding. Since the force of attraction between alkyl halide molecules and water molecules are weaker than the forces of attraction between alkyl halide and alkyl halide molecules and water –water molecules, hence alkyl halides are immiscible with water.

Ques 4) Why are haloalkanes very less soluble in water ?

Ans : Although haloalkanes are very polar molecule but neither they from 'H' bonds with water molecules nor they can break 'H' bonding between water molecules. As a result haloalkanes are very less soluble in water.

Ques 5) Out of ethyl bromide and ethyl chloride which has higher B.P. and Why?

Ans: Because of more mass and bigger size of 'Br' than 'Cl' the Vander wall force & attraction are stronger in ethyl bromide than in ethyl chloride. Hence ethyl bromide has higher B.P. than ethyl chloride.

Ques 6) Haloalkanes dissolve easily in organic solvents. Why?

Ans : Haloalkanes dissolve in organic solvents of low polarity, like petroleum-there, benzene, diethyl ether, chloroform, CCl4, etc. because new force of attraction setup between haloalkanes and solvent molecules are some as the force between haloalkanes-haloalkanes and between solvent-solvent molecules.

Ques 7) p-Dichlorobenzene has more melting point (323k) than orhto and meta isomers. Why?

Ans : p-Dichlorobenzene has more melting point than ortho and meta isomers due to better symmetry and better molecular packing in crystal lattice than other two isomers.

Ques 8) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes?

Ans : Haloalkanes are more reactive than haloarenes towards nucleophilic substitution reaction due to following reasons –

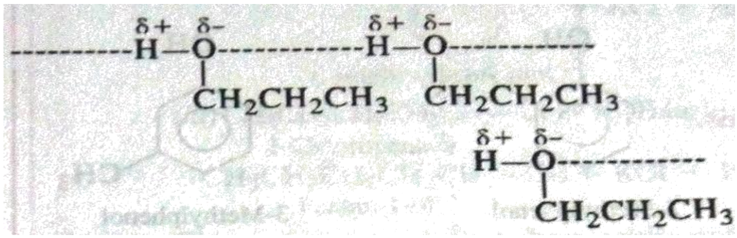
(a) Due to resonance in haloarenes, then C-X bond acquires a partial double bond character. It makes the bond cleavage in haloarenes more difficult than in haloalkanes.

(b) The carbon of C-X bond is sp^3-hybridised in haloalkanes while it is sp^2-hybridiesed in haloarenes. As such the C-X bond length in haloarenes in less than in haloalkenes. A shorter bond is more difficult to break.

(c) The benzene ring is haloarenes is electron rich. This make it difficult for electron rich nucleophiles to attack haloarenes.

Ques 9) Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

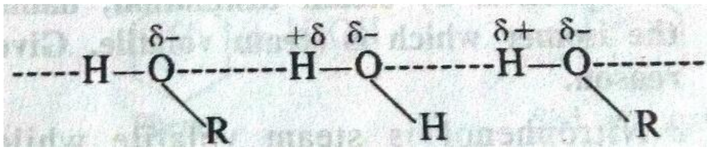
Ans: As butane is non-polar, the molecules of butane are held together by weak van der Waal's force of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding as shown below :



Therefore, the b. p. of propanol is much higher than that if butane.

Ques 10) Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

Ans: Alcohols can form H-bonds with water and break the H-bonds already existing between water molecules. Therefore, they are in general, soluble in water.



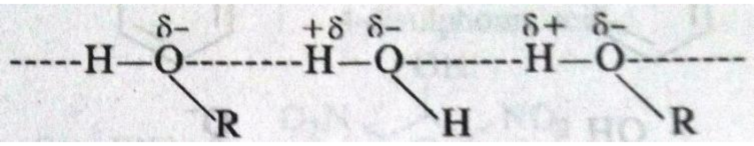
On the other hand, hydrocarbons cannot from H-bonds with water and hence are insoluble in water.

Ques 11) Which of the following will have a higher boiling point and why: CH_3NH_2 or CH_3OH?

Ans: CH_3OH will have a higher boiling point than CH_3NH_2. This can be explained as follows. Oxygen is more electronegative than nitrogen and atomic size of oxygen is less than that of nitrogen. As such, the intermolecular forces in CH_3OH are stronger than in CH_3NH_2. Therefore, boiling point of CH_3OH will be more than CH_3NH_2.

Ques 12) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

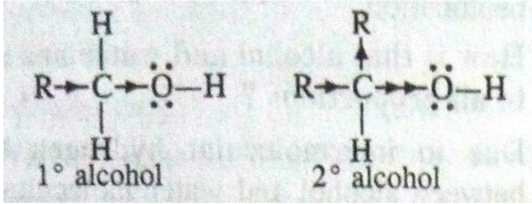
Ans: Alcohols can from H-bonds with water and break the H-bonds already existing between water molecules. Therefore, they are in general, soluble in water.



On the other hand, hydrocarbons cannot form H-bonds with water and hence are insoluble in water.

Ques 13) Why primary alcohols are more acidic than secondary alcohols?

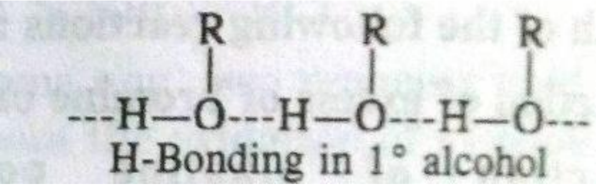
Ans: As we move from primary to secondary alcohol, the number of alkyl groups attached to the carbon having the –OH group increases.



Due to +I effect of alkyl group, the electron density on oxygen will be more in case of 2^{o} alcohols than in case of 1^{o} alcohol. Hence the shared pair of electron of the O-H bond will be more displaced towards the O atom in case of 1^{o} alcohol than in case of 2^{o} alcohol. Thus the release of proton (H^{+}) is easier in case of 1o alcohols than in case of 2^{o} alcohol. Therefore, 1^{o} alcohol is more acidic than 2^{o} alcohol.

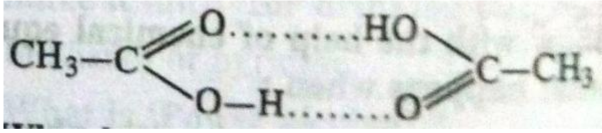
Ques 14) Why are alcohols higher boiling point compounds than hydrocarbons of corresponding molecular masses but have lower boiling point than corresponding acids?

Ans: The higher boiling point of alcohols than corresponding hydrocarbon are due to intermolecular hydrogen bonding.


H-Bonding in 1° alcohol

No such hydrogen bonding is present in hydrocarbons.

But alcohols have lower boiling points than corresponding acids because in acid there is stronger intermolecular H-bonding due to the presence of two electronegative oxygen atoms. Thus acid molecule dimerises.



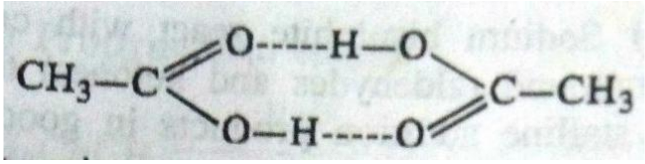
Ques 15) Give reasons for the following :

- **(a) Benzoic acid does not give Friedel-Craft's reaction.**
- **(b) Carboxylic acid with more than five carbon atoms are insoluble in water.**
- **(c) Acetic acid in vapors state shows a molecular mass of 120.**

Ans: (i) The carboxylic group (-COOH) is an electron withdrawing group and therefore, deactivates the benzene ring towards electrophilic attack. Therefore benzoic acid does not give Friedel Craft's reaction.

(ii) Carboxylic acid (RCOOH) dissolve in water due to hydrogen bonding between H-atom of –COOH group and O-atom of water. As alkyl portion R- is non-polar and hydrophobic, this effect predominates as –R gets larger (over five carbon atoms).

(iii) CH3COOH typically undergoes dimeric intermolecular hydrogen bonding as shown ahead.



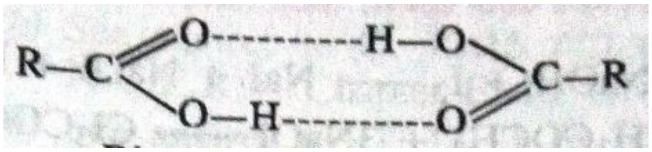
It exists as a dimer in the vapour state. Therefore, its molecular mass comes out to be double than the actual molecular mass of acetic acid (mol. Mass=60).

Ques 16) How would you account for the following:

- **(a) Aldehydes are more reactive than ketones towards nucleophiles.**
- **(b) The boiling point of aldehydes and ketones are lower than of the corresponding acids.**
- **(c) The aldehydes and ketones undergo a number of addition reaction.**

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

(ii) Carboxylic acids are higher boiling liquids than aldehydes and ketones of comparable molecular masses and ketones of comparable molecular masses. This is due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acid exist as dimer as simmer in vapour phase or in the aprotic solvents.



Dimer in vapour state or in aprotic solvent

(iii) Aldehydes and ketones undergo a bumbler if nucleophilic addition reaction reactions such as addition of HCN, $NaHSO_3$, Grignard reagent etc. This can be explained as follows.

A nucleophilic attack the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp2-hybridised orbitals of carbonyl carbon.

The hybridization of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result in addition of Nu- and H+ across the carbon oxygen double bond.

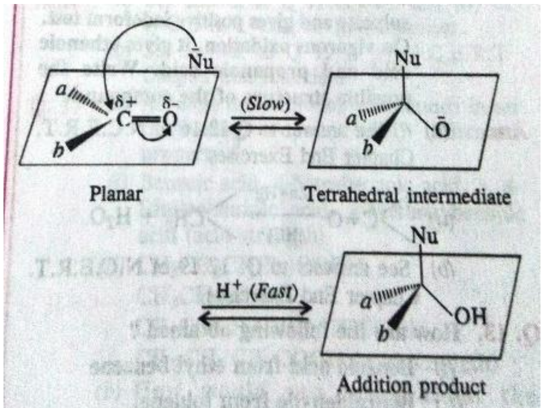
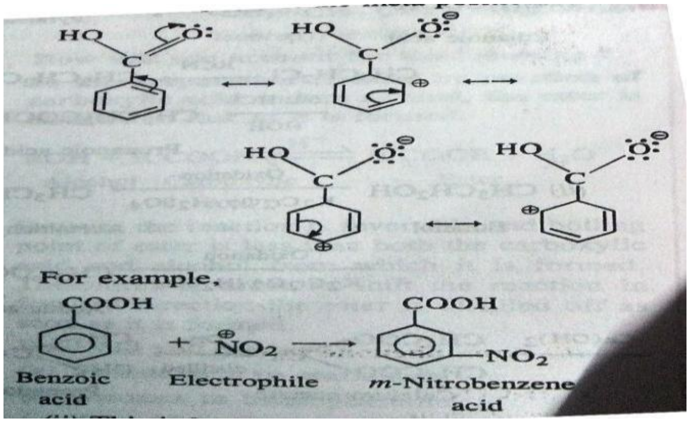


Fig. Nucleophilic attack on carbonyl carbon

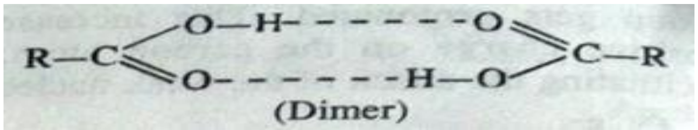
Ques 17) Account for the following:

- **(a) Electrophilic substitution in benzoic acid takes place at meta position.**
- **(b) Carboxylic acids have higher boiling point than alcohols of comparable molecular masses.**

Ans : Due to resonance in benzoic acid, there is comparatively higher electron density at meta position than at ortho and para positions. Therefore, electrophilic substation in benzoic acid takes place at the meta position.

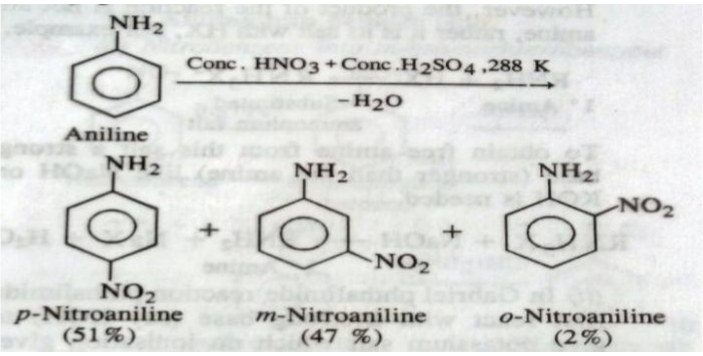


(ii) This is because of stronger intermolecular hydrogen bonding in carboxylic acids than in alcohols. This is due to the fact that O-H bond in carboxylic acid is more strongly polarized due to the presence of adjacent electron withdrawing carbonyl group.



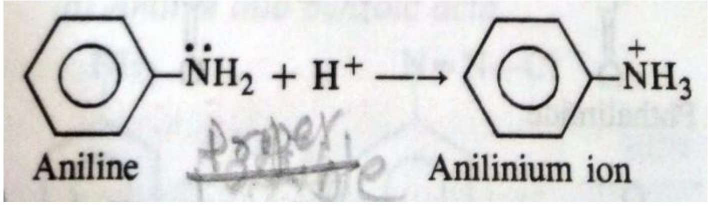
Ques 18) NH_2 group is ortho and para-directing group, nitration of aniline give along with ortho and para derivative, a good proportion of meta derivative also.

Ans: Direct narration of aniline with nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives a fair amount of m-derivative along with o-and p-product.



The NH_2 group in aniline is o and p-directing. As such only o and p-substituted products are expected in this reaction. The formation of a fair amount of m-derivative can be explained as follows:

In strongly acidic medium (conc. HNO_3+ conc. $H2SO_4$-nitrating mixture) aniline is protonated to form anilinium ion, which is meta directing.



Ques 19) Give plausible explanation for each of the following:

- **(a) The presence of a base in needed in the ammonolysis of alkyl halides.**
- **(b) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.**

Ans: (i) Ammonolysis of alkyl halides involves reaction of alkyl halide with ammonia to produce 1^o, 2^o or 3^o amines (along with quaternary ammonium salts).

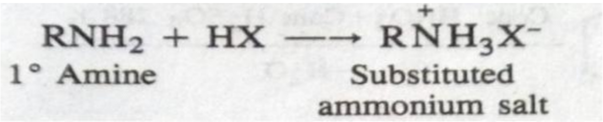
$$\underset{\text{Alkyl halide}}{RX} + NH_3 \longrightarrow \underset{1^\circ\text{ Amine}}{RNH_2} + HX$$

$$RX + RNH_2 \longrightarrow \underset{2^\circ\text{ Amine}}{R_2NH} + HX$$

$$RX + R_2NH \longrightarrow \underset{3^\circ\text{ Amine}}{R_3N} + HX$$

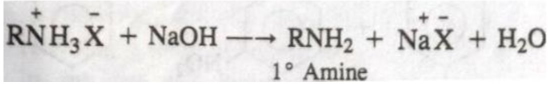
$$RX + R_3N \longrightarrow \underset{\substack{\text{Quaternary}\\ \text{ammonium salt}}}{[R_4N]^+ + X^-}$$

However, the product of the reaction is not an amine, rather it is its salt with HX, For example,



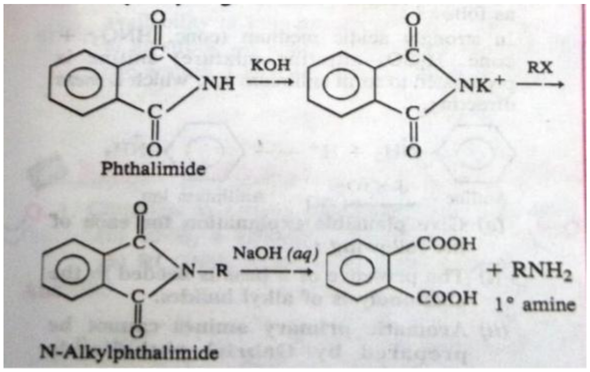
$$\underset{1^\circ\text{ Amine}}{RNH_2} + HX \longrightarrow \underset{\substack{\text{Substituted}\\\text{ammonium salt}}}{R\overset{+}{N}H_3X^-}$$

To obtain free amine from this salt a strong base (stronger than the amine) like NaOH or KOH is needed.



$$R\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow \underset{1^\circ\text{ Amine}}{RNH_2} + \overset{+}{Na}\overset{-}{X} + H_2O$$

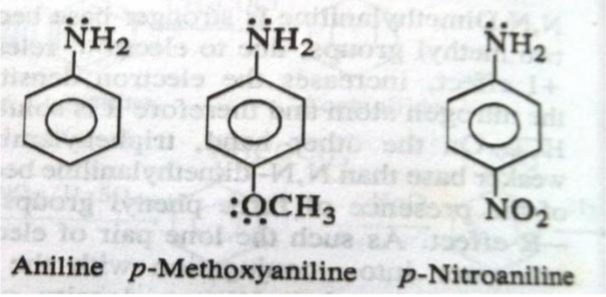
(ii) In Gabriel phthalimide reaction phthalimide first react with a strong base (say KOH) to give potassium salt which on ionization gives phthalimide ion. It is followed by nucleophilic substitution of alkyl halide by phalimide ion to give N-alkyl phthalimide which on alkaline hydrolysis gives the 1^{o} amine.



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

Ques 19) p-Methoxy aniline is a stronger base than aniline while p-nitroaniline is a weaker base than aniline. Why?

Ans: Methoxy group is an electron donating group. In p-methoxy aniline, methoxy group will increase the availability of lone pair of electrons on nitrogen, thus making it more basic than aniline. Nitro group is an electron it will decrease the availability of lone pair of electrons on nitrogen, thus making it less basic than online.

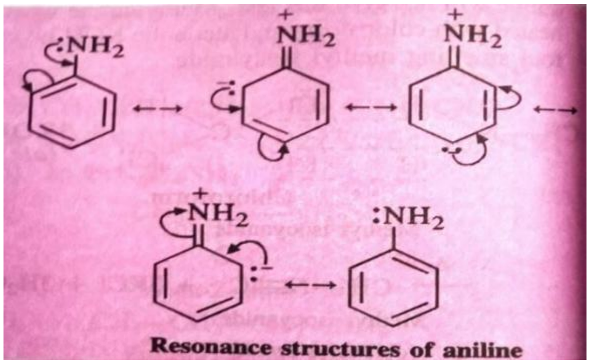


Ques 20) Account for the following:

- **(a) pKb of aniline is more than that of methylamine.**
- **(b) Ethylamine is soluble in water whereas aniline is not.**
- **(c) Methylamine in water reacts with ferric chloride to precipitate hydrate ferric oxide.**
- **(d) Aniline does not undergo Friedel-Crafts reaction.**
- **(e) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.**
- **(f) Gabriel phthalimide synthesis is preferred for synthesizing primary amines.**

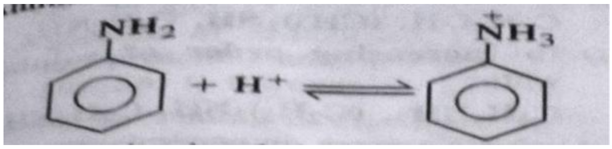
Ans: (a) Aniline is a weaker base than methylamine in other words, Kb of aniline is less than Kb of methylamine or pKb of aniline is more than pKb of methylamine (pKb=-log Kb or pKb=log 1/kb).

This can be explained on the basis of resonance and greater stability of aniline than anilinium ion. Aniline is a resonance hybrid of following structure:

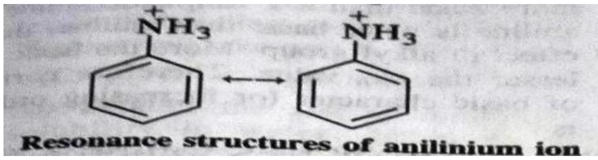


Resonance structures of aniline

As a result of resonance, the lone pair on nitrogen gets delocalized over the ring. This decreased the availability of electron pair for protonation. Therefore, aniline is weaker base than ammonia. Aniline accepts a proton to form anilinium ion.



Anilinium ion is relatively less stable than aniline as it has only two resonating structures



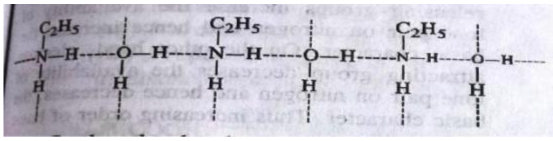
Resonance structures of anilinium ion

On other hand, methylamine is a stronger base than ammonia. This is due to the +I effect of methyl group which increases the availability of lone pair on nitrogen atom

CH3--------->---------NH_2

Thus, methylamine is much stronger base than aniline.

(b) Lower aliphatic amines like ethylamine are soluble in water. This is due to their ability to from hydrogen bonds with water. This is due to their ability to form hydrogen bonds with water.



On the other hand, aromatic amines like aniline are insoluble in water. This is due to their larger hydrocarbon part which hinders the formation of hydrogen bonds with water.

(c) Methylamine dissolve in water to give methylammonium hydroxide, which ionizes to give methylammonium and hydroxide ions.

$$\underset{\text{Methylamine}}{CH_3\ddot{N}H_2} + H_2O \rightleftharpoons \underset{\text{Methylammonium hydroxide}}{[CH_3NH_3]^+ \bar{O}H} \rightleftharpoons [CH_3NH_3]^+ + OH^-$$

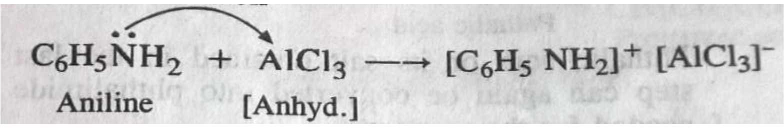
Due to the formation of OH-, ions they can precipitate out iron, aluminum, chromium etc., from their salts.

$$[CH_3NH_3]^+OH^- + FeCl_3 \longrightarrow Fe(OH)_3 \downarrow + CH_3NH_3Cl$$

Ferric hydroxide being unstable can be considered as hydrated ferric oxide.

$$2\ Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

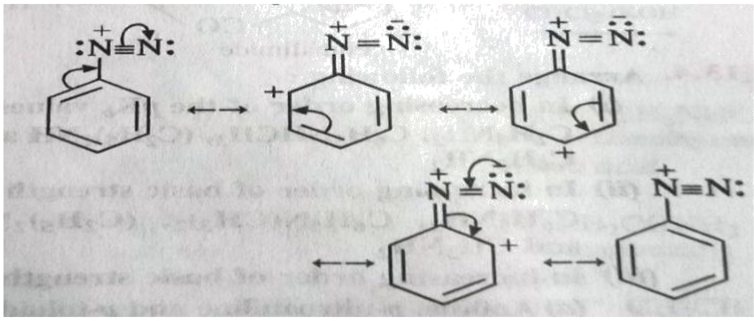
(d) Aniline does not undergo Friedel-Crafts acylation or alkylation. This is due to salt formation between base i.e. aniline and Lewis acid i.e. anhydrous AICI3 used as catalyst in the reaction.



$$\underset{\text{Aniline}}{C_6H_5\ddot{N}H_2} + \underset{\text{[Anhyd.]}}{AlCl_3} \longrightarrow [C_6H_5\ NH_2]^+ [AlCl_3]^-$$

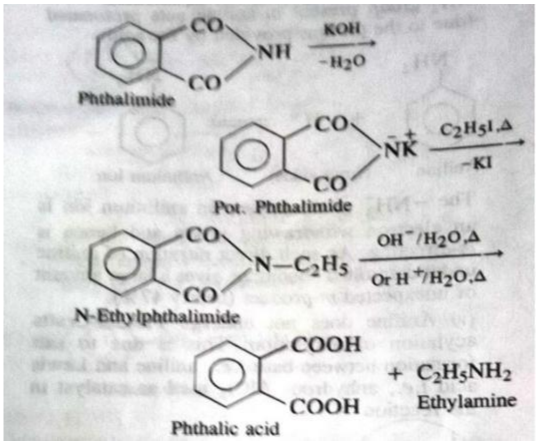
Due to this, nitrogen of aniline acquires positive charge and thus acts as a strong deactivating group. This does not allow Friedel-Crafts reaction to occur.

(e) This greater stability of aromatic diazonium compounds than aliphatic diazonium compounds is due to dispersal of the positive charges on the benzene ring, due to resonance.

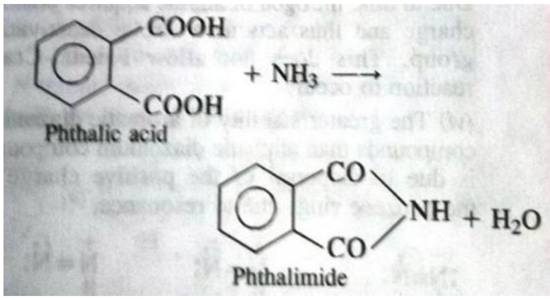


Such resonance structure are not possible in case of aliphatic diazonium salts. As such aliphatic diazonium salts are much less stable than aromatic diazonium salts.

(f) A reaction between alkyl halide and ammonia gives a mixture of amines (1o,2o, 3o) along with tetraallyl ammonium halide. The components of this mixture are not easy to separate. To get pure 1o amine, Gabriel phthalimide synthesis is preferred. This is because in this case pure 1o amine is obtained from alkyl halide and ammonia as shown below.



Phthalic acid or its salt obtained in the last step can again be converted into phthalimide needed for the reaction.

