STUDENTS SUPPORT MATERIAL

CLASS-XII

CHEMISTRY

SESSION-2020-21

KENDRIYA VIDYALAYA SANGTHAN
REGIONAL OFFICE
AHMEDABAD

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 physicaland 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.**

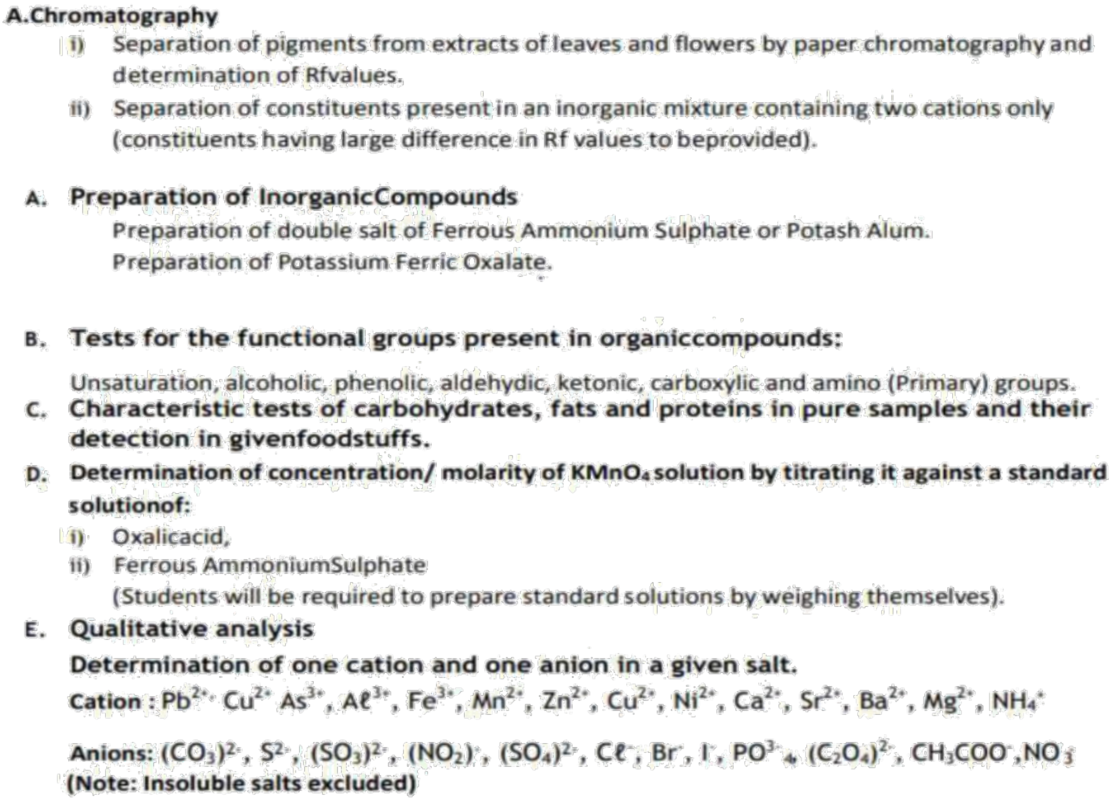
UNIT–4 CHEMICAL KINETICS Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), 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**

UNIT -1 “THE SOLID STATE”

TERMS	EXPLANATIONS
Amorphous and Crystalline Solids	Amorphous- short range order, Irregular shape, istropic. No sharp MP, so also called pseudo solids or super cooled liquids eg-glass Crystalline Solids- long range order, regular shape, anisotropic. Sharp MP, so called true solids. 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 -8, 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:	Cation 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 defects. The number of missing cations and anions are equal. Density decreases. For example, NaCl, KCl, CsCl and **AgBr.**
Impurity Defects	If molten NaCl containing a little amount of SrCl2 is crystallized, it creates cationic vacancies. The cationic vacancies thus produced are equal in number to that of Sr2+ ions.
Metal excess defect due to anionic vacancies (F-centres)	When alkali metal halides are heated in an atmosphere of alkali metal vapor, they become colored. During heating electrons released by metal diffuse into the crystal and occupy anionic sites, which is called **F^-centres.** NaCl, LiCl, KCl acquires yellow,

	pink, violet color when heated in vapors of Na. Li and K respectively.
Metal excess defect due to the presence of extra cations at interstitial sites:	Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow. The excess Zn2+ ions move to interstitial sites and the electrons to neighbouring interstitial sites.

Question - Answers

1. Which of the following statement is not true about amorphous solids?
   (i) On heating they may become crystalline at certain temperature.
   (ii) They may become crystalline on keeping for long time.
   (iii) Amorphous solids can be moulded by heating.
   (iv) They are anisotropic in nature.
2. Which of the following is not the characteristic of ionic solids?
   (i) Very low value of electrical conductivity in the molten state.
   (ii) Brittle nature.
   (iii) Very strong forces of interactions.
   (iv) Anisotropic nature.
3. Graphite is a good conductor of electricity due to the presence of __________.
   (i) lone pair of electrons (ii) free valence electrons (iii) cations (iv) anions
4. Which of the following point defects are shown by AgBr(s) crystals?
   (A) Schottky defect (B) Frenkel defect (C) Metal excess defect (D) Metal deficiency defect
   (i) (A) and (B) (ii) (C) and (D) (iii) (A) and (C) (iv) (B) and (D)
5. An excess of potassium makes KCl crystals violet or lilac in colour on heating, because_
   (i) some of the anionic sites are occupied by an unpaired electron.
   (ii) some of the anionic sites are occupied by a pair of electrons.
   (iii) there are vacancies at some anionic sites.
   (iv) F-centers are created which impart colour to the crystals.
6. Which of the following defects decrease the density?
   (i) Interstitial defect (ii) Frankel defect (iii) Schottky defect
   Assertion and Reason Type [7-9]

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

(i) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(ii) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(iii) Assertion is correct statement but reason is wrong statement.
(iv) Assertion is wrong statement but reason is correct statement.

7. Assertion : Graphite is a good conductor of electricity however diamond belongs to the category of insulators.
   Reason : Graphite is soft in nature on the other hand diamond is very hard and brittle.
8. Assertion : The total number of atoms present in a simple cubic unit cell is one.
   Reason : Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.
9. Assertion : The packing efficiency is maximum for the fcc structure.

Reason : The coordination number is 12 in fcc structures.

Ques	1	2	3	4	5	6	7	8	9
Ans	iv	i	ii	i	iv	iii	ii	i	ii

Short Answer Type:

10. Silver crystallizes in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3} , calculate the atomic mass of silver.

Ans: It is given that the edge length, a = 4.07×10^{-8} cm and density is d = 10.5 g cm^{-3}
As the lattice is fcc type, the number of atoms per unit cell, z = 4

$$d = \frac{zM}{a3N_A}$$

$$\Rightarrow M = \frac{da^3N_A}{z}$$

$$= \frac{10.5\,gcm^{-3} \times \left(4.077 \times 10^{-8} cm\right)^3 \times 6.022 \times 10^{23} mol^{-1}}{4}$$

$= 107.13$ $gmol^{-1}$
Therefore, atomic mass of silver = 107.13u

11. A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body centre. What is the formula of the compound? What are the coordination numbers of P and Q?

Ans: Number of atoms of Q in one unit cell = 8 × (1/8) = 1
Number of atoms of P in one unit cell = 1. So, the ratio of the number of P atoms to the number of Q atoms, P:Q = 1:1 Hence, the formula of the compound is PQ
The coordination number of both P and Q is 8.

12. Aluminium crystallizes in a cubic close-packed structure. Its metallic radius is 125 pm. (i) What is the length of the side of the unit cell? (ii) How many unit cells are there in 1.00 cm^3 of aluminium?

(i) For cubic close-packed structure:

$a = 2\sqrt{2}r$

$= 2\sqrt{2} = 125\ pm$

$= 353.55$ pm

$= 354$ pm (approximately)

(ii) Volume of one unit cell $= (354 \text{ pm})^3$

$= 4.4 \times 10^7 \text{ pm}^3$

$= 4.4 \times 10^7 \times 10^{-30} \text{cm}^3$

$= 4.4 \times 10^{-23} \text{ cm}^3$

Therefore, number of unit cells in $1.00 \text{ cm}^3 = \dfrac{1.00 \text{ cm}^3}{4.4 \times 10^{-23} \text{cm}^3}$

$= 2.27 \times 10^{22}$

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13. If NaCl is doped with 10^{-3}mol % of SrCl2 , what is the concentration of cation vacancies?

Ans:

It is given that NaCl is doped with 10^{-3}mol % of $SrCl_2$.

This means that 100 mol of NaCl is doped with 10^{-3}mol of $SrCl_2$.

Therefore, 1 mol of NaCl is doped with $\dfrac{10^{-3}}{100}$ mol of $SrCl_2$

$= 10^{-5}$mol of $SrCl_2$

Cation vacancies produced by one Sr^{2+} ion = 1

$\therefore$ Concentration of the cation vacancies

Produced by 10^{-5}mol of Sr^{2+} ions $= 10^{-5} \times 6.022 \times 10^{23}$

$= 6.022 \times 10^{18} \text{ mol}^{-1}$

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CHAPTER-2-"SOLUTION"

GIST OF THE LESSON

Conc. of Solutions w/w% omposition:	Mass of solute present per 100 g. of solution $\text{w/w\% Composition} = \frac{\text{w Solute}}{\text{w Solution}} \times 100$
Molarity [M]:	No. of moles of solute present per liter of solution in called 'molarity of solution'. . It is temperature dependent.M= No. of Moles of solute / Volume of solution in litre
Molality [m]:	No. of moles of solute present per kg. of solvent is called molality. It is temperature independent. m= No. of Moles of solute / Mass of Solvent in Kg
Normality[N]:	No. of gram equivalent of solute present per liter of solution is called normality of solution. N = No. of gm equivalent of solute / Volume of solution in litre
Parts Per Million[ppm]:	It is used for very dilute solutions, Parts of solute in per million parts of solution are called ppm. Ppm = Part of solute x10^6 / Part of solution
Mole Fraction:	Ratio of number of moles of a component in solution to the total no. of moles of all the components is called mole fraction (x) of the component.

Henry's law :-"The partial pressure of the gas in vapour phase *p* is proportional to the mole fraction of the gas *x* in the solution." $\mathbf{P=K_Hx}$

Applications of Henery Law(1) In Packing of soda/ Soft drinks(2) In Deep see diving(He = 11.7 % , N_2 = 56.2 % and O_2 =32.1%)(3) Functions of lungs (4)At high altitudes pressure is low there for breathing problems lead to ANOXIA (unable to think and weak)

Vapour Pressure: The pressure exerted by vapours over the liquid surface at equilibrium is called *vapour pressure* of the liquid.

Raoult'sLaw:"*TheV.P. of any volatile component in the solution is directly proportional to its mo fraction*".

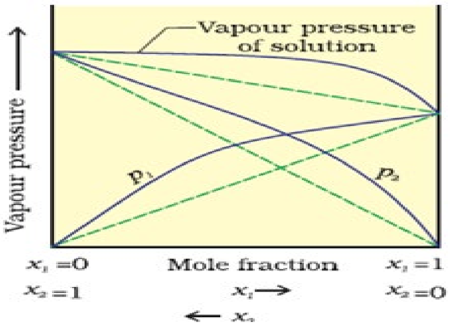
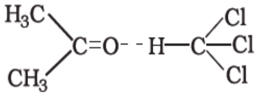
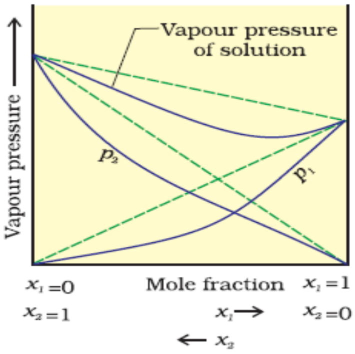
Raoult's law for a solution containing two miscible liquids:	**Raoult's law for a solution containing a non-volatile solute:**
The partial vapour pressure of each component of a solution is directly proportional to its mole fraction at a given temperature. Suppose A and B are two volatile components of a solution. Therefore according to Raoult's law $P_A \propto \chi_A$, $P_A = P_A^0 \times \chi_A$ and $P_B \propto \chi_B$, $P_B = P_B^0 \times \chi_B$ Therefore total vapour pressure of the solution: $P_s = P_A + P_B$	The relative lowering of vapour pressure for a solution containing a non-volatile solute is equal to mole fraction of the solute when solvent alone is volatile. $\chi_B = \frac{P_A^0 - P_A}{P_A^0}$ Where P_A^0 is vapour pressure of pure component 'A' P_A is partial vapour pressure of component 'A'

For a binary solution $\chi_A + \chi_B = 1$, if $\chi_A = 1 - \chi_B$ Ps = $P_A^0 + (P_B^0 - P_A^0)\chi_B$ and if $\chi_B = 1 - \chi_A$ Ps = $P_B^0 + (P_A^0 - P_B^0)\chi_A$	$P_A^0 - P_A$ is lowering of vapour pressure $\frac{P_A^0 - P_A}{P_A^0}$ is relative lowering of vapour pressur

Ideal and Non-Ideal Solutions:

Ideal Solution	Non Ideal Solution
Follows Raoult's law at all temperature and concentrations. $P = P_A + P_B$	Does not follow Raoult's law at all temperature and pressure. $P \neq P_A + P_B$
Intermolecular forces in resulting solution are same as in pure components. A – B = A – A = B – B	Intermolecular forces in resulting solution are different from the inter molecular force of pure components.A – B ≠ A – A, B – B
No change in volume while mixing components. $\Delta V_{mix} = 0$	Change in volume while mixing components. $\Delta V_{mix} \neq 0$
No heat change take place while mixing the components. $\Delta H_{mix} = 0$	Heat changes take place while mixing the components. $\Delta H_{mix} \neq 0$
Eg: n – hexane + n – heptanes & benzene + toluene	Eg: Acetone + Water & Acetone + $CHCl_3$

Non Ideal Solution

Showing Positive elevation from Raoult's Law	**Showing Negative Deviation from Raoult's Law**
Vapour pressure of resulting solution is greater than sum of partial pressure of components. $P > P_A + P_B$	Vapour pressure of resulting solution is less than sum of the partial pressure of pure components. $P < P_A + P_B$
Resulting intermolecular force is weaker than pure components.	Resulting intermolecular force is stronger than pure components.
ΔV_{mix} = +ve	ΔV_{mix} = –ve
Volume of solution > Sum of volume of pure components	Volume of solution < Sum of volume of pure components
ΔH_{mix} = +ve Endothermic mixing process	ΔH_{mix} = –ve Exothermic process
Eg: Acetone + Water, Alcohol + Water Carboxylic Acid + Water 	Eg: Acetone + $CHCl_3$, HNO_3 + H_2O  

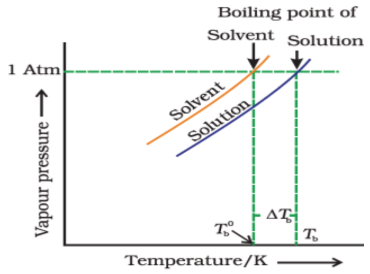
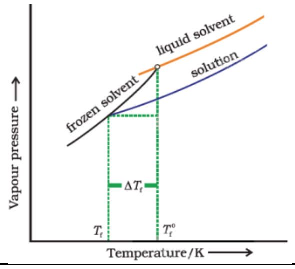
Azeothrpes: :- The mixture of liquids which boils at a constant temperature like a pure liquid and posses same composition of the components in liquid as well as in vapour

⊙ **Minimum Boiling Azeothrpes:** Boils at a temperature lower than b.ps. of pure components. **[95% Alcohol by volume]**

◉ **Maximum Boiling Azeothrpes:** Boils at a temperature higher than b.p.s. of pure components. [68% HNO_3 by mass]

Colligative Properties:-The properties of dilute solutions which depend only on number particles of solute present in the solution and not on their identity are called *colligative properties*

1-Relative Lowering of Vapour Pressure $\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$	**The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute present in the solution.**

3- Elevation of Boiling Point: Difference between boiling of solution containing non volatile solute and B.P. of pure solvent is called elevation of B.P. **$\Delta T_b = T_b - T^o_b$**		$\Delta T_b \propto$ m [molality] $\Delta T_b = K_b$ m K_b=MolalElevationConstant $\boxed{\Delta T_b} = K_b \frac{W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$
4-Depression of Freezing Point: Difference in freezing point of pure solvent and freezing point of solution is called 'Depression in Freezing Point'. **$\Delta T_f = T^0_f - T_f$**		$\Delta T_f \propto$ m [molality] $\Delta T_f = K_f m$ K_f =Molal Depression Constant $\Delta T_f = K_f \frac{W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$

Osmotic Pressure: Excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane. $\pi V = nRT$ π = Osmotic pressure R =Gas constant.

Reverse Osmosis: If pressure greater than osmotic pressure is applied then, flow of solvent molecules is reversed, i.e. from a higher concentration solution to lower concentrated solution. This phenomenon is called "Reverse Osmosis**". It is used in water purification and desalination of water.**

[1] MULTIPLE CHOICE QUESTIONS:

Q1. **The value of Henry's constant K_H is**:
(a) greater for gases with higher solubility (b) greater for gases with lower solubility.
(c) constant for all gases. (d) not related to the solubility of gases.

Q2. **Increasing the temperature of an aqueous solution will cause:**
(a) decrease in molality (b) decrease in molarity (c)
decrease in mole fraction (d) decrease in % (w/w)

Q3. **Colligative properties depend on:**
(a) the nature of the solute (b) the number of solute particles in solution (c) the physical properties of solute (d) the nature of the solvent

Q4. **The unit of ebullioscopic constant is:**
(a) K kg mol^{-1} (b) K^{-1} kg mol (c) K kg^{-1} mol^{-1} (d) K kg^{-1} mol $^{-1}$

Q5. **The most suitable colligative property to determine molecular weight of bimolecules is:**
(a) Lowering of vapour pressure (b) Osmotic pressure
(c) Elevation of boiling point (d) Depression of freezing point

Q6. **The number of moles of NaCl in 3 litres of 3M solution is:**
(a) 1 (b) 3 (c) 9 (d) 7

Q7. **Which has highest freezing point:**
(a) 1 M Glucose (b) 1 M NaCl (c) 1 M $CaCl_2$ (d) 1 M AlF_3

Q8. Which of the following condition is not satisfied by an ideal solution?
(a) $\Delta H_{mixing} = 0$ (b) $\Delta V_{mixing} = 0$ (c) Raoult's Law is obeyed
(d) Formation of an azeotropic mixture

Q9. **Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a negative deviation from Raoult's law?** (a) Methanol and acetone. (b) Chloroform and acetone. (c) Phenol and aniline. (d) Cyclohexane and ethanol

Q10. **The boiling point of an azeotropic mixture of water and ethanol is less than that of water and ethanol. The mixture shows:**
(a) no deviation from Raoult's Law. (b) positive deviation from Raoult's Law. (c) negative deviation from Raoult's Law. (d) that the solution is unsaturated. **[<u>Ans: 1 (b), 2 (b), 3 (b), 4 (a), 5 (b), 6 (c), 7 (a), 8 (d), 9 (b), 10 (b)</u>]**

[2] ASSERTION & REASON TYPE QUESTIONS:

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following 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 and reason both are incorrect statements.

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

2. Assertion: If on mixing the two liquids, the solution becomes hot, it implies that it shows negative deviation from Raoult's law.
Reason: Solution which shows negative deviation from Raoult's law are accompanied by decrease in volume.

3. Assertion: Greater the value of Henry's constant of a gas in a particular solvent, greater is the solubility of the gas at the same pressure and temperature.
Reason: Solubility of a gas is directly proportional to its Henry's constant at the same pressure and temperature.

4. Assertion: When a solution is separated from the pure solvent by a semi-permeable membrane, the solvent molecules pass through it from pure solvent side to the solution side.
Reason: Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

5. Assertion: Azeotropic mixtures are formed only by non-ideal solutions and they may have boiling points either greater than or less than both the components.
Reason: The composition of the vapour phase is same as that of liquid phase of the azeotropic mixture.

[Ans: 1 (a), 2 (b), 3 (d), 4 (c), 5 (b)]

[3] Some important descriptive questions of 2 and 3 marks

1. State the following with one application of each: Henry law and Reverse osmosis. (2M)

2. Wrte down four important points of differences between an ideal and a non ideal solution. (2M)

3. State Raoult's law for a solution containing a non volatile solute. Also give its mathematical expression. (2M)

Note: Answers of questions 1 to 3 are as such available in this support material.

4**.** A solution containing 18 g of non-volatile solute in 200g of water freezes at 272.07 K. Calculate the molecular mass of solute (given K_f = 1.86 K/m) (3M)

Ans. W_2 = 18 g W_1= 200g, k_f = 1.86k/m ΔT_f= 273K – 272.07K = 0.93K

$$\Delta T_f = \frac{1000 \times k_f \times W_2}{M_2 \times W_1} \qquad \therefore M_2 = \frac{1000 \times k_f \times W_2}{\Delta T_f \times W_1}$$

$$M_2 = \frac{1000 \times 1.86 \times 18}{0.93 \times 200} = 180 \text{ amu}$$

5. **Calculate the temperature at which a solution containing 54 g of glucose ($C_6H_{12}O_6$) in 250 g of water will freeze (k_f for water =1.86 KKg/mol).**

Ans. Given- W solute = 54 g ,W solvent = 250 g, M solute = 180

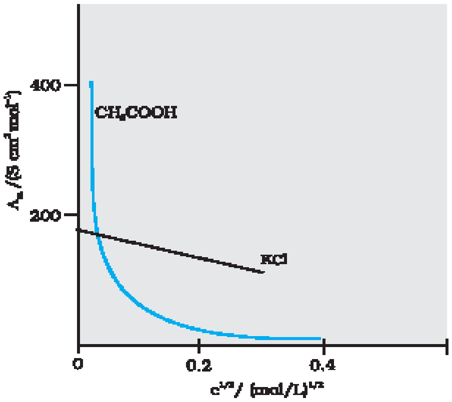
$$\Delta T_f = \frac{k_f \times w_{solute} \times 1000}{M_{solute} \times w_{solvent}}$$ **(substitute values and solve)**

ΔT_f = 2.232 K

$T_f = T^0_f - \Delta T_f T_f$ = 273- 2.232= 270.768 K

CHAPTER 3 -"ELECTROCHEMISTRY"

GIST OF THE LESSON

1.	**Conductance** : Reciprocal of the resistance $C = \frac{1}{R}$ **Unit is** Ω^{-1}	
2	**Specific Resistance/Resistivity** : **Unit is ohm.cm** $\rho = R\,A/l$	
3	**Specific Conductance or Conductivity** : **unit: S cm^{-1}** $k = 1/\rho = l/RA = 1/R \times l/A$ Conductivity of any conductor is the reciprocal of specific resistance and is denoted by κ (Greek work Kappa) $k = C \times G^*$ ($G^* = l/A$ = **Cell constant**, **Unit Cm^{-1}**) **Variation of k (Conductivity) with concentration:** k directly proportional to concentration.	
4	**Molar Conductivity** : It is defined as the conducting power of all the ions produced by one gram mol of an electrolyte in a solution. It is denoted by $\wedge_m$. $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$ **unit Scm^{2}mol^{-1}**	
5	**Variation of molar conductivity with concentration** In case of strong electrolyte like KCl, $\wedge_m$ does not increase appreciably because number of ions does not increase much whereas mobility of ions increases on dilution. In case of weak electrolyte like CH_3COOH, $\wedge_m$ increases appreciably with decrease in concentration because both number of ions as well as mobility of ions increase with decrease in concentration i.e. on dilution.	
6	**Kohlrausch's Law** : According to this law, molar conductivity of an electrolyte, at infinite dilution can be expressed as the sum of contributions from its individual ions e.g. $\wedge_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$ or $\wedge_m^o = \nu_+ \lambda_+^o + \nu_- \lambda_-^o$ Where ν_+ and ν_- are the number of cations and anions per formula of electrolyte (e.g. $\nu_+ = \nu_- = 1$ in NaCl but $\nu_+ = 1$ and $\nu_- = 2$ for $CaCl_2$). **Application ofKohlrausch's Law** 1. For calculation of limiting molar conductivity $\wedge_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$ 2. For calculation of degree of dissociation $\alpha = \frac{\Lambda}{\Lambda^o}$ 3. For calculation of dissociation constant.$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda^2}{\Lambda^o(\Lambda^o - \Lambda)}$	
7	**Nernst equation for half cell** (Single electrode): $E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$ OR $\mathbf{E_{M^{n+}/M} = E^o_{M^{n+}/M}} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$	**Solve,** **Intext question:** **3.4, [H$^+$] = 10^{-pH}** **Ans: = -0.951 V**

