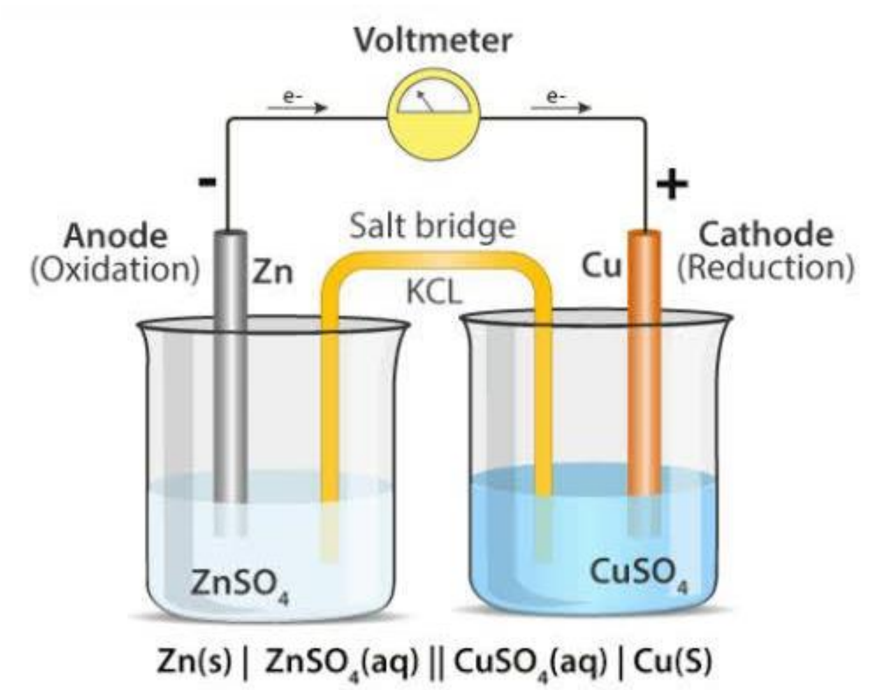
तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन

केन्द्रीय विद्यालय संगठन
KENDRIYA VIDYALAYA SANGATHAN
An autonomous body under MoE, Govt of India

KVS REGIONAL OFFICE JABALPUR

STUDY MATERIAL
CLASS – XII
CHEMISTRY (043)
2024-25



Zn(s) | ZnSO$_4$(aq) || CuSO$_4$(aq) | Cu(S)

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केन्द्रीय विद्यालय संगठन

STUDY MATERIAL
(2024 – 25)
CLASS - XII

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UNDER THE SUPERVISION OF

Sh. AMIT SHRIVASTAV
PRINCIPAL
PM SHRI KENDRIYA VIDYALAYA OF KHAMARIA, JABALPUR

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	MS. POONAM	No 1 Rewa
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	MR SHIVSHANKAR MATE	No. 1 Chhindwara S-1
	Mr. Prajesh Kumar Chourasia	Mandla
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	Ms.Seeta Goutam	Panna
	Ms. Sanjita Chakravarty	Seoni
9	**MS. Manju Nikhare (Group Leader)**	No.II GCF Jabalpur
	MS. NIDHI SINGH	Sidhi
	MS. RACHNA SRIVASTAV	Singrauli
10	**MR. RAMANUJ JHARIA (Group Leader)**	VF Jabalpur (S-1)
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	MR. NIRAJ KALWANI	No. 1 Satna

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CHEMISTRY (Code No. 043)
XI-XII (2024-25)

Rationale Higher Secondary is the most crucial stage of school education because at this juncture specialized discipline based, content -oriented courses are introduced. Students reach this stage after 10 years of general education and opt for Chemistry with a purpose of pursuing their career in basic sciences or professional courses like medicine, engineering, technology and study courses in applied areas of science and technology at tertiary level. Therefore, there is a need to provide learners with sufficient conceptual background of Chemistry, which will make them competent to meet the challenges of academic and professional courses after the senior secondary stage. The new and updated curriculum is based on disciplinary approach with rigour and depth taking care that the syllabus is not heavy and at the same time it is comparable to the international level. The knowledge related to the subject of Chemistry has undergone tremendous changes during the past one decade. Many new areas like synthetic materials, bio -molecules, natural resources, industrial chemistry are coming in a big way and deserve to be an integral part of chemistry syllabus at senior secondary stage. At international level, new formulations and nomenclature of elements and compounds, symbols and units of physical quantities floated by scientific bodies like IUPAC and CGPM are of immense importance and need to be incorporated in the updated syllabus. The revised syllabus takes care of all these aspects. Greater emphasis has been laid on use of new nomenclature, symbols and formulations, teaching of fundamental concepts, application of concepts in chemistry to industry/ technology, logical sequencing of units, removal of obsolete content and repetition, etc.

Objectives : The curriculum of Chemistry at Senior Secondary Stage aims to:

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

- integrate life skills and values in the context of chemistry.