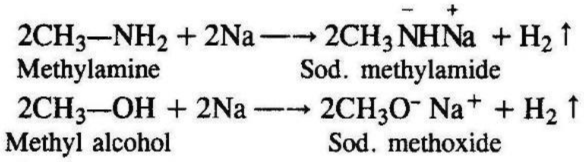


Ques 21) Give plausible explanation for each of the following:

- **(a) Why are amines less acidic than alcohols of comparable molecular masses?**
- **(b) Why do primary amines have higher boiling point than tertiary amines?**
- **(c) Why are aliphatic amines stronger bases than aromatic amines?**

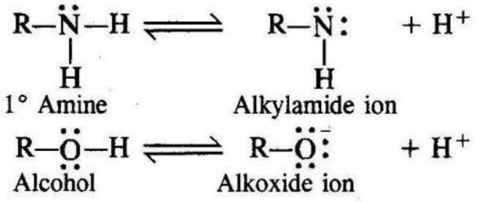
Ans: (a) Consider a 1 ° amine and an alcohol of comparable molecular masses.

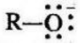
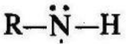
Due to the presence of lone pair of electrons. These can act as Lewis bases. However both 1 ° amine (say methylamine) and alcohol (say methyl alcohol) can also act as Bronsted acids. For example, they react with sodium metal to give hydrogen.


$$2CH_3{-}NH_2 + 2Na \longrightarrow 2CH_3\overset{-}{N}H\overset{+}{Na} + H_2\uparrow$$
$$2CH_3{-}OH + 2Na \longrightarrow 2CH_3O^- Na^+ + H_2\uparrow$$

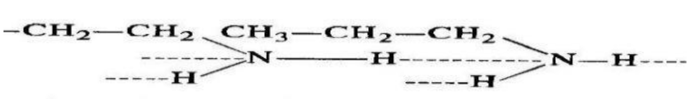
However, 1 ° amines are less acidic than alcohols of comparable molecular masses. This can be explained as follows :

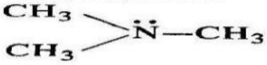
Loss of proton form a 1° amine gives an alkyl amide ion while loss of a proton from alcohol gives alkoxide ion. R—NT R—N + H+ 1° Amine Alkyl amide ion.



Since 0 is more electronegative than N, therefore, 0 in alkoxide ion can accommodate the -ve charge more easily than N in alkyl amide ion. In other words  is more stable than  Thus we can say that alcohols are more acidic than amines or amines are less acidic than alcohols. It should be noted that only 1' and 2° amines show acidic character. As nQ H-atom is attached to N-atom is 3° amines, 3°-amines cannot show acidic character.

(b) Boiling point of 1' amine is much higher than a tertiary amine of equal molecular mass. For example l.p. of $CH_3CH_2CH_2NH_2$(n-propylamine - a 1' amine) is much higher than l.p. of $(CH_3)_3$ N (trimethylamine - a 30 amine). Due to the presence of two H-atoms, attached to N-atom there is extensive intermolecular H-bonding in 1 ° amine. On the other hand in 3^0 amines as there is no H-atom attached to N-atom, H-bonding is absent in 3^0 amine. More the H-bonding stronger the intermolecular forces, and hence higher the boiling point.


Extensive H-bonding in *n*-propylamine

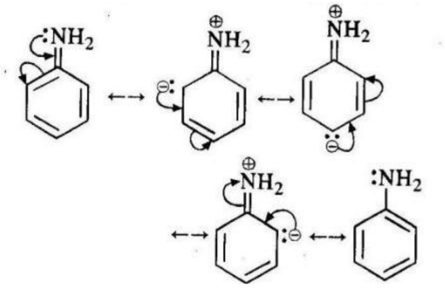

No H-bonding in trimethylamine

(c) Alkyl amines are stronger bases than ammonia : All the three types of aliphatic amines are stronger bases than ammonia (K_b = 1.8 x 10^{-5}). This can be explained on the bases of the + I effect or electron-donating effect of alkyl group or alkyl groups attached to the nitrogen atom. This increases the electron density on the nitrogen atom. Thus, amines can donate the lone pair of electrons more easily than ammonia. Moreover, electron releasing effect of alkyl groups stabilizes the alkyl ammonium ion formed and hence, shifts the equilibrium in the forward direction making the alkylamines stronger bases than ammonia.

$$\rightarrow\!- \ddot{N}H_2 + H_2O \rightleftharpoons [R{-}NH_3]^+ + OH^-$$

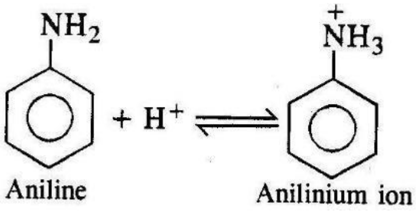
Aromatic amines such as aniline are less basic than ammonia. Aromatic amines such as aniline (K_b = 4.2 x 10^{-10}) are less basic than ammonia (Kb = 1.8 x 10^{-5}). The weaker basic character of aniline can be explained as follows.

(i) Resonance effect : Resonance effect : Aromatic ring has electron withdrawing nature due to resonance. This decreases the availability of electron pair on nitrogen, thereby, making it less basic than ammonia. For example, aniline can I be regarded as a resonance hybrid of the following structures.

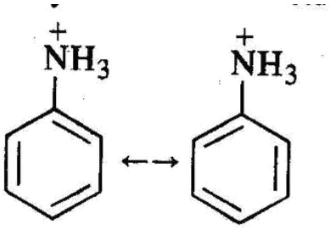


As a result of resonance, the lone pair on nitrogen atom gets delocalized over the benzene ring. This decreases the availability of electron pair for protonation. Therefore, aniline is a weaker base than ammonia.

(ii) Lower stability of aryl ammonium ion than aryl amine : Amines accept a proton to form conjugate acid,. For example, aniline accepts hydrogen to form anilinium ion.



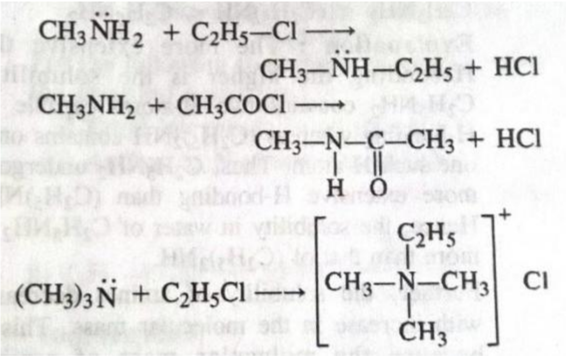
Anilinium ion is relatively less stable than aniline because it is a resonance hybrid of only two structures, whereas aniline is a resonance hybrid of five structures.



Thus we find that resonance stabilization of aniline is more than that of anilinium ion. Hence the proton acceptability or basic nature of aniline would be less than that of ammonia. As such basic character of aliphatic amines, aromatic amines and ammonia, in general, is in the order ; aromatic amines < ammonia < aliphatic amines Thus, we can say that aliphatic amines are stronger bases than aromatic amines.

Ques 22) Why do amines behave as nucleophiles?

Ans : Amines behave as nucleophiles. For example, amines react with alkyl halides, acid chlorides etc.



$$CH_3\ddot{N}H_2 + C_2H_5{-}Cl \longrightarrow CH_3{-}\ddot{N}H{-}C_2H_5 + HCl$$

$$CH_3NH_2 + CH_3COCl \longrightarrow CH_3{-}\underset{\displaystyle H}{\underset{|}{N}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3 + HCl$$

$$(CH_3)_3\ddot{N} + C_2H_5Cl \longrightarrow \left[CH_3{-}\overset{\displaystyle C_2H_5}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{N}}}}{-}CH_3 \right]^+ Cl$$

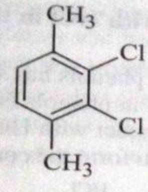
It is due to the presence of lone pair of electrons on nitrogen.

Ques 23) Why is an alkyl amine more basic than ammonia?

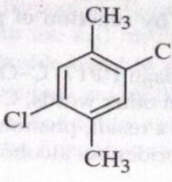
Ans: This is because of the presence of electron releasing alkyl group (+I effect) which increase the electron density on nitrogen.

Ques 24) Which of the following compounds will have the highest melting point and why?

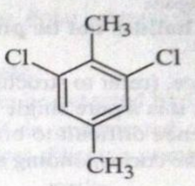
Ans : Compound (II) is most symmetrical because it has both the CH3 group and Cl atoms p- to each other. Therefore, it fits in the crystal lattice better than the other two isomers and hence it has the highest melting point.



(I)



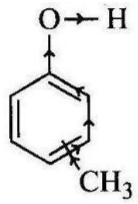
(II)



(III)

Ques 25) Which is a stronger acid, phenol or cresol? Explain.

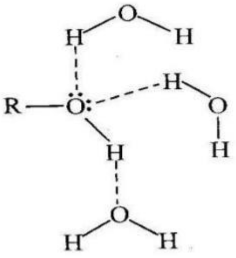
Ans : Cresol is methyl phenol. It has three positional isomers : o-cresol, m-cresol and p-cresol, Due to +I-effect of CH_3 group, electron density in the O-H bond increases. Therefore, it becomes difficult to break the O-H bond as compared to that in phenol and hence all cresols are less acidic than phenol or phenol is a stronger acid than cresols.



(Due to +I-effect of CH_3 group, electron density in the O — H bond increases thereby making the cleavage of O — H bond difficult)

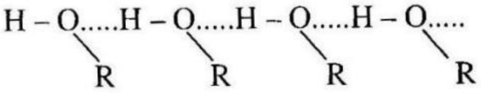
Ques 26) How is that alcohol and water are miscible in all proportions?

Ans: Due to intermolecular H-bonding (as shown below) alcohol and water are miscible in all proportions.



Ques 27)Why do alcohols have higher boiling points than haloalkanes of comparable molecular mass ?

Ans: Alcohols undergo extensive intermolecular H-bonding. As a result, alcohols exist as associated molecules as shown below:



$$\mathrm{H-\underset{\diagdown R}{O}.....H-\underset{\diagdown R}{O}.....H-\underset{\diagdown R}{O}.....H-\underset{\diagdown R}{O}.....}$$

Quite a large amount of energy is needed to break these H-bonds. Therefore, the boiling points of alcohols are much higher than haloalkanes of comparable molecular mass because the molecules of haloalkanes are held together only by weak dipole-dipole and van der Waals forces of attraction. For example, the b.p. of methyl chloride is 249 K while that of methanol is 337.5.

Ques 28) Why is sulphuric acid not used during the reaction of alcohols with K1 in the conversion of an alcohol to the alkyl iodide?

Ans: Alkyl iodides are formed when alcohols are heated with constant boiling hydriodic acid (57%)

$$R\text{—}OH + HI \xrightarrow{\text{Heat}} R\text{—}I + H_2O$$

The HI needed for the purpose, however, cannot be prepared in situ by heating KI with H_2SO_4. The reason being that H_2SO_4 being an oxidizing agent, oxidizes HI to I_2 before it is able to react with alcohols to form alkyl iodides.

$$KI + H_2SO_4 \xrightarrow{\text{Heat}} KHSO_4 + HI$$

$$2\,HI + H_2SO_4 \xrightarrow{\text{Heat}} I_2 + SO_2 + 2\,H_2O.$$

Ques 29) Why are phenols more acidic than alcohols? Give two reactions to show that phenols are acidic in nature.

Ans: Since the phenoxide ion left after the removal of a proton is stabilized by resonance (refer to page, 11/25) whereas alkoxide ion (left after the removal of a proton from alcohol) is riot. Therefore, phenols are more acidic than alcohols.

The two reactions of phenol showing its acidic nature are :

(i) Phenols dissolve in NaOH forming sodium phenoxide.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

(ii) Phenols react with metallic sodium to evolve H_2 gas

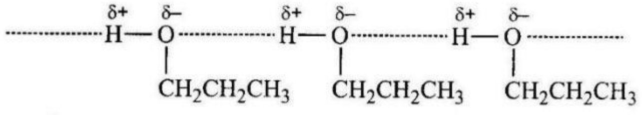
$$2\,C_6H_5OH + 2\,Na \longrightarrow 2\,C_6H_5ONa + H_2$$

Ques 30) Explain why phenols do not undergo Substitution of the -OH group like alcohols?

Ans: The C-0 bond in phenols has some double bond character due to resonance and hence cannot be easily cleaved by a nucleophile. In contrast, the C-O bond in alcohols is a pure single bond and hence can be easily cleaved by a nucleophile.

Ques 31) Explain why propanol has higher boiling point than that of the hydrocarbon, butane ?

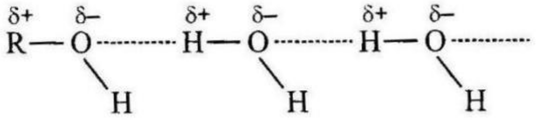
Ans: The molecules of butane are held together by weak van der Waals forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.



Therefore, the b.p. of propanol is much higher than that of butane.

Ques 32) Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

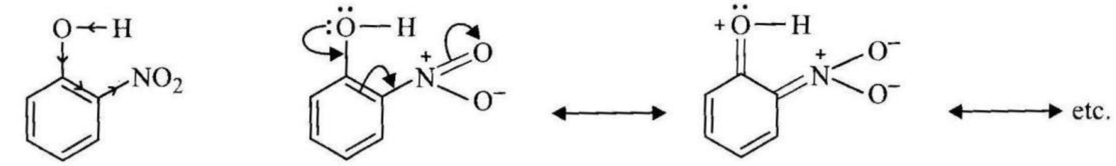
Ans: Alcohols can form H-bonds with water and can also break the H-bonds already existing between water molecules. Therefore, they are soluble in water.



On the other hand, hydrocarbons can neither form H-bonds with water nor can break the H-bonds already existing between water molecules and hence are insoluble in water.

Ques 33) Explain why is ortho-nitrophenol more acidic than ortho-methoxyphenol?

Ans: Due to strong –R and –I-effect of the NO_2 group, electron density in the O-H bond decreases and hence the loss of a proton becomes easy.



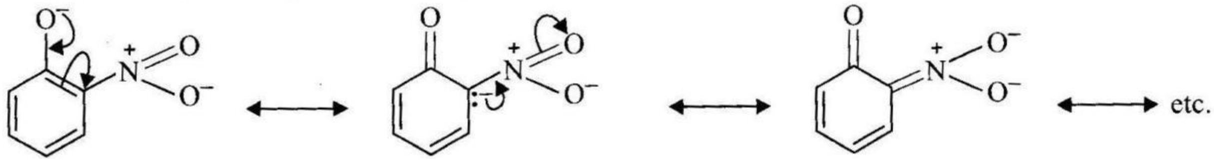
–I-Effect

decreases electron density in the O—H bond, makes release of proton easy

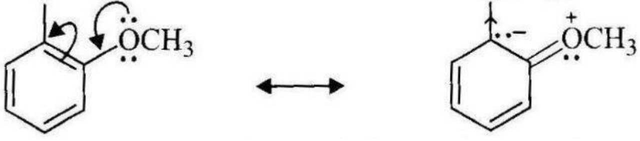
–R-Effect

puts a + ve charge on the phenolic O-atom, facilitates the release of a proton

Further, after the loss of a proton, the-nitro phenoxide ion left behind is stabilized by resonance, thereby making o-nitrophenol a stronger acid.



In contrast, due to +R effect of the OCH_3 group, the electron density in the O-H bond increases thereby making the loss of a proton difficult.



Furthermore, the o-methoxy phenoxide ion left after the loss of a proton is destabilized by resonance

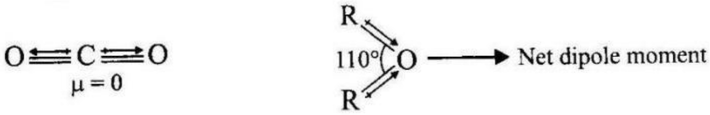
Because the two negative repel each other thereby making o-methoxyphenol a weaker acid. Thus, o-nitrophenol is more acidic than o-methoxyphenol.

Ques 34) Explain how does —OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

Ans: Phenol may be regarded as a resonance hybrid of structures, 1-V. "As a result of +R-effect of the OH group, the electron density in the benzene ring increases thereby facilitating the attack by an electrophile. In other words, presence of OH group, activates the benzene ring towards electrophilic substitution reactions. Further since the electron density is relatively higher at the two o- and one p- position, therefore, electrophilic substitution occurs mainly at o- and p-positions.

Ques 35) Explain why is O = C = O nonpolar while R-O-R is polar.

Ans: CO_2 is a linear molecule. The dipole moments of the two C = O bonds being equal and opposite cancel out each other and hence CO_2 is a non-polar molecule.



In contrast, in R-O-R molecule, the two dipoles of the R-O bonds are inclined to each other at angle of 110°, i.e., the two dipoles do not cancel out and hence have a finite resultant. In other words, R-O-R is a polar molecule.

Ques 36) Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different ?

Ans: The reaction of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) occurs through intermediate formation of carbocations. Obviously, more stable the carbocation, more reactive is the alcohol. Since the stability of carbocations follows the order : 3° > 2° > 1^0, therefore, reactivity of alcohols towards Lucas reagent follows the same order, i.e. , 3° > 2° > 1°.

Ques 37) Dipole moment of phenol is smaller than that of methanol. Why ?

Ans: In phenol, C-O bond is less polar due to electron-withdrawing effect of the benzene ring whereas in methanol, C-O bond is more polar due to +I-effect of the CH_3 group. As a result, phenol has lower dipole moment (1.54 D) than methanol (1.71 D).

Ques 38) Why are aldehydes more reactive than ketones ?

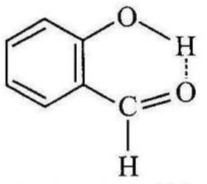
Ans: Aldehydes are more reactive than ketones due to the following two reasons :

(i) Due to smaller +1-effect of one alkyl group in aldehydes as compared to larger +1-effect of two alkyl groups, the magnitude of positive charge on the carbonyl carbon is more in aldehydes than in ketones. As a result, nucleophilic addition reactions occur more readily in aldehydes than in ketones.

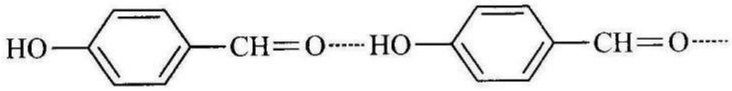
(ii) Due to presence of a H-atom on the carbonyl group, aldehydes can be more easily oxidized than ketones. As a result, aldehydes act as reducing agents and thus reduce Tollens' reagent, Fehling's solution, etc.

Ques 39) Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

Ans: Due to intramolecular H-bonding (chelation), o-hydroxybenzaldehyde exists as discrete molecules while due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules. To break these intermolecular H-bonds, a large amount of energy is needed. Consequently, p-hydroxy-benzaldehyde has a much higher m.p. and b.p. than that of o-hydroxybenzaldehyde. As a result, o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.



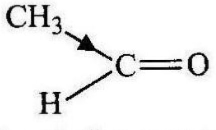
o-Hydroxybenzaldehyde



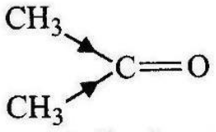
p-Hydroxybenzaldehyde (*intermolecular H–bonding*)

Ques 40) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN ? Explain. Or Propanone is less reactive than ethanal towards nucleophilic addition reactions. Give reasons.

Ans: Due to electron-donating inductive effect (+ I-effect) of the two CH_3 groups in CH_3COCH_3 as compared to smaller + I-effect of one CH_3 group in CH_3CHO, the magnitude of the +ve charge on the carbon atom of the carbonyl group in CH_3CHO is more than in CH_3COCH_3. As a result, nucleophilic addition reactions occurs more readily in CH_3CHO than in CH_3COCH_3.



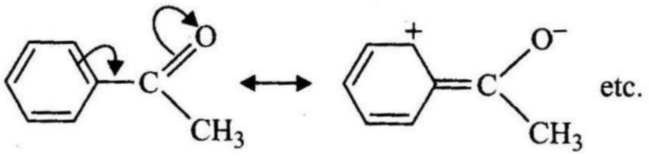
(*Smaller +I-effect, more +ve charge on the carbonyl carbon,* **more reactive**)



(*Stronger +I-effect, less +ve charge on the carbonyl carbon,* **less reactive**)

Ques 41) $C_6H_5COCH_3$ is much less reactive than CH_3COCH_3 towards nucleophilic addition reactions. Explain.

Ans: In $C_6H_5COCH_3$, the electron-donating resonance effect (+R-effect) of the benzene ring reduces the +ve charge on the carbon atom of the carbonyl group. Since +R-effect of benzene ring is more pronounced than +I-effect of the CH_3 groups, therefore, magnitude of the +ve charge on the carbon atom of the carbonyl group in $C_6H_5COCH_3$ is reduced to a much greater extent than in CH_3COCH_3. As a result, $C_6H_5COCH_3$ is much less reactive than CH_3COCH_3.



Ques 42) Acetone is highly soluble in water but benzophenone is not. Give reasons.

Ans: In acetone, C = O group easily forms H-bonds with water and hence acetone is highly soluble in water. However, in benzophenone, the phenyl groups are bulky and hence C = O group cannot form H-bonds with water due to steric hindrance and hence benzophenone is insoluble in water.

Ques 43) Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have the same solubility in water.

Ans: The b.p. of butanol is higher than that of butanal because butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole attraction. However, both of them form H-bonds with water and hence are soluble.

Ques 44) Why is benzoic acid less soluble in water than acetic acid ?

Ans: Due to polar nature of the C = O and O-H parts of COOH group, both CH_3COOH and C_6H_5COOH form H bonds with water. But due to large hydrocarbon part the extent of H-bonding is much lower in benzoic acid than in acetic acid and hence benzoic acid is much less soluble in water than acetic acid.

****

SOME IMPORTANT CHEMICAL REACTIONS IN ORGANIC CHEMISTRY

1. What happens when

I) Ethyl chloride is treated with Sodium Iodide (NaI)
II) Chlorobenzene is treated with Sodium metal in presence of dry ether.
III) Methyl Chloride is treated with KNO_3
IV) n-butyl chloride is treated with alcoholic KOH.
V) 2,4,6-trinitrochlorobenzene is subjected to hydrolysis.
VI) Methyl chloride is treated with AgCN.
VII) Chlorobenzene is treated with Cl_2 /$FeCl_3$
VIII) Ethyl Chloride is treated with $AgNO_2$
IX) 2-bromopentane is treated with alcoholic KOH.
X) Ethyl Chloride is treated with aqueous KOH

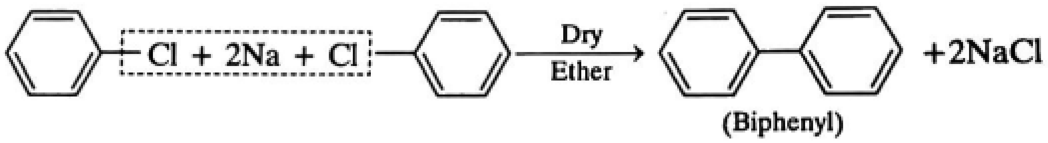
XI) Chlorobenzene is treated with CH_3COCl in presence of anhydrous $Alcl_3$
XII)Methyl chloride is treated with $AgNO_2$.
XIII) Bromobenzene is treated with Ch_3Cl in presence of anhydrous $AlCl_3$
XIV) Ethyl chloride is treated with alcoholic KOH
XV) Chlorobenzene is treated with Ch_3Cl in the presence of anhydrous $AlCl_3$

ANSWERS

I) Ethyl Iodide is formed.

$$C_2H_5-Cl + NaI \xrightarrow{\text{Acetone}} C_5H_5I + NaCl$$

II- Biphenyl will be formed.



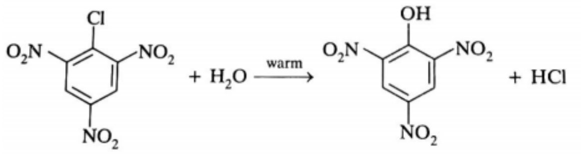
III- Methyl nitrite is formed.

$$CH_3Cl + \overset{+}{K} \vdots \overset{-}{O}-N=O \longrightarrow CH_3-O-N=O + KCl$$

IV-

$$CH_3CH_2CH_2CH_2Cl + KOH(alc) \longrightarrow CH_3-CH_2-CH=CH_2 + KCl + H_2O$$

V-

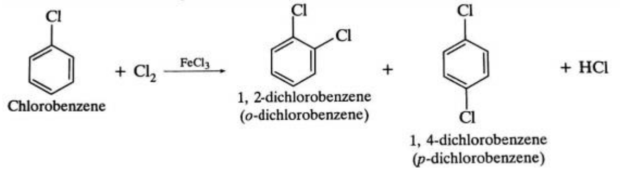


VI-

$$CH_3Cl + AgCN \longrightarrow CH_3N \equiv C + AgCl$$

VII-

o-dichlorobenzene and *p*-dichlorobenzene are formed.



VIII-

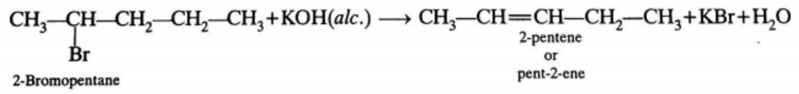
Nitroethane will be formed.

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + AgNO_2 \longrightarrow \underset{\text{Nitroethane}}{C_2H_5NO_2} + AgCl$$

Nitroethane will be formed.