8	**Nernst equation for complete cell** $Ecell = E^o cell - \frac{0.059}{n} \log \frac{[product]}{[react.]}$	**Equilibrium constant (K_c)** At equilibrium $Q_c = K_c$ and $E_{cell} = 0$ $E^o cell = \frac{0.059}{n} \log Kc$
9	**Electrochemical Cell and Gibbs energy of the reaction:** $\Delta_r G = -nFE$ $\Delta_r G^o = -nFE^o$ $\Delta_r G^o = -2.303RT \log K_c$	

[1]

MULTIPLE CHOICE QUESTIOS:

Q1 If limiting molar conductivity of Ca^{2+} and Cl^- are 119.0 and 76.3 S cm^2 mol^{-1}, then the value of limiting molar conductivity of $CaCl_2$ will be: (a) 195.3 S cm^2 mol^{-1} (b) 271.6 S cm^2 mol^{-1} (c) 43.3 S cm^2 mol^{-1} (d) 314.3 S cm^2 mol^{-1}

Q2. Why does the conductivity of a solution decrease with dilution? (a) No. of inons per cubic cm of solution increases (b) No. of ions per cubic cm of solution decreases (c) No. of inons per cubic cm of solution remains constant (d) Non of these

Q3.$\Lambda^o m$ (H_2O) is equal to:
(a) $\Lambda^o m(HCl) + \Lambda^o m(NaOH) - \Lambda^o m(NaCl)$
(b) $\Lambda^o m(HCl) - \Lambda^o m(NaOH) + \Lambda^o m(NaCl)$ (c) $\Lambda^o m(HCl) + \Lambda^o m(NaOH) + \Lambda^o m(NaCl)$
(d) $\Lambda^o m(HCl) - \Lambda^o m(NaOH) - \Lambda^o m(NaCl)$

Q4. The ration of distance between electodes and area of cross section is referred to as: (a) Faraday constant (b) Cell Constant (c) Electrochemical equivalent (d) Specific resistance

Q5. The conductance of electrolyte, when distance between elctrodes is 1 cm and and area of cross section is 1 cm^2, is referred to as: (a) Molar conductance (b) Equivalent conductance (c) Specific Conductance (d) Specific Resistance

Q6. The euation which gives the rlationship between molar conducance and concentration of strong electrolyte is known as: (a) Nernst equation (b) Electrochemical equation (c) Debye equation (d) Debye-Hukel-Onsager equation

Q7. Relation between molar conductivity of an electrolyte to its degree of dissociation is given by the relation:
(a) $\alpha = K/ \Lambda m$ (b) $\alpha = \Lambda m/ K$ (c) $\alpha = \Lambda^0 m/ \Lambda m$ (d) $\alpha = \Lambda m/ \Lambda^0 m$

Q8. An increase in molar conductance of a strong electrolyte with dilution is mainly due to: (a) increase in both i.e. number of ions and ionic mobility of ions. (b) Increase in number of ions (c) increase in ionic mobility of ions (d) 100% ionization of electrolyte at normal dilution

Q9. An increase in molar conductance of a weak electrolyte with dilution is mainly due to: (a) increase in both i.e. number of ions and ionic mobility of ions. (b) Increase in number of ions (c) increase in ionic mobility of ions (d) 100% ionization of electrolyte at normal dilution

Q10. The law that states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte is known as: (a) Farady Law (b) Kohlrausch law (c) Avogadro Law (d) Daltons law

[Ans: 1 (b), 2 (b), 3 (a), 4 (b), 5 (c), 6 (d), 7 (d), 8 (c), 9 (a), 10 (b)]

[2] ASSERTION & REASON TYPE QUESTIONS:

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following 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 and reason both are incorrect statements.

1. Assertion: Conductivity of all electrolytes decreases on dilution.
Reason: On dilution number of ions per unit volume decreases.

2. Assertion: Λm for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
Reason: For weak electrolytes degree of dissociation increases with dilution of solution.

3. Assertion: Current stops flowing when $E_{Cell} = 0$.
Reason: Equilibrium of the cell reaction is attained.

4. **Assertion:** Cu is less reactive than hydrogen.
Reason: E^0Cu^{2+}/Cu is negative.

5. **Assertion:** An electrochemical cell can behave like an electrolytic cell when $E_{ext} > E_{cell}$
Reason: When $E_{ext} > E_{cell}$, anode start functions as a cathode and cathode as an anode.

[Ans: 1 (d), 2 (a), 3 (a), 4 (c), 5 (a)]

[3] Some important descriptive questions of 2 and 3 marks

Q1. State Kohlrausch's law and give its applications. (2M)

Q2. (i) What is meant by cell constant? (2M)
(ii) Write an expression to relate $\wedge_m$ in terms of degree of dissociation.

Q3. Define conductivity and molar conductivity for the solution of an electrolyte. (2M)

Q4. The **conductivity** of **0.20 M** solution of KCl at 298 K is **0.0248 S cm^{-1}**. Calculate its **molar conductivity**. (2M)

Q5. Discuss the variation of conductivity and molar conductivity with dilution. (3M)

For answers of questions 1,2,3 and 5 refer the gist of this support materials.
For answer of question 4 refer point 4 of the gist. Get formula, substitute values and solve. The answer will come out to be 142 Scm^{2}mol^{-1}

Q6. Calculate the e.m.f. of the following cell at 298 K: (3M)

$Fe_{(s)} \mid Fe^{2+}(0.1M) \parallel Ag^+(0.1M) \mid Ag_{(s)}$ (Given $E^0_{Fe^{2+}/Fe} = -0.44$ V, $E^0_{Ag+/Ag} = +0.80$ V)
$R = 8.31\ JK^{-1}\ mol^{-1}$, $F = 96500$ C.

Solution:

$$\mathbf{Fe_{(s)}} \rightarrow Fe^{2+}_{(aq)} + 2e^-$$
$$\mathbf{2Ag^+ +} 2e^- \rightarrow 2Ag_{(s)}$$
$$\mathbf{Fe_{(s)} + 2Ag^+} \rightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)}$$

E $_{(cell)}$ = E^0 $_{(cell)}$ **-** $\frac{0.0591}{n}\log\frac{[Fe^{2+}]}{[Ag^+]^2}$**, n = 2, E** $_{(cell)}$ = [0.80-(-0.44)] **-** $\frac{0.0591}{2}\log\frac{[0.1]}{[0.01]^2}$

E $_{(cell)}$ = +1.205 V (ans)

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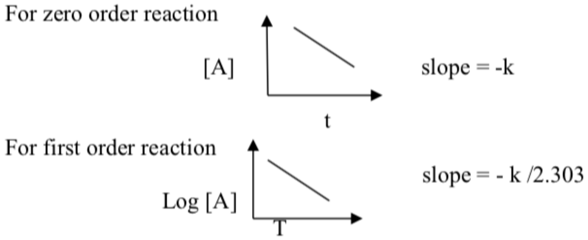
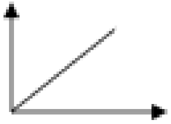
CHAPTER-4-"CHEMICAL KINETICS"

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)

S.No.	CONCEPT	THEORY AND FORMULA
1	Rate of reaction (r)	Change in concentration of reactant or product per unit time $A \longrightarrow B$, r = decrease in concentration of A / time = Increase 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) $t_{1/2}$ = 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	
10	Graph between r and [A]	For zero order reaction r 
		[A] For first order reaction r [A] 
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. $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$ Molecularity =2 and order of reaction =1

(C) ONE MARK QUESTIONS

1. What is the order of reaction whose rate constant has the same unit as the rate of reaction?

Ans. Zero order

2. Calculate overall order of reaction which has the rate expression r = k $[A]^{3/2}$ $[B]^{-1}$ **Ans**. Order = 3/2+(-1) =1/2

3. What is the unit of rate constant for a pseudo first order reaction ? **Ans.** Sec $^{-1}$

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.

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 r**1 **= k [1/2 A] =1/2 r**

(D) TWO MARKS QUESTIONS

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 = $-\Delta[R]/\Delta t$ = - (.02M - .05M) /30 sec =.03M /30 sec = .001M/ sec =10^{-3} moleL^{-1} sec^{-1}

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 = (2.303/k) log $[A_0]/[A]$
t= (2.303/60)log (1/(1/10))
t = (2.303/60) log10
t = (2.303/60) = 3.83 x 10^{-2} sec

3. A first order reaction is found to have a rate constant k =5.5 x 10^{-12} sec $^{-1}$. Find the half-life of the reaction.

Ans. Half life for a first order reaction is $t_{1/2}$ = (0.693/k) = 0.693 / 5.5 x 10^{-12} sec^{-1}

= 1.26 x 10^{+11} sec

4. A first order reaction has a rate constant 1.15 x10^{-3} 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 x10^{-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.

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)

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)

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)

4. Assertion: 50% of a reaction is completed in 50 sec, 75% of the reaction will be completed in 75 sec.

Reason: The rate constant of a zero-order reaction depends upon time

ANS: c)

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)

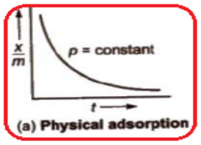
CHAPTER 5 -"Surface Chemistry"

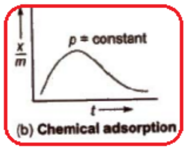
Adsorption:-The accumulation of molecular species at the surface rather in the bulk of a solid or liquid

- The substances upon which adsorption occurs, is called absorbent.
- The substance get adsorbed on the surface is call adsorbate.

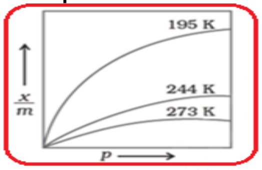
Physisorption	Chemisorption
Only van der Waals force are present between adsorbate and surface of adsorbent	Chemical bonds are formed between adsorbate and surface of adsorbent
Low enthalpy of adsorption ie, 20-40 kjmol^{-1}.	High enthalpy of adsorption i.e, 80-240 kjmol^{-1}.
Reversible and Not specific.	Irreversible and Highly specific.
It is usually takes place at **low temperature** and does not require any activation energy.	It takes place at **high temperature** and require activation energy..
Multi molecular layer of adsorbate are formed	Only **monomolecular layers** are formed.

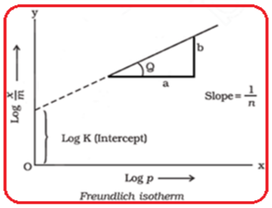
Adsorption Isobars:- plots between x / m (Extent of adsorption **v/s** temp at constant pressure.





Adsorption isotherm:- plots between x / m (Extent of adsorption) **v/s** pressure at constant temp.





Freundlich 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. (x= Mass of the gas adsorbed m = Mass of absorbent)

(i) At low Pressure x/m α P

(ii) At High Pressure x/m α P^0

(iii)At intermediate Pressure x/m α $P^{(1/n)}$

x/m =k.p(1/n) [n >1]

[logx/m = logK +1/n log p] (for gas)

[logx/m = logK +1/n log c] (for conc.)

SHAPE SELECTIVE CATALYSIS:-The catalytic reaction that depends upon the pore structure of the catalyst and the size of reactant and product molecules is called shape selective catalysis. e.g. Zeolites are good shape selective catalyst.ZSM-5 used to convert alcohol into gasoline.

Colloids:- Particle size between 1-1000nm **Dispersed Phase:**The phase which is dispersed or scattered through the dispersion medium is called Dispersed phase or discontinuous phase.**Dispersion Medium:-**The phase in which the scattering is done is called the dispersion medium or continuous medium.

Classification (interaction between dispersed phase and dispersion medium.)Lyophobic and Lyophilic Colloids:

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

(b) Lyophilic colloid-solvent loving these colloids can be prepared by simply mixing of dispersed phase into dispersion medium. e.g. Starch sol.

On the basis of types of particles of the dispersed phase

(a) Multimolecular colloid-on dissolution, a large 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 in suitable solvent form 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 conc. 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.

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

Critical micelle concentration (cmc) – conc. above which micelle formation takes place is known as cmc.

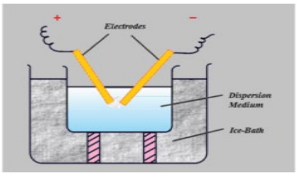
Methods of preparation of colloids: Chemical Methods:-

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decompostion}} As_2S_3(sol) + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S(sol) + 2H_2O$$

$$2\ AuCl_3 + 3\ HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\ (sol) + 3HCl$$

Bredig's method: An electric arc is struck between two metallic electrodes immersed in dispersion medium. The arc produced vapourises the metal which on further condensation produces particles of colloidal size	

Peptization: **Process of converting a precipitate into colloidal sol by shaking it with electrolyte in dispersion medium. Example:- (i) A reddish brown coloured solution is obtained by adding small quantity of Ferric chloride solution to freshly precipitated hydroxides**

PURIFICATION OF COLLIODAL SOLUTION :-

(a) **Dialysi**s-it is a process of removing a dissolved electrolytes from a colloidal solution by semi permeable membrane.

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

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

Colloidian: 4% cellulose nitrate in Alcohol- Ether mixture

PROPERTIES OF COLLOIDAL SOLUTION

(1)Brownian movement-zig-zag motion of colloidal particles **Cause of Brownian moment:-** reason is the molecules of dispersion medium due to their kinetic motion strike the dispersed phase with different forces.

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

a) The diameter of the dispersed particles is not much smaller as compared to wavelength of light used.

b) There should be a large difference in refractive indices of dispersed phase and dispersion medium.

(3) Charge on colloidal particles – Colloidal particles carry charges due to preferential adsorption.

(4)Electro kinetic or Zeta Potential:- when one type of the ions of the electrolyte are adsorbed on the surface of colloidal particles it forms a "Fixed layer". It attracts the opposite ions to form another layer called "diffused layer".

The double layer of opposite charge thus formed is called **Helmholtz electrical double** layer. As a result, a difference of potential exists between the fixed layer and the diffused layer. This potential difference is known as **zeta potential.**

(5) Electrophoresis or cataphoresis:- - Movement of Colloidal particles towards opposite electrode in presence of external electric field.

Electro-osmosis:- When the movement of dispersed phase particles are prevented by suitable means , then molecules of the dispersion medium are allowed to move under influence of an electric field

(6) Coagulation – The process of setting of colloidal particles is called coagulation of the sol.

Hardy Schulze Rule: Greater the valency of ion, greater will be the coagulating power.

Eg: $Na^+ < Ca^{2+} < Al^{3+}$ for negatively charged sol.; $Cl^- < CO_3^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}$ for positive sol.

Coagulation or Flocculation Value:-The minimum of an electrolyte (in millimoles) that must be added to one litre of a colloidal solution leads to bring about the complete coagulation is called coagulation or Flocculation Value

Protective action of lyophilic colloids:-Lyophilic sols like those of metals (Au, Ag etc) are unstable and are easily precipitated by addition of electrolytes. The lyophobic sols can be protected from coagulation by adding a small amount of lyophilic sols this process is called as "protection" and lyophilic colloid act as "protective colloids"

Application of colloids in everyday life:-

1. Medicines:- most of medicines used are in colloidal form (a) Argyrol used as an eye lotion is silver sol

2. Artificial rain:-Artificial rain can be brought by spraying electrified sand on clouds

3. Formation of Delta:– River water contains charged colloidal particles .Thus river water comes in contact with sea water the colloidal particles or river water gets coagulated to form a huge mass of sand known delta.

4. Blue Colour of Sky:-due to scattering of light by colloidal particles.

5. Smoke Precipitator: Cottrell precipitator based on coagulation of smoke particle under influence of electric field.

(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 ©

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

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) FeCl3 b) NaCl c) CaCl2?
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 anelectric 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. Why is it essential to wash the precipitate with water before estimating it quantitatively?
4.. Comment on the statement that “colloid is not a substance but state of a substance.”

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. 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 itquantitatively.
4. 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.

Questions carrying 3 marks

1. Explain what is observed when

(i) An electrolyte, NaCl is added to hydrated ferric oxide sol.
(ii) Electric current is passed through a colloidal sol.

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

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) $H2S$ is passed through arsenic oxide solution.

Answer key

1. (i)Coagulation (ii) Electrophoresis resulting in to coagulation. (iii) Tyndal effect

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. Alcohol 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

ASSERTION -REASON TYPE

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 : A colloidal sol scatters light but a true solution does not.

Reason : The particles in a colloidal sol move slowly than in a true solution.
(Ans - b)

4. Assertion : Hydrated ferric oxide can be easily coagulated by sodium phosphate in comparison to KCl.
Reason : Phosphate ions has higher negative charge than chloride ions. Hence, they are more effective for coagulation.
(Ans - a)

Note- Question number 1 to are case-based questions. Read the paragraph carefully and answer the questions

The colloidal state is considered to be an intermediate state between true solution and suspension. Depending upon the physical state of the dispersed phase and dispersion medium they are given specific names. They are further classified as lyophilic and lyophobic or multimolecular or macromolecular or associate colloids depending upon their specific character.A number of methods are available for their preparation andpurification.Their mechanical ,optical and electrical properties have been studied experimentally,coagulation being the most important studied by Hardy and Schulze.

1.What is the range of particle size in cooloidal solution in nm ?
Ans . 1-1000 nm

2.Write two difference between multimolecular and macromolecular colloids ?
Ans .Multimolecular colloids are formed by aggregation of small molecules (diameter<1). While macromolecular colloids are formed by macromolecules (polymers) and consists of single molecules(size of the macromoleculemay be in the colloidal range)

3.Hydrophobic sol is easily coagulate .Give reason.
Ans .Hydrophobic sols are not stable because they do not undergo hydration.

4.Name the type of the colloid formed when a liquid is dispersed in a solid
Ans . Gel .
5Which of the following is most effective electrolyte in coagulation of $Fe_2O_3.H_2O/Fe^{3+}$ sol?
KCl ,$AlCl_3$, $MgCl_2$,$K_4[Fe(CN)_6]$
Ans . $K_4[Fe(CN)_6]$

CHAPTER- 7 "THE P BLOCK ELEMENTS"

QUESTION ANSWER:-

Multiple Choice questions (with one correct answer)

1. Which of the following is planar?
   (a) XeO_4 (b) XeO_3F (c) XeO_2F_2 (d) XeF_4
2. Which of the following substances has the highest proton affinity?
   (a) PH_3 (b) H_2O (c) H_2S (d) NH_3
3. The acid having O – O bond is –
   (a) $H_2S_2O_3$ (b) $H_2S_2O_6$ (c) $H_2S_2O_8$ (d) $H_2S_4O_6$
4. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimize –
   (a) lone pair-bond pair repulsion only
   (b) bond pair- bond pair repulsions only
   (c) lone pair-lone pair and lone pair-bond pair repulsions
   (d) lone pair-lone pair repulsions only
5. Which of the following is the increasing order of enthalpy of vaporization?
   (a) NH_3, PH_3, AsH_3 (b) AsH_3 PH_3, NH_3
   (c) NH_3, AsH_3, PH_3 (d) PH_3, AsH_3, NH_3

6. Which among the following factors is most important in making fluorine the strongest oxidizing agent?
   (a) electron affinity (b) ionization energy
   (c) hydration energy (d) bond dissociation energy
7. Which one of the following oxides is expected to exhibit paramagnetic behavior?
   (a) CO_2 (b) ClO_2 (c) SO_2 (d) SiO_2
8. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species?
   (a) $F < Cl < O < S$ (b) $S < O < Cl < F$
   (c) $O < S < F < Cl$ (d) $Cl < F < S < O$

9. In which of the following molecules/ ions are all the bonds not equal?
   (a) SF_4 (b) SiF_4 (c) XeF_4 (d) BF_4^-
10. Which products are expected from the disproportion reaction of hypochlorous acid?
    (a) $HClO_3$ and Cl_2O (b) $HClO_2$ and $HClO_4$ (c) HCl and Cl_2O (d) HCl and $HClO_3$
11. The decreasing values of bond angles for NH_3 (106) to SbH_3 (101^0) down group 15 of the periodic table is due to –
    (a) Increasing bond pair-bond pair repulsion
    (b) Increasing p-orbital character in sp^3
    (c) Decreasing bond pair-bond pair repulsion
    (d) Decreasing electro negativity

12. Which inert gas has abnormal behavior on liquefaction?
    (a) Xe (b) He (c) Ar (d) Kr

13. The bleaching action of $CaOCl_2$ is due to –
(a) nascent oxygen (b) chlorine (c) HClO (d) HCl

14. Nitrogen forms a variety of compounds in all oxidation states ranging from –
(a) – 3 to + 5 (b) – 3 to + 3 (c) – 3 to + 4 (d) – 3 to + 6

15. Which of the following orders is not in accordance with the property stated against it?
(a) $F_2 > Cl_2 > Br_2 > I_2$; bond dissociation energy
(b) $F_2 > Cl_2 > Br_2 > I_2$; oxidizing power
(c) HI > HBr > HCl > HF; acidic property power
(d) $F_2 > Cl_2 > Br_2 > I_2$; electronegativity

16. The angular shape of molecule (O_3) consists of –
(a) 1 sigma and 1 pi pond (b) 2 sigma and 1 pi bond
(c) 1 sigma and 2 pi bonds (d) 2 sigma and 1 pi bonds

Multiple Choice questions (with one of more than one correct answer)

17. When Cl_2 gas is passed through hot NaOH, oxidation number of Cl changes from –
(a) – 1 to 0 (b) 0 to – 1 (c) 0 to + 7 (d) 0 to + 5

18. The noble gases which form clathrates are –
(a) He (b) Ar (c) Kr (d) Xe

19. SO_2 acts as a/an –
(a) Bleaching agent (b) Oxidising agent
(c) Reducing agent (d) Disinfectant

Multiple choice questions (based on the given passage/comprehension)
Comprehension:

Noble gases are chemically inert due to high ionization enthalpy, positive electron gain enthalpy and presence of completely filled orbitals. However, Xe forms a umber of compounds as $XePtF_6$, XeF_2, XeF_4, XeF_6 and a number of xenon oxides and oxyfluorides. Xenon fluorides react with fluoride ion acceptors such as PF_5, AsF_5, SbF_5, etc. to form cationic species but with fluoride ion donors such as alkali metal fluorides they form anionic fluoroanions. They are also hydrolyzed by water but their reactivity increases with the oxidation state of Xe.

20. The shape and hybridization of some xenon oxyfluorides are given below. Choose the wrong answer.
(a) $XeOF_2$ – T – shaped – sp^3d
(b) $XeOF_4$ – Square pyramidal – sp^3d^2
(c) XeO_2F_2 – Trigonal bipyramidal – sp^3d
(d) XeO_3F_2 – Tetrahedral – sp^3

21. The number of lone pairs and bond pairs of electrons around Xe in $XeOF_4$ respectively are –
(a) 0 and 5 (b) 1 and 5 (c) 1 and 4 (d) 2 and 3

22. Which of the following is not formed by Xe?
(a) XeF_5 (b) XeF (c) XeF_3 (d) all of these

23. When XF_4 is treated with water, it forms –
(a) Only Xe (b) both Xe and XeO_3
(c) only XeO_3 (d) Both XeO_3 and $XeOF_4$

24. Which of the followign statements is correct about the fluorides of xenon?
   - (a) $XePtF_6$ was the first noble gas compound isolated
   - (b) With SbF_5, XeF_2 acts as a Lewis base
   - (c) With RbF, XeF_6 acts as a Lewis acid
   - (d) all correct

Assertion – Reason type questions

Directions: In each of the following questions, a statement of Assertion (A) is given followed by a corresponding statement of Reason (R) just below it. Of the statements, mark the correct answer as –

(a) If both assertion and reason are true, and reason is the correct explanation of the assertion.

(b) If both assertion and reason are true, but reason is not the correct explanation of the assertion.

(c) If assertion is true, but reason is false.

(d) If both assertion and reason are false.