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + AgNO_2 \longrightarrow \underset{\text{Nitroethane}}{C_2H_5NO_2} + AgCl$$

IX- 2-pentene will be formed as major product

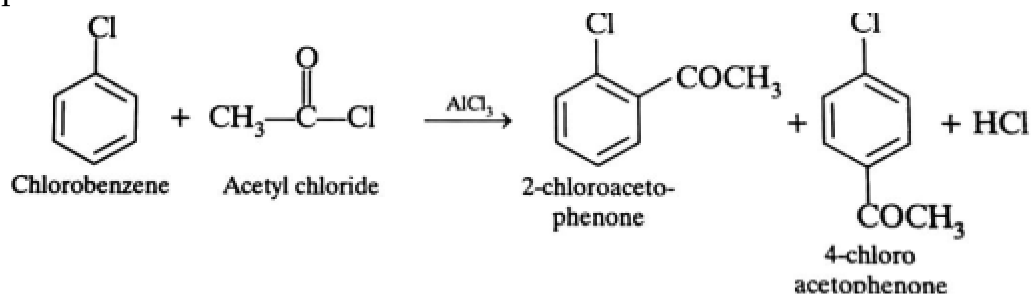


$$\underset{\text{2-Bromopentane}}{CH_3-\underset{Br}{CH}-CH_2-CH_2-CH_3} + KOH(alc.) \longrightarrow \underset{\text{2-pentene or pent-2-ene}}{CH_3-CH=CH-CH_2-CH_3} + KBr + H_2O$$

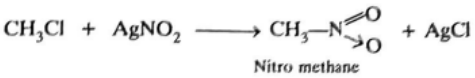
X- Ethyl Alcohol (ethanol) is formed

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + KOH\ (aq) \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KCl$$

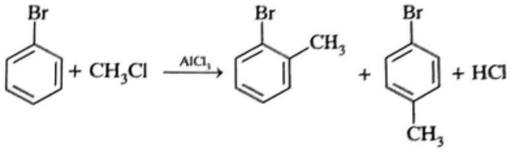
XI-



XII- Nitro methane is formed



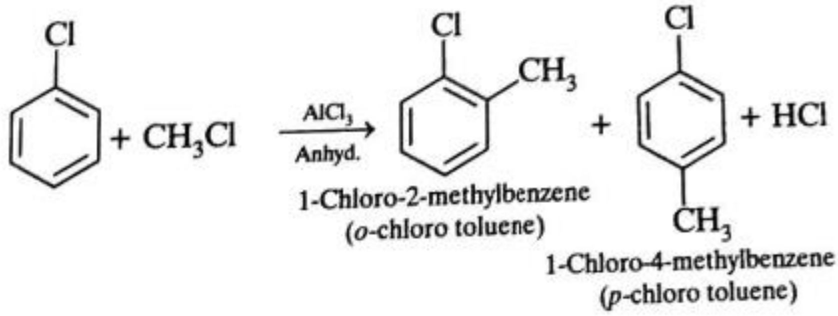
XIII-



XIV-

$$CH_3CH_2Cl \xrightarrow{\text{alc. KOH}} CH_2{=}CH_2 + KCl + H_2O$$

XV-



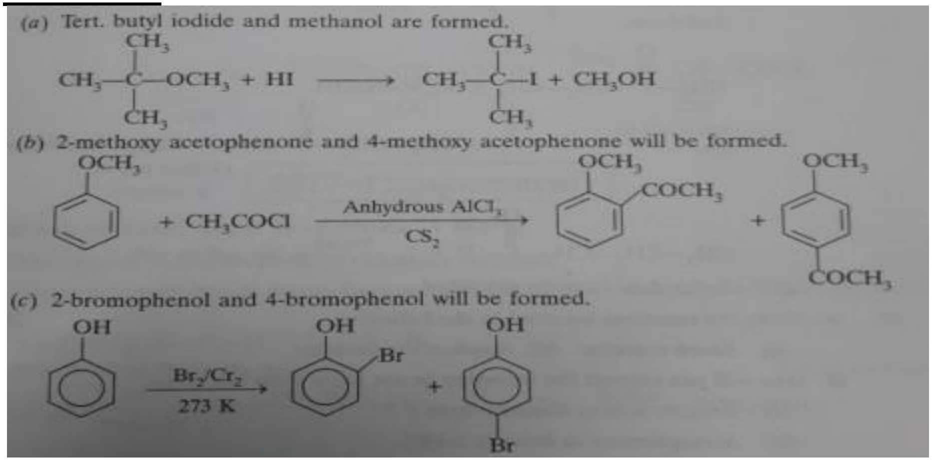
2 .What happens when:

A). $(CH_3)_3OCH_3$ is treated with HI

B). Anisole is treated with CH_3COOCl/anhydrous $ALCl_3$

C). Phenol is treated with Br_2/CS_2

ANSWERS



(a) Tert. butyl iodide and methanol are formed.

(b) 2-methoxy acetophenone and 4-methoxy acetophenone will be formed.

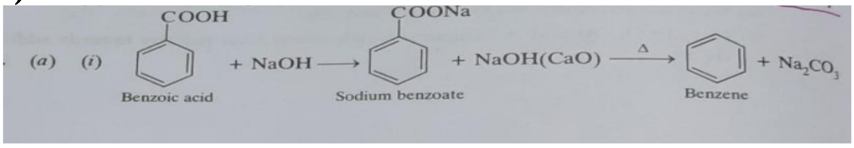
(c) 2-bromophenol and 4-bromophenol will be formed.

3. Convert the following:

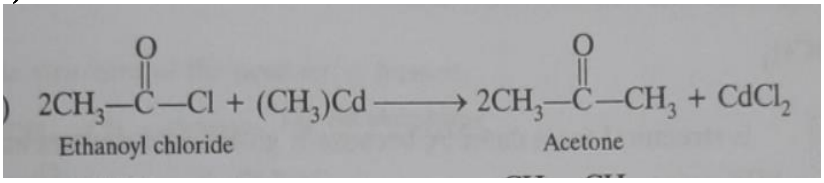
A). benzoic acid to Benzene
B). Ethanoyl chloride to Acetone
C). Acetophenone to Ethyl benzene
D). propanone to propene
E). benzyl chloride to phenyl ethanoic acid
F). Propene to acetone
G). Propanoic acid to 2-hydroxypropanic acid

ANSWERS

A).



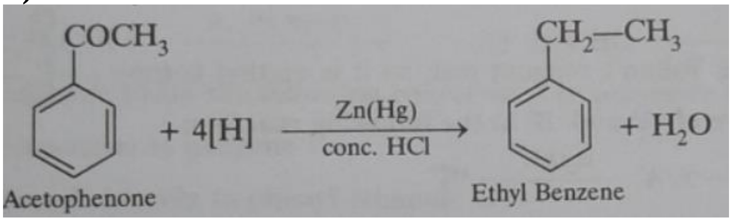
B).



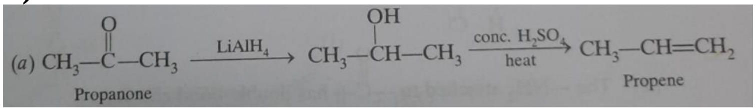
$$2CH_3-\overset{O}{\overset{\|}{C}}-Cl + (CH_3)Cd \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CdCl_2$$

Ethanoyl chloride Acetone

C).



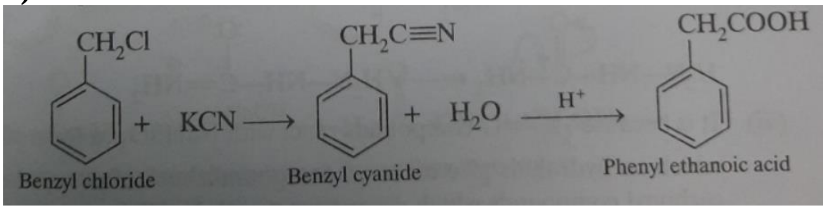
D).



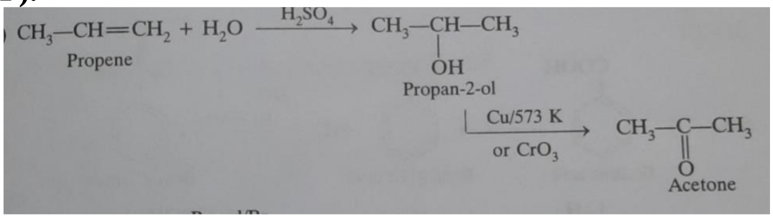
$$(a)\ CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{LiAlH_4} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow[heat]{conc.\ H_2SO_4} CH_3-CH=CH_2$$

Propanone Propene

E).



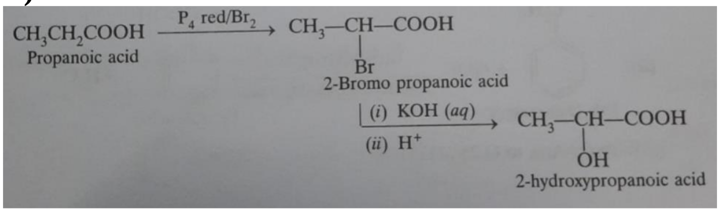
F).



$$CH_3-CH=CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3-\underset{OH}{\underset{|}{C}H}-CH_3 \xrightarrow[or\ CrO_3]{Cu/573\ K} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

Propene Propan-2-ol Acetone

G).

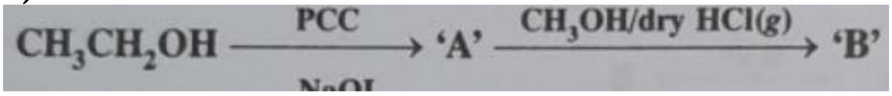


$$CH_3CH_2COOH \xrightarrow{P_4\ red/Br_2} CH_3-\underset{Br}{\underset{|}{C}H}-COOH \xrightarrow[(ii)\ H^+]{(i)\ KOH\ (aq)} CH_3-\underset{OH}{\underset{|}{C}H}-COOH$$

Propanoic acid 2-Bromo propanoic acid 2-hydroxypropanoic acid

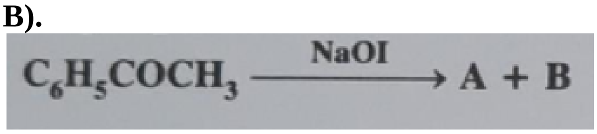
4.FILL IN THE BLANK:

A).



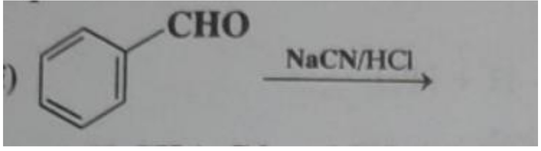
$CH_3CH_2OH \xrightarrow{PCC} \text{'A'} \xrightarrow{CH_3OH/\text{dry } HCl(g)} \text{'B'}$

B).

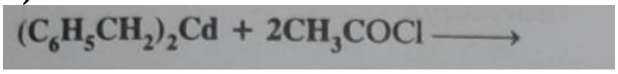


$C_6H_5COCH_3 \xrightarrow{NaOI} A + B$

C).

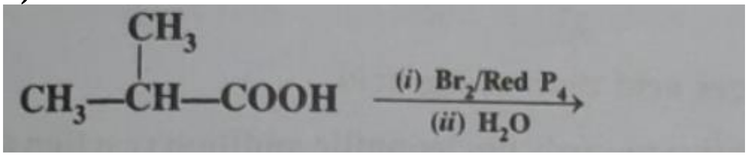


D).



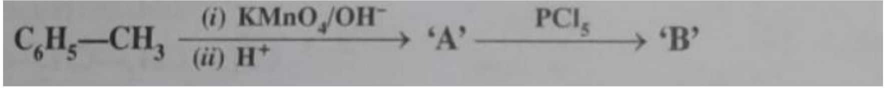
$(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$

E).



$CH_3-\overset{\overset{\large CH_3}{|}}{C}H-COOH \xrightarrow[(ii)\ H_2O]{(i)\ Br_2/\text{Red } P_4}$

F).

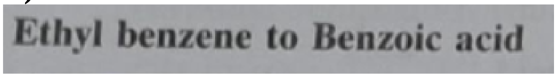


$C_6H_5-CH_3 \xrightarrow[(ii)\ H^+]{(i)\ KMnO_4/OH^-} \text{'A'} \xrightarrow{PCl_5} \text{'B'}$

G).

Benzoic acid to benzaldehyde

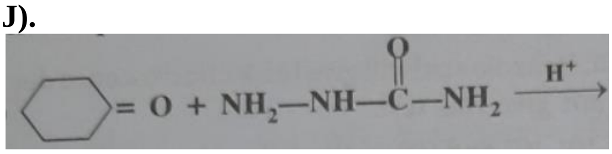
H).



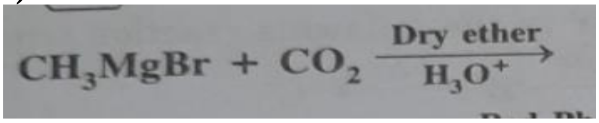
Ethyl benzene to Benzoic acid

I). Propanone to propene

J).

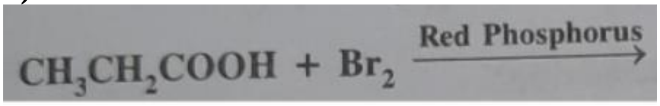


K).



$CH_3MgBr + CO_2 \xrightarrow[H_3O^+]{\text{Dry ether}}$

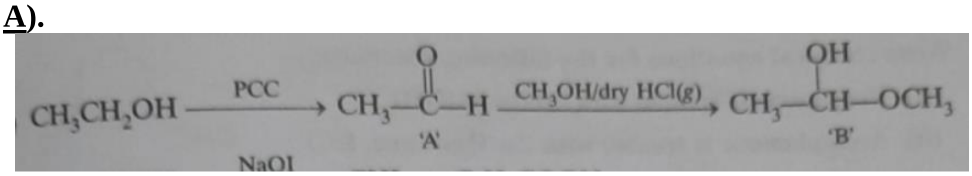
L).



$CH_3CH_2COOH + Br_2 \xrightarrow{\text{Red Phosphorus}}$

ANSWERS

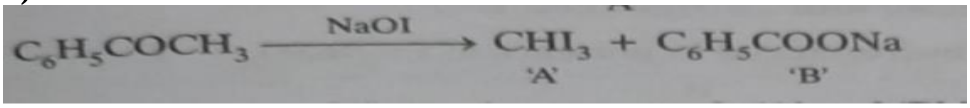
A).



$CH_3CH_2OH \xrightarrow{PCC} \underset{\text{'A'}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{CH_3OH/\text{dry } HCl(g)} \underset{\text{'B'}}{CH_3-\overset{\overset{OH}{|}}{C}H-OCH_3}$

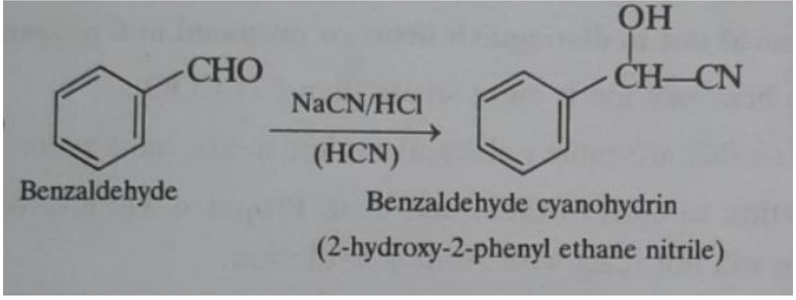
NaOI

B).

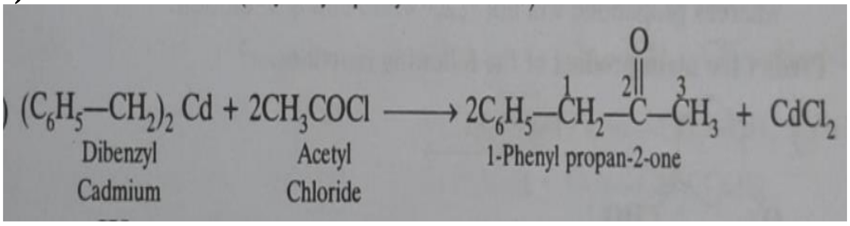


$C_6H_5COCH_3 \xrightarrow{NaOI} \underset{\text{'A'}}{CHI_3} + \underset{\text{'B'}}{C_6H_5COONa}$

C).

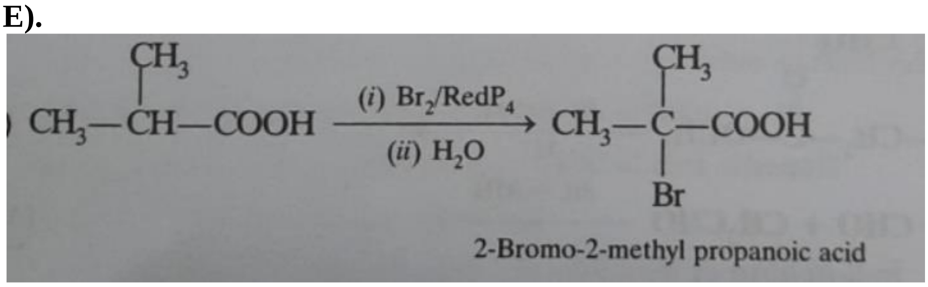


D).



$$\underset{\text{Dibenzyl Cadmium}}{(C_6H_5-CH_2)_2Cd} + \underset{\text{Acetyl Chloride}}{2CH_3COCl} \longrightarrow \underset{\text{1-Phenyl propan-2-one}}{2C_6H_5-\overset{1}{C}H_2-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{3}{C}H_3} + CdCl_2$$

E).



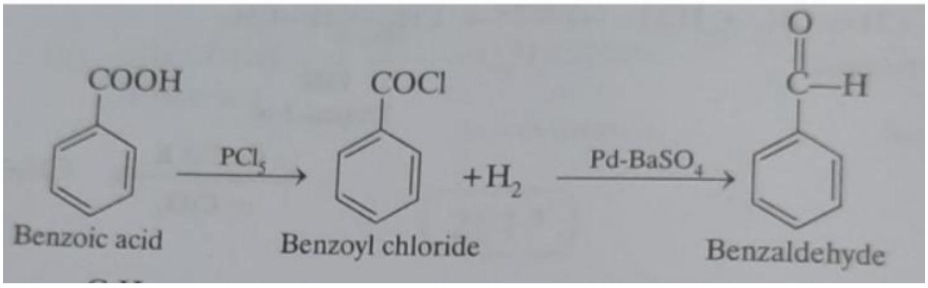
$$CH_3-\overset{\overset{CH_3}{|}}{C}H-COOH \xrightarrow[(ii)\ H_2O]{(i)\ Br_2/RedP_4} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOH$$

2-Bromo-2-methyl propanoic acid

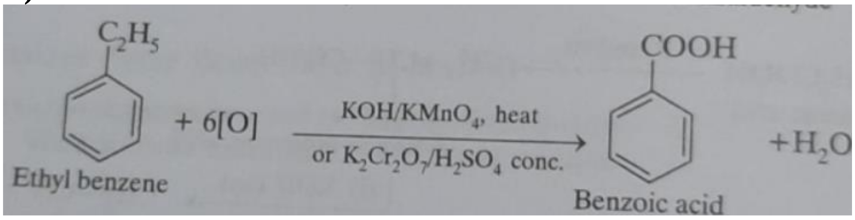
F).

$$C_6H_5-CH_3 \xrightarrow[(ii)\ H^+]{(i)\ KMnO_4/OH^-} \underset{\text{'A'}}{C_6H_5COOH} \xrightarrow{PCl_5} \underset{\text{'B'}}{C_6H_5COCl}$$

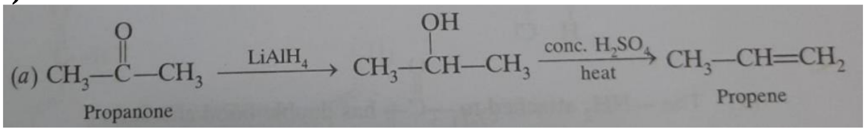
G).



H).

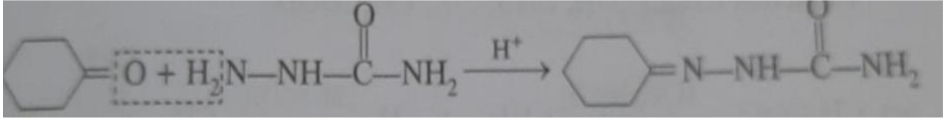


I).



$$(a)\ \underset{\text{Propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{LiAlH_4} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

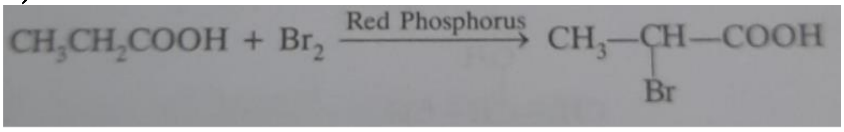
J).



K).

$CH_3MgBr + CO_2 \xrightarrow[H_3O^+]{\text{Dry ether}} CH_3COOH$

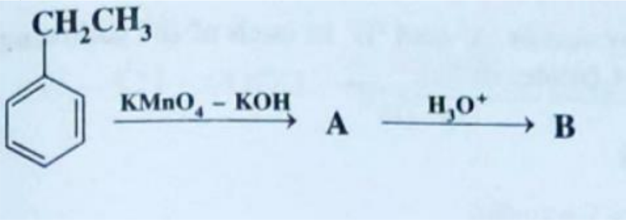
L).



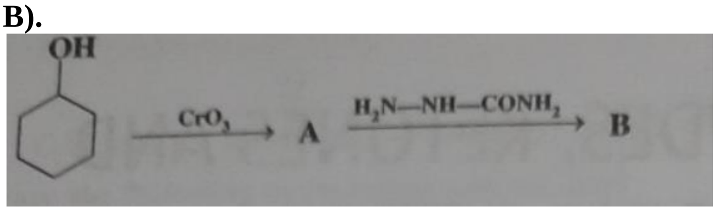
$CH_3CH_2COOH + Br_2 \xrightarrow{\text{Red Phosphorus}} CH_3\text{—}\underset{Br}{CH}\text{—}COOH$

5.WRITE THE PRODUCT

A).



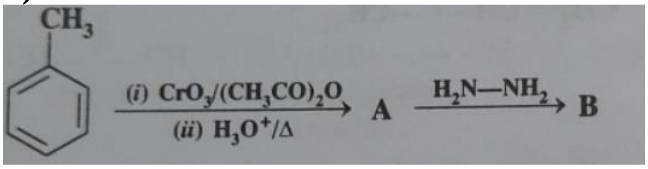
B).



C).

$CH_3CH_2CN \xrightarrow{CH_3MgBr/H_3O^+} A \xrightarrow{LiAlH_4} B$

D).



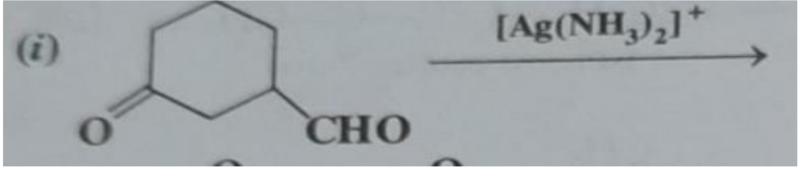
E).

$C_6H_5COOH \xrightarrow{PCl_5} \text{'A'} \xrightarrow{H_2/Pd\text{-}BaSO_4} \text{'B'}$

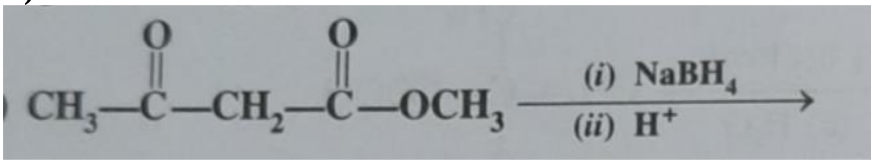
F).

$CH_3C\equiv N \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} \text{'A'} \xrightarrow[\text{Conc. HCl}]{Zn(Hg)} \text{'B'}$

G).

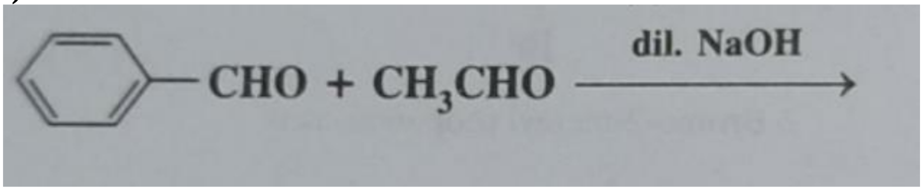


H).

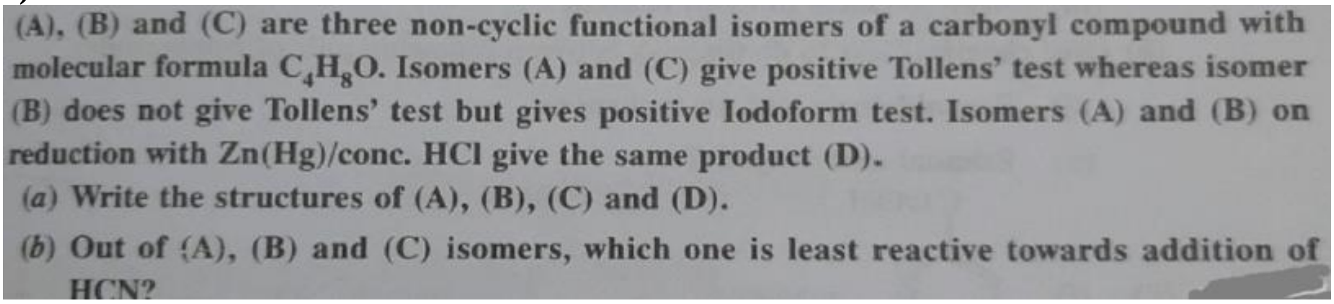


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4}$$

I).



J).

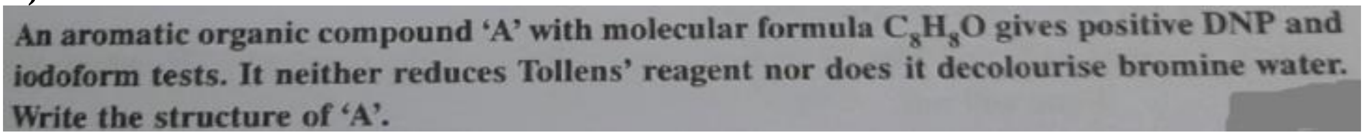


(A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollens' test whereas isomer (B) does not give Tollens' test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/conc. HCl give the same product (D).

(a) Write the structures of (A), (B), (C) and (D).

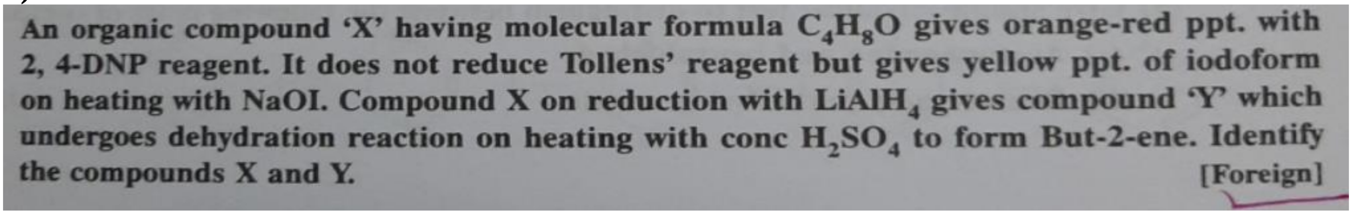
(b) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN?

K).



An aromatic organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It neither reduces Tollens' reagent nor does it decolourise bromine water. Write the structure of 'A'.

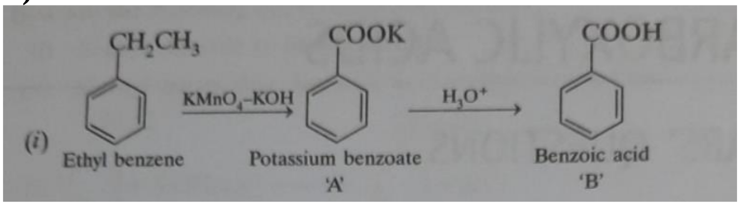
L).



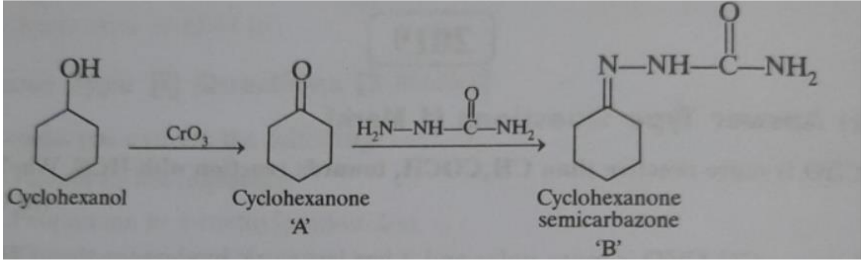
An organic compound 'X' having molecular formula C_4H_8O gives orange-red ppt. with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow ppt. of iodoform on heating with NaOI. Compound X on reduction with $LiAlH_4$ gives compound 'Y' which undergoes dehydration reaction on heating with conc H_2SO_4 to form But-2-ene. Identify the compounds X and Y. [Foreign]

<u>ANSWERS</u>

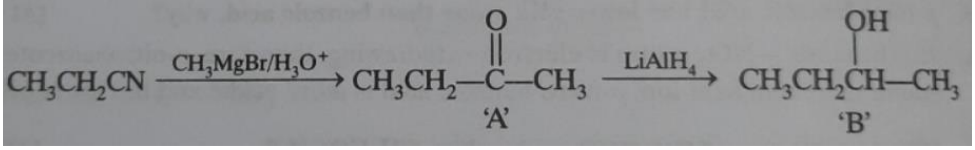
A).



B).

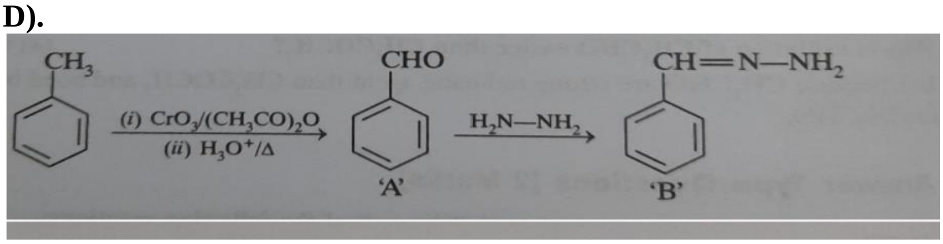


C).

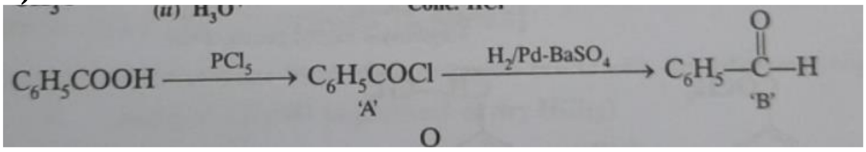


$$CH_3CH_2CN \xrightarrow{CH_3MgBr/H_3O^+} \underset{\text{'A'}}{CH_3CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3} \xrightarrow{LiAlH_4} \underset{\text{'B'}}{CH_3CH_2\overset{\overset{OH}{|}}{C}H-CH_3}$$

D).

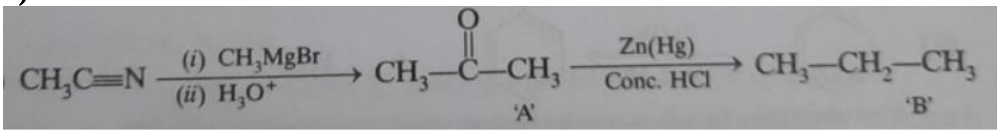


E).



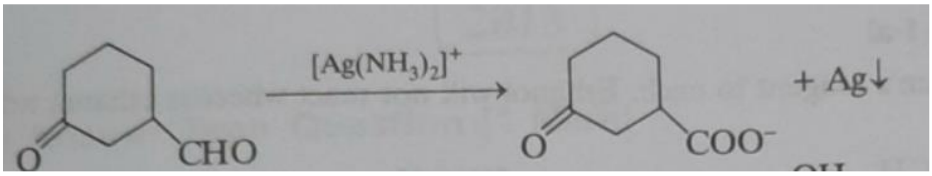
$$C_6H_5COOH \xrightarrow{PCl_5} \underset{\text{'A'}}{C_6H_5COCl} \xrightarrow{H_2/Pd\text{-}BaSO_4} \underset{\text{'B'}}{C_6H_5-\overset{\overset{O}{\parallel}}{C}-H}$$

F).

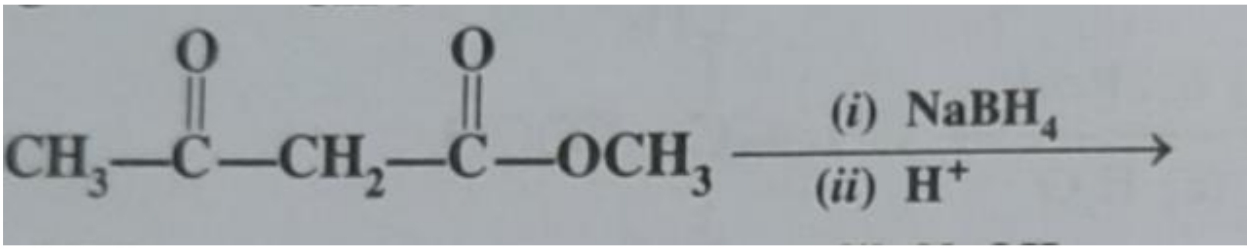


$$CH_3C\equiv N \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} \underset{\text{'A'}}{CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3} \xrightarrow[\text{Conc. HCl}]{Zn(Hg)} \underset{\text{'B'}}{CH_3-CH_2-CH_3}$$

G).

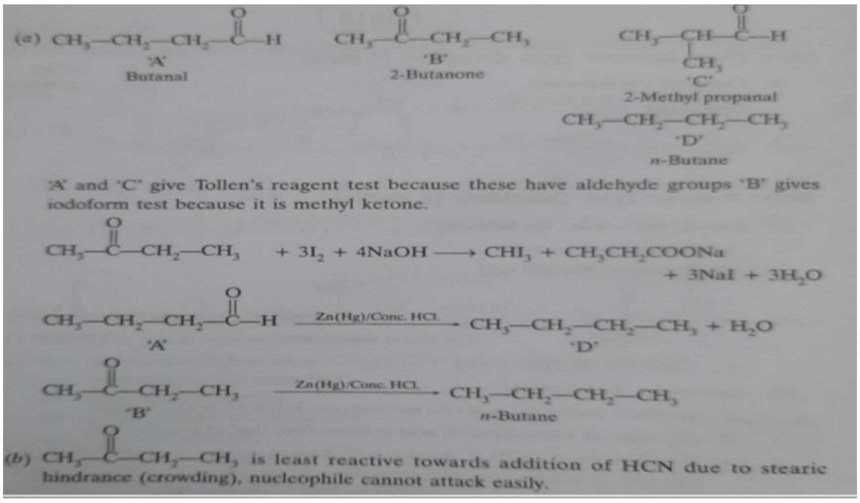


H).



$$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{O}{\parallel}}{C}-OCH_3 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4}$$

J).



(a) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$ 'A' Butanal

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ 'B' 2-Butanone

$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H$ 'C' 2-Methyl propanal

$CH_3-CH_2-CH_2-CH_3$ 'D' *n*-Butane

'A' and 'C' give Tollen's reagent test because these have aldehyde groups 'B' gives iodoform test because it is methyl ketone.

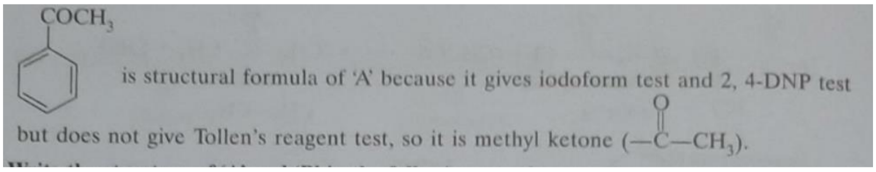
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3CH_2COONa + 3NaI + 3H_2O$$

$$\underset{\text{'A'}}{CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{Zn(Hg)/Conc.\ HCl} \underset{\text{'D'}}{CH_3-CH_2-CH_2-CH_3} + H_2O$$

$$\underset{\text{'B'}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3} \xrightarrow{Zn(Hg)/Conc.\ HCl} \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3}$$

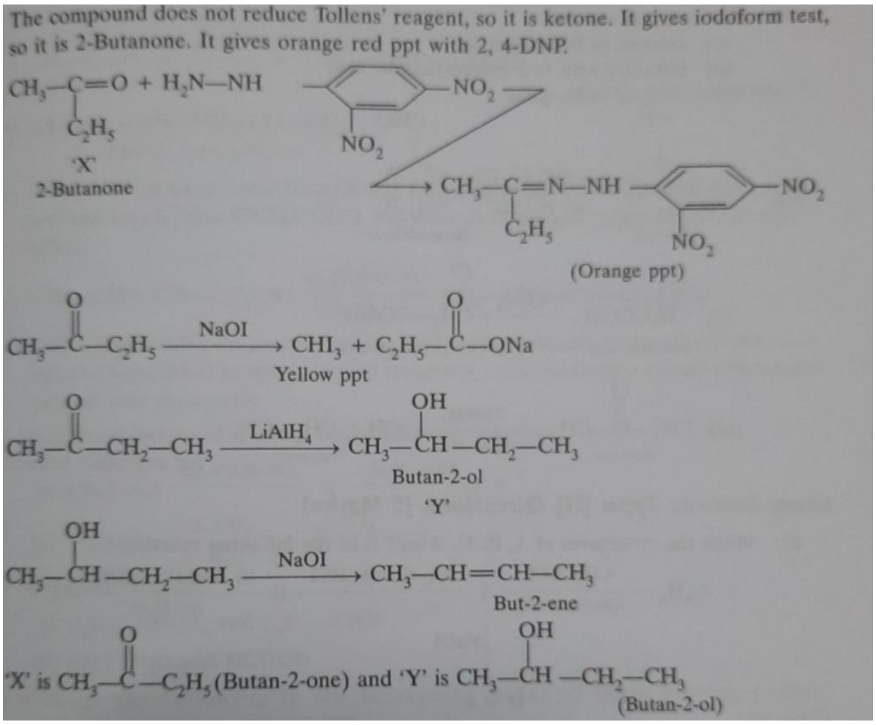
(b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ is least reactive towards addition of HCN due to stearic hindrance (crowding), nucleophile cannot attack easily.

K).



$C_6H_5COCH_3$ is structural formula of 'A' because it gives iodoform test and 2, 4-DNP test but does not give Tollen's reagent test, so it is methyl ketone ($-\overset{O}{\overset{\|}{C}}-CH_3$).

L).



The compound does not reduce Tollens' reagent, so it is ketone. It gives iodoform test, so it is 2-Butanone. It gives orange red ppt with 2, 4-DNP.

$$\underset{\text{'X'}\ \text{2-Butanone}}{CH_3-\underset{C_2H_5}{\underset{|}{C}}=O} + H_2N-NH-C_6H_3(NO_2)_2 \longrightarrow \underset{\text{(Orange ppt)}}{CH_3-\underset{C_2H_5}{\underset{|}{C}}=N-NH-C_6H_3(NO_2)_2}$$

$$CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5 \xrightarrow{NaOI} \underset{\text{Yellow ppt}}{CHI_3} + C_2H_5-\overset{O}{\overset{\|}{C}}-ONa$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow{LiAlH_4} \underset{\text{Butan-2-ol 'Y'}}{CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_3}$$

$$CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_3 \xrightarrow{NaOI} \underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3}$$

'X' is $CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5$ (Butan-2-one) and 'Y' is $CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_3$ (Butan-2-ol)

BIOMOLECULES

KEY WORDS AND THEIR EXPLANATION

Carbohydrates	Optically active, poly hydroxy aldehydes or ketones or the compounds which yield such units upon hydrolysis.
Monosaccharides	Cannot be hydrolyzed further. e.g.-glucose, fructose, ribose
Reducing sugars	Aldehydic/ ketonic groups free so reduce Fehling's/ Tollen's solution . e.g.- all monosaccharides, maltose and lactose
Non reducing sugars	Aldehydic/ ketonic groups are bonded so cannot reduce Fehling's/ Tollen's solution. Eg sucrose
Anomers.	The two cyclic hemiacetal forms of glucose that 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.
Invert sugar	Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and levorotatory fructose. Since the levorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is levorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar.
Essential amino acids	Which cannot be synthesized in the body and must be obtained through diet. Eg valine,leucine
Non-essential amino acids	Which can be synthesized in the body, eg-Glycine, Alanine
Zwitter ion	In aqueous solution, amino acids exist as a dipolar ion known as zwitter ion.
Peptide linkage	Peptide linkage is an amide formed between –COOH group and –NH2 group of two successive amino acids in peptide chain.
Primary (1^0) str. Of proteins:	Sequence of amino acids that is said to be primary structure of proteins.
Secondary (2^0) str. Of proteins	secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two types of structures viz. α-helix andβ-pleated sheet structure.
Tertiary structure of proteins:	further folding of the secondary structure. It gives rise to two major molecular shapes viz fibrous and globular.
Fibrous proteins	Polypeptide chains run parallel, held together by hydrogen and disulphide bonds, fiber– like structure. Water insoluble. Eg- keratin (inhair, wool, silk) myosin (present in muscles).
Globular proteins	chains of polypeptides coil around to give a spherical shape. water soluble. Eg-Insulin and albumin
Stable forces 2°& 3° structure of proteins	Hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
Denaturation of Proteins	When a protein is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. (During denaturation 2° and 3^0 structures are destroyed but 1^0 structure remains intact.) eg- The coagulation of egg white on boiling, curdling of milk etc.
DNA	pentose sugar (D-2-deoxyribose) + phosphoric acid + nitrogenous bases (A , G , C, T)
RNA	pentose sugar (ribose) + phosphoric acid + nitrogenous bases (A, G, C, U)
Phosphodiester link	Linkage between two nucleotides in polynucleotides

Functions of Nucleic Acids	DNA reserve genetic information, maintain the identity of different species is capable of self-duplication during cell division, protein synthesis.

Very Short Answer Questions

1. How many asymmetric carbon atoms are present in D (+) glucose?
2. Give the significance of (+)-sign in the name D- (+)-glucose.
3. Give the significance of prefix 'D' in the name D- (+)-glucose.
4. Name the linkage present in proteins.
5. Write the Zwitter ion form of amino acetic acid. (H_2NCH_2COOH).
6. How would you explain the amphoteric behavior of amino acids?
7. Which nucleic acid is responsible for carrying out protein synthesis in the cell?
8. The two strands in DNA are not identical but complementary. Explain.
9. What type of linkage holds together the monomers of DNA and RNA?
10. Mention the number of hydrogen bonds between adenine and thymine.

ANSWERS

1. 4
2. (+) sign indicates dextrorotatory nature of glucose.
3. 'D' Signifies that –OH group on C-5 is on the right-hand side
4. Peptide linkage
5. $NH_3^+CH_2COO^-$
6. Amino acids are amphoteric due to the presence of both acidic and basic functional groups.
7. RNA
8. complementary bases are prepared.
9. Phosphodiester linkage.
10. Two

Assertion –Reason based questions

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) Both assertion and reason are false.

1. Assertion : D - glucose is dextrorotatory whereas L - glucose is levorotatory.
   Reason : D - compounds are always dextro and L - compounds are always laevo. (Ans - b)
2. Assertion : Purine bases present in DNA are adenine and guanine.
   Reason : The base thymine is present in RNA while base uracil is present in DNA. (Ans - c)
3. Assertion : α - Amino acids are the building blocks of proteins.
   Reason : Natural amino acids are mostly α - amino acids. (Ans - b)
4. Assertion : The two strands of DNA are complementary.
   Reason : Cytosine always pairs with guanine and thymine pairs with adenine. (Ans- a)
5. Assertion : Keratin is a globular protein.
   Reason : Globular shape is due to secondary structure of proteins. (Ans- c)

Multiple Choice Questions

1. Antibodies are –

(a) carbohydrates (b) Proteins
(c) Lipids (d) Enzymes
Ans b

2. Which statement is incorrect about peptide bond?
(a) N bond length in proteins is longer than usual bond length of C – N bond
(b) Spectroscopic analysis shows planar structure of – CO – NH – group
© C – N bond length in proteins is smaller than usual bond length of C – N bond
(d) None of the above Ans a

3. The functional group which is found in amino acid is
(a) – COOH (b) – NH2
(c) – CH3 (d) both (a) and (b) Ans – d

4. Which base is present in RNA but not in DNA?
(a) Uracil (b) Cytosine
(c) Guanine (d) Thymine Ans d

5. ADP and ATP differ in the number of
(a) adenine base (b) ribose units
(c) phosphate units (d) nitrogen atoms Ans c

6. In both DNA and RNA, heterocyclic base and phospho diester linkages are at –
a. C5' and C2' respectively of the sugar molecule
b. C2' and C5' respectively of the sugar molecule
c. C1' and C5' respectively of the sugar molecule
d. C5' and C1' respectively of the sugar molecule
Ans c

6. Protein is a polymer made of
(a) carbohydrates (b) amino acids
© nucleic acids (d) carboxylic acids Ans- b

7. Nucleic acids are the polymers of
(a) Nucleosides (b) Nucleotides
© Bases (d) Sugars Ans- b

8. The specific sequence of amino acids in a polypeptide chain is known as
(a) Primary structure of proteins
(b) Secondary structure of proteins
(c)Tertiary structure of proteins
(d) Quaternary structure of proteins

9. Which of the following properties of glucose can be explained only by its cyclic structure
(a) Glucose forms pentaacetate
(b) Glucose reacts with hydroxylamine to form an oxime.
© Pentaacetate of glucose does not react with hydroxylamine.
(d) Glucose is oxidized by nitric acid to gluconic acid. Ans – c

10. Which of the following statements is not true about glucose ?
(a) It is an aldohexose
(b) On heating with HI it forms n- hexane
© It is present in furanose form
(d) It does not give 2,4-DNP test. Ans- c

Short Answer Questions

Q1. What is difference between reducing and non-reducing sugars or carbohydrates?
(Ans) All those carbohydrates which contain aldehydic and ketonic group in the hemiacetal or hemiketal form and reduce Tollen's reagent or Fehling's solution are called reducing carbohydrates while others which do not reduce these reagents are called non-reducing sugars.

Q2. Explain the term mutarotation?
(Ans) Mutarotation is the change in the specific rotation of an optically active compound with time, to an equilibrium mixture.

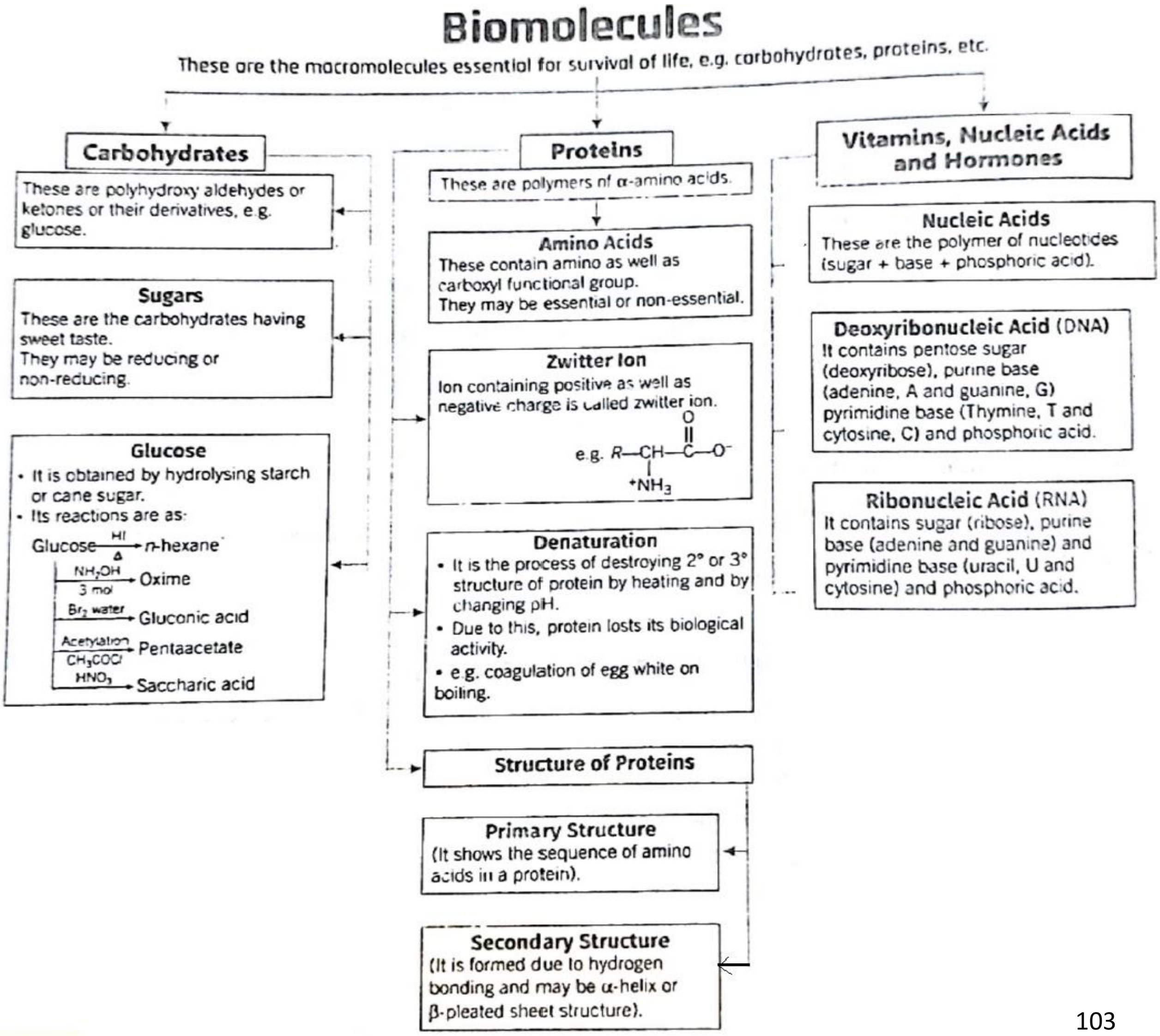
Q3. Why are carbohydrates generally optically active?
Ans. It is due to the presence of Chiral Carbon atoms in their molecules

Q4. How is globular protein different from fibrous protein?
Ans–

Globular Protein	Fibrous Protein
1.they form α-helix structure	. 1. they have β-pleated structure
2.they are water soluble.	2. they are water insoluble
3 they involve H bonding**.**	**3. they have strong intermolecular forces of attraction**

Q5. (i) What products would be formed when a nucleotide from DNA containing thymine is hydrolyzed?
Ans. Complete hydrolysis of DNA yields a pentose sugar, phosphoric acid and thymine.
(ii)How will you distinguish 1° and 2° hydroxyl groups present in glucose?
Ans- On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid,

Q6. Explain tertiary structure of Protein.
Ans. Tertiary structure of proteins: The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. The main forces which stabilize the 2° and 3° structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic force of attraction.