25. Assertion: The O – O bond length in H_2O_2 is shorter than that of O_2F_2
    Reason: H_2O_2 is an ionic compound.
26. Assertion: NF_3 is weak ligand than $N(CH_3)_3$.
    Reason: NF_3 ionizes to give F^- ion in aqueous solution.
27. Assertion: $HClO_4$ is a stronger acid than $HClO_3$.
    Reason: Oxidation state of Cl in $HClO_4$ is + 7 and in $HClO_3$ is +5.

28. Assertion: All F – S – F bond angles in SF_4 are greater than 90^0 but less than 180^0.
    Reason: The lone pair-bond pair repulsion is weaker than bond pair-bond pair repulsion.

ANSWER KEY P BLOCK ELEMENTS:-

1	D	6	C	11	D	16	B	21	B	26	C				
2	D	7	B	12	B	17	B,D	22	D	27	A				
3	C	8	C	13	A	18	B,C,D	23	B	28	C				
4	C	9	A	14	A	19	A,B,C,D	24	D						
5	D	10	D	15	A	20	D	25	D						

GROUP 15 ELEMENTS

1 Mark Questions-

1. Nitrogen does not form penta halides. 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 pΠ-pΠ interaction(weak interaction), Nitrogen is a gas. Phosphorous on the other hand, has the ability to form dΠ-dΠ 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. PH3 has lower boiling point than NH3. Why?
Ans. Unlike NH3, PH3 cannot form Hydrogen bond, so its boiling point is less than NH3.
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 BiH3 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 H2 gas, which is a reducing agent.
10. What happens when Sodium Azide is heated?
Ans. It gives off Dinitrogen gas. 2NaN3 --------------> 2Na + 3N2
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 Cu2+?
Ans. Cu2+(aq)+4NH3-------> [Cu(NH3)4]2+(Deep blue)
16. What is the Covalency of Nitrogen in N2O5?
Ans. 4
17. Why does NO2 dimerise?
Ans. NO2 contains odd number of valence electrons. It is converted to stable N2O4 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-
4NH3 + 5O2---Pt/Pd--------> 4NO + 6H2O
2NO + O2----------------> 2NO2
3NO2 + H2O--------------> 2HNO3 + NO
2. Give the reaction of dilute Nitric acid with Copper and Zinc.
Ans. 3Cu +8HNO3 (dil) --------------->3Cu(NO3)2 + 2NO + 4H2O

$4Zn + 10HNO_3$ (dil) -------------------->$4Zn(NO_3)_2 + N_2O + 5H_2O$

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. $NO + O_3$-------------> $NO_2 + O_2$

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. $2Fe^{3+} + SO_2 + 2H_2O$------------> $2Fe^{2+} + SO_4^{2-} + 4H^+$

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.
$SO_2 + Cl_2 \text{------------>} SO_2Cl_2$.

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. $Cl_2 + 2NaOH(dil.) \longrightarrow NaCl + NaOCl + H_2O$
b. $3Cl_2 + 6NaOH(conc.) \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

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. $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
b. $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
c. $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$ ..

6. Give the equations for partial hydrolysis of XeO_6.
Ans.
$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$
$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

CHAPTER-8-"THE D BLOCK ELEMENTS"

(A) General electronic configuration, Occurrence , Character sticks OF Transition metals.

(B) General trends in properties of First Transition series – metallic property, Oxidation states , Ionization enthalpy , Ionic radius , Colour, catalytic property, Magnetic property , Alloy formation , Interstitial compounds

(C) Lanthanides – Electronic configuration , Oxidation states , Lanthanoid contraction and its consequences .

MCQ on d and f block elements

Q1.Which of the following arrangements does not represent the correct order of the property stated against it?

A $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behavior
B $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
C $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
D Sc < Ti < Cr < Mn : number of oxidation states

Q. 2 Which of the following lanthanoid ions is diamagnetic?

(At. nos. Ce = 58, Sm = 62, Eu = 63, Yb = 70)

A Ce^{2+}
B Sm^{2+}
C Eu^{2+}
D Yb^{2+}

Q. 3

Which of the following statements about the interstitial compounds is incorrect?

A They retain metallic conductivity
B They are chemically reactive
C They are much harder than the pure metal
D They have higher melting points than the pure metal

Q. 4

All the metals form oxides of the type MO except

A copper
B barium
C silver
D lead

Q.5

Among the following, the coloured compound is

A CuCl
B $K_3 [Cu(CN)_4]$
C CuF_2
D $[Cu(CH_3CN)_4]BF_4$

Q6. How many 'd' electrons are in present Cr^{2+} ion

AAAA 4
5
C 6
3

Q.7
Cyanide process is used for extraction of
A Ag
Ni
C Pt
Zn

Q.8
Extraction for zinc blende is achieved by
A electrolytic reduction
roasting followed by reduction with carbon
C roasting followed by reduction with another metal
roasting followed by self reduction

Q.9
Formation of coloured solution is possible when metal ion in the compound contains
A paired electrons
unpaired electrons
C lone pair of electrons
none of these

Q.10
Identify the incorrect statement among the following
A d-Block elements show irregular and erratic chemical properties among themselves
La and Lu have partially filled d orbitals and no other partially filled orbitals
C The chemistry of various lanthanoids is very similar
4f and 5f orbitals are equally shielded

Q.11 Which one of the following ions exhibits colour in aqueous solution
A Sc^{3+}
Ni^{2+}
C Ti^{4+}
Zn^{2+}

Q.12
Which one of the following is a diamagnetic ion?
A CO^{2+}
Cu^{2+}
C Mn^{2+}
Sc^{3+}

Q.13

Which ore contains both iron and copper?

A Cuprite
Chalcocite
C Chalcopyrite
Malachite

Q.14

Which pair of compounds is expected to show similar colour in aqueous medium?

A $FeCl_2$ and $CuCl_2$
$VOCl_2$ and $CuCl_2$
C $VOCl_2$ and $FeCl_2$
$FeCl_2$ and $MnCl_2$

Q.15

Zn does not show variable valency because of

A complete d sub-shell
inert pair effect
C $4s^2$ sub-shell
None of these

Q.16

'Hydride Gap' is referred to which region of the periodic table?

A Groups 3, 4 and 5
Groups 5, 6 and 7
C Groups 4, 5 and 6
Groups 7, 8 and 9

Q.17

Which one of the following sets correctly represents the increase in the paramagnetic property of the ion?

A $Cu^{2+} < V^{2+} < Cr^{2+} < Mn^{2+}$
$Cu^{2+} < Cr^{2+} < V^{2+} < Mn^{2+}$
C $Mn^{2+} < V^{2+} < Cr^{2+} < Cu^{2+}$
$Mn^{2+} < Cu^{2+} < Cr^{2+} < V^{2+}$

Answers: Answers: 1. A 2. D 3 C 4 C 5 B 6 A 7 A 8 B 9 B
10 D 11. B 12. D 13. C 14. B 15. A 16. D 17. A

……

CHAPTER-9-"CO-ORDINATION 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, $K_4[Fe(CN)_6]$. **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, $FeSO4{\cdot}(NH_4)_2SO_4 . 6H_2O$ get dissociated into Fe^{2+}, NH^{+4} and $SO^{2-}{}_4$ ions.

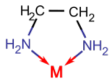
Terms Related to Coordination Compounds

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., $[Pt(NH3)_4]^{2+}$ (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 $[NiCI_2(H2O)_4]$. Ni is central metal atom.

Ligands: an ion or molecule capable of donating a pair of electrons to the central atom via a donor atom.

- **Unidentate ligands:** Ligands with only one donor atom, e.g. NH_3, Cl^-, F^- etc.
- **Bidentate ligands:** Ligands with two donor atoms, e.g. ethylenediamine, $C_2O_4^{2-}$ (oxalate ion) etc.
- **Tridentate ligands:** Ligands which have three donor atoms per ligand, e.g. (dien) diethyl triamine.
- **Hexadentate ligands:** Ligands which have six donor atoms per ligand, e.g. EDTA.

Chelating Ligands:

• Multidentate ligand simultaneously coordinating to a metal ion through more than one site is called chelating ligand. Example: Ethylenediamine ($NH_2CH_2CH_2NH_2$)	

Werner's Theory: Metals possess two types of valencies

primary valency – ionizable	secondary valency- nonionizable
It is equal to oxidation number.	It is equal to coordination number.
It is satisfied by negative ions	It may be satisfied by neutral, negative or positive ions.

Eg. $\mathbf{[Co(NH_3)_6]Cl_3}$ Primary Valencies = **3 Cl^-** Secondary Valencies(coordination no.) = **6 NH_3**

Nomenclature of Complexes: ∘ Naming of complex

No of ligands	**Name of ligand**	**Name of central Metal/ion**	**Oxidation No. of Metal**
2= di 3= tri 4 tetra 5=penta	Negative ligands are named by suffix **– o** Positive ligands are named by prefix – **ium.** Neutral ligands are named as such ***** Ligands are named in	Suffix **"ate"** is used in negative	In Roman in brackett [ ] $[Co(NH_3)_6]Cl_3$ Hexaamminecobalt(III)chloride $K_2[Cu(SCN)_4]$ Potassium

Valence Bond Theory: **Hybridization:** Find out the hybridization of central metal ion using following steps:

- Write down the electronic configuration of metal atom.
- Find out oxidation state of metal atom.
- Write down the electronic configuration of metal ion.
- Write down the configuration of complex to find out hybridization.
- Strong field ligands cause the pairing of electrons.
- When the d orbital taking part in hybridization is inside the s and p orbital taking part in hybridization with respect to the nucleus, it is called an inner orbital complex.
- When the d orbital taking part in hybridization outside the s and p orbital taking part in hybridization with respect to the nucleus, it is called an outer orbital complex.

Example: (i) d^2sp^3 hybridization of $[Co(NH_3)_6]^{3+}$ involves 3d, 4s and 4p orbital, hence it is an inner orbital complex.

(ii) sp^3d^2 hybridization of $[CoF_6]^{3-}$ involves, 4*s* ,4*p* and 4*d* orbital, hence it is an outer orbital complex.

Geometry: sp^3 = Tetrahedral

dsp^2 = Square Planar

d^2sp^3 & sp^3d^2 = Octahedral

Magnetic Properties:

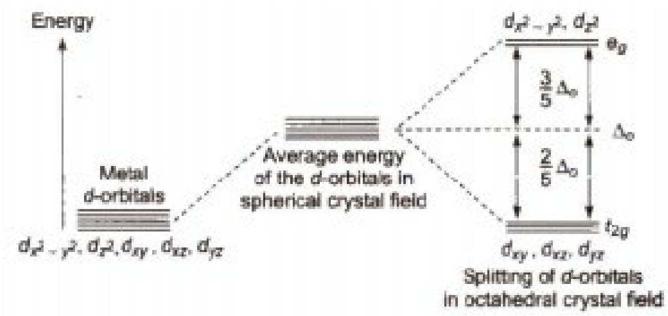
- Diamagnetic: All the electrons paired.
- Paramagnetic: Contains unpaired electron.

Crystal Field Theory:

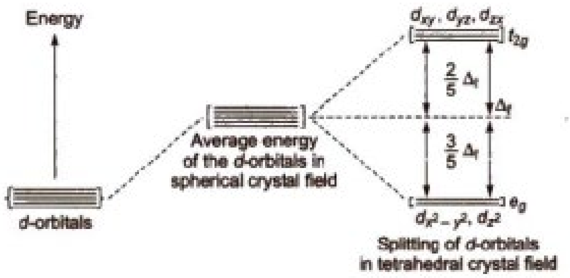
Strong field ligand causes greater repulsion and thus results in the formation of low spin complexes by pairing of electrons. **Strong Field Ligands:** CO, CN^-, NO_2^-, en, py, NH_3. **Weak Filed Ligands:** H_2O, OH^-, F^-, Cl^-, Br^-, I^-

- Weak field ligands result in the formation of high spin complexes
- strength of ligands: (Spectrochemical series)CO > CN^- > NO_2^- > en > py = NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-

Octahedral Complexes: e_g orbital are of higher energy than t_{2g} orbital. $\Delta_t = (4/9)\ \Delta_o$



Tetrahedral Complexes: e_g orbitals are of lower energy than t_{2g} orbitals.



Applications of Coordination Compounds

1. Hardness of water is estimated by simple titration with Na_2 EDTA.

2. Purification of metals can be achieved through formation of coordination compounds (Mond Process). 3. They have great importance in biological systems

i) Chlorophyll – complex of Mg ii) Haemoglobin – complex of Fe iii) Vitamin B-12 – complex of Co

4. Lead poisoning by EDTA.

5. As medicines: Cisplatin [Cancer Treatment]

Coordination Compounds

[1 marks questions]

1. Write the formula of the following coordination compounds

(a)Tetraamminediaquacobalt(III)chloride
Ans. $[Co(NH_3)_4(H_2O)_2]Cl_3$
(b)Potassium tetracyanidonickelete(II)
Ans. $K_2[Ni(CN)_4)]$
(c) Tris (ethane 1,2 diamine) Chromium(II)chloride
Ans.$[Cr(en)_3]Cl_3$
(d) Amminebromidochloridonitrito-N-platinate(II)
Ans. $[Pt(NH_3)BrCl(NO_2)]^-$
(e)Iron(III)hexacyanoferrate(II)
Ans.$Fe_4[Fe(CN)_6]_3$
(f) Dichloridobis(ethane-1,2-diamine)platinum(iv)nitrate
Ans. $[PtCl_2(en)_2](NO_3)_2$
(g)hexamminecobalt(III)chloride
Ans. $[Co(NH_3)_6]Cl_3$
(h)pentaamminechloridocobalt(III)chloride
Ans.$[Co(NH_3)_5Cl]Cl_2$
(i) potassiumhexacyanoferrate(III)
Ans.$K_3[Fe(CN)_6]$
(j) Potassium trioxalatoferrate(IIIS)
Ans.$K_3[Fe(C_2O_4)_3]$
(k) bis(cyclopentadienyl)Iron Ans : $[Fe(C_5H_5)_2]$

2. $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colouress .why

Ans. In $[Ti(H_2O)_6]^{3+}$ Ti^{3+} ion has one electron in t_{2g} d –orbital ,which can absorb light in the visible region resulting into d-d transition and show coloured . But Sc^{3+}has no d electron thus it is colourless .

3. Which type of ligands form chelates?

Ans. Polydentate ligands

4.What is crystal field splitting energy?

Ans. The difference of energy between two sets of d orbitals after splitting is called CFSE.

5. Define coordinationnumber.

Ans.Coordination number is a number of coordinate bonds formed by the ligands with the central metal atom.

6. Give one example of ambidentate ligand

Ans. CN^-

[2 marks questions]

1 $CuSO_4.5H_2O$ is blue in colour while $CuSO_4$ is colouress. Why?

Ans. In $CuSO_4.5H_2O$; $4H_2O$ molecules are present as ligand, Crystal field splitting occurs and hence d-d transition occurs which gives blue colour, In $CuSO_4$,there are no H_2o molecules present as ligand .No CFS occurs and hence it has no colour .

2 Magnetic moment of $[MnCl_4]^{2-}$is 5.92BM. Explain giving reason.

Ans. Magnetic moment is 5.92BM. means n=5 ie 5 unpaired electron .$Mn^{2+}=3d^5\ 4s^0 4p^0$. To form $[MnCl_4]^{2-}$, hybridisation will be sp^3. Hence the structure will be tetrahedral.

3. Explain the drawbacks of VBT?

Ans. (a) It can not explain why some complexes of a metal ion in a particular oxidation state are low spin. (b)It does not distinguish between weak and strong ligands.

4. Explain the limitation of CFT?

Ans. (a) As ligands are considered as point charges, the anioic ligands should exerts greater splitting effect , However actually the anionic ligands are present at the low end of the spectrochemical series .

(b) It treats the metal ligand bonds as purely ionic and does not take into account the covelent character of the bond.

5.The values of dissociation constants of $[Cu(NH_3)_4]^{2+}$ and $[Co(NH_3)_6]^{3+}$are $1.0x10^{-12}$ and $6.2x10^{-36}$ respectively .which complex would be more stable and why ?

Ans.Smaller the value of the dissociation constant, more stable is the complex in the solution. Hence $[Co(NH_3)_6]^{3+}$ismore stable than $[cu(NH_3)_4]^{2+}$ ion.

6. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers?

Ans. When they are dissolved in water ,they will give different ions in the solution which can be tested by adding $AgNO_3$ solution and $BaSO_4$ solution . when Cl^- ions are counter ions a white ppt will be obtained with $AgNO_3$ solution , If SO_4^{2-} ions are counter ions a white ppt will be obtained with $BaCl_2$ solution .

7. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6\ ]^{3-}$ is weakly paramagnetic Why?

Ans In both the complexes Fe is in +3 oxidation state with the configuration $3d^5$. CN^- is a strong ligand .In Its presence, 3d electrons pair up leaving only one unpaired electron .The hybridisation is d^2sp3 forming Inner orbital complex .H_2O is a weak ligand, in its presence, 3d electron do not pair up.The hybridisation is $sp^{\mathbf{3}}d^{\mathbf{2}}$ forming an outer orbital complex containing five unpaired electrons. Hence it is strongly paramagnetic.

8. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral,why ?

Ans. In $[NiCl_4]^{2-}$, Ni is +2 oxidation state with the configuration $3d^84S^0$, Cl^- is weak ligand. it cannot pair up the electron in3d orbitals, Hence it is paramagnetic .In $[NI(CO)_4$,Ni is in zero oxidation state with the configuration $3d^84s^2$,In the presence of CO ligand , the 4s electrons shift to 3d to pair up 3d electrons .thus ,there is no unpaired electron present . Hence it is diamagnetic.

9. Calculate the over all complex dissociation equilibrium constant for the$[Cu(NH_3)_4]^{2+}$ion , given that B_4 for this complex is $2.1\ x(10)^{13}$?

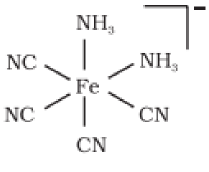
Ans. Overall stability constant $(B)=2.1x(10)^{13}$

Overall dissociation constant is the reciprocal of the overall stability constant .Hence overall dissociation constant= $1\backslash B_4= 1\backslash 2.1X\ (10)^{13}=4.7X\ (10)^{-14}$.

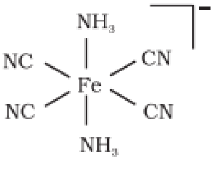
10. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Ans: Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

11. . Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

Ans: 

cis

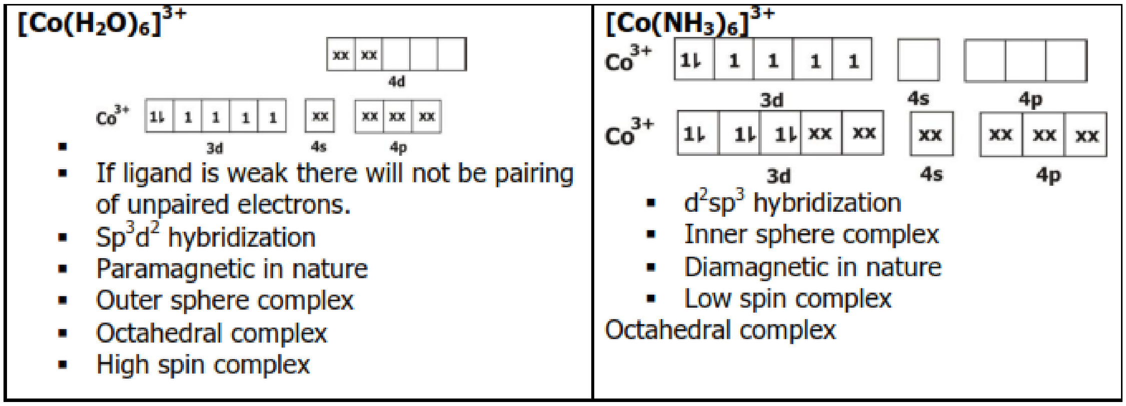


trans

[3Marks questions]

(i) Compare the magnetic behaviour of (a)$[Co(H_2O)_6]^{3+}$ and $[Co(NH_3)_6]^{3+}$

(b) $[NiCl_4]^{2-}$ and $[Ni(CO)_4$



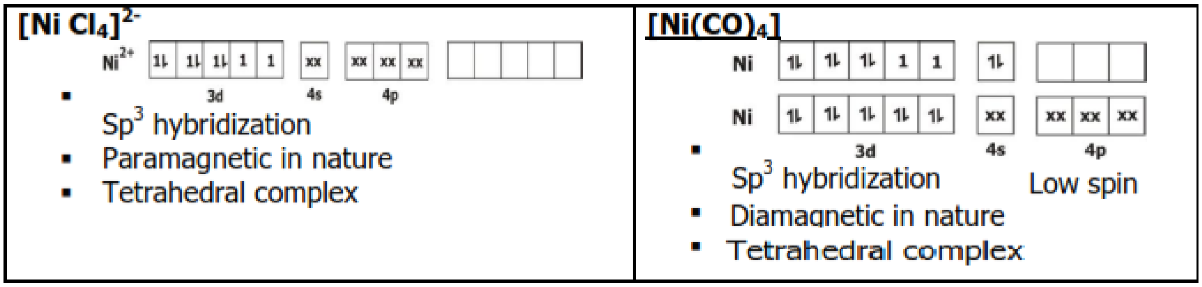
$[Co(H_2O)_6]^{3+}$

- If ligand is weak there will not be pairing of unpaired electrons.
- Sp^3d^2 hybridization
- Paramagnetic in nature
- Outer sphere complex
- Octahedral complex
- High spin complex

$[Co(NH_3)_6]^{3+}$

- d^2sp^3 hybridization
- Inner sphere complex
- Diamagnetic in nature
- Low spin complex

Octahedral complex



$[Ni\ Cl_4]^{2-}$

- Sp^3 hybridization
- Paramagnetic in nature
- Tetrahedral complex

$[Ni(CO)_4]$

- Sp^3 hybridization Low spin
- Diamagnetic in nature
- Tetrahedral complex

Passage-1

Coordination compounds plays many important roles in animals and plants. They are essential in the storage and transport of oxygen, as electrons transfer agents, as catalysts, and in photosynthesis. Wide range of application in daily life takes place through formation of complexes.

Photographic fixing, qualitative and quantitative analysis, purification of water, metallurgical extraction are some specific worth mentioning.

1. Oxalic acid is commonly used to remove rust stains. Justify.
   Ans: rust is hydrated iron III oxide ,Fe2O3.xH2O. iron (III)forms soluble complex with chelating oxalate ion furnished by oxalic acid.
2. Calcium dihydrogen salt of EDTA is used as an antidote for lead poisioning, why?
   Ans: EDTA coordinates lead in the body because of more soluble lead EDTA complex, which can be eliminated in urine without causingany harmful effects. The calcium salt of EDTA will not remove Ca2+ ions from the body.
3. What is cis-platin?
   Ans: cis-platin stands for cis-dichloridodiammineplatinum(II) used to treat cancer.
4. Write the use of Zeigler-Natta catalyst.
   Ans: Zeigler Natta catalyst is a coordination compound of Pt and Al which is used to convert ethylene.

Passage-2

Valence bond theory describes the bonding in complexes in terms of coordinate covalent bonds resulting from overlap filled ligand orbitals with vacant metal hybrid orbitals. This theory explains magnetic behaviour and geometrical shape of coordination compounds. Magnetic moment of a complex, acompound can be determined experimentally and theoretically experimentally and theoretically by using spin only formula.

Magnetic moment $\sqrt{n(n+2)}$ BM

(where ,n=no. of unpaired electrons)

1. Write the state of hybridization, shape and magnetic behaviour of the $[Cr(H_2O)_2(C_2O_4)]^-$
   Ans: $[Cr(H_2O)_2(C_2O_4)]^-$
   In the complex, Cr is present as Cr^{3+}
   Hybridization is d^2sp^2 as oxalate is bidentate ligand, one oxalate occupies two orbitals.
2. Why s-orbital does not show preference to any direction ?
   Ans: the s- orbital is spherically symmetric in shape so it does not show preference to any direction.it is the same from all the directions.
3. Describe the type of hybridization ,shape and magnetic properties of $[Co(NH_3)_4 Cl_2]Cl$. (given: At. No. of Co=27)
   Ans: hybridization is d^2sp^2
   Shape is octahedral
   Magnetic properties: diamagnetic
4. Explain the geometry and magnetic character of complex $[Cr(NH_3)_6]^{3+}$
   Ans: Octahedral complex including d^2sp^2 hybridisation. It is paramagnetic due to the presence of three unpaired electrons.