Biomolecules

These are the macromolecules essential for survival of life, e.g. carbohydrates, proteins, etc.

Carbohydrates

These are polyhydroxy aldehydes or ketones or their derivatives, e.g. glucose.

Sugars

These are the carbohydrates having sweet taste.
They may be reducing or non-reducing.

Glucose

- It is obtained by hydrolysing starch or cane sugar.
- Its reactions are as:

$$\text{Glucose} \xrightarrow[\Delta]{HI} n\text{-hexane}$$
$$\xrightarrow[3\ mol]{NH_2OH} \text{Oxime}$$
$$\xrightarrow{Br_2\ water} \text{Gluconic acid}$$
$$\xrightarrow[CH_3COCl]{Acetylation} \text{Pentaacetate}$$
$$\xrightarrow{HNO_3} \text{Saccharic acid}$$

Proteins

These are polymers of α-amino acids.

Amino Acids

These contain amino as well as carboxyl functional group.
They may be essential or non-essential.

Zwitter Ion

Ion containing positive as well as negative charge is called zwitter ion.

e.g. $R-\underset{{}^{+}NH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^-$

Denaturation

- It is the process of destroying 2° or 3° structure of protein by heating and by changing pH.
- Due to this, protein losts its biological activity.
- e.g. coagulation of egg white on boiling.

Structure of Proteins

Primary Structure

(It shows the sequence of amino acids in a protein).

Secondary Structure

(It is formed due to hydrogen bonding and may be α-helix or β-pleated sheet structure).

Vitamins, Nucleic Acids and Hormones

Nucleic Acids

These are the polymer of nucleotides (sugar + base + phosphoric acid).

Deoxyribonucleic Acid (DNA)

It contains pentose sugar (deoxyribose), purine base (adenine, A and guanine, G) pyrimidine base (Thymine, T and cytosine, C) and phosphoric acid.

Ribonucleic Acid (RNA)

It contains sugar (ribose), purine base (adenine and guanine) and pyrimidine base (uracil, U and cytosine) and phosphoric acid.

SOME VERY-VERY IMPORTANT TOPICS FOR QUICK REVISION & PRACTICE

SOLID STATE

Formula and Points.

	Value of z	Lattice Point	Relation	Internuclear Distanc
FCC	$z=4$	$8+6=14$	$4r=\sqrt{2}a$	$2r$
BCC	$z=2$	$8+1=19$	$4r=\sqrt{3}a$	$2r$
Simple	$z=1$	8	$2r=a$	$2r$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A} = \frac{Z \times \text{mass given}}{a^3 \times \text{No. of atoms in given mass}}$$

$$\text{No. of unit cells} = \frac{\text{Volume given}}{\text{Volume of one unit cell}}$$

$$= \frac{\text{Volume}}{a^3} \text{ (in same unit)}$$

$$= \frac{\text{mass given}}{\text{mass of each unit cell}}$$

$$= \frac{\text{mass}}{Z \times \frac{\text{Atomic Mass}}{N_A}}$$

NOTE:- For NaCl type (Rock salt structure)

1. FCC structure, $Z=4$
2. $r_{Na^+} + r_{Cl^-} = a/2$

For CsCl type (BCC structure)

1. $z = 1$
2. $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$

For other ionic solid $z = 4$

Solution

1. Molarity = moles/Lit. of Solution

$$M = \frac{\text{mass}}{\text{molar mass}} \times \frac{1000}{\text{Volume in ml}}$$

2. Molality = moles / kg of Solvent

$$m = \frac{\text{mass}}{\text{molar mass}} \times \frac{1000}{\text{mass of solvent in gm.}}$$

3. mole fraction = $\frac{n_{solute}}{n_{solute} + n_{solvent}}$

n = no. of moles.

4. Rault's Law -

$$P_A = P_A^\circ x_A \quad , \quad P_B = P_B^\circ x_B$$

$$P_S = P_A + P_B$$

$$= P_A^\circ x_A + P_B^\circ x_B$$

5. Henry Law

$$P = K_H \cdot x$$

P - Partial pressure
K_H - henry constant
x - mole fraction

6. Calligative property

$$\frac{P^\circ - P_s}{P^\circ} = \frac{w_2/m_2}{\frac{w_1}{m_1} + \frac{w_2}{m_2}} = x_2 = \text{mole fraction of Solute}$$

where
w_2 - mass of Solute
m_2 - molar mass of Solute
w_1 - mass of Solvent
m_1 - molar mass of Solvent

7. $\pi = CRT$, where $c = \text{molarity} = \frac{w_2}{m_2} \times \frac{1000}{V(ml) \text{ of Solution}}$

$= \frac{n}{V} RT$

Volume(V) in Liter

$$= \left(\frac{w_2}{m_2} \times \frac{1000}{V \text{ in } ml}\right) RT$$

$R = 0.0821 \ L\,atm^{-1}$ if π is in atm.
T- in kelving
1 atm = 760 mm
= 760 torr
= 76 Cm

8. $\Delta T_b = K_b \cdot \text{molality}$

$$\text{molality} = \frac{w_2}{m_2} \times \frac{1000}{\text{mass of Solvent in gm.}}$$

9. $\Delta T_f = K_f \cdot \text{molality}$

~~10. Dissociation~~, ~~α~~

Electrochemistry

1. $E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log Q$

n = from cell reaction no. of electron , $Q = \frac{[\text{Product}]^{\text{Coeff.}}}{[\text{Reactant}]^{\text{Coeff.}}}$

2. $E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{anode}$

$= \text{more} - \text{less}$

3. $\Delta G^\circ = -2.303\, RT \log K$ K = equilibrium constant

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

$1F = 96500\,C$

n = no. of e^- in cell reaction

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

= (Always Positive)

ΔG° = Standard Gibb's energy change

Teacher's Signature

Page No.

Electrolysis →

4. $m = ZQ$ Q= Quantity of charge in ~~Col~~ Coulumb(C)

$= Zit$

$Z = \frac{A}{nF} = \frac{\text{Atomic mass}}{\text{Valency} \times 96500}$.

5. $\frac{m_1}{E_1} = \frac{m_2}{E_2} = \frac{m_3}{E_3}$

$E = \frac{A}{n} = \frac{\text{Atomic mass}}{\text{Valency}}$

Conductance →

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

7. Conductance $G = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{A}{l}$ $\left[\because K = \frac{1}{\rho} \right]$

8. Conductance $= K \cdot \frac{A}{l}$, K → Conductivity (Kappa)

Unit – $Ohm^{-1}\ cm^{-1}$

$K = G \cdot \frac{l}{A}$ G-Conductance.

Unit- $Ohm\ cm^2\ mole^{-1}$

$K = G \cdot G^*$

$G^* = \frac{l}{A} =$ Cell Constant

Unit = cm^{-1}.

9. molar Conductivity - $\Lambda_m = \frac{K \times 1000}{M}$

M - molarity

Degree of dissociation -

$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$

Λ_m = molar Conductivity

Λ_m° = limiting molar conductance.

10. Kohlrausch's Law, for Λ_m°

$$\Lambda_m^\circ = \Sigma \lambda_+^\circ + \Sigma \lambda_-^\circ$$

CHEMICAL KINETICS

1. Rate of reaction

Change in concentration of product and reactant.

Let a reaction-

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Rate of Reaction $= -\frac{d}{dt} N_2$ = Rate of decomposition of N_2.

$= -\frac{1}{3} \frac{d}{dt} H_2$

$= \frac{1}{2} \frac{d}{dt} [NH_3]$, Rate of formation of NH_3

$= \frac{d}{dt} NH_3$.

2. Rate Law :-

$$aA + bB \longrightarrow \text{Product}$$

Rate of reaction $= K[A]^{\alpha}[B]^{\beta}$

Order of reaction $= \alpha + \beta$

3. Molecularity -

Let a reaction,

$$aA + bB \longrightarrow \text{Product}$$

Molecularity $= a + b$

4. Integrated Rate expression -

For zero order -

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

$[R_0]$ - initial Conc. of reactant

$[R]$ - Conc. of reactant after t time

$t_{1/2} = \frac{[R_0]}{2K}$ = half life time.

5. For first order

$$K = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

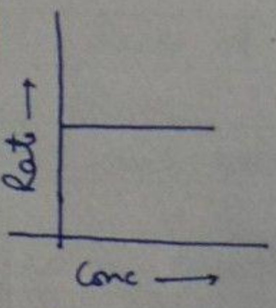
$$t_{1/2} = \frac{0.693}{K.}$$

Unit of K = $(\text{Conc.})^{1-n}\, t^{-1}$

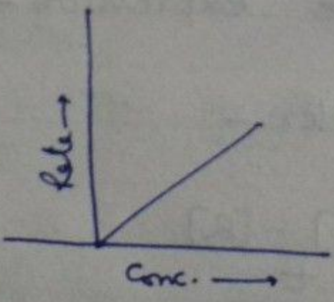
= $(\text{mole Lit}^{-1})^{1-n}\, t^{-1}$

For
1st order Unit of K = Sec^{-1}
2nd order " " = $\text{L mole}^{-1}\, \text{sec}^{-2}$
3rd order " " = $\text{L}^{2}\, \text{mole}^{-2}\, \text{sec}^{-1}$
zero order " " = $\text{mole Lit}^{-1}\, \text{sec}^{-1}$

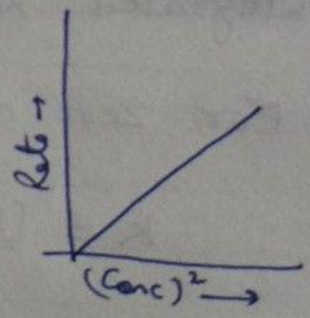
Graphical Method :→



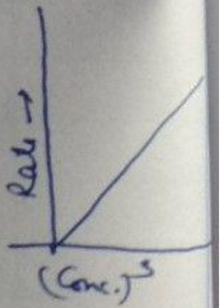
Zero order



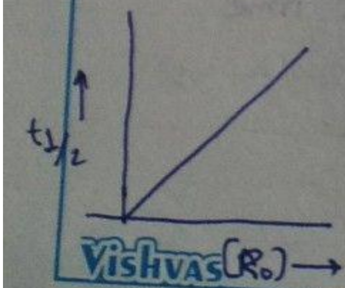
first orde



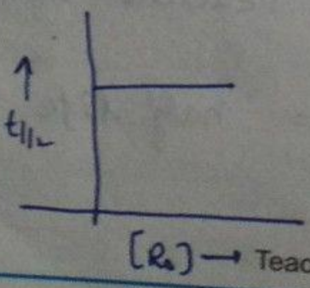
Second ordo



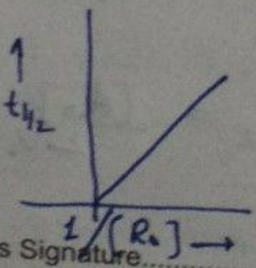
Third order



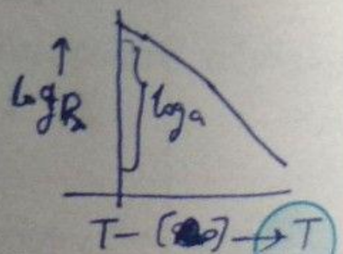
Zero order



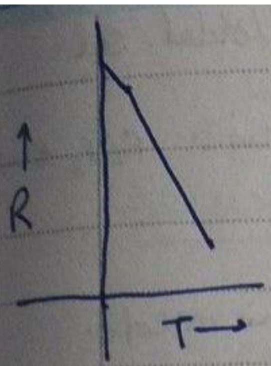
firstorder



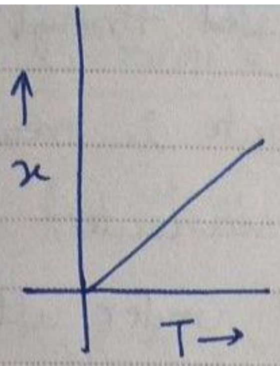
Second order



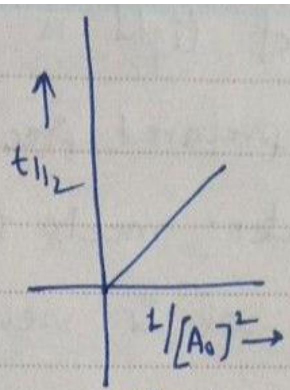
First order



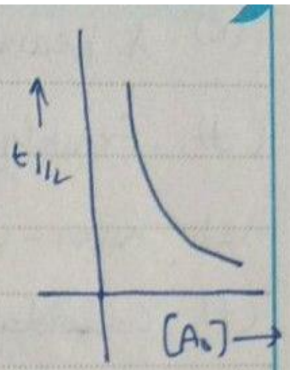
zero order



Zero order



Third order



Second order.

Surface Chemistry

Q:-1 Define the following -

(a) Coagulation (b) Electrophoresis (c) Tyndal effect

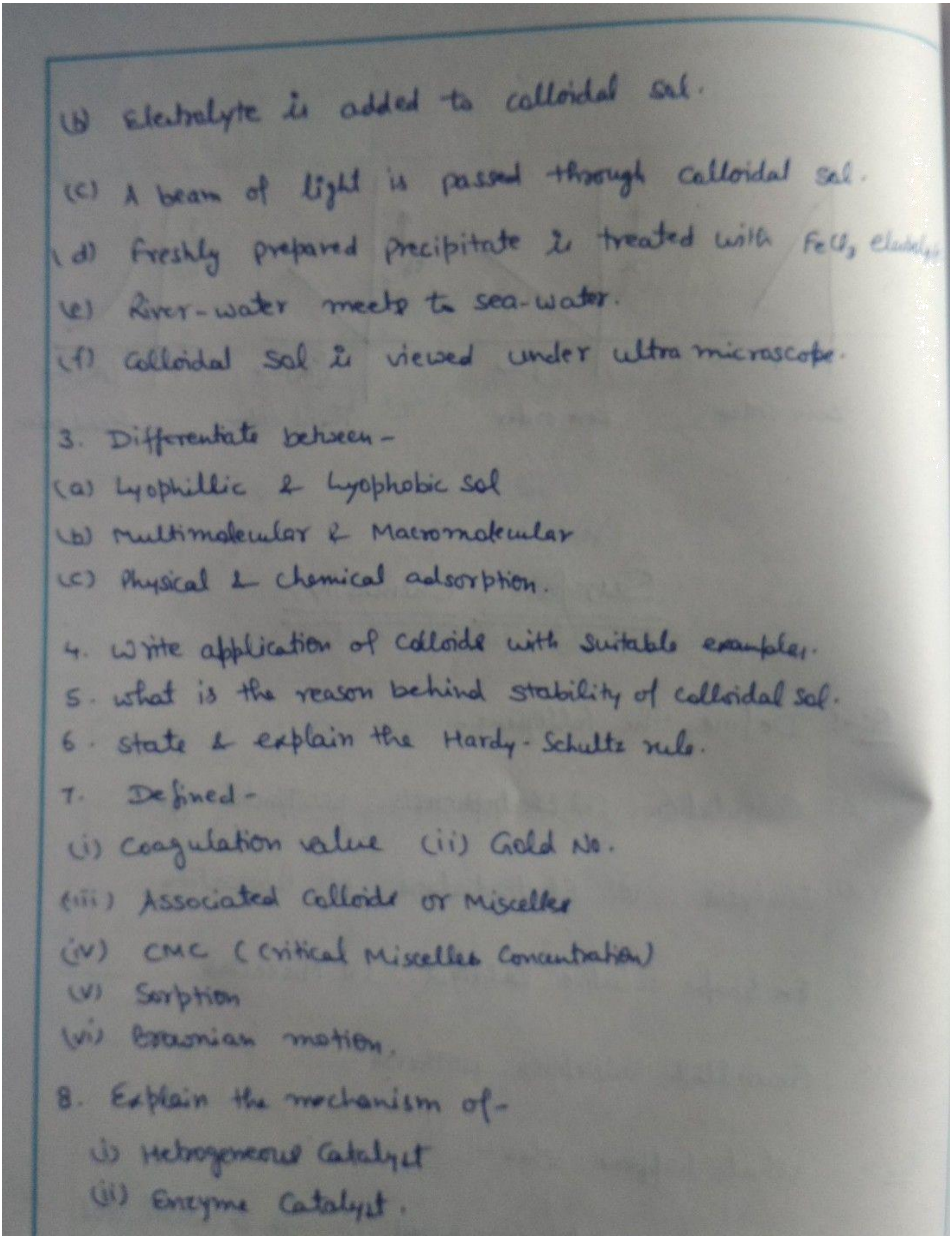
(d) Dialysis (e) Electrodialysis (f) Peptisation

(g) ~~Em~~ Shape selective catalyst (h) Miscelles

(i) Freundlich adsorption isotherm.

Q2:- What happens when -

(a) Electric current is passed through colloidal sol.



(b) Electrolyte is added to colloidal sol.

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

(d) Freshly prepared precipitate is treated with $FeCl_3$ electroly

(e) River-water meets to sea-water.

(f) Colloidal sol is viewed under ultra microscope.

3. Differentiate between -

(a) Lyophillic & Lyophobic sol

(b) Multimolecular & Macromolecular

(c) Physical & chemical adsorption.

4. Write application of colloids with suitable examples.

5. what is the reason behind stability of colloidal sol.

6. state & explain the Hardy-Schultz rule.

7. Defined -

(i) Coagulation value (ii) Gold No.

(iii) Associated Colloids or Miscelles

(iv) CMC (Critical Miscelles Concentration)

(v) Sorption

(vi) Brownian motion.

8. Explain the mechanism of -

(i) Hetrogeneous Catalyst

(ii) Enzyme Catalyst.

The P-Block Elements

Reasoning Questions →

1. Nitrogen is least reactive at room temperature. why?
2. Oxygen exists as O_2(gas) but sulpher exists as S_8(Solid).
3. Sulpher in vapour state is paramagnetic.
4. Phosphorous shows more catenation than Nitrogen.
5. The negative electron gain enthalpy of:
   $N < P$, $O < S$, $F < Cl$
6. Bond dissociation enthalpy of F_2 is even less than Cl_2 and Br_2.
7. NF_3 is exothermic compound but NCl_3 is endothermic.
8. SF_6 is Formed, but SCl_6 is not formed.
9. Nitrogen, oxygen and fluorine form hydrogen bonds.
10. H_2O is a liquid, while H_2S is a gas at room temp.
11. Nirogen does not form pentahalides.
12. $R_3P=O$ is formed but $R_3N=O$ is not formed
13. Inspite of fluorine having less negative electron gain enthalpy than chlorine, F_2 has more oxidising power than Cl_2.
14. Ozone (O_3) is a strong oxidising agent.
15. Bismuth (Bi) in pentavalent state is oxidising agent.
16. PbO_2 is a oxidising agent.
17. Interhalogen compounds are less stable than halogens.
18. Fluorine does not play the role of central element in interhalogen compounds.

19. Ionisation enthalpy of Group 15 elements is more than that of Group 16 elements.

20. Boiling point of inert gas is very less.

21. Inert gas do not form compounds.

22. Xe forms ~~the~~ its compounds, but only with fluorine and oxygen.

23. Even though Lithium has very high ionisation enthalpy, it is a strong reducing agent

24. SF_6 is more stable than SF_4.

25. SbF_5 is less stable than SbF_3.

26. H_3PO_3 is a dibasic acid and it undergoes disproportionation

27. Electron gain enthalpy of noble gas is positive and their ionisation enthalpy is very high.

28. NH_3 is more basic than PH_3.

29. NH_3, H_2O, HF exists in liquid state and have high boiling point than corresponding PH_3, H_2S, HCl.

30. why the acidic strength order is as–

(i) $HF < HCl < HBr < HI$

(ii) $H_2O < H_2S < H_2Se < H_2Te$

(iii) $HClO_4 > HClO_3 > HClO_2 > HClO$.

(iv) $HOCl > HOBr > HOI$.

31. Arrange the following in decreasing order of property mentioned:

i) LiCl, LiBr, LiI (Covalent character)
(ii) MF, MCl, MBr, MI (Ionic character)
(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Basic Strength)
(iv) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Reducing Power)

Important structure

H_2SO_4, $H_2S_2O_3$, $H_2S_2O_7$, $H_2S_2O_8$,

H_2SO_5, H_2SO_3, H_3PO_4, H_3PO_3, H_3PO_2,

$H_4P_2O_7$, $H_4P_2O_5$, $(HPO_3)_3$, HNO_3, HNO_2,

$HClO_4$, $HClO_3$, $HClO_2$, HClO, N_2O_5,

NO_2, N_2O_4, N_2O_3, NO, N_2O, [illegible] NH_3,

NH_4^+, NO_3^-, SO_3, SO_2, SF_4, SF_6, ICl_2^+,

I_3^-, IF_5, IF_7, ICl_4^-, XeF_2, XeF_4

Complete the following Reactions

1. $HNO_2 \longrightarrow HNO_3 + H_2O + NO$

2. $NH_4Cl + NaNO_2 \longrightarrow N_2 + H_2O + NaCl$

3. $H_2O + NO_2 \longrightarrow HNO_3 + NO$

4. $ZnSO_4 + NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$

5. $PH_3 + HgCl_2 \longrightarrow Hg_3P_2 + HCl$

6. $P_4 + NaOH \longrightarrow PH_3 + NaH_2PO_2$

7. $H_3PO_3 \xrightarrow{\Delta} PH_3 + H_3PO_4$

[redacted]

8. $N_2O_5 + H_2O \longrightarrow HNO_3$

9. $SO_3 + H_2O \longrightarrow H_2SO_4$

10. $H_2S_2O_7 + H_2O \longrightarrow H_2SO_4$

11. $Cl_2O_7 + H_2O \longrightarrow HClO_4$

12. $XeF_2 + H_2O \longrightarrow Xe + HF + O_2$

13. $XeF_4 + H_2O \longrightarrow Xe + XeO_3 + HF + O_2$

14. $XeF_6 + H_2O \longrightarrow XeO_3 + HF$

15. $H_2SO_4 + C \longrightarrow CO_2 + SO_2 + H_2O$

16. $I_2 + HNO_3 \longrightarrow HIO_3 + NO_2 + H_2O$

17. $Cu + \text{dil. } HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$.

18. Cu + Conc. $HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

19. $NH_3 + O_2 \longrightarrow NO + H_2O$

20. $Cu^{+2} + NH_3 \longrightarrow [Cu(NH_3)_4]^{+2}$

21. $CuSO_4 + NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4$

22. $AgCl + NH_4OH \longrightarrow Ag(NH_3)_2Cl$

23. Cl_2 + dil. $NaOH \longrightarrow NaCl + NaClO + H_2O$

24. Cl_2 + Con. $NaOH \longrightarrow NaCl + NaClO_3 + H_2O$

25. $SO_2 + Fe^{+3} + H_2O \longrightarrow Fe^{+2} + H_2SO_4$

26. $H_2S + SO_2 \longrightarrow S + H_2O$

27. $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

28. $AgCl + NH_3 \longrightarrow [Ag(NH_3)_2]Cl$

29. $HNO_2 \xrightarrow{\Delta} HNO_3 + H_2O + NO$

30. $XeF_6 + MF$ ($M = Na, K, Rb, Cs$) $\longrightarrow M^+[XeF_7]^-$

31. $Xe + F_2$ (excess Xe) $\longrightarrow XeF_2$

32. $Xe + F_2$ (1:5) $\longrightarrow XeF_4$

33. $Xe + F_2$ (1:20) $\longrightarrow XeF_6$

34. $MnO_2 + HCl \xrightarrow{\Delta} MnCl_2 + Cl_2 + H_2O$

35. $FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + HCl$

36. $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + HF$

37. $ZnS + O_2 \longrightarrow ZnO + SO_2$

38. $AgNO_3 + H_2O + H_3PO_2 \longrightarrow Ag + HNO_3 + H_3PO_4$

39. $POCl_3 + H_2O \longrightarrow H_3PO_4 + HCl$

40. $NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$

41. $NH_4Cl + Ca(OH)_2 \longrightarrow NH_3 + H_2O + CaCl_2$

42. $C + HNO_3 \longrightarrow CO_2 + H_2O + NO_2$

43. $S_8 + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$.

44. $P_4 + HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$

45. $NH_3 + O_2 \xrightarrow{Pt/Rh} NO + H_2O$

46. $NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

47. $HCl + O_2 \xrightarrow{Cu_2Cl_2} Cl_2 + H_2O$

48. $NaCl + MnO_2 + H_2SO_4 \longrightarrow MnCl_2 + NaHSO_4 + Cl_2 + H_2O$.

d & f block elements

Reasoning Questions →

Account for the following –

(i) Transition metals are hard and high enthalpy of atomisation? why?