Assertion/Reason type questions

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below.

(a) Both the assertion and reasonis the correct and reason is the correct explanation of assertion.
(b) Both the assertion and reason is the correct and 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: $[Ti(H_2O)_6]^{3+}$is coloured while $[Sc(H_2O)_6]^{3+}$is colourless.
   Reason: d-d transition is not possible in $[Sc(H_2O)_6]^{3+}$
   Ans: (a)
2. Assertion: Linkage isomerism arises in coordination compounds containing ambidentate ligand.
   Reason: ambidentate ligands have two different donors.
   Ans: (a)
3. Assertion: toxic metal ions are removed by chelating ligands.
   Reason: chelate complex tend to be more stable.
   Ans.(a)

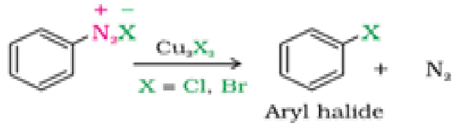
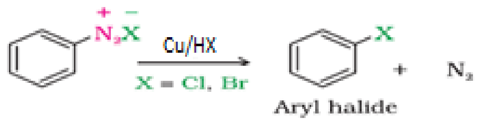
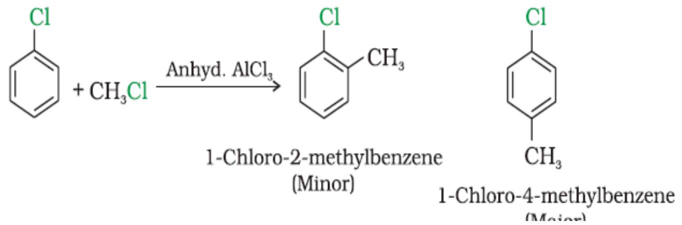
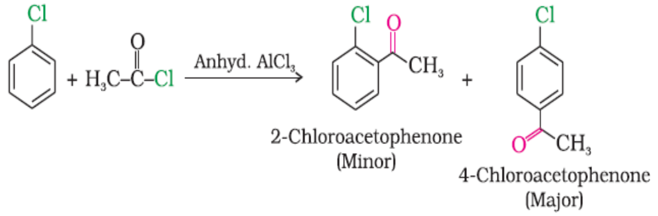
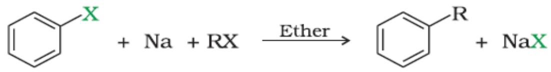
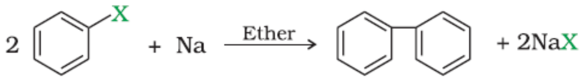
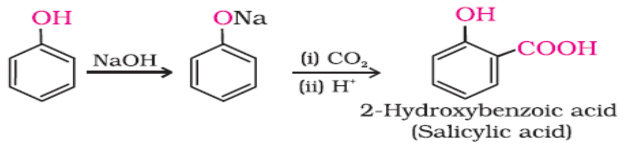
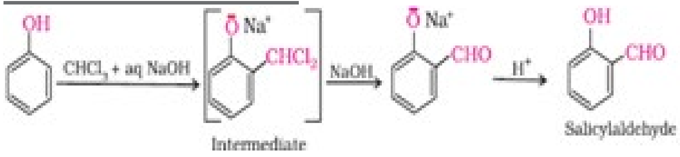
4. Assertion:[Fe(CN)$_6$]$^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
   Reason: because it has d^2sp^3 type hybridization
   Ans: (b)
5. Assertion:[Ni(CO)$_4$] is diamagnetic complex.
   Reason:it involves sp^3 hybridisation and has no unpaired electron.
   Ans: (a)

Multiple choice questions

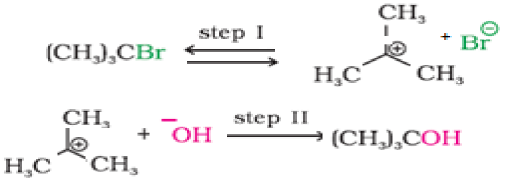
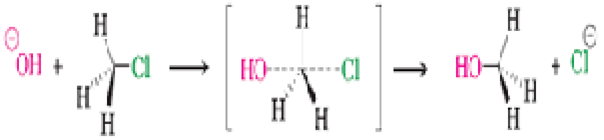
1. Due to presence of ambidentate ligands coordination compounds show isomerism.palladium complexes of the type[Pd(C$_6$H$_5$)$_2$(SCN)$_2$] and [Pd(C$_6$H$_5$)$_2$(NCS)$_2$] are
   a) Ionization isomers
   b) Linkage isomers
   c) Coordination isomers
   d) No isomers Ans: (b)
2. A chelating ligand has more thantwo donor atoms to bind a single metal ion. Which of the following is not a chelating agent?
   a) Thiosulphate
   b) Oxalate
   c) Glycinato
   d) Ethane 1,2-diamine Ans: (a) thiosulphate as it is a monodentate ligand
3. Which of the following is not expected to be a ligand?
   a) NO
   b) NH_4^+
   c) $NH_2CH_2CH_2NH_2$
   d) CO Ans: (b)
4. IUPAC name of [Pt(NH$_3$)$_2$Cl(NO$_2$)] is
   a) Platinum diaminechloronitrate
   b) Chloronitrito-N-amineplatinum(II)
   c) Diaminechloridonitrito-N-platinum(II)
   d) Diaminechloronitrito-N-platinate(II) Ans: (c), Diaminechloridonitrito-N-platinum(II)

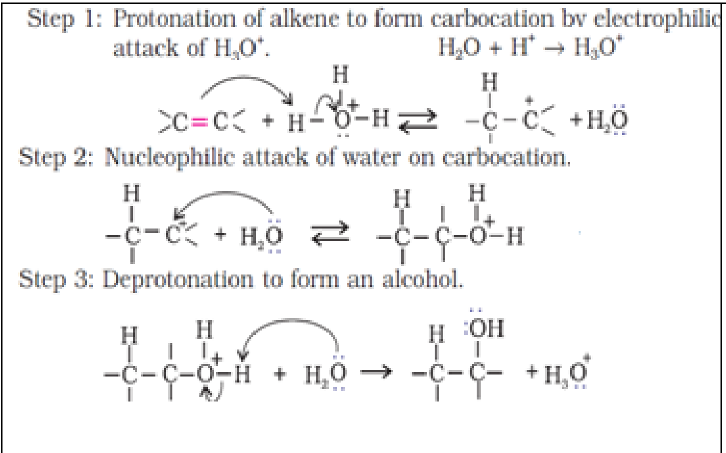
5. What kind of isomerism exists between [Cr(H$_2$O)$_6$]Cl$_3$ (violet) and [Cr(H$_2$O)$_5$Cl]Cl$_2$.H$_2$O (greyish green)
   a) Linkage isomerism
   b) Solvate isomerism
   c) Ionisation isomerism
   d) Coordination isomerism Ans: (b) solvate isomerism

CHAPTER-10-"Haloalkanes and Haloarenes "
AND
CHAPTER-11-ALCOHOL, PHENOL & ETHER

Sandmeyer's reaction:- Aryl halide	**Gatterman reaction.** Aryl halide
Finkelstein reaction:- $R-X + NaI \xrightarrow[X=Cl,\,Br]{} R-I + NaX$	***Swart Reaction:-*** $H_3C-Br + AgF \longrightarrow H_3C-F + AgBr$
Freidel Craft alkylation:- 1-Chloro-2-methylbenzene (Minor) 1-Chloro-4-methylbenzene (Major)	***Freidel Craft acylation:-*** 2-Chloroacetophenone (Minor) 4-Chloroacetophenone (Major)
Wurtz fittig reaction 	***Fittig reaction*** 
Wurtz reaction:- $2R-X + 2Na \xrightarrow{Ether} R-R + 2NaX$	***Williamson Synthesiss*** $R-X + R'-\ddot{O}\,Na \longrightarrow R-\ddot{O}-R' + Na\,X$
Kolbe's reaction:- 2-Hydroxybenzoic acid (Salicylic acid)	***Reimer Tiemann:-*** Intermediate Salicylaldehyde

Mechanism

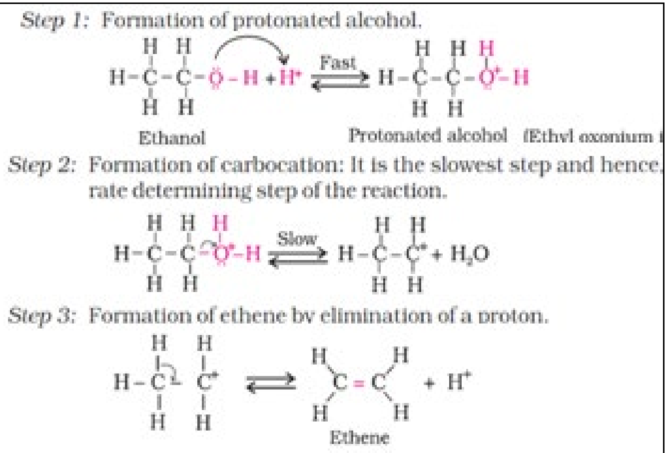
SN1 	***SN2*** 
Acid catalyse hydration of alkene	***Acid Catalysis dehydration alkene formation(443K)***



Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+. $H_2O + H^+ \rightarrow H_3O^+$

Step 2: Nucleophilic attack of water on carbocation.

Step 3: Deprotonation to form an alcohol.

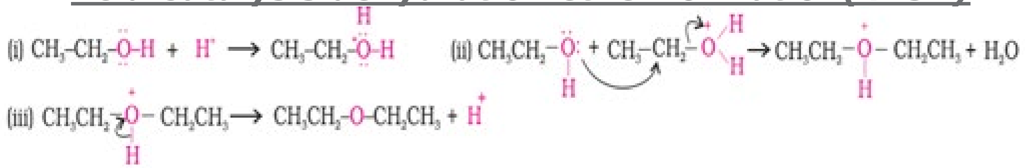


Step 1: Formation of protonated alcohol.

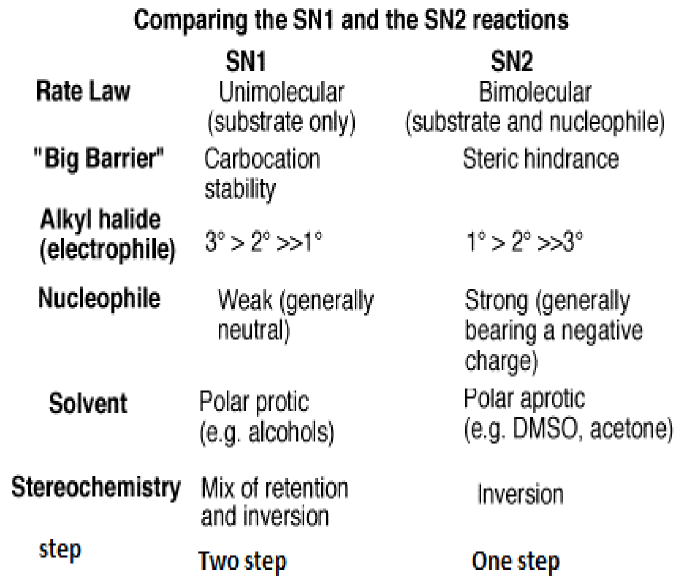
Step 2: Formation of carbocation: It is the slowest step and hence, rate determining step of the reaction.

Step 3: Formation of ethene by elimination of a proton.

Acid Catalysis dehydration ether formation(413K)



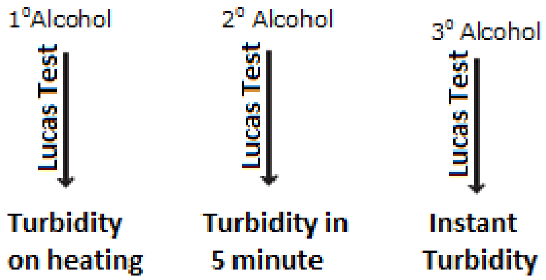
Comparing the SN1 and the SN2 reactions



	SN1	SN2
Rate Law	Unimolecular (substrate only)	Bimolecular (substrate and nucleophile)
"Big Barrier"	Carbocation stability	Steric hindrance
Alkyl halide (electrophile)	3° > 2° >>1°	1° > 2° >>3°
Nucleophile	Weak (generally neutral)	Strong (generally bearing a negative charge)
Solvent	Polar protic (e.g. alcohols)	Polar aprotic (e.g. DMSO, acetone)
Stereochemistry	Mix of retention and inversion	Inversion
step	Two step	One step

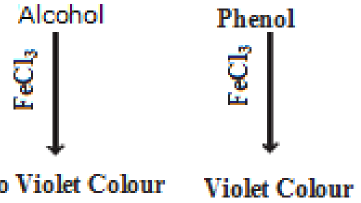
Lucas test to distinguish 1° 2° 3° Alcohol

Lucas Reagent = Anhy.ZnCl2 + Con.HCl



1°Alcohol	2° Alcohol	3° Alcohol
Turbidity on heating	**Turbidity in 5 minute**	**Instant Turbidity**

Distinguish between Alcohal and Phenol

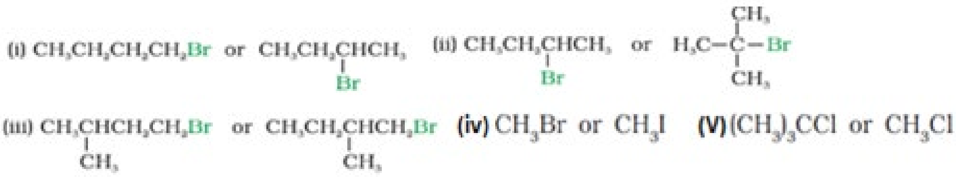
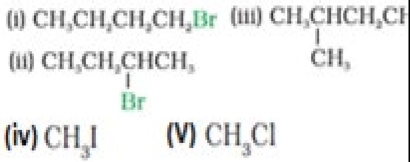
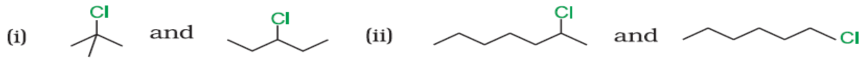
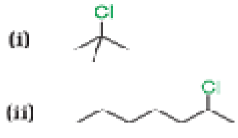


Alcohol	**Phenol**
No Violet Colour	**Violet Colour**

Important Reasoning Question

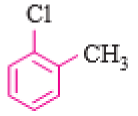
What Happen When

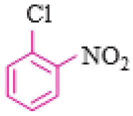
Question	Answer
n-butyl chloride is treated with alcoholic KOH,	Elimination reaction to form butene
bromobenzene is treated with Mg in the presence of dry ether,	Grignard reagent
chlorobenzene is subjected to hydrolysis,	Doesnot undergo hydrolysis
ethyl chloride is treated with aqueous KOH,	Ethyl alcohal

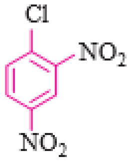
methyl bromide is treated with sodium in the presence of dry ether,	Ethane
methyl chloride is treated with KCN?	Methyl cyanide
Oxidation of propan-1-ol with alkaline KMnO4 solution.	Propanoic acid
Bromine in CS_2 with phenol.	o/p Bromo phenol
Dilute HNO_3 with phenol.	o/p nitro phenol
Treating phenol wih chloroform in presence of aqueous NaOH.	Salicaldihyde
Which alkyl halide from the following pairs would you expect to react more rapidly by an SN_2 mechanism? Explain your answer.  (i) $CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2\underset{Br}{C}HCH_3$ (ii) $CH_3CH_2\underset{Br}{C}HCH_3$ or $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br$ (iii) $CH_3\underset{CH_3}{C}HCH_2CH_2Br$ or $CH_3CH_2\underset{CH_3}{C}HCH_2Br$ (iv) CH_3Br or CH_3I (V) $(CH_3)_3CCl$ or CH_3Cl	 (i) $CH_3CH_2CH_2CH_2Br$ (iii) $CH_3\underset{CH_3}{C}HCH_2Br$ (ii) $CH_3CH_2\underset{Br}{C}HCH_3$ (iv) CH_3I (V) CH_3Cl SN2 reactivity inversely proportional to steric hindrance and I^- is better leaving group than Br^-
In the following pairs of halogen compounds, which compound undergoes faster SN1 reaction? 	

MULTIPLE CHOICE QUESTIONS

1. **Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:**

(i) 

(ii) 

(iii) 

(a) i < ii < iii (b) i < iii < ii

(c) ii < i < iii (d) iii < ii < i

2. **In a SN^1 reaction on chiral centers, there is -**

(a) 100 % retention (b) 100 % inversion

(c) 100 % racemization (d) No racemization

3. **In SN ^{2} reactions, the correct order of reactivity fo the following compounds**

(i) CH_3Cl (ii) $(CH_3)_3CCl$

(iii) $(CH_3)_2CHCl$ (iv) $CH_3CH_2—Cl$

(a) i > ii > iii > iv (b) iv > iii > ii > i

(c) i > iv > iii > ii (d) iv > i > ii > iii

4. **Arrange the following compounds in increasing order of their boiling point :**

(i) $(CH_3)_2CH_2CH_2—Br$ (ii) $CH_3—(CH_2)_3—Br$ (iii) $(CH_3)_3C—Br$

(a) ii < i < iii (b) i < ii < iii

(c) iii < i < ii (d) iii < ii < i

5. **The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives 'X' and the reaction with Cl_2 in presence of light gives 'Y'. Thus 'X' and 'Y' are:**

(a) 'X' = benzyl chloride and 'Y' = m-chlorotoluene

(b) 'X' = benzyl chloride and 'Y' = o-chlorotoluene

(c) 'X' = m-chlorotoluene and 'Y' = p-cholorotoluene

(d) 'X' = p-chlorotoluene and 'Y' = benzyl chloride.

6. **Aryl halides are less reactive toward nucleophilic substitution reaction than alkyl halides due to-**

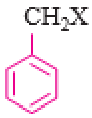
(a) the formation of stable carbocation

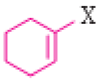
(b) Partial double bond character due to resonance

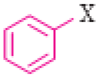
(c) longer carbon-halogen bond

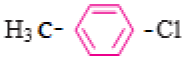
(d) sp^3 hybridised carbon attached to halogen

7. **Which of the following contain sp^3 hybridised carbon bonded to X ?**

(a) 

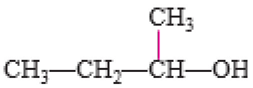
(b) 

(c) 

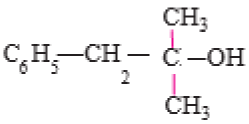
(d) 

8. **The order of reactivity of following alcohols with halogen acid (HX) is -**

(i) $CH_3—CH_2—CH_2—OH$

(ii) 

$CH_3—CH_2—CH(CH_3)—OH$

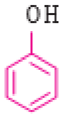
(iii) 

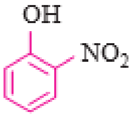
$C_6H_5—CH_2—C(CH_3)_2—OH$

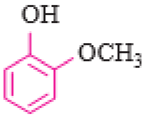
(a) i > ii > iii (b) iii > ii > i

(c) ii > i > iii (d) i > iii > ii

9. **The correct order of decreasing acid strength of the following compound is:**

(i) 

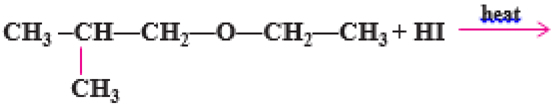
(ii) 

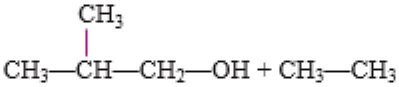
(ii) 

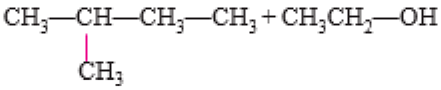
(a) i > ii > iii (b) iii > ii > i

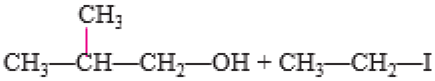
(c) ii > i > iii (d) ii > iii > i

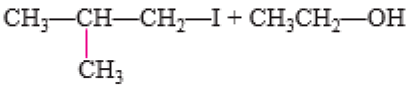
10. **In the reaction :**


$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}O{-}CH_2{-}CH_3 + HI \xrightarrow{heat}}$

(a) 
$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{CH}{-}CH_2{-}OH + CH_3{-}CH_3}$

(b) 
$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_3{-}CH_3 + CH_3CH_2{-}OH}$

(c) 
$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{CH}{-}CH_2{-}OH + CH_3{-}CH_2{-}I}$

(d) 
$\mathrm{CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}I + CH_3CH_2{-}OH}$

11. **The major product obtained on interaction of phenol with NaOH and CO$_2$ is**

(a) Benzoic acid (b) Salicaldehyde

(c) Salicylic acid (d) Pthalic acid

12. **Iodoform can be prepared from all except**

(a) butan-2-one (b) acetophenone

(c) propan-2-ol (d) propan-1-ol

13. **Which of the following alcohol on dehydration with conc H$_2$SO$_4$ gives but-2- ene?**

(b) 2-methylpropan-2-ol (b) Butan-1-ol

(c) Butan-2-ol (d) b & d both

14. **Correct statements in case of n-butanol and tert-butanol are:**

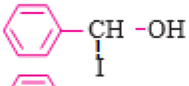
(a) both are having equal solubility in water

(b) tert-butanol is less soluble in water than n-butanol

(c) boiling point of tert-butanol is lower than n-butanol

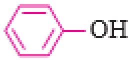
(d) boiling point of n-butanol is lower than tert-butanol

15. **The ether C_6H_5-O-$CH_2C_6H_5$ when treated with HI produce :**

(a) 

(b) 

(c) 

(d) 

Answers :

(1) a (2) c (3) c (4) c (5) d

(6) b (7) a (8) b (9) c (10) c

(11) c (12) d (13) d (14) c (15) d

Assertion and Reasoning

1. **Assertion :** SN ^{2} reaction proceeds with inversion of configuration.

   Reason : SN ^{2} reaction occurs in one step

2. **Assertion :** Treatment of chloroethane with saturated solution of AgCN give ethyl cyanide as major product.

   Reason : Cyanide ion (CN^-) is an ambident nucleophile.

3. **Assertion:** The boiling point of alcohol is higher than those of hydrocarbons of comparable molecular mass.

   Reason: Alcohol show intramolecular hydrogen bonding.

4. **Assertion:** O and p-nitrophenols can be separated by steam distillation.

   Reason: O-isomer is steam volatile due to intramolecular hydrogen bonding and p-isomer is not steam volatile due to intermolecular hydrogen bonding.

5. Assertion : **Bond angle in ethers is slightly less than the tetrahedral angle. Reason : There is a repulsion between the two bulky (-R) groups.**

6. **Assertion : p-Nitrophenol is more acidic than phenol.**
   Reason : Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.

Answers:- 1- b 2- d 3 – c 4 – a 5-d 6-a

Word Problem

1 . An alcohol A ($C_4H_{10}O$) on oxidation with acidified $K_2Cr_2O_7$ gives carboxylic acid 'B' ($C_4H_8O_2$). Compound 'A' when dehydrated with conc. H_2SO_4 at 443 K gives compound 'C' with aqueous H_2SO_4. 'C' gives compound 'D' ($C_4H_{10}O$) which is an isomer of 'A'. Compound 'D' is resistant to oxidation but compound 'A' can be easily oxidized. Identify A, B, C and D and write their structure

Ans. A : $(CH_3)_2CHCH_2OH$ B : $CH_3CH(CH_3)COOH$
C : $(CH_3)_2C = CH_2$ D : $(CH_3)_3 - C - OH$

2. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis from compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E

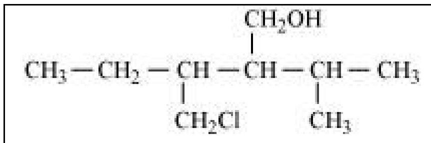
Ans. A : $CH_3CH_2OCH(CH_3)_2$ B : CH_3CH_2OH
C : $CH_3CHOHCH_3$ D : CH_3COOH E
: CH_3COCH_3

3. A primary alkyl halide (A), C_4H_9Br reacted with hot alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give (C), which is an isomer of (A). When (A) was reacted with sodium metal, it gave a compound (D), C_8H_{18} which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write equations of all the reactions.

Ans. (A) isobutyl bromide
(B) 2−methyl−1−propene
(C) tert−butylbromide
(D) 2,5-dimethylhexane

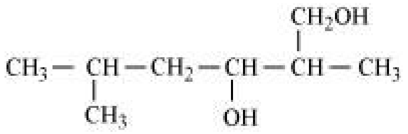
IUPAC Nomenclature & Conversation

IUPAC Nomenclature	**Conversation**



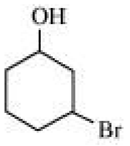
$CH_3-CH_2-\underset{\underset{CH_2Cl}{|}}{CH}-\overset{\overset{CH_2OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(ii)

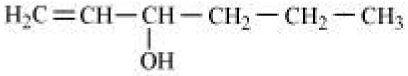


$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-\overset{\overset{CH_2OH}{|}}{CH}-CH_3$

(iii)

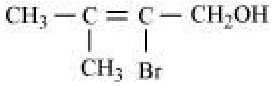


(iv)



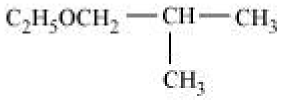
$H_2C=CH-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3$

(v)



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

(vi)



$C_2H_5OCH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Answer

(i) 3-Chloromethyl-2-(1’methyl ethyl) pentan-1-ol

(ii) 2, 5-Dimethylhexane-1, 3-diol

(iii) 3-Bromocyclohexanol

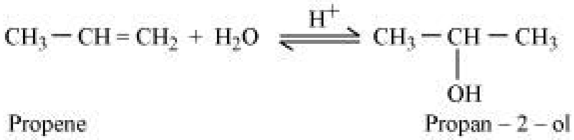
(iv) Hex-1-en-3-ol

(v) 2-Bromo-3-methylbut-2-en-1-ol

(vi) 1-Ethoxy-2-methylpropane

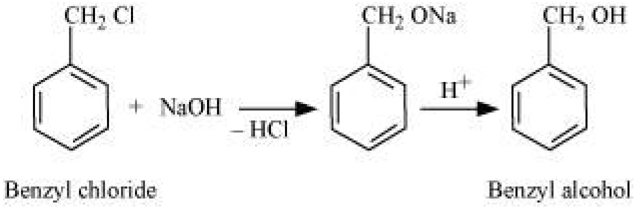
(a) How are the following conversions carried out?

(i) Propene → Propan-2-ol

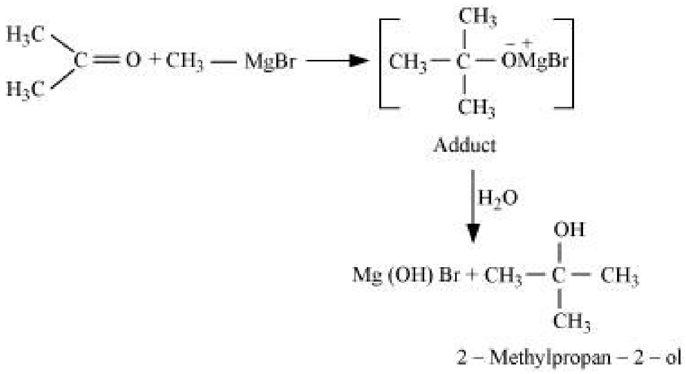


$CH_3-CH=CH_2 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(ii) Benzyl chloride → Benzyl alcohol



(iii) Ethyl magnesium chloride → Propan-1-ol.



(b) Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

(iv) Butan-2-one to butan-2-ol.

Answer

(i) Acidified potassium permanganate

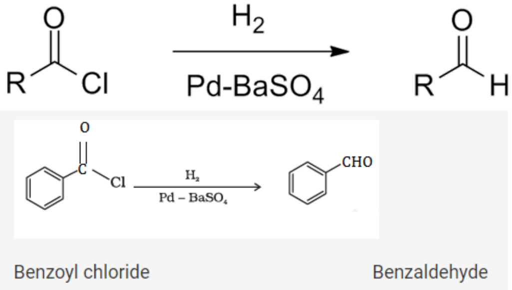
(ii) Pyridinium chlorochromate (PCC)

(iii) Bromine water (iv) $NaBH_4$ or $LiAlH_4$

UNIT-12
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

IMPORTANT REACTIONS:

ROSENMUND REDUCTION:



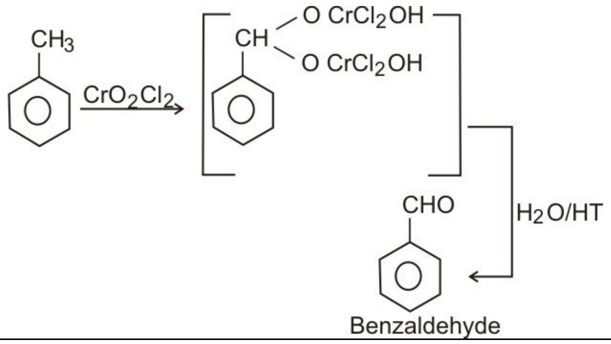
STEPHEN REACTION

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

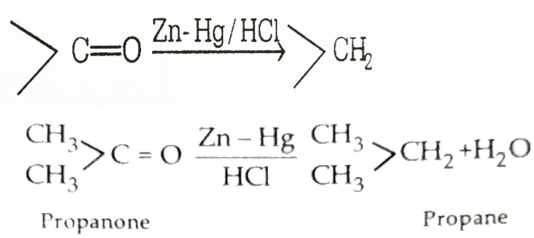
OR

$$RCN \xrightarrow[(ii)\ H_3O^+]{(i)\ SnCl_2+HCl} RCHO$$

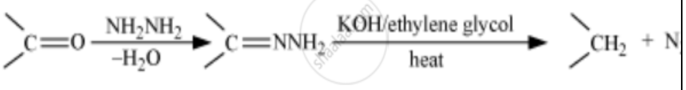
ETARD REACTION



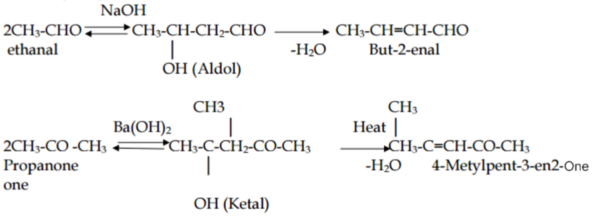
CLEMMENSEN REDUCTION



WOLFF- KISHNER REDUCTION



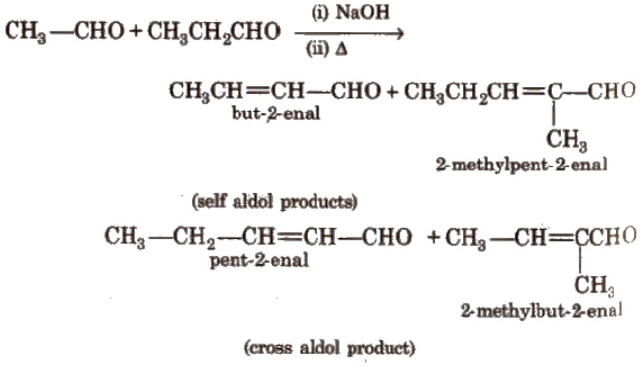
ALDOL CONDENSATION



$$\underset{\text{ethanal}}{2CH_3\text{-}CHO} \xrightleftharpoons{NaOH} \underset{\text{OH (Aldol)}}{CH_3\text{-}\underset{|}{CH}\text{-}CH_2\text{-}CHO} \xrightarrow[-H_2O]{} \underset{\text{But-2-enal}}{CH_3\text{-}CH{=}CH\text{-}CHO}$$

$$\underset{\text{Propanone one}}{2CH_3\text{-}CO\text{-}CH_3} \xrightleftharpoons{Ba(OH)_2} \underset{\text{OH (Ketal)}}{CH_3\text{-}\overset{CH3}{\underset{|}{\overset{|}{C}}}\text{-}CH_2\text{-}CO\text{-}CH_3} \xrightarrow[-H_2O]{Heat} \underset{\text{4-Metylpent-3-en2-One}}{CH_3\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH\text{-}CO\text{-}CH_3}$$

CROSS- ALDOL CONDENSATION



$$CH_3—CHO + CH_3CH_2CHO \xrightarrow[(ii)\ \Delta]{(i)\ NaOH}$$

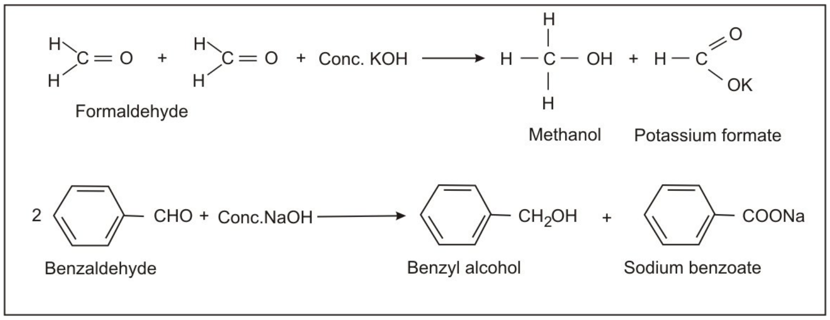
$$\underset{\text{but-2-enal}}{CH_3CH{=}CH—CHO} + \underset{\text{2-methylpent-2-enal}}{CH_3CH_2CH{=}\underset{CH_3}{\underset{|}{C}}—CHO}$$

(self aldol products)

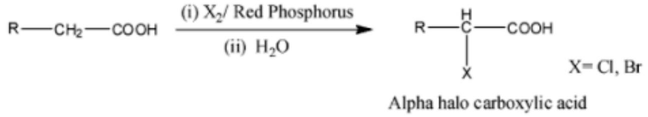
$$\underset{\text{pent-2-enal}}{CH_3—CH_2—CH{=}CH—CHO} + \underset{\text{2-methylbut-2-enal}}{CH_3—CH{=}\underset{CH_3}{\underset{|}{C}}CHO}$$

(cross aldol product)

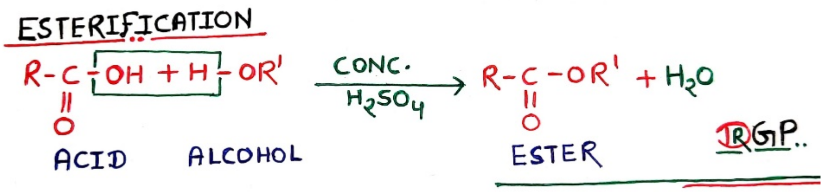
CANNIZZARO REACTION



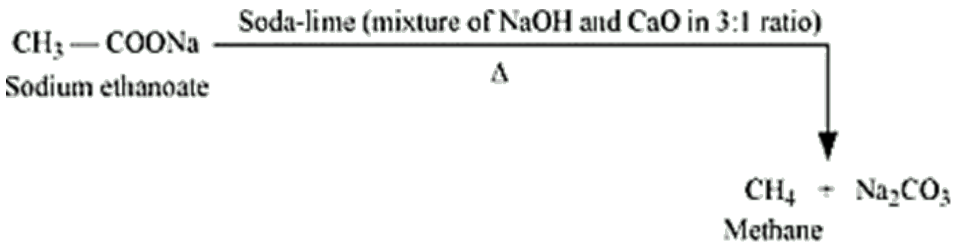
HELL-VOLHARD-ZELINSKY REACTION (HVZ)



ESTERIFICATION



DECARBOXYLATION:



MECHANISMS

i) $H_2SO_4\ H^+ + HSO_4^-$ $\longrightarrow$

ii) $CH_3\ CH_2\ OH + H^+ \longrightarrow CH_3-CH_2-\underset{\underset{H}{|}}{O^+}-H$

(iii) $CH_3CH_2-\underset{\underset{H_2O\ H}{|}}{O^+}-H \longrightarrow CH_3\ CH_2^+ +$

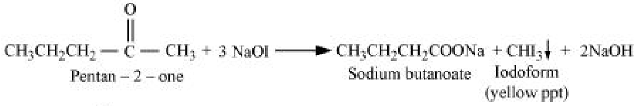
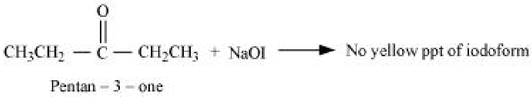
iv) $CH_3\ CH_2-O-H + CH_3\ CH_2^+ \longrightarrow CH_3-CH_2-\underset{\underset{CH_2CH_3}{|}}{O^+}-H$

v) $CH_3CH_2-\underset{\underset{CH_2CH_3}{|}}{O^+}-H \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

$HSO_4^- + H^+\quad H_2SO_4$ $\longrightarrow$

<u>DISTINGUISH</u>

ii) Acetophenone and Benzophenone ANS: (a) Iodoform test:	(i)Propanal and Propanone: ANS: By (a) Tollen's test

$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + CHI_3 + 2NaO$ Acetophenone, Sodium hypoiodite, Sodium benzoate, Iodoform (yellow ppt) $C_6H_5COC_6H_5 + NaOI \longrightarrow$ No yellow ppt of CHI_3 Benzophenone	$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + Ag\downarrow + 4N$ Propanal, Tollen's reagent, Propanoate ion, Silver mirro (b) Fehling's test $CH_3CH_2CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + Cu_2O\downarrow +$ Propanal, Propanoate ion, Cuprous oxi (Red – brow
Phenol and Benzoic acid: Ferric chloride test:given by phenol $6C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{3-} + 3H^+ + 3Cl^-$ Phenol, Iron-phenol complex (Violet colour)	Benzoic acid and Ethyl benzoate By NaHCO3 test – given by benzoic acid $C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O$ Benzoic acid, Sodium benzoate $C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow$ No effervescence due to evolution of CO_2 gas
Pentan-2-one and Pentan-3-one By Iodoform test:  $CH_3CH_2CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3 + 3NaOI \longrightarrow CH_3CH_2CH_2COONa + CHI_3\downarrow + 2NaOH$ Pentan – 2 – one, Sodium butanoate, Iodoform (yellow ppt)  $CH_3CH_2-\overset{O}{\overset{\Vert}{C}}-CH_2CH_3 + NaOI \longrightarrow$ No yellow ppt of iodoform Pentan – 3 – one	Benzaldehyde and Acetophenone By (a)Tollen's Test $C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow C_6H_5COO^- + Ag\downarrow + 4NH_3 + 2H_2O$ Benzaldehyde, Tollen's reagent, Benzoate ion, Silver mirror (b)Iodoform test $C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + CHI_3 + 2NaOH$ Acetophenone, Sodium benzoate, Iodoform (yellow ppt)
Ethanal and Propanal By Iodoform test- given by ethanal $CH_3CHO + 3NaOI \longrightarrow HCOONa + CHI_3 + 2NaOH$ Ethanal, Sodium methanoate, Iodoform (yellow ppt)	

+

CONCEPTUAL QUESTIONS

Q 1.Arrange the following compounds in increasing order of their property as indicated.

1. CH3CHO, C6H5CHO, HCHO (reactivity towards nucleophilic addition reaction).

2. 2,4-dinitrobenzoic acid, 4 methoxybenzoic acid, 4 nitrobenzoic acid(acidic character).Answer : 1. C6H5CHO < CH3CHO < HCHO

4-methoxybenzoic acid < 4-nitrobenzoic acid < 2, 4-dinitrobenzoic acid

Q 2. CH3CHO is more reactive than CH3COCH3 towards reaction with HCN.

Answer : CH3CHO is more polar and has less stearic hindrance, therefore, more reactive with HCN than CH3COCH3.

Q 3. Carboxylic acid is a stronger acid than phenol.

Answer : Carboxylate ions are more stable than phenoxide ions as negative charge is delocalised on two oxygen atoms in carboxylate ions.

Q 4. Why is oxidation of alcohals to get aldehydes carried out under controlled conditions?

Answer : It is because aldehydes get further oxidised to acids, oxidation of alcohals to aldehydes needs to be controlled.

Q 5. Melting point of an acid with even no. of carbon atoms is higher than those of its neighbour with odd no. of carbon atoms.

Answer : They fit into crystal lattice more readily than odd ones that is why they have higher lattice energy and higher melting point.

Q 6. Why formaldehyde cannot be prepared by Rosenmund'S reduction?

Answer : Because the formyl chloride thus formed is unstable at room temperature so cannot be prepared by Rosenmund reduction

Q 7. Why does methanal undergo cannizaro's reaction?

Answer :because it does not possesses ɑ-hydrogen atom.

Q 8.Which acid is stronger and why?

F_3C-C_6H_4COOH and $CH_3C_6H_4COOH$

Answer :CF_3^- has strong (-I)effect Whereas,
CH_3^- has strong (+I)effect
Due to greater stability of $F_3CC_6H_4COO^-$ ion over CH_3-$C_6H_4COO^-$ ion $CF_3C_6H_4COOH$ is much stronger acid than CH_3-C_6H_4COOH.

Q 9.Why HCOOH does not give HVZ reaction while CH_3COOH does?

Answer: CH_3COOH contains α-hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction.

Q 10.Why PCC cannot oxidise methanol to methanoic acid and while $KMNO_4$ can?

Answer:This is because PCC is a mild oxidising agent and can oxide methanol to methanal only. While $KMNO_4$ being strong oxidising agent oxidises it to methanoic acid.

ASSERTION - REASON TYPE QUESTIONS

1. Question 1. Assertion (A): Formaldehyde is a planar molecule.
   Reason (R): It contains sp^2 hybridised carbon atom.
   Solution: (a) Formaldehyde is a planar molecule because it contains sp^2 hybridised carbon atom.

2. Question 2. Assertion (A): Compounds containing -CHO group are easily oxidized to corresponding carboxylic acids.
   Reason (R): Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.
   Solution: (e) Due to electron withdrawing nature of -C = O group, C — H bond in aldehydes is weak and thus can be easily oxidized to the corresponding carboxylic acids even with mild oxidizing agents like Fehling's solution and Tollens reagents.

3. Question 3. Assertion (A): The a-hydrogen atom in carbonyl compounds is less acidic.
   Reason (R): The anion formed after the loss of a-hydrogen atom in carbonyl compounds is more acidic.
   Solution: (d) The a-hydrogen atom in carbonyl compounds is more acidic.

4. Question 4. Assertion (A): Aromatic aldehydes and formaldehyde undergo Cannizzaro's reaction.
   Reason (R): Aromatic aldehydes are almost as reactive as formaldehyde.
   Solution: (c) Aromatic aldehydes and formaldehyde do not contain a-hydrogen and thus undergo Cannizzaro's reaction. Formaldehyde is more reactive than aromatic aldehydes.

5. Question 5. Assertion (A): Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.
   Reason (R): Both, aldehydes and ketones contain a carbonyl group.
   Solution: (d) Both aldehyde and ketones have carbonyl group but only aldehydes react with Tollen's reagent to give silver mirror.

MCQ

Question 1.
Which of the following reactions will give benzolphenone?
(i) Benzoyl chloride + Benzene + $AlCl_3$
(ii) Benzoyl chloride + Phenylmagnesium bromide
(iii) Benzoyl chloride + Diphenyl cadmium.

(a) (i)and(ii)
(b) (ii) and (iii)
(c) (i) and (iii)
(d) (i), (ii) and (iii)

Answer: (c) (i) and (iii)

Question 2.
Propanone can be prepared from ethyne by
(a) passing a mixture of ethyne and steam over a catalyst, magnesium at 420°C
(b) passing a mixture of ethyne and ethanol over a catalyst zinc chromite
(c) boiling ethyne with water in the presence of $HgSO_4$ and H_2SO_4
(d) treating ethyne with iodine and NaOH

Answer: (c) boiling ethyne with water in the presence of $HgSO_4$ and H_2SO_4

Question 3.
The oxidation of toluene to benzaldehyde by chromyl, chloride is called
(a) Etard reaction
(b) Riemer-Tiemann reaction
(c) Wurtz reaction
(d) Cannizzaro's reaction

Answer: (a) Etard reaction
Question 4.
There is a large difference in the boiling points of butanal and butanal-1-oldueto
(a) intermolecular hydrogen bonding in butan-1-ol
(b) intermolecular hydrogen bonding in butanal
(c) higher molecular mass of butan-1-ol
(d) resonance shown by butanal

Answer: (a) intermolecular hydrogen bonding in butan-1-ol

Question 5.
The addition of HCN to carbonyl compounds is an example of

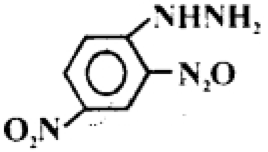
(a) nucleophilic addition
(b) electrophilic addition
(c) free radical addition
(d) electromeric addition

Answer: (a) nucleophilic addition
Question 6.
Aldehydes other than formaldehyde react with Grignard’s reagent to give addition products which on hydrolysis give
(a) tertiary alcohols
(b) secondary alcohols
(c) primary alcohols
(d) carboxylic acids

Answer: (b) secondary alcohols
Question 7.
Which of the following will not give aldol condensation?
(a) Phenyl acetaldehyde
(b) 2-Methylpentanal
(c) Benzaldehyde
(d) 1-Phenylpropanone

Answer: (c) Benzaldehyde
Question 8.
Which of the following compounds does not react with $NaHSO_3$?
(a) HCHO
(b) $C_6H_5COCH_3$
(c) CH_3COCH_3
(d) CH_3CHO

Answer: (b) $C_6H_5COCH_3$

Question 9.
Which of the following compounds will ive a coloured crystalline compound with


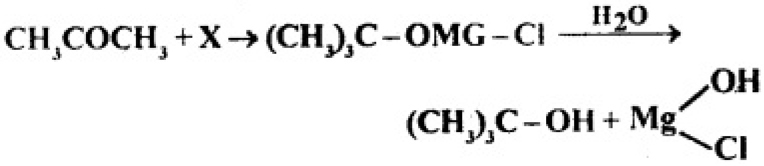
(a) CH_3COCl
(b) $CH_3COOC_2H_5$
(c) CH_3COCH_3
(d) CH_3CONH_2

Answer: (c) CH_3COCH_3
Question 10.
The product of hydrolysis of ozonide of 1-butene are

(a) ethanol only
(b) ethanal and methanal
(c) propanal and methanal
(d) methanal only

Answer: (c) propanal and methanal

Question 11.
Identify reactant (X) in the given reaction sequence



$$CH_3COCH_3 + X \rightarrow (CH_3)_3C-OMG-Cl \xrightarrow{H_2O} (CH_3)_3C-OH + Mg\begin{matrix} OH \\ Cl \end{matrix}$$

(a) CH_3MgCl
(b) CH_3COCl +Mg
(c) $MgCl_2$
(d) CH_3CH_2MgCl

Answer: (a) CH_3MgCl
Question 12.
The best oxidising agent- for oxidation of
CH_3-CH = CH-CHO to CH_3-CH = CH-COOH is
(a) Baeyefs reagent
(b) Tollen’s reagent
(c) SchifFs reagent
(d) Acidified dichromate

Answer: (b) Tollen’s reagent

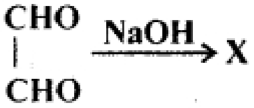
Question 13.
In order of reactivity of CH_3CHO, $CH_3COC_2H_5$ and CH_3COCH_3 is
(a) $CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$
(b) $C_2H_5COCH_3 > CH_3COCH_3 > CH_3CHO$
(c) $CH_3COCH_3 > CH_3CHO > C_2H_5COCH_3$
(d) $CH_3COCH_3 > C_2H_5COCH_3 > CH_3CHO$

Answer: (a) $CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$
Question 14.
The final product (Y) in the following sequence of chemical reaction is

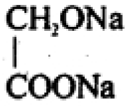
$$CH_3OH \xrightarrow[300°C]{Cu} X \xrightarrow{NaOH} Y + CH_3OH$$

(a) An alkene
(b) a carboxylic acid
(c) an aldehyde
(d) sodium salt of carboxylic acid

Answer: (d) sodium salt of carboxylic acid
Question 15.