(ii) why transition metal shows variable oxidation State?

(iii) Transition metal form coloured compounds? why

(iv) Transition metal form interstitial Compounds? why

(v) T.M. is used as catalysts? why

(vi) T.M. is used for making alloys? why

(vii) T.M. and its Compounds are paramagnetic? why

(viii) 3rd I.E. of Mn is exceptionally high. why?

(ix) T.M. form Complex Compounds why?

(x) E° value for Fe^{+2}/Fe^{+3} is more feasible than Mn^{+2}/Mn^{+3}, why

(xi) Cr^{+3} is more stable than Cr^{+3}? why

(xii) Sc^{+3} form Colourless and dimagnetic Compound?

(xiii) Zn, Cd & Hg are not transition elements.

(xiv) Chemical properties of 4d and 2nd transition series Similar with 5d or 3rd transition series.

Page No.

(XV) Unlike Lanthanoids the elements of actinoids show large range of variable oxidation state?

(XVi) Cu^+ undergoes dis proportination reaction in aq. state?

(XVii) Cu^{+2} is more stable than Cu^+?

(XViii) Why $[Ti(H_2O)_6]^{3+}$ is Coloured but $[Sc(H_2O)_6]^{+3}$ is Colourless?

(X ix) Mn^{+3} (d^4) is oxidising agent but Cr^{+2} (d^4) is reducing agent. why?

(XX) what is Lanthanoid Contraction? what is its reason? what are its Consequences.

(Xxi) Mn has maximum Paramagnetism? Explain

Organic Chemistry

Name Reaction →

1. finkelsteen reaction 2. Swartz reaction
3. Fittig reaction 4. Williamson's Synthesis
5. Rosenmund reaction 6. Clemensen's reduction
7. Aldol Condensation 8. Cannizaro reaction
9. Kolbe's reaction 10. Gabriel phthalimide rxn
11. Iodoform 12. Carbylamine reaction
13. Hoffman bromamide reaction 14. Etard reaction.
15. Reimer-Tiemann reaction 16. Esterification
17. Gatterman Koch reaction.

Distinction Test :→

1. Alcohol Phenol Carboxylic acid

Phenol $\xrightarrow{FeCl_3}$ Violet Colour

Carboxylic acid $\xrightarrow{NaHCO_3}$ Brisk effervescence of CO_2

2. 1°, 2°, 3° alcohol

$\downarrow$

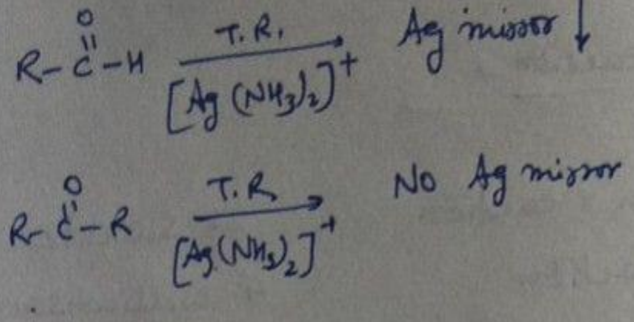
Lucas Test (Anhyd. $ZnCl_2$ & Conc HCl)

③ Aldehyde & Ketone

↓

Tollen's Reagent & Fehling Solution Test.

[illegible]



$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[{[Ag(NH_3)_2]^+}]{T.R.} Ag \text{ mirror} \downarrow$$

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[{[Ag(NH_3)_2]^+}]{T.R.} \text{No } Ag \text{ mirror}$$

④ Aliphatic Aldehyde & Aromatic Aldehyde.

↓ Fehling Test → Reddish Brown ppt (CH_2O)

↓ Fehling Test → No ppt.

⑤ Iodoform Test → $I_2 | NaOH \longrightarrow CHI_3$ Yellow ppt.

Condition - Aldehyde & ketone having $(CH_3-\overset{O}{\overset{\|}{C}}-)$ group and alcohol containing $(CH_3-\overset{OH}{\overset{|}{C}H}-)$ group

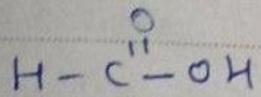
e.g. Ethanal & propanal

acetophenone & benzophenone

[redacted]

Methanal & Ethanal.

⑥ Tollen's Reagent test
or F.S test.



$H-\overset{O}{\overset{\|}{C}}-OH$

Aldehydic gp.

Methanoic acid $\longrightarrow$ +ve test

Ethanoic acid or any other acid $\longrightarrow$ No Test.

⑦ 1°, 2° & 3° amine. - Hinsberg Test.

⑧ 1° aliphatic & 1 aromatic amine - HNO_2 Tes

$\downarrow HNO_2$ N₂ gas

$\downarrow HNO_2$ (B.D.C)

Q:- Distinguish the fallowing pair of organic Compounds.

1. Phenol & propanol
2. Benzoic acid & Ethyl benzoate
3. Ethanoic acid & Methanoic acid
4. 1-propanol & 2-propanol
5. Propanal & propanone
6. Ethanal & propanal

[redacted]

⑦ 2-pentanone & 3-pentanone

⑧ Propanal & benzaldehyde.

⑨ Acetophenone & benzophenone.

⑩ Methyl amine & Aniline

⑪ Aniline & N, N Dimethyl propanamine.

⑫ Benzaldehyde & Acetophenone

⑬ formaldehyde & formic acid.

Give Reason in brief →

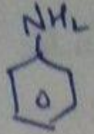
1. Carboxylic acid has more boiling point than alcohol.
2. Orthonitrophenol is steam volatile but p-nitrophenol has more B.Pt.
3. Phenol is acidic? Carboxylic acid has more Ka value than phenol.
4. Aniline has more pK_b value than CH_3-NH_2
5. 2° amine is more basic in aqueous Solution but in gas phase 3° amine is more basic.
6. P-nitrophenol is more acidic than p-methoxyphenol.
7. Trifluoro acetic acid is more acidic than trichloro acetic acid.

8. Chlorobenzene give less electrophilic substitution reaction but ortho and para directing.
9. Chlorobenzene does not give nucleophilic Substitution reaction.
10. Tertiary butyl chloride gives faster SN^1 reaction but chloromethane gives SN^2 reaction faster.
11. Aldehyde is more reactive towards nucleophilic addition reaction than ketone.
12. Aniline does not give friedal craft rxn.
13. Aniline on nitration gives meta product.
14. Phenol undergoes less protonation than aliphatic alcohol.
15. Methoxy benzene (anisole) is more reactive towards electrophilic substitution reaction than benzene but less reactive than phenol.

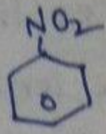
Q!- Identify A, B, C, D, E ----

1. 

$\xrightarrow[AlCl_3]{CH_3Cl} A \xrightarrow[KMnO_4]{[O]} B \xrightarrow{NaOH} C \xrightarrow[CaO,\ \Delta]{NaOH} D$

2. 

$\xrightarrow[H-Cl\ \ 0-5^\circ C]{HNO_2} A \xrightarrow[\Delta]{H_3O^+} B \xrightarrow[\Delta]{Zn} C \xrightarrow[AlCl_3]{CO/HCl} D \xrightarrow[KOH]{Con} E+F$

3. 

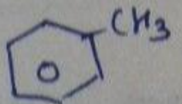
$\xrightarrow[[H]]{Sn/HCl} A \xrightarrow[HCl]{HNO_2} B \xrightarrow{CuCN} C \xrightarrow[HCl]{H_2O/dil} D$

4. 

$\xrightarrow{Con.\ H_2SO_4} A \xrightarrow[Dil]{NaOH} B \xrightarrow[fusion]{NaOH} C \xrightarrow{H^+} D \xrightarrow[HNO_3]{Conc} E$

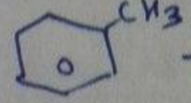
5. 

$\xrightarrow{Cl_2/AlCl_3} A \xrightarrow[623K\ \ H^+]{NaOH} B \xrightarrow[\Delta,\ H^+]{CO_2/NaOH} C \xrightarrow{CH_3COCl} D$

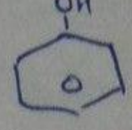
6. 

$\xrightarrow{HF} A$

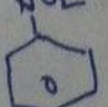
7. $CH_3-CH=CH_2 \xrightarrow[H_2O_2]{HBr} A \xrightarrow[KOH]{aq.} B \xrightarrow[H_2SO_4]{Conc.} C \xrightarrow{H_2O/H^+} D \xrightarrow{PCl_5} E$

8. 

$\xrightarrow[KOH]{KMnO_4} A \xrightarrow{H_3O^+} B \xrightarrow{PCl_5} C \xrightarrow[Pd-BaSO_4]{H_2} D \xrightarrow{NaOH} E+F$

9. 

$\xrightarrow{CO_2/NaOH} A \xrightarrow{H^+} B \xrightarrow[(CH_3CO)_2O]{CH_3COCl\ \ or} C$

10. 

$\xrightarrow[[H]]{Sn/HCl} A \xrightarrow[HCl]{HNO_2} B \xrightarrow[\Delta]{H_3O^+} C \xrightarrow{Zn,\ \Delta} D$

Conversion →

1. Ethane to propanoic acid
2. 1-Bromopropane to 1-propanal
3. 2-propanal to 1 propanal
4. Propanoic acid to propenoic acid
5. Ethanal to But-1-yne
6. Ethanol to ethane
7. Ethanol to ethene
8. Ethanol to propane nitrile
9. Ethanal to But-2-enal
10. Ethanal to Butan-1-ol
11. Ethanol to But-2-en-1-ol
12. Ethanal to 3-hydroxybutanal
13. Benzyl chloride to Benzyl alcohol
14. Chloroethane to iodoethane
15. propanoic acid to ethanamine,

Biomolecule

1. what happens when D-glucose reacts with
   $HI, HNO_3, Br_2, (CH_3CO)_2O, HCN, NH_2OH$
   write chemical rxn with name and structure of
2. Product.

2. IUPAC name of (i) D-glucose (ii) D-fructose

3. what do you mean by glycosidic linkage, Explain giving example of sucrose, Lactose, Maltose. why Sucrose is non-reducing but lactose and maltose is reducing.

4. Draw the open chain structure & ring structure of α- Dglucose & β-D glucose.

5. Differentiate between-
   - (i) Nucleotide and Nucleoside
   - (ii) DNA & RNA
   - (iii) Fibrous and Globular protein
   - (iv) Essential & non-essential α amino acid
   - (v) Primary & Secondry structure of protein

6. Define with example-
   - (i) Denaturation of protein
   - (ii) Anomers
   - (iii) Inversion of Cane sugar
   - (iv) Peptide
   - (v) Zwitter ion

CASE STUDY BASED QUESTIONS

PHYSICAL CHEMISTRY

Case Study-Based question on Solid State:

Any deviation from orderly arrangement in crystal lattice leads to development of imperfections or defects in crystalline solids. These imperfections not only modify the properties but also sometimes impart new properties to the solids. These defects may be either of point nature or of line nature. Point defects may be classified as stoichiometric and nonstoichiometric. Due to stoichiometric defects formula of the compound remains same as the ideal formula whereas in case of nonstoichiometric defects it changes. In some cases, these defects are introduced in crystals to have the desired properties.

1. Which of the following defects does not affect the density of the crystal?
   a) Schottky defect
   b) Interstitial defect
   c) Frankel defect
   d) Both b) and c)
2. Schottky defect mainly arises in ionic solids where
   a) Positive ion is bigger in size
   b) Negative ion is small in size
   c) Positive and negative ions are of similar sizes
   d) Positive ions are big and negative ions are small
3. The appearance colour in solid alkali metal halides is mainly due to
   a) Frankel defect
   b) Interstitial defects
   c) F- centres
   d) Schottky defects
4. Cations are present in interstitial sites in
   a) Frankel defects
   b) Schottky defects
   c) Vacancy defects
   d) Metal deficiency defects
5. When electrons are trapped are crystal in anionic vacancy, the defect is known as
   a) Schottky defect
   b) Frankel defect
   c) Stoichiometric defect
   d) F- centres

ANSWERS

1. c
2. c
3. c
4. d
5. d

Case Study-Based question on Electrochemistry

(1) Read the given passage and answer the following questions

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

7. Write the mathematical expression for molar conductivity.
8. What are the units of molar conductivity?

3.how does molar conductivity varies with the concentration for strong as well as weak electrolytes?

4.Give the graphical representation of variation of conductivity with concentration for weak electrolytes?

(2) Read the given passage and answer the following questions

A substance which accelerate the rate of a chemical reaction and itself remains chemically quantitatively unchanged after the reaction, is known as catalyst and this process is know catalyst. There are two type of catalyst i.e.homogenrous catalyst and heterogeneous catalyst. Most important type of catalysis is enzyme catalyst. Number of reactions that occur in the body of organism are catalyzed by enzymes. Mechanism of enzyme- catalyzed reactions completed in two steps

1. What is the homogeneous catalysis?

2.Write a chemical reaction which involves homogeneous catalysis.

3.Name two industrial process in which heterogeneous catalyst are used.

4.What is the role of desorption in the process of catalysis?

5. Write any two characteristics of enzyme catalysis.

(3) Read the given passage and answer the following questions

When a non-volatile solute is added to a solvent, the freezing point of thus formed solution is always lower than that of pure solvent. this difference in freezing point is known as depression in freezing point is known as freezing point. If difference in temperature of pure solvent and Tf is the freezing point temperature of solution when non-volatile solute is dissolved in it then depression in freezing point ΔTf is given by

Depression of freezing point $= \Delta T_f = T_f^\circ - T_f$

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

1-Why the freezing point of solution is always lower than that of a pure solvent?

2-Write the formula relating depression in freezing point with molar mass of solute.

3-Define the proportionality cosstsnt(Kf).centre Kf.

4-Write the unit of Kf.

5-Calculate the depression in freezing point of 5% glucose in water.

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

* *

SURFACE CHEMISTRY

Passage based question

surface studies meticulously, it becomes imperative to have a really clean surface. Under very high vacuum of the order of 10–8 to 10–9
pascal, Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen. surface of a solid has the tendency to attract and retain the molecules of the phase with which is comes into contact.

Q1-What is meant by interfacial phenomenon?

Q2- define adsorption and classify it
into physical and chemical
adsorption
Q3- Solid materials must have ultra clean surface. Why?

Q-4 Name some phenomenon taking place on surface of solids mostly.

Q5-What are active sites present on the surface of metals? Write mechanism of catalysis.

* *

INORGANIC CHEMISTRY

Case Study Questions

Topic: p-Block Elements

1- Read the given passage and answer the following questions :

The common oxidation states of elements of group 15 are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group. Further due to inert pair effect, the stability of +5 oxidation state decreases while that of +3 oxidation state increase down the group. Nitrogen is restricted to a maximum covalency of 4 while heavier elements expand their co-valence due to vacant of d-abitalsas in PF_6^-

All the elements of group 15 from hydrides of the type EH_3 (Where E=N,P,As, Sb, Bi). The stability of hydrides decreases from NH_3 to BiH_3. Consequently, reducing character of hydrides increases. Basicity of hydrides also decrease from NH_3 to BiH_3.

Q.1 Maximum co-valency of Nitrogen is -
(a) 3 (b) 4 (c) 5 (d) 6

Q.2 Maximum co-valency of phosphorus is -
(a) 3 (b) 4 (c) 5 (d) 6

Q.3 Correct among the following hydrides, the correct decreasing order of basic strength is
(a) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
(b) $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
(c) $PH_3 > NH3 > AsH_3 > SbH_3 > BiH_3$
(d) $SbH_3 > AsH_3 > BiH_3 > PH_3 > NH_3$

Q.4 Correct order of reducing character of hydrides of Group 15 is –
(a) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
(b) $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
(c) $PH_3 > NH3 > AsH_3 > SbH_3 > BiH_3$
(d) $SbH_3 > AsH_3 > BiH_3 > PH_3 > NH_3$

2- Read the following passage and answer the questions that follow:

Group 18 elements are called noble gases and not inert gases because compounds of Kr, Xe and Rn have been prepared. Their general electronic configuration is ns2 np6 except He (1s2). They have highest ionization enthalpy and positive electron gain enthalpy due to stable electronic configuration. Helium is found in sun and stars. Noble gases have low boiling points due to weak van der Waals' forces of attraction. Xenon forms XeF2, XeF4, XeF6, XeOF4, XeO3, XeO2F2, their structures can be drawn on the basis of VSEPR theory. Helium is mixed with oxygen by deep sea divers to avoid pain. Neon is used in colored advertising lights.

Argon is used in bulbs as inert gas. Kr and Xe are used in high efficiency lamps, head light of cars. Radon is radioactive formed by α-decay of Radium. Argon is most abundant (0.9%) noble gas in atmosphere

How do boiling points of noble gases vary down the group?

Ans. Boiling point of noble gases increase down the group due to increase in atomic size, Surface area and increase in van der Waals' forces of attraction.

Which noble gas has highest ionization enthalpy and why?
Ans. Helium. It is due to smallest atomic size. Removal of electron is difficult
Which was first noble gas compound prepared by Neil Bartlett?
Ans. $Xe^+ PtF_6^-$
Draw the shapes of (i) XeF_2 (ii) $XeOF_4$.
Ans. (i) Linear – Structure as per NCERT (ii) Square pyramidal – Structure as per NCERT

Complete the following reactions: (i) $XeF_6 + KF \rightarrow$
(ii) $XeF_6 + 2H_2O \rightarrow$
Ans. (i) $XeF_6 + KF \rightarrow K^+ [XeF_7]^-$
(ii) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

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

The d-block of the periodic table contains the elements of the groups 3 to 12 and are known as transition elements. In general, the electronic configuration of these elements is $(n – 1)d^{1 – 10} ns^{1-2}$. The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals i.e. 3d, 4d and 5d series. However, Zn, Cd and Hg are not regarded as transition elements. Transition elements exhibit certain characteristic properties like variable oxidation stables, complex formation, formation of colored ions, alloys formation, catalytic activity etc. Transition metals are hard (except Zn, Cd and Hg) and have a high melting point and high boiling points

Why are Zn, Cd and Hg non-transition elements?
Ans. It is because neither they nor their ions in most stable oxidation state have incompletely filled d-orbitals.
Which transition metal of 3d series does not show variable oxidation state?
Ans. Scandium (Sc) Atomic No 21 and Zinc (Zn) Atomic No 30
Why do transition metals and their compounds are very good catalysts?
Ans. It is because they show (i) variable oxidation state, (ii) can form intermediate complexes and (iii)have large surface area for adsorption of gases.

Why are melting points and boiling points of transition metals high?
Ans. It is due to strong interatomic forces of attraction due to presence of unpaired electrons.
Why is Cu^{2+} ion colored while Zn^{2+} ion is colorless in aqueous solution?
Ans. It is because Cu^{2+} has one unpaired electron and undergoes d-d transition by absorbing light from visible region and radiate blue color, whereas Zn^{2+} is colorless due to absence of unpaired electron.

****

d and f block elements

1- **Read the paragraph carefully and answer the Questions given below**

- The transition elements are those elements having a partially filled d subshell in any common oxidations state. The term “transition elements” most commonly refers to the d-block elements. The elements zinc , cadmium & mercury do not strictly meet the defining properties but are usually included with the transition elements because their similar properties. The general properties of transitions elements are
  - They are high melting point metals
  - They have several oxidation states
  - They usually from coloured compounds
  - They are often paramagnetic

The transition elements include the important metals iron, copper and silver. Iron & titanium are the most abundant transition elements. Many catalysts for industrial reactions involve transition elements.

Q1 -Iron is a transition element

A. Iron has fully filled d orbitals
B. Iron has partially filled d orbitals
C. Iron has partially filled d subshell in metallic state
D. None of Above.

Q2 . Zn2+ salts are colourless due to
A. d-d transition of electrons
B. Fully filled d orbitals
C. No d-d transition of electrons
D. Fully filled d orbitals and no d-d transition of electrons

Q3. Out of Sc3+,Cr3+,Zn2+,Mn2+which is highly paramagnetic
A. Sc3+
B. Cr3+
C. Zn2+
D. Mn2+

Q4.transition Metals are known to form complexes
A. They have vacant d orbitals
B. They hey high nuclear charge

C. They can accept electrons from ligands
D. All of above

Answer Key
1-C
2-D
3-D
4-D

2-Pratham went to chemistry lab and he observed some pink, blue, green and yellow coloured solutions in lab. His teacher explains that when an electron from lower energy d orbital is excited to higher energy d orbital (d-d transition),it absorbs light of visible range. The colour observed corresponds to the complementary colour of the light absorbed.

1. What is the colour of hydrated copper sulphate and why?
   Ans ..Hydrated CuSO4 is blue in colour because of d-d transition.

2. Predict which of the following will be coloured in aqueous solution and why?
   Sc^{3+}, Ti^{3+}, V^{3+} , Cu^{+} , Fe^{3+}

Ans Ti^{3+}, V^{3+} ,Fe^{3+} are coloured because they have unpaired d electrons which can undergo d-d transition.

3. Which of the following is a coloured salt before heating ?
   (i) $CuCO_3$ (ii) $PbCO_3$ (iii) $ZnCO_3$ (iv) Na_2CO_3

   Ans. $CuCO_3$
4. Explain why $ZnSO_4$ solution is colourless although it is a‘d’ block element?
   Ans .Zn^{2+} ions have completely filled d^{10} electronic configuration.

3- Pooja and Tanya were discussing about oxidation states .Pooja got confused about oxidation state of iron. Then Tanya explained to her that Transition metals show great variety of oxidation state in their compounds, e.g. Manganese exhibits all the oxidation states from +2 to +7. At the other end the only oxidation state of Zinc is +2 (no d electrons are involved).The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons up to manganese.

1. Name a transition metal which doesn’t exhibit variable oxidation states.
   Ans. Scandium (Z=21)
2. Which of 3d series of transition metals exhibits the largest number of oxidation states and why?
   Ans. Manganese exhibit the largest number of oxidation states. It shows the oxidation states +2, +3, +4, +5 ,+6, and + 7. The reason for that is the maximum number of unpaired electrons present in its outermost shell i.e. $3d^5 4s^2$.

3. Why Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to +3 states?
Ans. Since **Mn^{2+}** has **stable** half-filled electronic configuration, therefore **Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation** to their +**3 state**. $Fe^{2+}(3d^6)$ can lose one electron easily to give $Fe^{3+}(3d^5$, **stable** configuration).

What may be stable oxidation state of transition metal having $3d^8$ ground state electronic configuration?

Ans. +2

* * *

Topic: d- and f- Block Elements

Read the given passage and answer the following questions :

The two series of inner transition elements, Lanthanoid and actinides constitute the f block of the periodic table. With the successive filling of inner orbitals, 4f, there is a gradual decrease in the atomic and iconic sizes of the metals along the series (Lanthanoid contraction). This contraction is similar to the observed in a ordinary transition series and it attributed to the same cause, the imperfect shielding on electron by another in this sub-shell due to shapes of these f- orbitals. The almost identical radii of Zr and Hf a consequence of the Lanthanoid contraction.

The typical oxidation state of Lanthanoid is +3. The oxidation states of +2 and +4 are exhibited by some of the elements to acquire a stable electronic configuration of f^0, f^7 or f^{14}.

Q.1 Which of the following is the most common oxidation state among the lanthanoid?

(a) +3 (b) +4 (c) +2 (d) +5

Q.2 Which of the following pair have same size ?

(b) Fe^{2+}, Ni^{2+}
(b) Zr^{4+} , Ti^{4+}
(c) Zr^{4+}, Hf^{4+}
(d) Zn^{2+}, Hf^{4+}

Q.3 Lanthanoid contraction is observed in -

(a) Gd (b) At (c) Xe (d) Ac

Q.4 Lanthanoid contraction is due to increase in –

(a) Effective shielding of f-elements
(b) Atomic number
(c) Effective nuclear charge
(d) Atomic radius

- **Coordination chemistry**

Read the paragraph carefully and answer the Questions given below
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.
Coordination compounds are molecules that poses one or multiple metal centers that is bound to ligands (atoms, ions or molecules that donate electrons to the metal). Monodentate ligands donate one pair of electrons to the central metal atoms.

An example of these ligands are the halide ions (F-, Cl-, Br-, I-). Polydentate ligands, also called chelates or chelating agents, donate more than one pair of electrons to the metal atom forming a stronger bond and a more stable complex. A common chelating agent is ethylene diamine (en), which, as the name suggests, contains two ammines or :NH2 sites which can bind to two sites on the central metal.

Q5 Assertion: the coordination number of Iron is six in Fe(CN)6]4-
Reason: cyanide is a bidentate ligand

Q6 Assertion: thiocyanate iron and isothiocyanate ions are ambidentate ligands
Reason :they have more than one donor atom which can coordinate.

Q7 Assertion: ethylenediamine is unidentate ligand

Reason: It forms stable complexes with metal
Q8 Assertion: bidentate, tridentate ligands form chelates.

Reason: they can donate more than two electron pairs to central atom and form a ring type of structure.