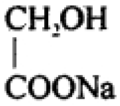

$$\begin{matrix}\mathrm{CHO}\\ |\\ \mathrm{CHO}\end{matrix}\xrightarrow{\mathrm{NaOH}}\mathrm{X}$$

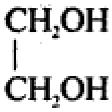
The product (X) will be

(a)

$$\begin{matrix}\mathrm{CH_2ONa}\\ |\\ \mathrm{COONa}\end{matrix}$$

(b)

$$\begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{matrix}$$

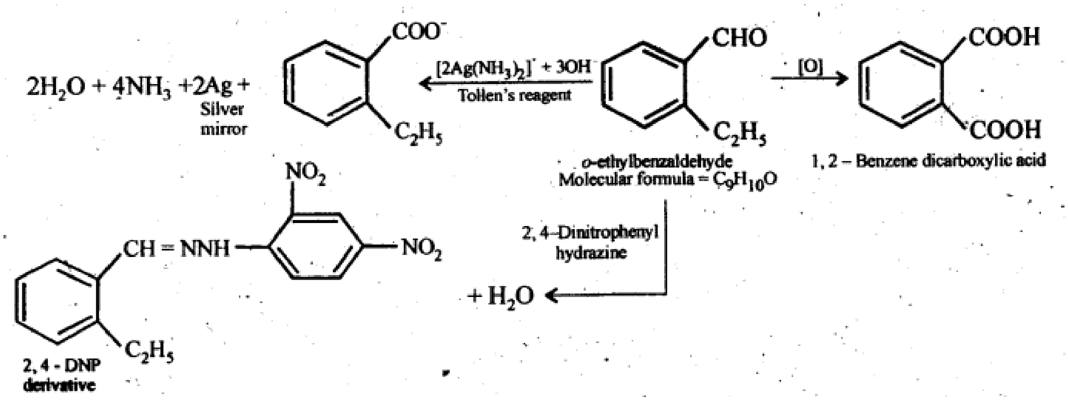
(c)

$$\begin{matrix}\mathrm{CH_2OH}\\ |\\ \mathrm{COONa}\end{matrix}$$

(d)

$$\begin{matrix}\mathrm{CH_2OH}\\ |\\ \mathrm{CH_2OH}\end{matrix}$$

Answer: (c)

WORD PROBLEM

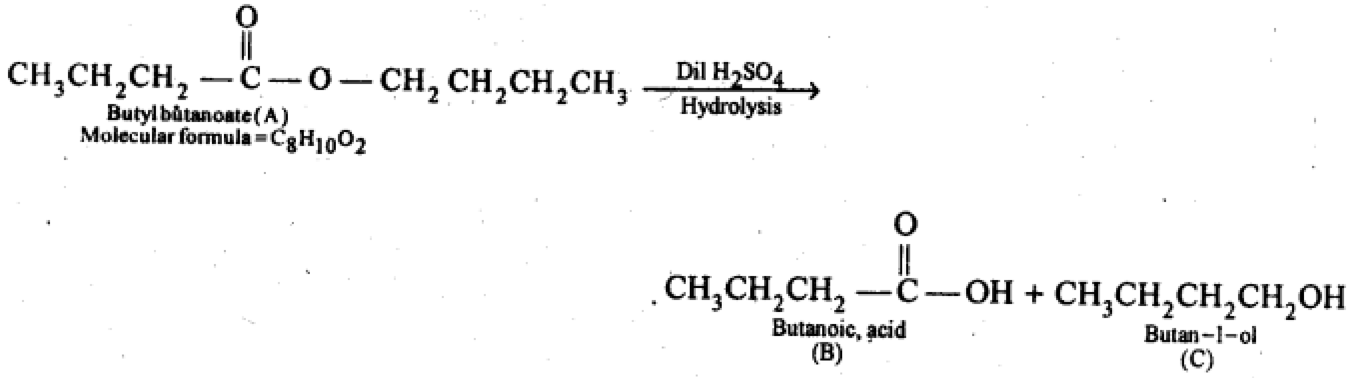
1.An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent, and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.
Ans: Since the given compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, it must be an aldehyde. Since it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to die benzene ring.
Since on vigorous oxidation, it gives 1, 2-benzene dicarboxylic acid, therefore, it must be an ortho- substituted benzaldehyde. The only o-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is o-ethyl benzaldehyde. Ail the reactions can now be explained on the basis of this structure.



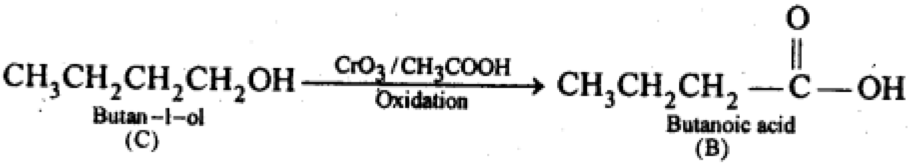
2. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B} and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (Q on dehydration gives but-l-ene. Write equations for the reactions involved.
Ans: Since an ester A with molecular formula $C_8H_{16}O_2$ upon hydrolysis gives carboxylic acid B and the alcohol C and oxidation of C with chromic acid produces the acid B, therefore, both the carboxylic acid B and alcohol C must contain the same number of carbon atoms.
Further, since ester A contains eight carbon atoms, therefore, both the carboxylic acid B and the alcohol C must contain four carbon atoms each.
Since the alcohol C on dehydration gives but-l-ene, therefore, C must be a straight chain

alcohol, i.e., butan-l-ol.

If C is butan-l-ol, then the acid B must be butanoic acid and the ester A must be butyl butanoate.The chemical equations are as follows:



$$\underset{\substack{\text{Butyl bûtanoate (A)}\\ \text{Molecular formula} = C_8H_{10}O_2}}{CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_2CH_2CH_3} \xrightarrow[\text{Hydrolysis}]{\text{Dil } H_2SO_4} \underset{\substack{\text{Butanoic, acid}\\ \text{(B)}}}{CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\substack{\text{Butan-l-ol}\\ \text{(C)}}}{CH_3CH_2CH_2CH_2OH}$$

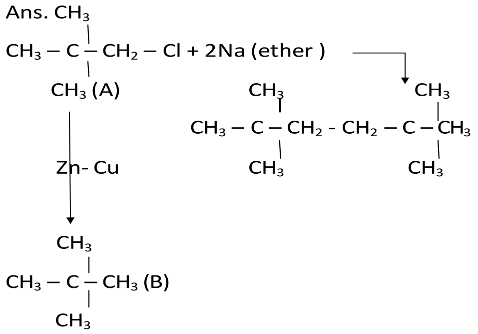


$$\underset{\substack{\text{Butan-l-ol}\\ \text{(C)}}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{CrO_3/CH_3COOH} \underset{\substack{\text{Butanoic acid}\\ \text{(B)}}}{CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

$$CH_3CH_2CH_2CH_2OH \xrightarrow[-H_2O]{\text{Dehydration}} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

3.A Chloro compound 'A' on reduction with Zn – Cu and alcohol gives the hydro carbon (B) with five carbon atom.When 'A' is dissolved in ether and treated with sodium 2,2,5,5 tetramethyl hexhane is formed structure of A and B?

Ans.

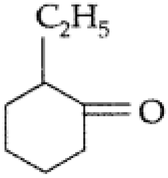
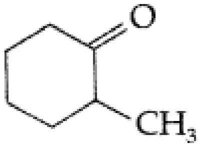
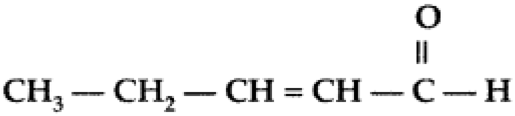
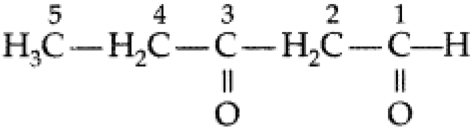
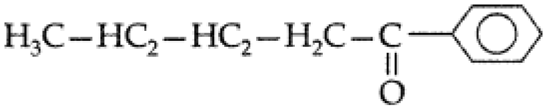


$$\underset{CH_3\ (A)}{CH_3-\overset{CH_3}{\underset{|}{\overset{|}{C}}}-CH_2-Cl} + 2Na\ (\text{ether}) \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

$$\xrightarrow{\text{Zn-Cu}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3\ (B)$$

NOMENCLATURE

Write IUPAC name of the following :

 I IUPAC name : 2-Ethyl cyclohexanone.	 2-methylcyclohexanone
 $CH_3-CH_2-CH=CH-\overset{\overset{O}{\parallel}}{C}-H$ Pent-2-enal	Ph – CH = CH – CHO 3-phenylprop-2-enal
 $\overset{5}{H_3C}-\overset{4}{H_2C}-\underset{\underset{O}{\parallel}}{\overset{3}{C}}-\overset{2}{H_2C}-\underset{\underset{O}{\parallel}}{\overset{1}{C}}-H$ 3-oxopentanal	 1-phenylpentan- 1-one
$PhCH_2CH_2COOH$ 3-Phenylpropanoic acid	$(CH_3)_2\ C=CHCOOH$ 3-Methylbut-2-enoic acid.

CONVERSIONS:

1How will you convert ethanal into the following compounds?
(i) Butane-1,3-diol
(ii) But-2-enal
(iii) But-2-enoic acid

Ans:

(*i*) $2CH_3CHO \xrightarrow{\text{Dil NaOH}} \underset{\text{3-Hydroxy butanal}}{CH_3CH(OH)CH_2CHO} \xrightarrow{NaBH_4} \underset{\text{Butan-1,3-diol}}{CH_3CHOHCH_2CH_2OH}$

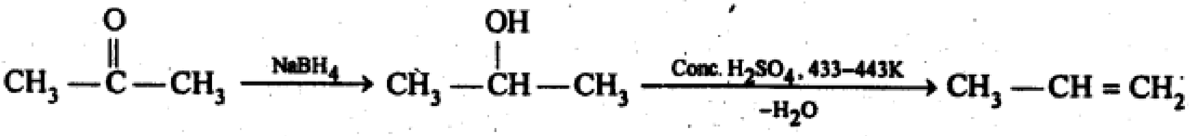
(*ii*) $2CH_3CHO \xrightarrow{\text{Dil NaOH}} CH_3CH(OH)CH_2CHO \xrightarrow[-H_2O]{H_3O^+} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$

(*iii*) $\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(ii) }H_3O^+]{\text{(i)Dil NaOH}} CH_3CH=CHCHO \xrightarrow[\text{Tollens' reagent}]{[Ag(NH_3)_2]^+OH^-} \underset{\text{But-2-enoic acid}}{CH_3CH = CHCO_2H}$

Q. How will you bring about the following conversions in not more than two steps?
(i) PropanonetoPropene
(ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal
(iv) Benzene to m-Nitroacetophenone
(v) Benzaldehyde to Benzophenone –
(vi) Bromobenzeneto 1-PhenylethanoL
(vii) Benzaldehyde to 3-Phenylpropan-1-ol.
(viii) Benzaldehyde to ɑ Hydroxyphenylacetk acid
(ix) Benzoic acid to m-Nitrobenzy 1 alcohol

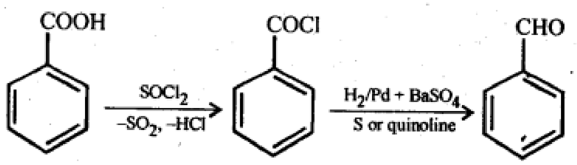
Ans:

(*i*) **Propanone to propene:**

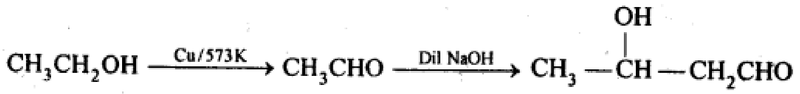


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{NaBH_4} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow[-H_2O]{\text{Conc. }H_2SO_4\text{, 433–443K}} CH_3-CH=CH_2$$

(*ii*) Benzoic acid to benzaldehyde:

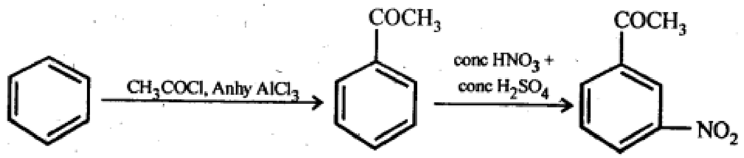


(*iii*) Ethanol to 3-hydroxy butanal:



$$CH_3CH_2OH \xrightarrow{Cu/573K} CH_3CHO \xrightarrow{Dil\ NaOH} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CHO$$

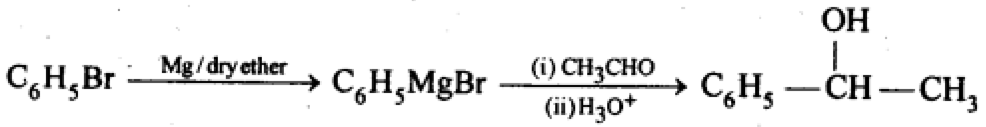
(*iv*) Benzene to *m*-nitroacetophenone:



(*v*) Benzaldehyde to benzophenone:

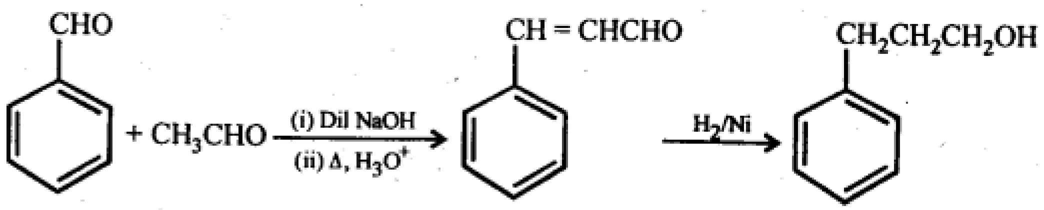
$$C_6H_5CHO \xrightarrow[(ii)\ CaCO_3]{(i)\ K_2Cr_2O_7/H_2SO_4} (C_6H_5COO)_2Ca \xrightarrow[-CaCO_3]{Dry\ Distillation} (C_6H_5)_2CO$$

(*vi*) Bromobenzene to 1-phenylethanol

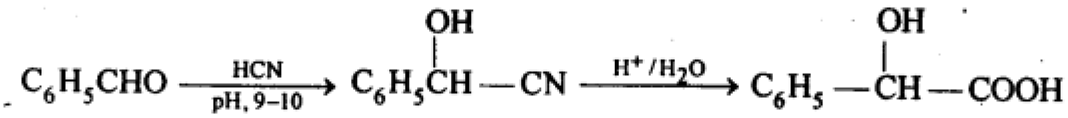


$$C_6H_5Br \xrightarrow{Mg/dry\ ether} C_6H_5MgBr \xrightarrow[(ii) H_3O^+]{(i)\ CH_3CHO} C_6H_5-\overset{OH}{\overset{|}{C}H}-CH_3$$

(*vii*) Benzaldehyde to 3-phenylpropan-1-ol

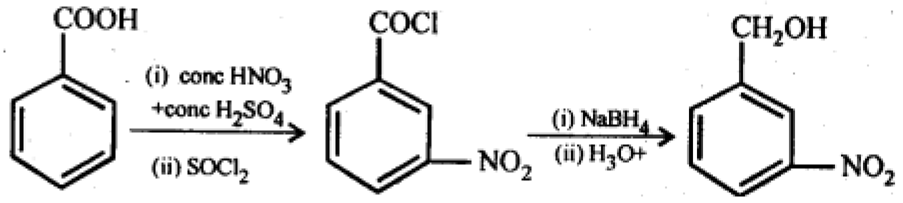


(*viii*) Benzaldehyde to α-hydroxyphenylacetic acid:



$$C_6H_5CHO \xrightarrow[pH,\ 9-10]{HCN} C_6H_5\overset{OH}{\overset{|}{C}H}-CN \xrightarrow{H^+/H_2O} C_6H_5-\overset{OH}{\overset{|}{C}H}-COOH$$

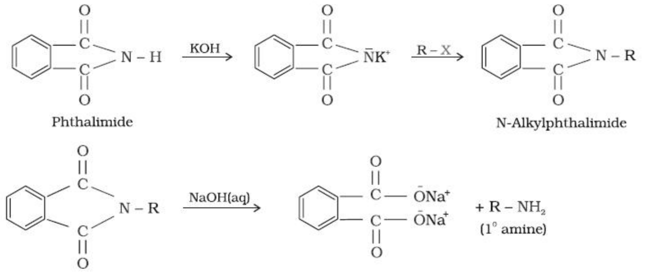
(*ix*) Benzoic acid to *m*-nitrobenzyl alcohol:



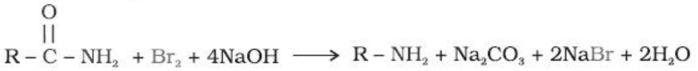
UNIT-13
AMINES

IMPORTANTS REACTIONS:

1. Gabriel phthalimide synthesis



2. Hoffmann bromamide degradation reaction



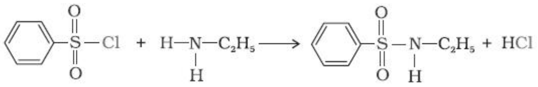
$$R-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

3.Carbylamine reaction

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

4.Hinsberg Test:

(a)with primary amines



N-Ethylbenzenesulphonamide
(soluble in alkali)

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

(i) Methylamine and dimethylamine

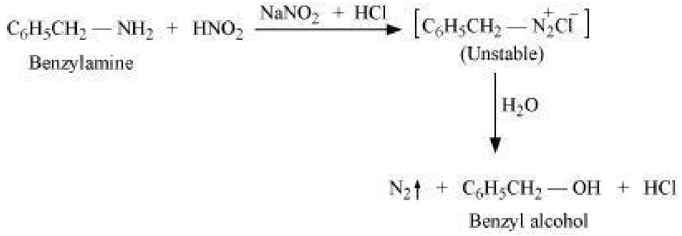
By Carbylamine test:

$$\underset{\text{Methylamine}(1^0)}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Methyl isocyanide}\\ \text{(foul smell)}}}{CH_3-NC} + 3KCl + 3H_2$$

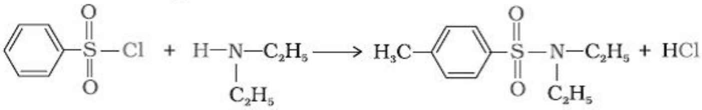
$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

(ii) Aniline and benzylamine

Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.



On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.

(iii) Secondary and tertiary amines	(iv) Aniline and N-methylaniline.
By **Hinsberg's reagent** (a)with sec. amines  *N,N*-Diethylbenzenesulphonamide (b)Tertiary amines do not react with benzenesulphonyl chloride	**By Carbylamine test:** $C_6H_5-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} C_6H_5-NC + 3KCl + 3H_2O$ Benzylamine (1^0) Benzyl isocyanide (foul smell) $C_6H_5NHCH_3 + CHCl_3 + 3KOH \xrightarrow{\Delta}$ No reaction N-Methylaniline

REASONING QUESTIONS

Q1. Account for the following:

(i) pKb of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

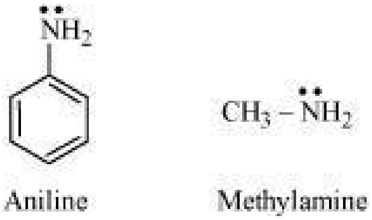
(iv) Although amino group is o– and p– directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

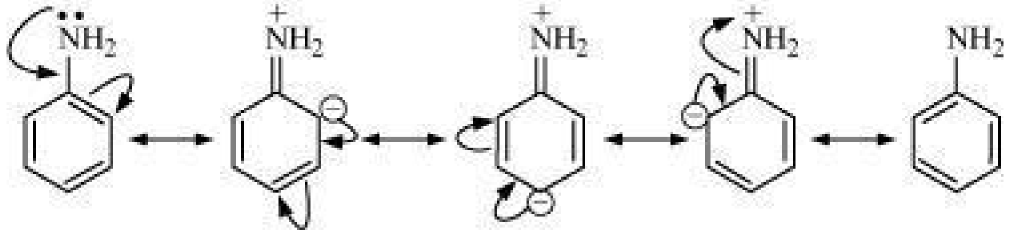
(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

ANS. (i) pK_b of aniline is more than that of methylamine:

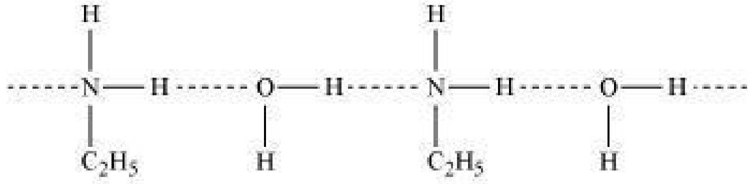


Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not:
Ethylamine when added to water forms intermolecular H−bonds with water. Hence, it is soluble in water.



Ethylamine

But aniline does not undergo H−bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:

$$\underset{\text{Methylamine}}{CH_3 \longrightarrow NH_2} \qquad \underset{\text{Water}}{H—OH}$$

Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces OH^- ions by accepting H^+ ions from water.

$$CH_3-NH_2+H-OH \longrightarrow CH_3-\overset{+}{N}H_3+OH^-$$

Ferric chloride ($FeCl_3$) dissociates in water to form Fe^{3+} and Cl^- ions.

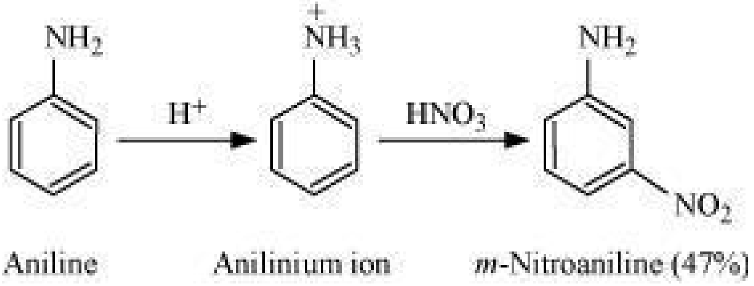
$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$$

Then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\substack{\text{Hydrated}\\ \text{ferric oxide}}}{Fe_2O_3 \cdot 3H_2O}$$

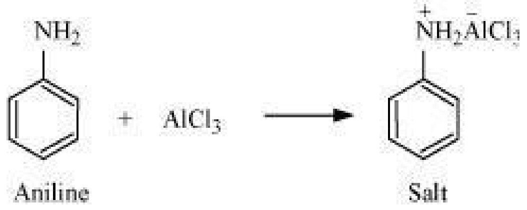
(iv) Although amino group is o,p− directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).



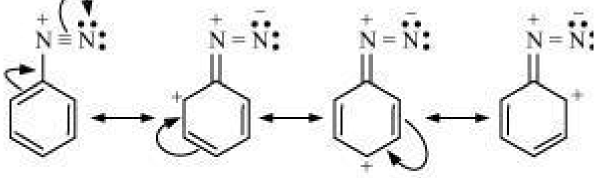
For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction:
A Friedel-Crafts reaction is carried out in the presence of $AlCl_3$. But $AlCl_3$ is acidic in nature, while aniline is a strong base. Thus, aniline reacts with $AlCl_3$ to form a salt (as shown in the following equation).



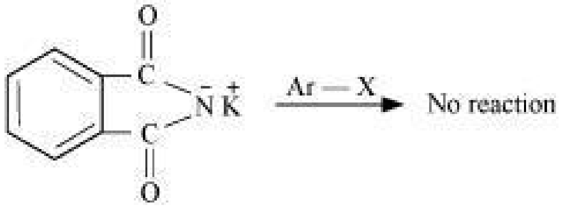
Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines: The diazonium ion undergoes resonance as shown below:



This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

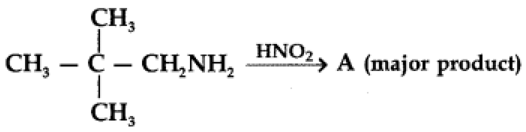
(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines: Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.



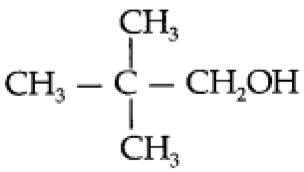
Hence, aromatic primary amines cannot be prepared by this process.

MCQ:

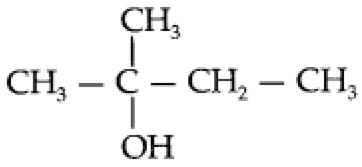
1.