Answer Key
5-C
6-A
7-D
8-A

ORGANIC CHEMISTRY

ALKYL HALIDE

1) The polarity of carbon-halogen bond of alkyl halide is responsible for their nucleophilic substitution and elimination reaction. Nucleophilic substitution reaction are categorised into SN1 and SN2 . Chiraity has a profound role in understanding the reaction mechanism of SN1 and SN2 reaction. SN2 reaction of chiral alkyl halide are characterized by inversion of configuration while SN1 reaction are categorised by racemization. Due to their tendency to undergo substitution by a large number of nucleofphiles ,they form a variety of product

a) Which will react faster in SN2 reaction
   (1) 1-bromopentane
   (2) 2bromopentane
   (3) Both of these
   (4) Non of these

b) Which will undergo SN1 reaction faster
   (1) 2- chloro -2- methyl propane
   (2) 2 chloro butane
   (3) None of these
   (4) Both of these

c) Which one is the correct statement
   (1) In SN2 racemization occur
   (2) SN1 is two step reaction
   (3) In SN1 reaction inversion takes place
   (4) SN2 is to step reaction

d) What happens when CH3BR is treated with KCN
   (1) Racemization occur
   (2) SN1 reaction takes place
   (3) SN2 reaction takes
   (4) More than one option correct

2) Molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to parent hydrocarbon the intermolecular forces of attraction (dipole-dipole and van Der Walls) are stronger in halogen derivatives. That is why the boiling point of chloride ,bromide and iodide are considerably higher than those of hydrocarbons of comparable molecular mass.

a) Boiling point depends upon ?
   (1) Polarity of compound
   (2) Molecular mass of compound
   (3) Intermolecular forces between compound
   (4) All of these

b) Which one has higher boiling point (1) *ethane* (2*) ethane chloride*
   (1) Option 1
   (2) Option 2
   (3) Same for both
   (4) Data insufficient

c) Which one has highest boiling point

(1) Bromoform (2 Bromoethane

(3) Chloromethane (4) Dibromomethane

D) Which has higher boiling point
   (1) Ethane chloride
   (2) Ethanol
   (3) Same for both
   (4) Can’t tell

Answers

1) a – 1
   b – 1

   c – 2

   d – 3

2) a – 4
   b – 2

   c – 1

   d – 2

****

CASE STUDY –ALCOHOLS
QUESTION-1

Read the passage given below and answer the following questions:
Alcohols are derivatives of hydrocarbons in which an –OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (–OH) functional groups, they do not behave like bases such as NaOH and KOH. NaOH and KOH are ionic compounds that contain OH– ions. Alcohols are covalent molecules; the –OH group in an alcohol molecule is attached to a carbon atom by a covalent bond. The term alcohol originally referred to the primary alcohol ethanol(ethyl alcohol), which is used as a drug and is the main alcohol present in alcoholic beverages. Alcohols are compounds find wide application in industries(preparation of dyes, drugs, solvents etc) and are of immense use in our daily life. They contain one or more –OH group (responsible for the variation in their properties). They are classified as primary, secondary and tertiary alcohol. During chemical reaction they undergoes Substitution, Dehydration , Dehydrogenation. Dehydrogenation is a chemical reaction that involves the removal of hydrogen, usually from an organic molecule. It is the reverse of hydrogenation. Dehydrogenation is important, both as a useful reaction and a serious problem. At its simplest, it is useful way

of converting alkanes, which are relatively inert and thus low-valued, to olefins, which are reactive and thus more valuable. Dehydrogenation of alcohols gives aldehyde, ketone and alkene , when alcohol is heated at 573K in the presence of copper.

1. The product of which alcohol gives positive Tollen's test –
   (a) Primary alcohol
   (b) Secondary alcohol
   (c) Tertiary alcohol
   (d) All of the abov Ans (a)
2. Which among primary, secondary and tertiary alcohol on oxidation gives carboxylic acid having same number of carbon atom?
   (a) Primary alcohol
   (b) Secondary alcohol
   (c) Tertiary alcohol
   (d) Isopropyl alcohol Ans (a)
3. An organic compound 'A' having molecular formula C_6H_4O is an isomer of alcohol with excess of HI forms two alkyl halides. On hydrolysis gives two compounds B and C . Oxidation B gives an acid D and C gives a mixed ketone. The name of D and E is-
   (a) Propanoic acid, Butan-2one
   (b) Ethanoic acid , Butan-2-one
   (c) Butanoic acid , Propan-2-one
   (d) Methanoic acid, 3Methyl But-2one Ans (b)
4. In all the following isomeric alcohols with molecular formula $C_5H_{12}O$, identify the isomers exhibit chirality.
   (a) Pentan-3-ol
   (b) 2- Methyl butan-2-ol
   (c) 3Methyl butan-2-ol
   (d) 2,2 Dimethylpropan-1-ol. Ans (c)

OR

In the acid catalyzed dehydration of alkene (ethane), water acts as-

(a)Electrophile
(b)Nucleophile
(c)Electrophile and nucleophile
(d)Free radical Ans (c)

QUESTION-2

Read the passage given below and answer the following questions:

"Lucas' reagent" is a solution of anhydrous zinc chloride in concentrated hydrochloric acid. This solution is used to classify alcohols of low molecular weight. The reaction is a substitution in which the chloride replaces a hydroxyl group. A positive test is indicated by a change from clear and colorless to turbid, signaling formation of a chloroalkane. Also, the best results for this test are observed in tertiary alcohols, as they form the respective alkyl halides fastest due to higher stability of the intermediate tertiary carbocation. The Lucas test in alcohols is a test to differentiate between primary, secondary, and tertiary alcohols. It is based on the difference in reactivity of the three classes of alcohols with hydrogen halides via an SN1 reaction. Iodoform (also known as triiodo methane and, inaccurately, as carbon triiodide) is the organ iodine compound with the formula CHI3. A pale yellow, crystalline, volatile substance, it has a penetrating and distinctive odor (in older chemistry texts, the smell is sometimes referred to as that of hospitals, where the compound is still commonly used) and, analogous to chloroform, sweetish taste. It is occasionally used as a disinfectant.

1. An unknown alcohol gives positive Lucas test in about 5 min. When this alcohol was heated with conc. sulphuric acid alkene was formed with the formula C_4H_8. Ozonolysis of this alkene gives a single product C_2H_4O.Identify the alcohol-
   (a)Butan-2-ol
   (b)2-Methyl propan-1-ol
   (c)2- Methyl propan-2-ol
   (d)Butan-1-ol Ans (a)

2.Which of the above alcohol does not give positive iodoform test?
(a) Butan-1-ol
(b) Butan-2-ol
(c) 2-Methyl propal-1-ol
(d) 2- Methyl propan-2-ol Ans (a)

3.Which isomer of the unknown alcohol forms alkene on dehydrogenation?
(a)Butan-1-ol
(b)Butan-2-ol
(c) 2-Methyl propal-1-ol
(d) 2- Methyl propan-2-ol Ans (d)

4. Which carbonyl compound is used to prepare 2-Methyl propan2-ol with methyl magnesium bromide?
(a) Methanol
(b)Ethanal
(c) 2-Propanone
(d) 2- Butanone Ans (c)

QUESTION-3

Read the passage given below, and answer the following questions:

Alcohol is very important organic compound widely used in industry to prepare paints, varnishes, Medicines and different types Liquor.

Ethanol is the main constituents of different types of wines. Commercial alcohols is made unfit for drinking by mixing in it copper sulphate(to give it color) and pyridine(a Foul smelling liquid) it is known as Denaturation of alcohols. Ingestion of small quantity of Methanol can cause blindness and large quantities cause even death.

Grignard Reagent can be used to prepare different types of alcohols. Methanol when treated with Grignard Reagent followed by hydrolysis forms primary alcohols. Ethanol and other aldehydes can be used to prepare Secondary alcohols. Ketones when treated with Grignard Reagent Followed by hydrolysis leads to the formation of tertiary alcohols.

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

(a) Assertion and reason both are correct statements. And reason is the correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not the correct explanation for assertion.
(c) Assertion is correct but reason is wrong statement.
(d) Assertion is wrong but reason is correct statement.

1. ASSERTION: denaturation of commercial Alcohols can be done by mining copper sulphate and Pyridine.
REASON : Denatured alcohol is unfit for drinking.

2. ASSERTION: Ethanol contaminated with methanol is not feet for drinking
REASON : Methanol is highly piousness for human body .

3. ASSERTION: Isopropyl Alcohol can be prepared by using grignard reagent
REASON : Methyl magnesium bromide reacts with ethanal followed by hydrolysis form isopropyl alcohol.

4. ASSERTION : Grignard reagent can be used to prepare tertiary alcohol.
REASON: Grignard reagent do not react with Ketone

ANSWERS

1-(b) ; 2 (a) ; 3(a) ;4(c)

Case Study: Grignard's Reagent

Grignard's Reagents (RMgX) are prepared by the reaction of organic halide and magnesium metal in Ether Solvent.

R-X + Mg -------------> R-MgX.

The solvent (usually diethyl ether or tetrahydrofuran) plays an important role in formation of Grignard's Reagent. Alkyl Halides are more reactive than aryl and vinyl halides. Indeed, aryl and vinyl halides do not form Grignard's Reagent in diethyl ether. However, an alkyl halidecontining an alcoholic group(-OH) is converted to Grignard's Reagent by first protecting the –OH group with tert-butyldimethylsilyl ether which is inert to Grignard's Reagent. The protecting group is finally ibrated by treatment with fluoride ion.

$ROH + SiCl(CH_3)_2\text{-}C(CH_3)_3$ -------> $ROSi(CH_3)_2C(CH_3)_2C(CH_3)_3$ ------> $ROH+F\text{-}Si(CH_3)_2C(CH_3)_3$
(tert-butylchlorodimethylsilane)

Q1. Grignard reaction generally occurs in dry ether because:

a) The stronger acid diethyl ether will displace the weaker RH acid from its salt.
b) The stronger acid H_2O will displace the weaker RH acid from its salt.
c) Water slows down the reaction.
d) Water mixes with ether preventing ether from performing its function.

Q2. The function of tetrahydrofuran in the preparation of Grignard's Reagent is that it:

a) Acts as solvent.
b) Helps in maintaining the reactivity of Mg.
c) Both
d) NOTA

Q3. Grignard's Reagent cannot be prepared from:

a) $CH_2(OH)CH_2CH_2Br$
b) Chlorobenzene
c) 1,2-dichlorobenzene
d) $C(CH_3)_3Cl$

Answers

1. (d) Water mixes with ether preventing ether to perform its functions
2. (c) Both
3. (a) $CH_2(OH)CH_2CH_2Br$

1. A chemist isolated a compound A with molecular formula $C_7H_{13}Br$. A undergoes very fast S_N1 reaction. Spectroscopic evidence indicated that compound A has the following structural characteristics.

It contains five sp^3 hybridized carbon atoms. Among these five sp^3 carbon atoms are three methyl groups, one CH_2 group and one CH group.

- It also contains two sp^2 -hybridized carbon atoms. Also, there is only one hydrogen atom attached to sp^2 carbons.
- The compound contains a total of six allylic hydrogen atoms.
- The carbon atom that holds the Br has one H attached to it.

When compound A reacts with boiling water, it undergoes an S_N1 reaction and produces two principal products B and C.

—

Both B and Care alcohols with their molecular formula $C_7H_{14}O$. Among the two alcohols, B has the OH group attached to a sp^3 carbon atom that has no H atoms bonded to it.

A. What can be said about the isomerism shown by the two alcohols B and C?

B. If the starting compound A is brominated in gas phase in presence of a Lewis acid catalyst, a tribromide would result from addition of Br_2 to $C{=}C$. How many different structures of stereo isomerism can be drawn for this tribromide?

C. If the original compound A is treated with $LiAlH_4$, a new compound D (C_7H_{14}) would be produced. How many different structure(s) can be drawn for this D?

ANSWERS

A. We can say that both B and C show stereoisomerism but only C can be resolved into enantiomers.

B. 4

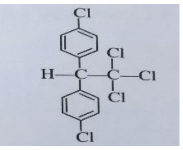
C. One(1)

2. An organic compound X which is manufactured by heating a mixture of chloral and chlorobenzene in the presence of concentrated H_2SO_4 is used as an insecticide. The use of compound X is banned in many countries. The compound is very effective against mosquitoes which spread malaria. Answer the following questions based on the information:
    A. Name the compound X.
    B. Give its structural formula.
    C. Write the IUPAC name of compound X.
    D. Why is the use of compound X banned in many countries? Should we also advocate the ban of this compound though it is banned in many countries?

ANSWERS

A. DDT

B.



C. IUPAC NAME: 2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane

D. It is banned in many countries as it has harmful effects on microorganisms and vegetation. Yes, we should advocate the ban of DDT

****

SAMPLE PAPER 1
CHEMISTRY THEORY (043)

MM:70 **Time: 3 Hours**

General Instructions:

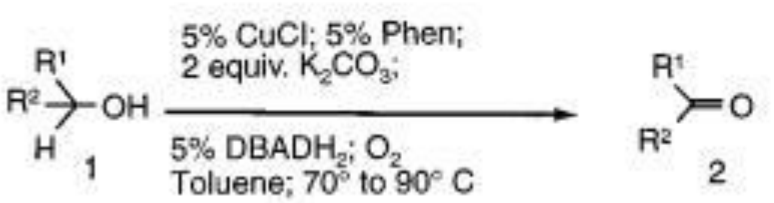
Read the following instructions carefully.

9. There are 33 questions in this question paper. All questions are compulsory.
10. Section A: Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
11. Section B: Q. No. 17 to 25 are short answer questions and carry 2 marks each.
12. Section C: Q. No. 26 to 30 are short answer questions and carry 3 marks each.
13. Section D: Q. No. 31 to 33 are long answer questions carrying 5 marks each.
14. There is no overall choice. However, internal choices have been provided.
15. Use of calculators and log tables is not permitted.

SECTION A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions: (1x4=4)

An efficient, aerobic catalytic system for the transformation of alcohols into carbonyl compounds under mild conditions, copper-based catalyst has been discovered. This copper-based catalytic system utilizes oxygen or air as the ultimate, stoichiometric oxidant, producing water as the only by-product



A wide range of primary, secondary, allylic, and benzylic alcohols can be smoothly oxidized to the corresponding aldehydes or ketones in good to excellent yields. Air can be conveniently used instead of oxygen without affecting the efficiency of the process. However, the use of air requires slightly longer reaction times.

This process is not only economically viable and applicable to large-scale reactions, but it is also environmentally friendly.

(*Reference:Ohkuma, T., Ooka, H., Ikariya, T., & Noyori, R. (1995). Preferential hydrogenation of aldehydes and ketones. Journal of the American Chemical Society, 117(41), 10417-10418.)*

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

(i)The Copper based catalyst mention in the study above can be used to convert:

(d) propanol to propanonic acid
(e) propanone to propanoic acid
(f) propanone to propan-2-ol
(g) propan-2-ol to propanone

(ii)The carbonyl compound formed when ethanol gets oxidised using this copper-based catalyst can also be obtained by ozonolysis of:

(d) But-1-ene
(e) But-2-ene
(f) Ethene
(g) Pent-1-ene

OR

Which of the following is a secondary allylic alcohol?

But-3-en-2-ol
But-2-en-2-ol
Prop-2-enol
Butan-2-ol

(d) Benzyl alcohol on treatment with this copper-based catalyst gives a compound ‘A’ which on reaction with KOH gives compounds ‘B’ and ‘C’. Compound ‘B’ on oxidation with $KMnO_4$- KOH gives compound ‘C’. Compounds ‘A’, ‘B’ and ‘C’ respectively are :

Benzaldehyde, Benzyl alcohol, potassium salt of Benzoic acid
Benzaldehyde, potassium salt of Benzoic acid, Benzyl alcohol
Benzaldehyde, Benzoic acid, Benzyl alcohol
Benzoic acid, Benzyl alcohol, Benzaldehyde

(iii) An organic compound ‘X’ with molecular formula C_3H_8O on reaction with this copper based catalyst gives compound ‘Y’ which reduces Tollen’s reagent. ‘X’ on reaction with sodium metal gives ‘Z’ . What is the product of reaction of ‘Z’ with 2-chloro-2-methylpropane?

$CH_3CH_2CH_2OC(CH_3)_3$
$CH_3CH_2OC(CH_3)_3$
$CH_2=C(CH_3)_2$
$CH_3CH_2CH=C(CH_3)_2$

Read the passage given below and answer the following questions: (1x4=4)

The amount of moisture that leather adsorbs or loses is determined by temperature, relative humidity, degree of porosity, and the size of the pores. Moisture has great practical significance because its amount affects the durability of leather, and in articles such as shoes, gloves and other garments, the comfort of the wearer. High moisture content accelerates deterioration and promotes mildew action. On the other hand, a minimum amount of moisture is required to keep leather properly lubricated and thus prevent cracking.

The study indicates that adsorption of moisture by leather is a multi-molecular process and is accompanied by low enthalpies of adsorption. Further at 75-percent relative humidity, the adsorption is a function of surface area alone.

Hide is tanned to harden leather. This process of tanning occurs due to mutual coagulation of positively charged hide with negatively charged tanning material. Untanned hide and chrome-tanned leathers have the largest surface areas. The leathers tanned with vegetable tanning materials have smaller surface areas since they are composed of less hide substance and the capillaries are reduced to smaller diameters, in some cases probably completely filled by tanning materials. The result of the study indicated that untanned hide and chrome-tanned leather adsorb the most water vapour.

(Source:Kanagy, J. R. (1947). Adsorption of water vapor by untanned hide and various leathers at 100 F. *Journal of Research of the National Bureau of Standards*, *38*(1), 119-128.)

(iv) In these questions (Q. No 5-8 , a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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

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

Assertion is correct statement but reason is wrong statement.

Assertion is wrong statement but reason is correct statement.

(c) Assertion: Vegetable tanned leather cannot adsorb a large amount of moisture.
Reason: Porous materials have higher surface area.

(d) Assertion: Animal hide soaked in tannin results in hardening of leather.
Reason: Tanning occurs due to mutual coagulation.

(e) Assertion: Adsorption of moisture by leather is physisorption.
Reason: It is a multimolecular process and is accompanied by low enthalpies of adsorption

(iii) Assertion: Leathers tanned with vegetable tanning materials have smaller surface areas
Reason: The capillaries present in leather are reduced to smaller diameters

OR

Assertion: Leather absorbs different amount of moisture.
Reason: Some moisture is necessary to prevent cracking of leather.

Following questions (No. 3 -11) are multiple choice questions carrying 1 mark each:

(c) Which of the following option will be the limiting molar conductivity of CH_3COOH if the limiting molar conductivity of CH_3COONa is 91 Scm^2mol^{-1}? Limiting molar conductivity for individual ions are given in the following table.

S.No	**Ions**	**limiting molar conductivity / Scm^2mol^{-1}**
1	H+	349.6
2	Na+	50.1
3	K+	73.5
4	OH^-	199.1

(iii) 350 Scm^2mol^{-1}

(iv) 375.3 Scm^2mol^{-1}

(v) 390.5 Scm^2mol^{-1}

(vi) 340.4 Scm^2mol^{-1}

(g) Curdling of milk is an example
of: a) breaking of peptide linkage
b) hydrolysis of lactose
c) breaking of protein into amino acids
d) denauration of proetin

OR

Dissachrides that are reducing in nature are:

(c) sucrose and lactose
(d) sucrose and maltose
(e) lactose and maltose
(f) sucrose, lactose and maltose

5.When 1 mole of benzene is mixed with 1 mole of toluene The vapour will contain: (Given : vapour of benzene = 12.8kPa and vapour pressure of toluene = 3.85 kPa).

(d) equal amount of benzene and toluene as it forms an ideal solution
(e) unequal amount of benzene and toluene as it forms a non ideal solution
(f) higher percentage of benzene
(g) higher percentage of toluene

6.Which of the following is the reason for Zinc not exhibiting variable oxidation state

b inert pair effect
c completely filled 3d subshell
d completely filled 4s subshell
e common ion effect

OR

Which of the following is a diamagnetic ion: (Atomic numbers of Sc, V, Mn and Cu are 21, 23, 25 and 29 respectively)

1 V^{2+}
2 Sc^{3+}
3 Cu^{2+}
4 Mn^{3+}

(f) Propanamide on reaction with bromine in aqueous NaOH gives:
Propanamine
Ethanamine
N-Methyl ethanamine
Propanenitrile

OR

IUPAC name of product formed by reaction of methyl amine with two moles of ethyl chloride

(g) N,N-Dimethylethanamine
(h) N,N-Diethylmethanamine
(i) N-Methyl ethanamine
(j) N-Ethyl - N-methylethanamine

8.Ambidentate ligands like NO_2^- and SCN^- are :
(d) unidentate
(e) didentate
(f) polydentate
(g) has variable denticity

OR

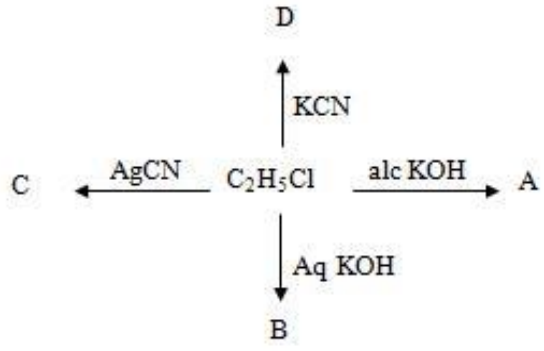
The formula of the coordination compound Tetraammineaquachloridocobalt(III) chloride is

(c) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(d) $[Co(NH_3)_4(H_2O)Cl]Cl_3$
(e) $[Co(NH_3)_2(H_2O)Cl]Cl_2$
(f) $[Co(NH_3)_4(H_2O)Cl]Cl$

9.Which set of ions exhibit specific colours? (Atomic number of Sc = 21, Ti = 22, V=23, Mn = 25, Fe = 26, Ni = 28 Cu = 29 and Zn =30)

(d) Sc^{3+}, Ti^{4+}, Mn^{3+}
(e) Sc^{3+}, Zn^{2+}, Ni^{2+}
(f) V^{3+}, V^{2+}, Fe^{3+}
(g) Ti^{3+}, Ti^{4+}, Ni^{2+}

10. Identify A,B,C and D:



(ii) A = C_2H_4, B= C_2H_5OH, C= C_2H_5NC, D= C_2H_5CN

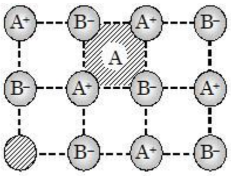
(iii) A= C_2H_5OH, B= C_2H_4, C = C_2H_5CN, D=C_2H_5NC

(iv) A = C_2H_4, B= C_2H_5OH, C= C_2H_5CN, D= C_2H_5NC

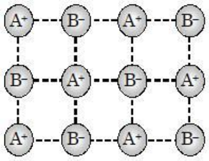
(v) A= C_2H_5OH, B= C_2H_4, C= C_2H_5NC, D= C_2H_5CN

11.The crystal showing Frenkel defect is :

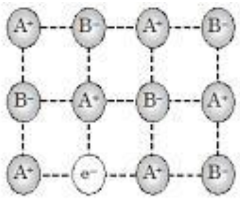
a)



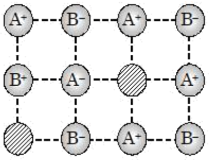
b)



c)



d)



In the following questions (Q. No. 12 - 16) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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

(iv) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(v) Assertion is correct statement but reason is wrong statement.

(vi) Assertion is wrong statement but reason is correct statement.

12.Assertion: The two strands of DNA are complementary to each other

Reason: The hydrogen bonds are formed between specific pairs of bases.

13.Assertion: Ozone is thermodynamically stable with respect to oxygen.

Reason:Decomposition of ozone into oxygen results in the liberation of heat

14.Assertion: Aquatic species are more comfortable in cold waters rather than in warm waters. Reason:Different gases have different K_H values at the same temperature

OR

Assertion: Nitric acid and water form maximum boiling azeotrope.

Reason: Azeotropes are binary mixtures having the same composition in liquid and vapour phase.

(iii)Assertion: Carboxylic acids are more acidic than phenols. Reason: Phenols are ortho and para directing.

16.Assertion: Methoxy ethane reacts with HI to give ethanol and iodomethane

Reason: Reaction of ether with HI follows S_N2 mechanism

SECTION B

The following questions, Q.No 17 – 25 are short answer type and carry 2 marks each.

(iii) With the help of resonating structures explain the effect of presence of nitro group at ortho position in chlorobenzene.

OR

Carry out the following conversions in not more than 2 steps:

(i)Aniline to chlorobenzene
(ii)2-bromopropane to 1- bromopropane

18. A glucose solution which boils at 101.04°C at 1 atm. What will be relative lowering of vapour pressure of an aqueous solution of urea which is equimolal to given glucose solution? (Given: K_b for water is 0.52 K kg mol^{-1})

19. (i) Using crystal field theory, write the electronic configuration of iron ion in the following complex ion. Also predict its magnetic behaviour :

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

(ii)Write the IUPAC name of the coordination complex: $[CoCl_2(en)_2]NO_3$

OR

(i)Predict the geometry of $[Ni(CN)_4]^{2-}$
(ii)Calculate the spin only magnetic moment of $[Cu(NH_3)_4]^{2+}$ ion.

20. For a reaction the rate law expression is represented as follows: Rate = k $[A][B]^{1/2}$

i. Interpret whether the reaction is elementary or complex. Give reason to support your answer.
ii. Write the units of rate constant for this reaction if concentration of A and B is expressed in moles/L.

OR

The following results have been obtained during the kinetic studies of the reaction:

$P+2Q \rightarrow R+2S$

Exp.	**Initial P(mol/L)**	**Initial Q (mol/L)**	**Init. Rate of Formation of R (M min^{-1})**
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

Determine the rate law expression for the reaction.

21. The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees. How old is that piece of wood? (log 3= 0.4771, log 7 = 0.8540 , Half-life of C-14 = 5730 years)

22. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{HBr} CH_3-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$

Give a mechanism for this reaction.

23. Give the formula and describe the structure of a noble gas species which is isostructural with IF_6^-.

24. The following haloalkanes are hydrolysed in presence of aq KOH.

(i) 2- Chlorobutane (ii) 2-chloro-2-methylpropane

Which of the above is most likely to give a racemic mixture? Justify your answer.

25. Atoms of element P form *ccp* lattice and those of the element Q occupy 1/3rd of tetrahedral voids and all octahedral voids. What is the formula of the compound formed by the elements P and Q?

SECTION C

Q.No 26 -30 are Short Answer Type II carrying 3 mark each.

26. Give reasons for the following:

i. Transition elements act as catalysts
ii. It is difficult to obtain oxidation state greater than two for Copper.
iii. $Cr_2O_7^{2-}$ is a strong oxidising agent in acidic medium whereas WO_3 and MoO_3 are not.

OR

Observed and calculated values for the standard electrode potentials of elements from Ti to Zn in the first reactivity series are depicted in figure (1):

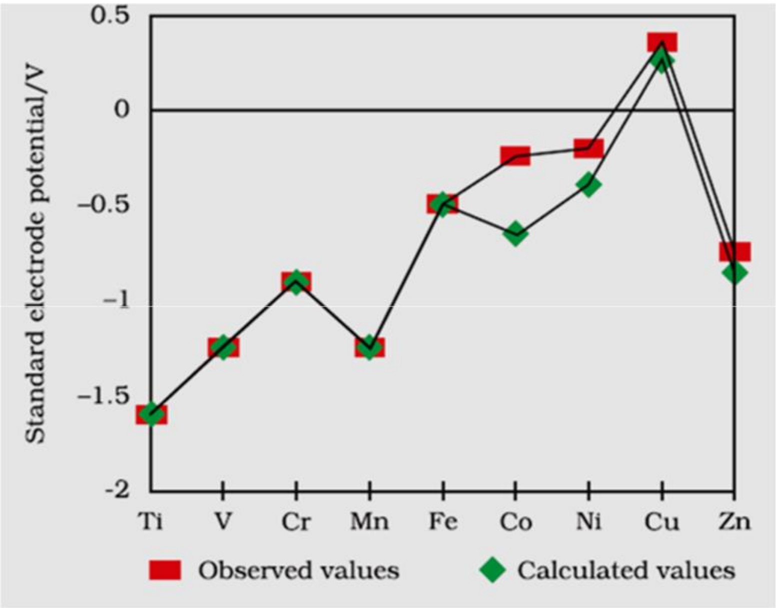


FIGURE 1 (source NCERT)

Explain the following observations:

i. The general trend towards less negative E^{o} values across the series
ii. The unique behaviour of Copper
iii. More negative E^{o} values of Mn and Zn

27. Arrange the following in increasing order of property specified:

i. Aniline, ethanamine, 2-ethylethanamine (solubility in water)
ii. Ethanoic acid, ethanamine, ethanol (boiling point)
iii. Methanamine, N, N- dimethylmethanamine and N- methylmethanamine (basic strength in aqueous phase)

OR

i. Give a chemical test to distinguish between N-methylethanamine and N,N-dimethyl ethanamine.
ii. Write the reaction for catalytic reduction of nitrobenzene followed by reaction of product so formed with bromine water.
iii. Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why?

28. A metal crystallizes into two cubic system-face centred cubic (fcc) and body centred cubic (bcc) whose unit cell lengths are 3.5 and 3.0Å respectively. Calculate the ratio of densities of fcc and bcc.

29. Three amino acids are given below:

Alanine $CH_3CH(COOH)(NH_2)$ Aspartic acid $HOOC\text{-}CH_2CH(COOH)(NH_2)$ and Lysine $H_2N\text{-}(CH_2)_4\text{-}CH(COOH)(NH_2)$

i. Make two tripeptides using these amino acids and mark the peptide linkage in both cases.
ii. Represent Alanine in the zwitter ionic form.

30. i. Arrange the following in decreasing order of bond dissociation enthalpy

F_2 , Cl_2 , Br_2 , I_2

ii. Bi does not form pπ-pπ bonds. Give reason for the observation.

iii.Electron gain enthalpy of oxygen is less negative than sulphur. Justify

SECTION D

Q.No 31 to 33 are long answer type carrying 5 marks each.

31. (i) Answer the following questions: **(2+3)**

a) Write the balanced chemical reaction for reaction of Cu with dilute HNO_3.

b) Draw the shape of ClF_3

(ii)'X' has a boiling point of 4.2K, lowest for any known substance. It is used as a diluent for oxygen in modern diving apparatus. Identify the gas 'X'. Which property of this gas makes it usable as diluent? Why is the boiling point of the gas 'X' so low?

OR

(i) Answer the following questions: **(2+3)**

a) Arrange the following in the increasing order of thermal stability:

H_2O, H_2S, H_2Se, H_2Te

b)Give the formula of the brown ring formed at the interface during the ring test for nitrate.

(ii) A greenish yellow gas 'A' with pungent and suffocating odour, is a powerful bleaching agent. 'A' on treatment with dry slaked lime it gives bleaching powder. Identify 'A' and explain the reason for its bleaching action. Write the balanced chemical equation for the reaction of 'A' with hot and concentrated NaOH.

32. An organic compound 'A' C_8H_6 on treatment with dilute H_2SO_4 containing mercuric sulphate gives compound 'B'. This compound 'B' can also be obtained from a reaction of benzene with acetyl chloride in presence of anhy $AlCl_3$. 'B' on treatment with I_2 in aq. KOH gives 'C' and a yellow compound 'D'. Identify A, B, C and D. Give the chemical reactions involved. **(5)**

OR

(i) Write the reaction for cross aldol condensation of acetone and ethanal.

(ii) How will you carry out the following conversions:

a) Benzyl alcohol to phenyl ethanoic acid
b) Propanone to propene
c) Benzene to *m*-Nitroacetophenone

33. (i) State Kohlrausch law. **(1+4)**

(ii) Calculate the emf of the following cell at 298 K: $Al(s)/Al^{3+}$ (0.15M)//Cu^{2+}(0.025M) /Cu(s)

(Given $E^o(Al^{3+}/Al) = -1.66$ V, $E^o(Cu^{2+}/Cu) = 0.34$V, log 0.15 = -0.8239, log 0.025 = -1.6020)

OR

(i) On the basis of E^o values identify which amongst the following is the strongest oxidising agent **(1+4)**

$Cl_2(g) + 2e^- \rightarrow 2Cl^-$ $E_o = +1.36$ V,

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^o = +1.51$ V $Cr_2O_7^{2-} + 14H^+$
$+ 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $E^o = +1.33$ V

(ii) The following figure 2, represents variation of (Λ_m) vs $\sqrt{c}$ for an electrolyte. Here Λ_m is the molar conductivity and c is the concentration of the electrolyte.

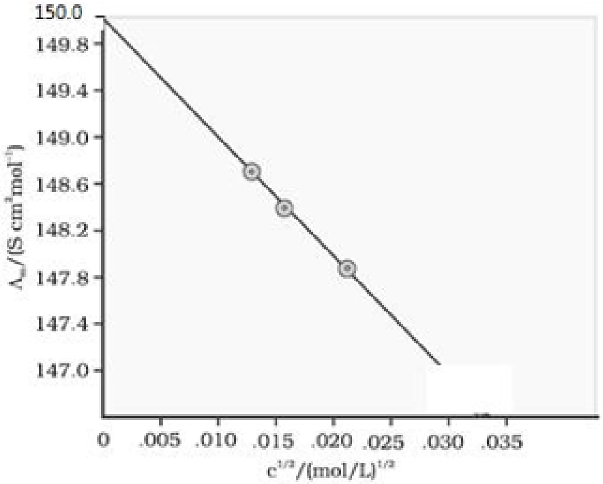


Figure 2

a) Define molar conductivity
b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
c) Determine the value of Λ_m^o for the electrolyte.
d) Show how to calculate the value of A for the electrolyte using the above graph.

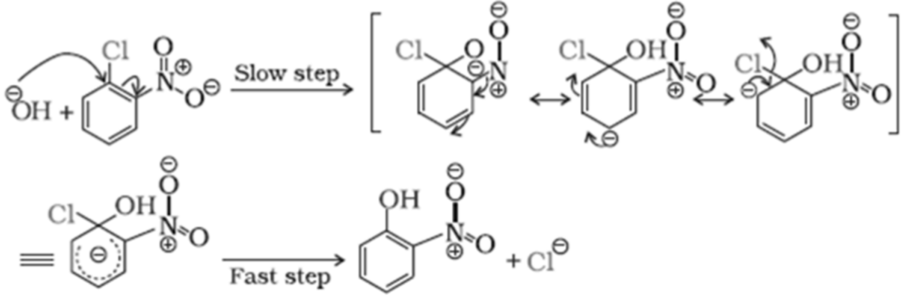
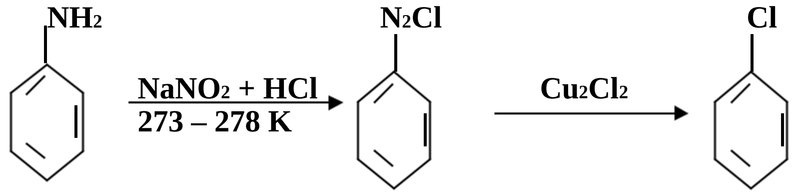
MARKING SCHEME

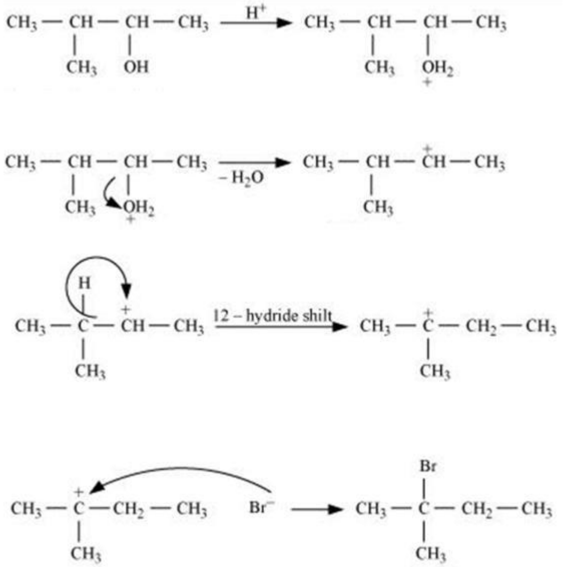
SAMPLE PAPER 1

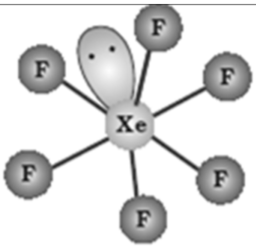
SECTION A

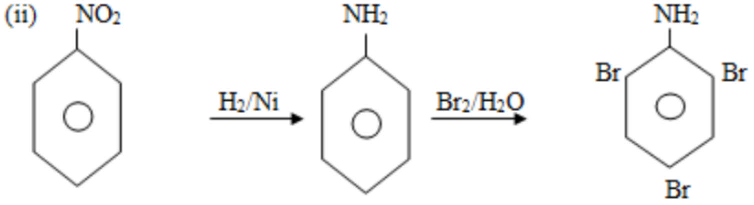
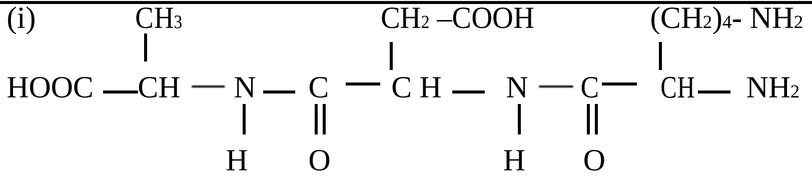
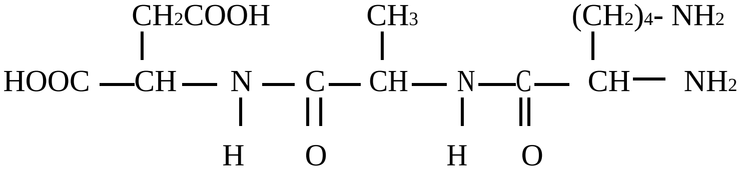
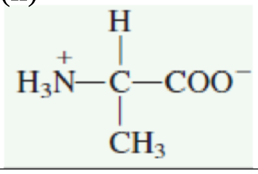
Q.No.	Value Point	Marks
1(i)	D	1
(ii)	B OR A	1
(iii)	A	1
(iv)	C	1
2(i)	B	1
(ii)	A	1
(iii)	A	1
(iv)	A OR B	1
3	C	1
4	D OR C	1
5	C	1
6	B OR B	1
7	B OR D	1
8	A OR A	1
9	C	1
10	A	1
11	A	1
12	A	1
13	D	1
14	B OR B	1
15	B	1
16	A	1

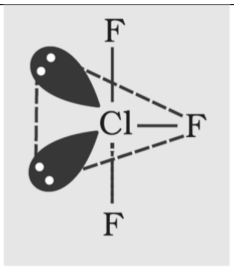
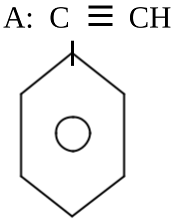
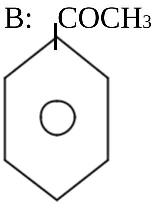
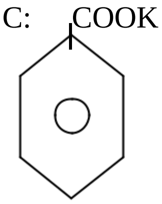
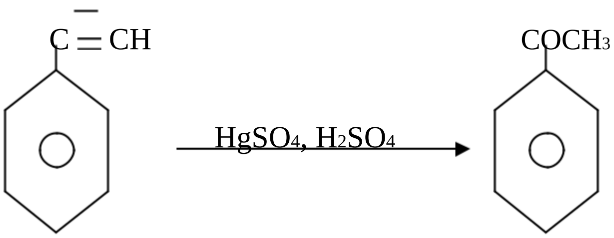
SECTION B, C, D

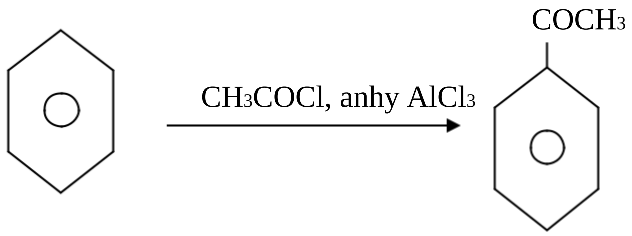
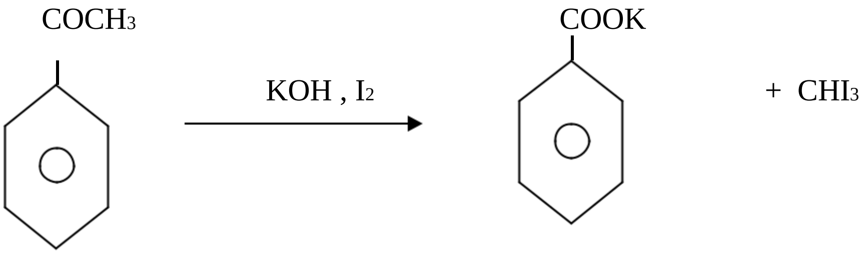
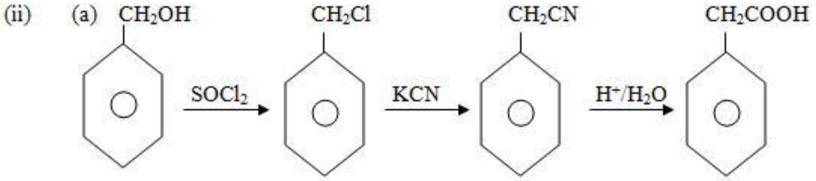
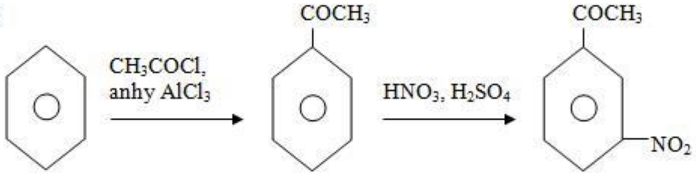
Q.No.	VALUE POINTS	MARKS
SECTION B		
17	Nitro group at ortho position withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene.  **OR** **(i)**  **(ii)** $CH_3CH(Br)CH_3 \xrightarrow{\text{alc KOH}} CH_3CH{=}CH_2 \xrightarrow{\text{HBr, organic peroxide}} CH_3CH_2CH_2Br$	2 1 1
18	$T_b = K_b\, m$ T_b = 101.04-100 = 1.04 ^oC or m= 1.04 /0.52 = 2 m 2 m solution means 2 moles of solute in 1 kg of solvent. 2 m aq solution of urea means 2 moles of urea in 1kg of water. No. of moles of water = 1000/18 = 55.5 Relative lowering of VP = x_2 (where x_2 is mole fraction of solute) Relative lowering of VP = n_2/n_1+n_2 (n_2 is no. of moles of solute , n_1 is no. of moles of solvent) = 2/ 2+55.5 = 2/57.5 = 0.034	1 1/2 1/2
19	(i)$t_{2g}^4e_g^2$ Paramagentic (ii)Dichloridobis(ethane-1,2-diamine)cobalt(III)nitrate OR (i)Square planar (ii)Cu^{2+} = $3d^9$ 1 unpaired electron so $\sqrt{1(3)}$ = 1.73BM	½, ½ 1 1 1
20	Reaction is a complex reaction. Order of reaction is 1.5. Molecularity cannot be 1.5, it has no meaning for this reaction. The reaction occurs in steps, so it is a complex reaction. (ii)units of k are $mol^{-1/2}L^{1/2}s^{-1}$	1/2 1/2 1

	OR Ans : let the rate law expression be Rate = k $[P]^x[Q]^y$ from the table we know that Rate 1 = 3.0×10^{-4} = k $(0.10)^x$ $(0.10)^y$ Rate 2 = 9.0×10^{-4} = k $(0.30)^x$ $(0.30)^y$ Rate 3 = 3.0×10^{-4} = k $(0.10)^x$ $(0.30)^y$ Rate 1/ Rate 3 = $(1/3)^y$ or 1 = $(1/3)^y$ So y = 0 Rate 2/ Rate 3 = $(3)^x$ or 3 = $(3)^x$ So x = 1 Rate = k [P]	½ ½ 1
21	k = $0.693/t_{1/2}$ k = 0.693/5730 years^{-1} t = $\frac{2.303}{k} \log \frac{Co}{Ct}$ let Co = 1 Ct = 3/10 so Co/Ct = 1/ (3/10) = 10/3 t = $\frac{2.303}{0.693} \times 5730 \log \frac{10}{3}$ t = 19042 x (1-0.4771) = 9957 years	½ ½ ½ ½
22		½ ½ ½ ½
23	XeF_6 Central atom Xe has 8 valence electrons, it forms 6 bonds with F and has 1 lone pair. According to VSEPR theory, presence of 6 bp and 1 lp results in distorted octahedral geometry	1 1

		
16.	Racemic mixture will be given by 2 chlorobutane as it is an optically active compound. When 2 chlorobutane undergoes S_N^1 reaction, both front and rear attack are possible, resulting in a racemic mixture	1 1
25	Let no. of Atoms of element P be x No. of tetrahedral voids = 2x No. Of octahedral voids = x Atoms of Q = 1/3 (2x) + x = 5x/3 $P_xQ_{5x/3}$ P_3Q_5	1/2 ½ 1
	SECTION C	
26	(i)Due to large surface area and ability to show variable oxidation states (ii)Due to high value of third ionisation enthalpy (iii) Mo(VI) and W(VI) are more stable than Cr(VI). **OR** (i) The general trend towards less negative E^o V values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. (h) The high energy to transform Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy. (iii) The stability of the half-filled *d* sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their more negative E^o V values	1 1 1 1 1 1
27	(i) Aniline, *N*-ethylethanamine, Etanamine (ii)Ethanamine, ethanol, ethanoic acid (iii) N, N dimethylmethanamine, methanamine, N-methylmethanamine **OR** (i) N-methyletahnamine is a secondary amine. When it reacts with benzenesulphonyl chloride, it forms N- Ethyl -N methyl sulphonamide while and	1 1 1 1

	N,N-dimethyl etahnanmine is a tertiary amine it does not react with benzenesulphonyl chloride.  (iii)Butan-1-ol Alcohol forms stronger hydrogen bonds with water than formed by amine due to higher electronegativity of O in alcohol than N in amine	1 ½ ½
28	We know that d = zM/ $N_a a^3$ For fcc, z=4 therefore d = 4 x M / Na $(3.5 \times 10^{-8})^3$ g/cm^3 For bcc, z=2 therefore d’ = 2 x M / Na $(3.0 \times 10^{-8})^3$ g/cm^3 d/d’ = $4/(3.5 \times 10^{-8})^3$ / $2/(3.0 \times 10^{-8})^3$ = 1.26:1	1/2 1 1 1/2
29	(i)  $HOOC-\overset{CH_3}{\overset{\vert}{C}H}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{CH_2-COOH}{\overset{\vert}{C}H}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{(CH_2)_4-NH_2}{\overset{\vert}{C}H}-NH_2$  $HOOC-\overset{CH_2COOH}{\overset{\vert}{C}H}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{CH_3}{\overset{\vert}{C}H}-\underset{H}{\underset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}}-\overset{(CH_2)_4-NH_2}{\overset{\vert}{C}H}-NH_2$ (ii) 	1 1 1
30	i. Arrange the following in decreasing order of bond dissociation enthalpy $Cl_2 > Br_2 > F_2 > I_2$ ii. Bi does not form pπ-pπ bonds as its atomic orbitals are large and diffuse so effective overlapping is not possible iii.Due to small size of oxygen, it has greater elecrton electron repulsions	1 1 1
	SECTION D	
(h)	(i) (a) $3Cu + 8 HNO_3$(dilute) → $3Cu(NO_3)_2 + 2NO + 4H_2O$ (b)	1

	 (ii)'X' is Helium It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. It monoatomic having no interatomic forces except weak dispersion forces and has second lowest mass therefore bp is lowest. OR (a) H_2Te, H_2Se, H_2S, H_2O (b) $[Fe(H_2O)_5(NO)]^{2+}$ (ii) A is chlorine gas Its bleaching action is due to oxidation. $Cl_2 + H_2O \rightarrow 2HCl + O$, Coloured substance + O → Colourless substance $6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$	1 1 1 1 1 1 1 1 1
32	A:  B:  C:  D: CHI_3 	½ each 1 1

	  **OR** (i) $CH_3COCH_3 + CH_3CHO$ $\downarrow$ dil NaOH $(CH_3)_2C(OH)CH_2CHO + CH_3CH(OH)CH_2COCH_3$ $\downarrow$ Heat $(CH_3)_2C=CHCHO + CH_3CH=CHCOCH_3$ (ii)  (b) $CH_3COCH_3 \xrightarrow{H_2,\ Pd} CH_3CH(OH)CH_3 \xrightarrow{H_2SO_4} CH_3CH=CH_2$ (c)  	1 1 1 1 1 1
33	(i) limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. (ii) E^ocell = E^ocathode -E^oanode = 0.34-(-1.66) = 2.00 V Ecell = E^ocell – $\underline{0.059}$ log $\underline{[Al^{3+}]}^2$	1 1/2

n $[Cu^{2+}]^3$

Here n = 6

$E_{cell} = 2 - \underline{0.059} \log \frac{[0.15]^2}{[0.025]^3}$

(iv) 2 – 0.059/6 (2log 0.15 – 3 log 0.025)

(v) 2 – 0.059/6 (-1.6478 +4.8062) = 2- 0.0311 = 1.9689V

OR

(e) MnO_4^-

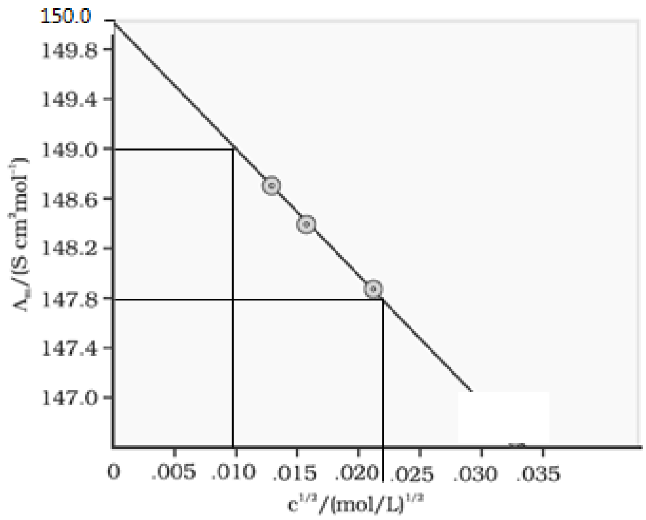
(ii)(a) Molar conductivity of a solution at a given concentration is the conductance of the volume *V* of solution containing one mole of electrolyte kept between two electrodes with area of cross section *A* and distance of unit length.

(b)Strong electrolyte, For strong electrolytes, Λm increases slowly with dilution

(c) $\Lambda m = \Lambda m° - A\, c^{½}$

Therefore $\Lambda m°$ = 150 S cm^2 mol^{-1}

(d)



A = – slope = - (149 – 147.8/ 0.010-0.022) = 100 S cm^2 mol^{-1}/(mol/L^{-1})$^{1/2}$.

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