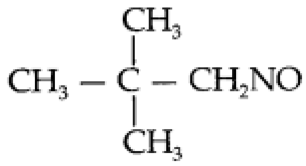
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2NH_2 \xrightarrow{HNO_2} A \text{ (major product)}$$

(*a*)


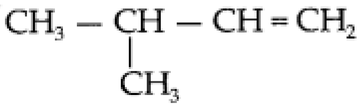
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH$$

(*b*)


$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2-CH_3$$

(*c*)


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2NO$$

(*d*)


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

Answer: b

2.

$$RCH_2OH \xrightarrow{K_2Cr_2O_7/\text{Conc. } H_2SO_4} X \xrightarrow[\text{(ii) Heat}]{\text{(i) } NH_3} Y \xrightarrow{H_2/Ni} Z$$

Answer: b

3.The correct decreasing order of boiling points among amines and their corresponding acids and alcohols is
(a) $R - CH_2 NH_2 > RCOOH > RCH_2OH$
(b) RCH2NH2 > $RCH_2OH > RCOOH$
(c) $R - CH_2OH > R - CH_2NH_2 > RCOOH$
(d) $R - COOH > R - CH_2OH > R - CH_2NH_2$

Answer: d

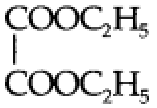
4.Aniline is less basic than ethylamine. This is due to
(a) Conjugation of lone pair of nitrogen with the ring
(b) The insoluble nature of aniline
(c) More Kfc value of aniline
(d) Hydrogen bonding

Answer: a

5.Primary amine reacts with carbon disulphide and $HgCl_2$ to produce alkyl isothiocyanate. This reaction is
- (a) Carbylanine reaction
  - (b) Hoffmann bromamide reaction
  - (c) Perkin reaction
  - (d) Hoffmann mustard oil reaction

Answer: d

6. Hinsberg's reagent is

(a) 
$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}$$
(b) $C_6H_5SO_2Cl$
(c) $C_6H_5SO_2NH_2$
(d) $CH_3COCH_2COOC_2H_5$

Answer b

7. Nitration of aniline is carried out after acylation because
(a) Acylation dectivates the — NH_2 group
(b) Oxidation can be prevented
(c) O-and p-products are obtained in good yield
(d) All of these
Answer d

8. NH_2 group in aniline is
(a) Ortho directing
(b) Meta directing
(c) Ortho and para directing
(d) Para directing
Answer c

9. Primary and secondary amines cannot be distinguished by
(a) Schiff's reagent
(b) Carbylamine reaction
(c) Hoffmann's bromamide reaction
(d) Iodoform test

Answer b

9. Which of the following cannot be identified by carbyl amine test?
   1. $C_2H_5NH_2$
   2. $C_6H_5NH_2$
   3. $C_6H_5 — NH — C_6H_5$
   4. $(C_2H_5)_3N$

(a) 1, 2
(b) 1, 2, 4
(c) 3, 4
(d) 2, 4
Answer c

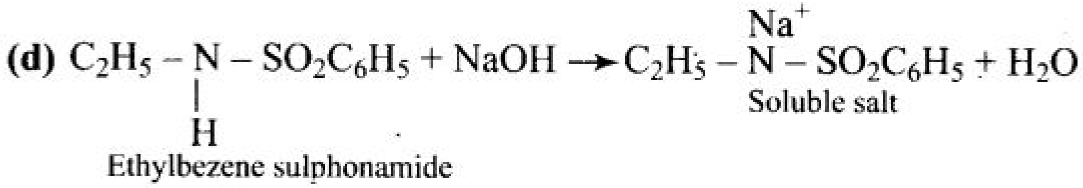
A/R : Assertion and Reason Type Questions

Question 1.Assertion (A): Acylation of amines gives a monosubstituted product, whereas alkylation of amines gives polysubstituted product.
Reason (R): Acyl group sterically hinders the approach of further acyl groups.
Solution: (c) Amines on acetylation give monosubstituted product, while on alkylation gives polysubstitution product as well.

Question 2. Assertion (A): Hofmann's bromamide reaction is given by primary amines. Reason (R): Primary amines are more basic than secondary amines.
Solution: (a) Hofmann's bromamide reaction is given by amides, not by amines. Moreover, primary amines are basic than secondary amines.

Question 3. Assertion (A): N-Ethylbenzene sulphonamide is soluble in alkali.
Reason (R): Hydrogen attached to nitrogen in sulphonamide is strongly **acidic.**

Solution:



$$\textbf{(d)}\ C_2H_5-\underset{\underset{H}{|}}{N}-SO_2C_6H_5+NaOH \rightarrow C_2H_5-\underset{\text{Soluble salt}}{\overset{Na^+}{N}}-SO_2C_6H_5+H_2O$$

Ethylbezene sulphonamide

Ethylbenzene sulphonamide is soluble in alkali because it has acidic hydrogen.

Question 4. Assertion (A): N, N-diethylbenzene sulphonamide is insoluble in alkalf. Reason (R): Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.
Solution: (b) N, N-diethyl benzene sulphonamide is insoluble in alkali because it has no acidic hydrogen.
Sulphonyl group attached to nitrogen atom is electron withdrawing group.

Question 5. Assertion (A): Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
Reason (R): $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.
Solution: (d) $Fe + 2HCl > FeCl_2 + 2[H]$
Nascent hydrogen reduces nitro compounds.
$FeCl_2 + H_2O(g) > FeO + 2HCl$

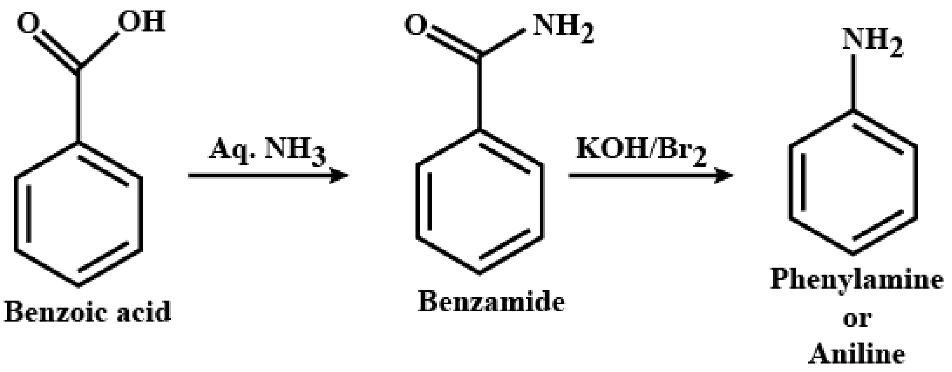
Question 6. Assertion (A): Aromatic 1° amines can be prepared by Gabriel phthalimide synthesis.
Reason (R): Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.
Solution: (a) Aromatic amines are never obtained by Gabriel phthalimide synthesis.

Question 7. Assertion (A): Acetanilide is less basic than aniline.
Reason (R): Acetylation of aniline results in decrease of electron density on nitrogen.
Solution: (d) Acetanilide is less basic than aniline because electron density of nitrogen is lowered by acetyl group.

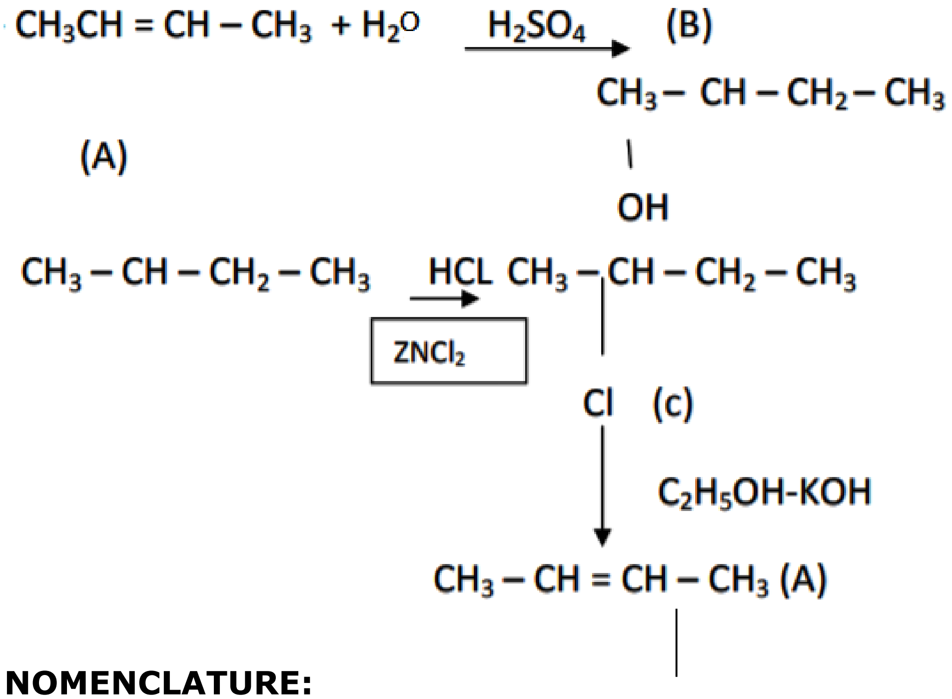
WORD PROBLEMS :

Q 1. An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N .Identify A,B,C .

Ans:-



Q 2. organic compound 'A' having molecular formula C_4H_8 on treatment with dil.H_2SO_4 gives 'B' . 'B' on treatment with conc. HCl and anhydrous $ZnCl_2$ gives C and on treatment with sodium ethoxide gives back A.Identify A,B,C.



$$CH_3CH=CH-CH_3 + H_2O \xrightarrow{H_2SO_4} (B)\ CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$$

(A)

$$CH_3-CH-CH_2-CH_3 \xrightarrow[\boxed{ZNCl_2}]{HCL} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3\ (c)$$

$$\downarrow C_2H_5OH\text{-}KOH$$

$$CH_3-CH=CH-CH_3\ (A)$$

IUPAC NOMENCLATURE:

Give the IUPAC name of the compound and classify into primary, secondary or tertiary amines.

$(CH_3)_2CHNH_2$	1-Methylethanamine (1^0 amine)
$CH_3(CH_2)_2NH_2$	Propan-1-amine (1^0 amine)
$CH_3NHCH(CH_3)_2$	N−Methyl-2-methylethanamine (2^0 amine)
$(CH_3)_3CNH_2$	2-Methylpropan-2-amine (1^0 amine)

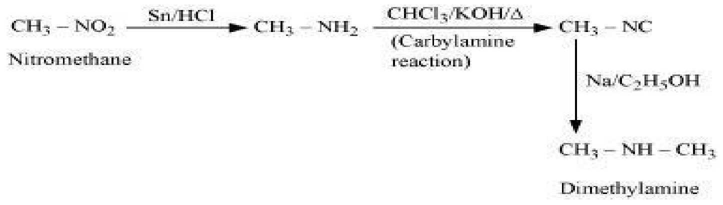
CONVERSIONS:

Q. How will you convert:

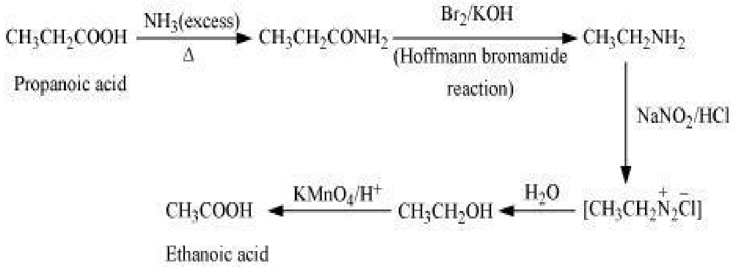
(i) Nitromethane into dimethylamine

(ii) Propanoic acid into ethanoic acid?

(i)

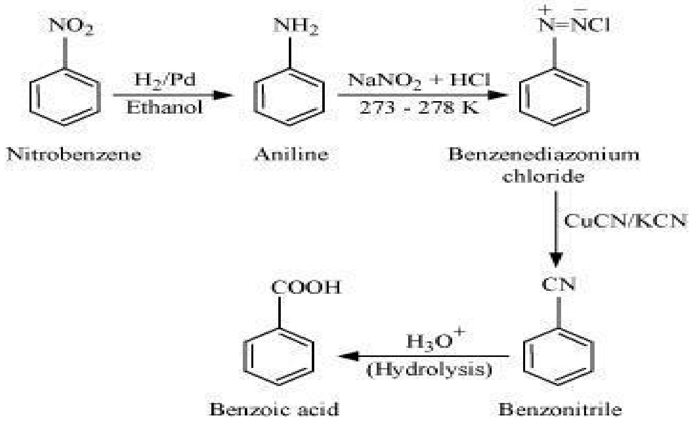


(ii)

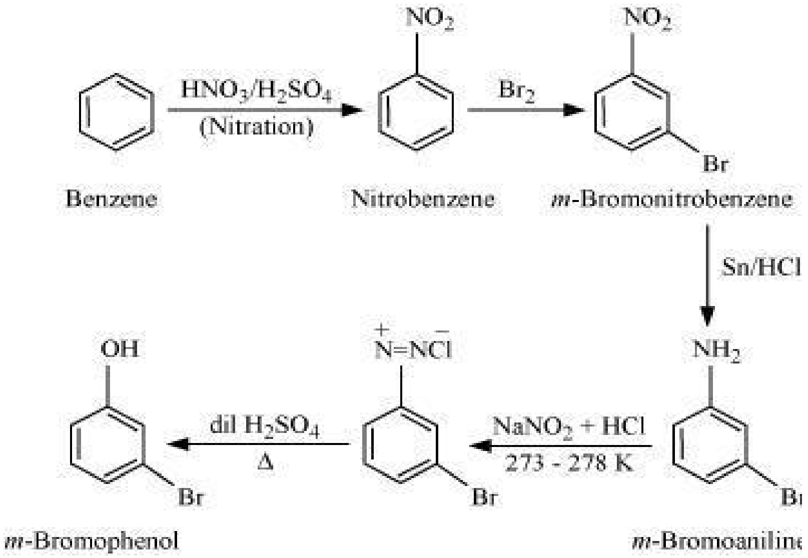


Q.Accomplish the following conversions:

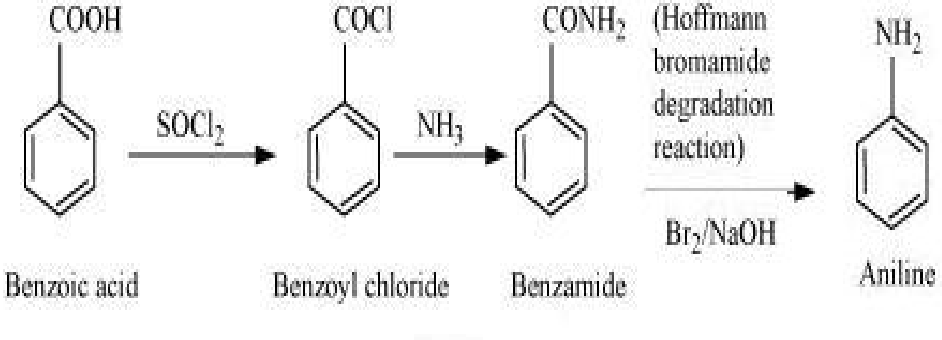
(i) Nitrobenzene to benzoic acid
(ii) Benzene to m-bromophenol
(iii) Benzoic acid to
aniline <u>ANS.</u> (i)



(ii)



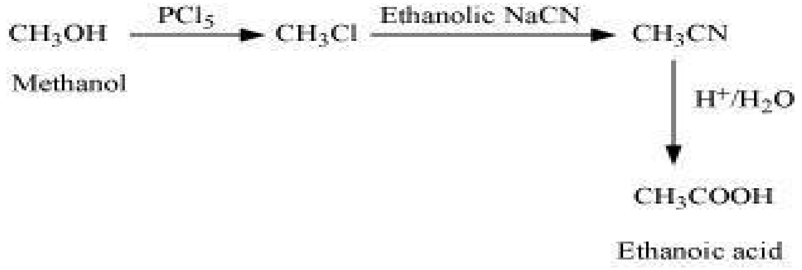
(iii)



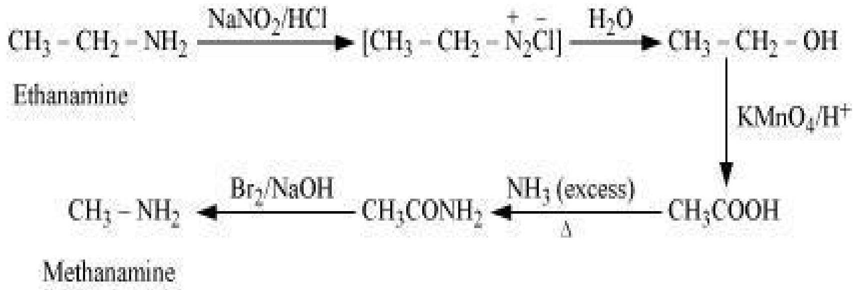
How will you convert:

(i) Methanol to ethanoic acid
(ii) Ethanamine into methanamine

<u>ANS.</u> (i)



(ii)



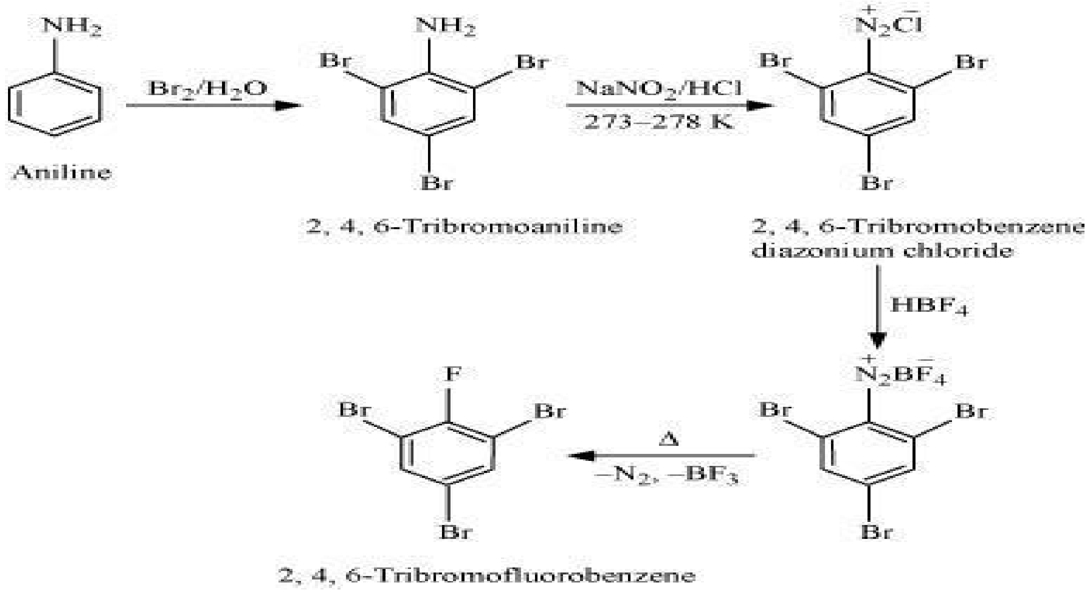
Accomplish the following conversions:

(i) Aniline to 2,4,6-tribromofluorobenzene

(ii) Benzyl chloride to 2-phenylethanamine

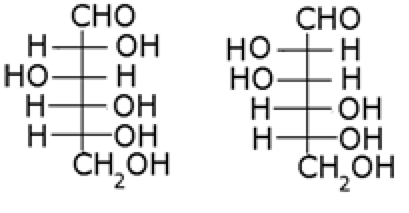
(iii) Chlorobenzene to p-chloroaniline

(i)



CHAPTER-14-"Biomolecules"

- **Carbohydrates:** Polyhydroxy aldehydes or polyhydroxy ketones or compounds on hydrolysis give carbohydrates.
- **Classification of carbohydrates:**
  Monosaccharides
  (a) Simplest carbohydrates
  (b) It cannot be hydrolysed into simpler compounds
  (c) Examples – Glucose, mannose
  Oligosaccharides
  (a) Carbohydrates which gives 2 to 10 monosaccharide units on hydrolysis
  (b) Examples – Sucrose, Lactose, Maltose
  Polysaccharides
  (a) Carbohydrates which on hydrolysis give large number of monosaccharide units.
  (b) Examples – Cellulose, starch
- **Anomers:** Pair of optical isomers which differ in configuration only around C1 atom are called anomers. Examples – α-D-glucopyranose and β-D-glucopyranose.
- **Epimers:** Pair of optical isomers which differ in configuration around any other C atom other than C1 atom are called epimers. E.g. D-glucose and D- mannose are C2 epimers.



D - Glucose D - Mannose

Preparation of glucose (also called dextrose, grape sugar):

$$\underset{Sucrose}{C_{12}H_{22}O_{11}}+H_2O\xrightarrow{H^+}\underset{Glucose}{C_6H_{12}O_6}+\underset{Fructose}{C_6H_{12}O_6}$$

- **From starch**

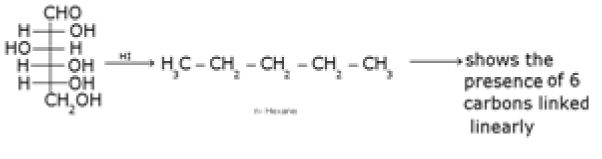
$$\underset{\substack{Sucrose\\Or\\Cellulose}}{(C_{12}H_{22}O_5)_n}+H_2O\xrightarrow{H^+/393k;2-3atm}n\underset{Glucose}{C_6H_{12}O_6}$$

- **Structure of glucose**

$$CHO-(CHOH)_4-CH_2OH$$

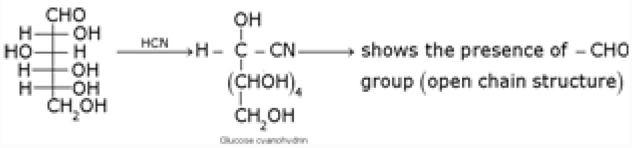
- **Structure elucidation of glucose:**

a) D – glucose with HI



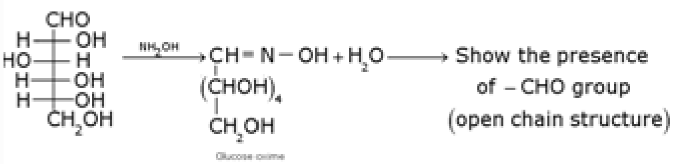
shows the presence of 6 carbons linked linearly

b) D – glucose with HCN



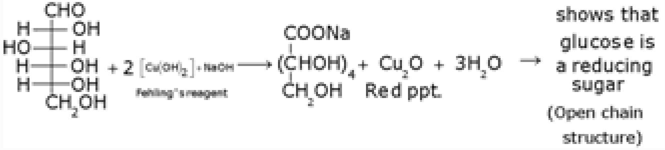
shows the presence of – CHO group (open chain structure)

c) D – glucose with NH_2OH



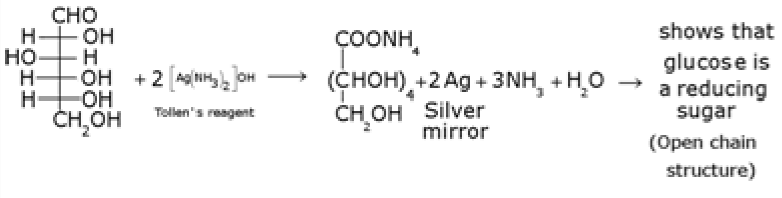
Show the presence of – CHO group (open chain structure)

d) D- glucose with Fehling's reagent



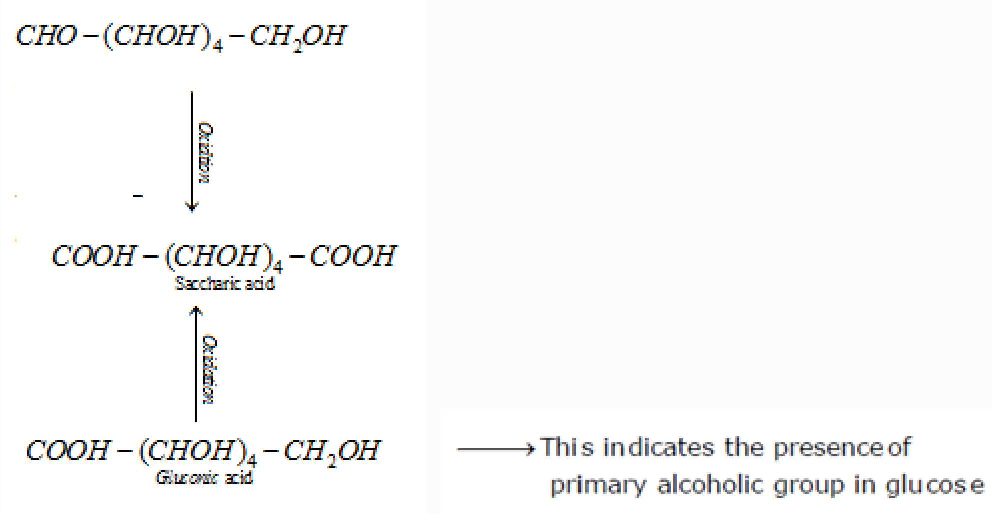
shows that glucose is a reducing sugar (Open chain structure)

e) D – glucose with Tollen's reagent



shows that glucose is a reducing sugar (Open chain structure)

f) D – glucose with nitric acid



This indicates the presence of primary alcoholic group in glucose

g) D – glucose with $(CH_3CO)_2O$ and $ZnCl_2$

$$\text{Glucose} \xrightarrow{5(CH_3CO)_2O/ZnCl_2}$$

$$\underbrace{CHO-(CHOCOCH_3)_4-CH_2OCOCH_3}_{\text{Pentaacetyl glucose}}+5CH_3COOH$$

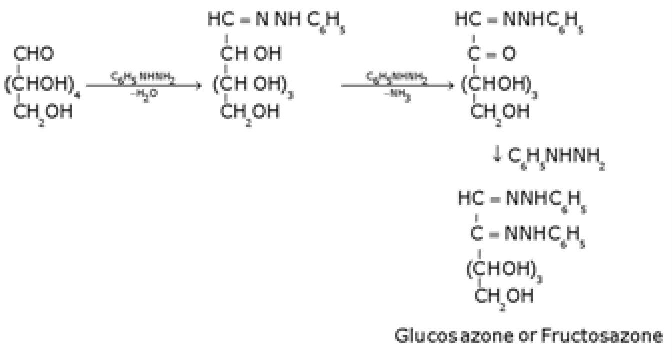
→

shows the presence of 5 -OH groups

h) D – glucose with bromine water

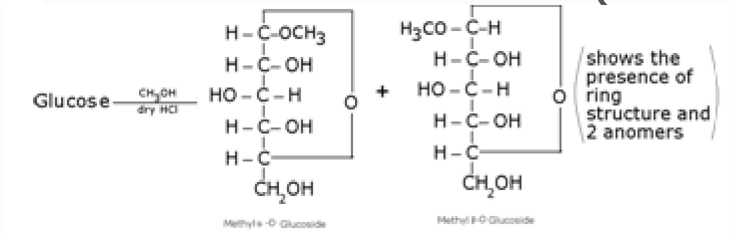
$$CHO-(CHOH)_4-CH_2OH \xrightarrow{Br_2\ \text{water}} \underbrace{COOH-(CHOH)_4-CH_2OH}_{\text{Gluconic acid}}$$

i) Glucose with phenylhydrazine to form osazone



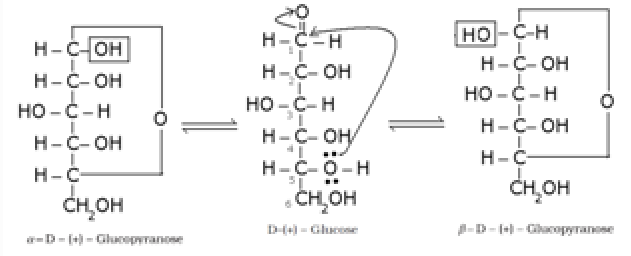
Glucose and fructose gives the same osazone because the reaction takes place at C1 and C2 only.

- **Other Reactions of Glucose (Presence of ring structure)**

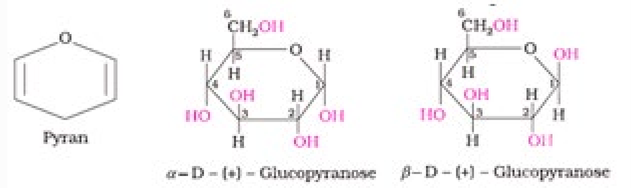


Glucose does not give Schiff's test and does not react with sodium bisulphite and NH3. Pentaacetyl glucose does not react with hydroxyl amine. This shows the absence of –CHO group and hence the presence of ring structure.

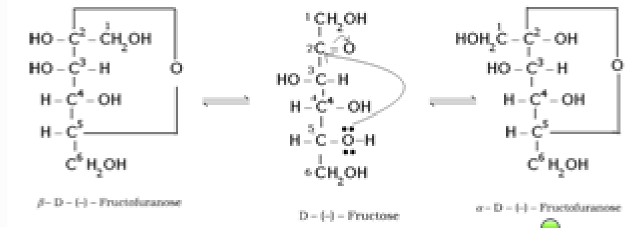
- **Cyclic structure of glucose:**



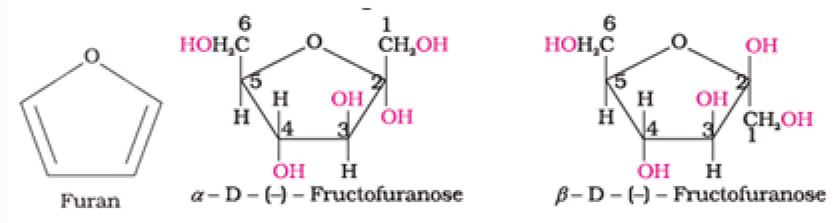
- **Haworth representation of glucose:**



- **Cyclic structure of fructose:**



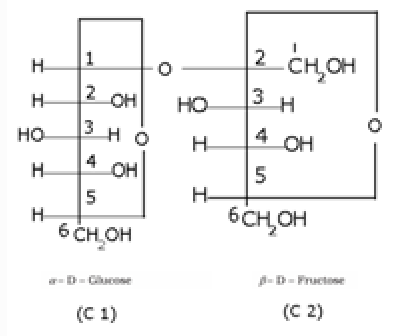
- **Haworth representation of fructose**



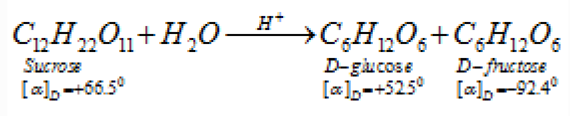
- **Glycosidic linkage:** The oxide linkage formed by the loss of a water molecule when two monosaccharides are joined together through oxygen atom is called glycosidic linkage.

- **Sucrose (invert sugar):**

a) Sucrose is a non-reducing sugar because the two monosaccharide units are held together by a glycosidic linkage between C1 of α-glucose and C2 of β– fructose. Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.

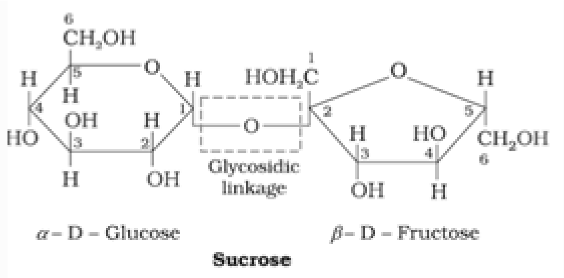


b) Sucrose is dextrorotatory but on hydrolysis it gives dextrorotatory & laevorotatory and the mixture is laevorotatory.



$$\underset{\substack{\text{Sucrose} \\ [\alpha]_D = +66.5^0}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{D\text{–glucose} \\ [\alpha]_D = +52.5^0}}{C_6H_{12}O_6} + \underset{\substack{D\text{–fructose} \\ [\alpha]_D = -92.4^0}}{C_6H_{12}O_6}$$

- **Haworth Projection of Sucrose:**

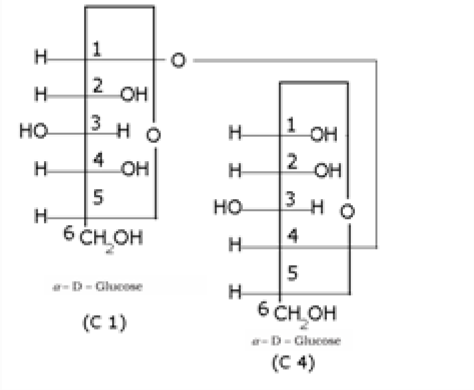


Sucrose

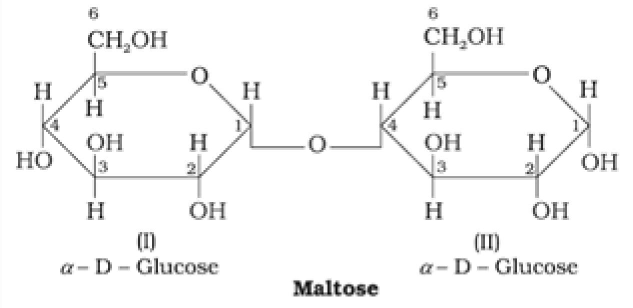
-
-
-
- **.Maltose:**

1. Maltose is composed of two α-D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II).
2. The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.

$$\text{Maltose} \xrightarrow{H_2O} \underset{C1\alpha}{\text{Glucose}} + \underset{C4\alpha}{\text{Glucose}}$$

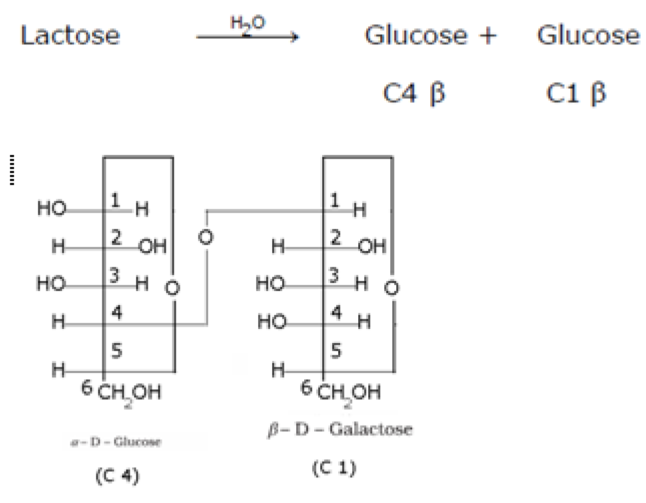


- **Haworth projection of maltose:**

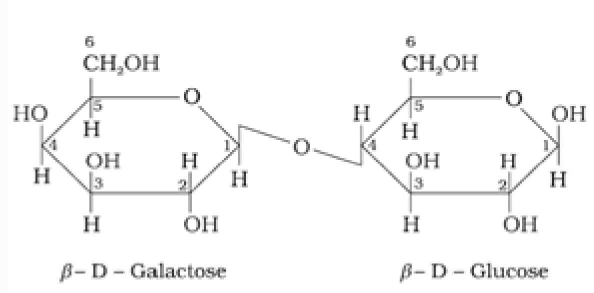


Maltose

- **Lactose (Milk sugar):**It is composed of β-D-galactose and β-D-glucose. The linkage is between C1 of galactose and C4 of glucose. Hence it is also a reducing sugar.



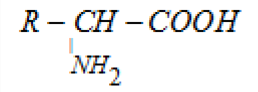
- **Haworth projection of lactose:**



Lactose

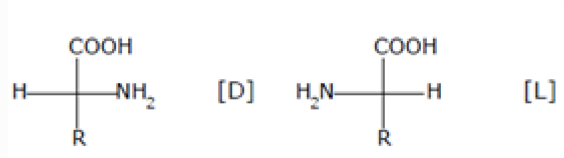
- **Amino acids:**

Amino acids contain amino (–NH2) and carboxyl (–COOH) functional groups.



$$R-\underset{NH_2}{\underset{|}{CH}}-COOH$$

Where R – Any side chain
Most naturally occurring amino acids have L – Config.

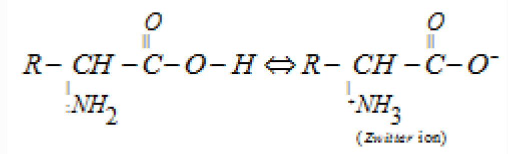


- **Types of amino acids:**

a). **Essential amino acids:** The amino acids which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids. Examples: Valine, Leucine
b). **Non-essential amino acids:** The amino acids, which can be synthesised in the body, are known as non-essential amino acids. Examples: Glycine, Alanine

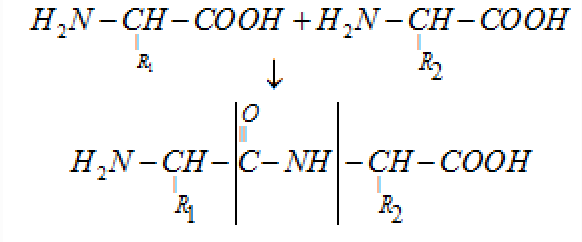
- **Zwitter ion form of amino acids:**

1. Amino acids behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule. In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion. This is neutral but contains both positive and negative charges.
2. In zwitterionic form, amino acids show amphoteric behaviour as they react both with acids and bases.



$$R-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-O-H \Leftrightarrow R-\underset{NH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-O^-$$

- **Isoelectronic point:** The pH at which the dipolar ion exists as neutral ion and does not migrate to either electrode cathode or anode is called isoelectronic point.
- **Proteins:** Proteins are the polymers of α-amino acids and they are connected to each other by peptide bond or peptide linkage. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein.
- **Peptide linkage:** Peptide linkage is an amide linkage formed by condensation reaction between –COOH group of one amino acid and –NH2 group of another amino acid.



$$H_2N-\underset{R_1}{\underset{|}{CH}}-COOH + H_2N-\underset{R_2}{\underset{|}{CH}}-COOH$$
$$\downarrow$$
$$H_2N-\underset{R_1}{\underset{|}{CH}}-\left|\overset{O}{\overset{||}{C}}-NH\right|-\underset{R_2}{\underset{|}{CH}}-COOH$$

Peptide link age

- **Primary structure of proteins:** The sequence of amino acids is said to be the primary structure of a protein.
- **Secondary structure of proteins:** It refers to the shape in which long polypeptide chain can exist. Two different types of structures:

α– Helix:

1. It was given by Linus Pauling in 1951
2. It exists when R- group is large.
3. Right handed screw with the NH group of each amino acid residue H – bonded to – C = O of adjacent turn of the helix.
4. Also known as 3.613 helix since each turn of the helix hasapproximately 3.6 amino acids and a 13 – membered ring is formed by H – bonding.
5. C = O and N – H group of the peptide bonds are trans to each other.
6. Ramchandran angles ($\Phi$and Ψ) – Φangle which $C_\alpha$makes with N – H and Ψangle which C_α makes with C = O.

β– pleated sheet:

1. It exists when R group is small.

2. In this conformation, all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by hydrogen bonds.

- **Tertiary structure of proteins:** It represents the overall folding of the polypeptide chain i.e., further folding of the 2° structure.
- **Types of bonding which stabilize the 3° structure:**

1. Disulphide bridge (-S – S-)
2. H – bonding – (C = O … H – N)
3. Salt bridge (COO– … + NH_3)
4. Hydrophobic interactions

- van der Waals forces

- **Two shapes of proteins:**

Fibrous proteins

a) When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre– like structure is formed.
b) These proteins are generally insoluble in water
c) Examples: keratin (present in hair, wool, silk) and myosin (present in muscles), etc

Globular proteins

a) This structure results when the chains of polypeptides coil around to give a spherical shape.
b) These are usually soluble in water.
c) Examples: Insulin and albumins

- **Quaternary structure of proteins:**

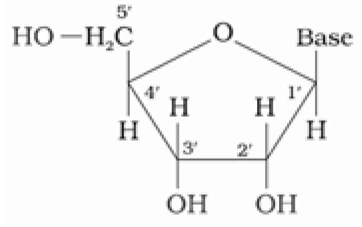
1. Some of the proteins are composed of two or more polypeptide chains referred to as sub-units.
2. The spatial arrangement of these subunits with respect to each other is known as quaternary structure of proteins.

- **Denaturation of proteins:**

1. The loss of biological activity of proteins when a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH. This is called denaturation of protein.
2. Example: coagulation of egg white on boiling, curdling of milk.

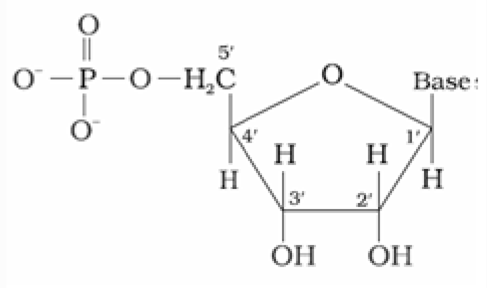
- **Nucleoside:**

1. Base + sugar



- **Nucleotide:**

1. Base + sugar + phosphate group



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- **Nucleic acids (or polynucletides):**

1. Long chain polymers ofnucleotides.
2. Nucleotides are joined by phosphodiester linkage between 5′ and 3′ C atoms of a pentose sugar.

- **Two types of nucleic acids:DNA**

1. It has a double stranded α-helix structure in which two strands are coiled spirally in opposite directions.
2. Sugar present is β–D–2-deoxyribose
3. Bases:
   i) Purine bases: Adenine (A) and Guanine (G)
   ii) Pyrimidine bases: Thymine (T) and cytosine (C)
4. It occurs mainly in the nucleus of the cell.
5. It is responsible for transmission for heredity character.**RNA**

1. It has a single stranded α-helix structure.
2. Sugar present is β–D–ribose
3. Bases:
   i) Purine bases: Adenine (A) and Guanine (G)
   ii) Pyrimidine bases: Uracil (U) and cytosine (C)
4. It occurs mainly in the cytoplasm of the cell.
5. It helps in protein synthesis.

Double helix structure of DNA:

1. It is composed of two right handed helical polynucleotide chains coiled spirally in opposite directions around the same central axis.
2. Two strands are anti-parallel i.e., their phosphodiester linkage runs in opposite directions.
3. Bases are stacked inside the helix in planes $\perp$to the helical axis.
4. Two strands are held together by H – bonds (A = T, G $\equiv$C).
5. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases.

6. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.
7. Diameter of double helix is 2 nm.
8. Double helix repeats at intervals of 3.4 nm. (One complete turn)
9. Total amount of purine (A + G) = Total amount of pyramidine (C + T)

Assertion/Reason type questions

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below.

(e) Both the assertion and reasonis the correct and reason is the correct explanation of assertion.
(f) Both the assertion and reason is the correct and reason is not the correct explanation of assertion.
(g) Assertion is true but reason is false.
(h) Both assertion and reason are false.

1. Assertion: All enzymes found in cells are invariably proteins which catalyse biological reactions.
   Reason: Enzymes act efficiently at a moderate temperature and pH.
   Ans: (b)
2. Assertion: D-glucose is dextrorotatory whereas L-glucose is laevorotatory.
   Reason: D-compounds are alwaysdextrowhereas L-compoundsare always laevorotatory.
   Ans: (b)
3. 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)
4. Assertion: α-Amino acids are the building blocks of proteins.
   Reason: natural amino acids are mostly α-Amino acids.
   Ans: (b)
5. Assertion:Maltose is a reducing sugar which gives two moles of D-glucose on hydrolysis.
   Reason: Maltose has a 1,4-β glycosidic linkage.
   Ans: (c)
6. Assertion: DNA undergoes replication.
   Reason:DNA contains cytosine and thymine as pyrimidine base.
   Ans: (b)
7. Assertion: disruption of natural structure of a protein is called denaturation.
   Reason: the change in colour and appearance of egg during cooking is due to denaturation.
   Ans: (b)

8. Assertion: the two strands in double strand helix structure of DNA are complementary to each other.
   Reason: disulphide bonds are formed between specific pair of bases.
   Ans: (c)
9. Assertion: glucose reacts with hydroxylamine to form an oxime and also adds a molecule of hydrogen cyanide to give cyanohydrin.
   Reason: the carbonyl group is present in the open chain structure of glucose.
   Ans: (a)

TEXT BASED QUESTIONS

1. **Read the passage carefully and answer the following questions**.

Carbohydrates are the polyhydroxy aldehydes and ketones and those compounds which on hydrolysis give such compounds are also carbohydrates. The carbohydrates which are not hydrolysed are called monosaccharides . Other carbohydrates are oligosaccharides and polysaccharides.

Monosaccharides with aldehydic group are called aldoses and those with free ketonic group are called as ketose.

Carbohydrates are optically active

Number of optical isomers are 2^n (where ,n=number of asymmetric carbons.)

carbohydrates are mainly synthesized by plants during photosynthesis.

I. Write the name of two compounds which are not carbohydrates but have the formula $C_x(H_2O)_y$.

Ans: Formaldehyde(CH_2O) and acetic acid($C_2H_4O_2$)

II. Write the name of two compounds which are carbohydrates but not have the formula $C_x(H_2O)_y$.

Ans: Rhamnose($C_6H_{12}O_5$) and deoyribose ($C_5H_{10}O_4$)

III. Which of the following cannot be hydrolysed further?

Glucose,fructose,sucrose , ribose?

Ans: glucose, fructose and ribose.

IV. What do you mean by a disaccharide?

Ans: The carbohydrates which on hydrolysis gives two units of monosaccharide is known as disaccharide. For ex.sucrose is a disaccharide which on hydrolysis give glucose and fructose.

V. What are the functional groups that can be present in monosaccharies?

Ans: monosaccharides have alcoholic groups (primary and secondary) and aldehydic and ketonic groups.

PASSAGE 2

Proteins are polymers of α-amino acids and these are connected by peptide bond. A polyeptide having higher molecular mass and specific structure is called protein.

Structure and shapes of protein can be studied at four levels.These levels are primary,secondary,tertiary and quarternary and each level being more complex than the previous one

a) An example of globular and fibrous proteins respectively is
   - (i) insulin and myosin
   - (ii) Albumin and insulin
   - (iii) keratin and myosin
   - (iv)primary and secondary

   Ans: (b)

b) Proteins are polymers of__________
   - (i)amino acids
   - (ii) nucleic acid
   - (iii) lipids
   - (iv) nucleotides

   Ans: (a)

c) When protein is treated with acid,bases or heated they undergo
   - (i) Denaturation
   - (ii) Change in the secondary structure of protein
   - (iii) Uncoiling
   - (iv) All of the above

   Ans: (a)

d) The two common type of secondary structure of proteins are
   - (i) Essential and non essential amino acids
   - (ii) DNA and RNA
   - (iii) α- helix and β-pleated sheets
   - (iv) dipetide and tripetide.

   Ans: (c)

Multiple choice questions

1. which of the following statement is not true about glucose?
   - a) It is an aldohexose
   - b) On heating with HI it forms n-hexane.
   - c) It is present in furanose structure
   - d) It doesnot give 2,4 DNP test.

   Ans: (c)
2. DNA and RNA contain four bases each. Which of the following bases is not present in RNA?
   - a) Adenine
   - b) Uracil
   - c) Thymine
   - d) Cytosine

   Ans: (c)

3. Proteins are found to have different types of secondary structures namely α-helix and β-pleated structure,α-helix of the protein is stabalised by
   a) Peptide bonds
   b) Vander waals forces
   c) Hydrogen bonds
   d) Dipole- dipole interactions
   Ans: (c)
4. Nucleic acids are the polymers of
   a) Nucleosides
   b) Nucleotides
   c) Bases
   d) Sugars
   Ans: (b)

<u>One mark questions</u>

1. Name the sugar present in milk. How many monosaccharides are γγpresent in it?
   Ans: lactose. Two monosaccharides(glucose and galactose)
2. How will you explain the presence of all six carbon atoms in glucose in a straight chain ?
   Ans: glucose on prolonged heating with HI and red phosphorus gives n-hexane.
3. Name the linkage connecting monosaccharides units in polysaccharides.
   Ans: glycosidic linkage.
4. Which sugar is called as invert sugar? Why is it so?
   Ans: sucrose is called as invert sugar. It is because on hydrolysis it gives D-(+) glucose and D-(-) fructose.
   Sucrose is dextrorotatory but after hydrolysis it gives leavorotatory fructose resulting in the inversion of the configuration.
5. Amino acids can be classified as α,β, γ, δ depending on the relative position of the aminoacids with respect to the carboxyl group. Which type of amino acids form polypeptide chains in protein?
   Ans: alpha amino acids.

<u>Two marks questions</u>

1. Mention one important function of nucleic acids.
   Ans: nucleic acids control the transmission of hereditary characters from one generation to another.
2. Explain the meaning of
   a) A peptide linkage
   b) A glycosidic linkage
      Ans: a) peptide linkage: a peptide linkage is an amide linkage formed between -COOH group of one amino acid and NH_2 of another amino acid by the loss of a molecule of water.

   b)Glycosidic linkage: the two monosaccharides units joined together through an oxide linkage formed by loss of a water molecule.

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