Time : 3 Hours **CLASS XII (2024-25) (THEORY)** **70 Marks**

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

Unit I: Solutions **10 Periods**

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

Unit II: Electrochemistry **12 Periods**

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

Unit III: Chemical Kinetics **10 Periods**

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

Unit IV: d and f Block Elements **12 Periods**

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

Unit V: Coordination Compounds **12 Periods**

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit VI: Haloalkanes and Haloarenes. **10 Periods**

Haloalkanes: Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions. Haloarenes: Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit VII: Alcohols, Phenols and Ethers **10 Periods**

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol. Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophillic substitution reactions, uses of phenols. Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit VIII: Aldehydes, Ketones and Carboxylic Acids **10 Periods**

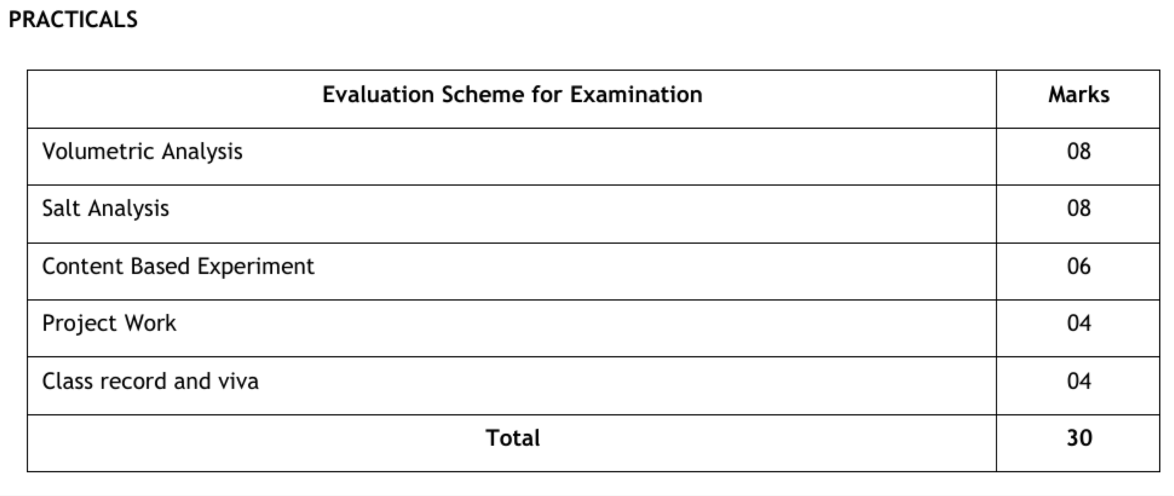
Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses. Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties;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

Unit IX: Amines **10 Periods**

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines. Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit X: Biomolecules **12 Periods**

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.



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**

PRACTICAL SYLLABUS 60Periods

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

A. Surface Chemistry

(a) Preparation of one lyophilic and one lyophobic sol Lyophilic sol - starch, egg albumin and gum Lyophobic sol - aluminium hydroxide, ferric hydroxide, arsenous sulphide.

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

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

B. Chemical Kinetics

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

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

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

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

C. Thermochemistry

Any one of the following experiments

i) Enthalpy of dissolution of Copper Sulphate or Potassium Nitrate.

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

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

D. Electrochemistry

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

E. Chromatography

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

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

F. Preparation of Inorganic Compounds

Preparation of double salt of Ferrous Ammonium Sulphate or Potash Alum.

Preparation of Potassium Ferric Oxalate.

G. Preparation of Organic Compounds P

reparation of any one of the following compounds

i) Acetanilide

ii) Di -benzalAcetone

iii) p-Nitroacetanilide

iv) Aniline yellow or 2 - Naphthol Anilinedye.

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

Unsaturation, alcoholic, phenolic, aldehydic, ketonic, carboxylic and amino (Primary) groups.
I. Characteristic tests of carbohydrates, fats and proteins in pure samples and their detection in given

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

i) Oxalic acid,

ii) Ferrous Ammonium Sulphate (Students will be required to prepare standard solutions by weighing themselves).

K. Qualitative analysis

Determination of one cation and one anion in a given salt. Cation : Pb2+, Cu2+ As3+, Aℓ3+, Fe3+, Mn2+, Zn2+, Cu2+, Ni2+, Ca2+, Sr2+, Ba2+, Mg2+, NH4+ Anions: (CO3)2-, S2-, (SO3)2-, (NO2)-, (SO4)2-, Cℓ-, Br-, I-, PO3-4, (C2O4)2-, CH3COO-,NO3-

(Note: Insoluble salts excluded)

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

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

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

CHEMISTRY (Code No. 043) QUESTION PAPER DESIGN CLASSES –XI and XII 2024-25

S	Domains	Total Marks	%
1	**Remembering and Understanding:** Exhibit memory of previously learned material by recalling facts, terms, basic concepts and answers. Demonstrate understanding of facts and ideas by organizing, comparing, translating, interpreting, giving descriptions and stating main ideas.	28	40
2	**Applying:** Solve problems to new situations by applying acquired knowledge, facts, techniques and rules in a different way.	21	30
3	**Analysing, Evaluating and Creating:** Examine and break information into parts by identifying motives or causes. Make inferences and find evidence to support generalizations. Present and defend opinions by making judgments about information, validity of ideas or quality of work based on a set of criteria. Compile information together in a different way by combining elements in a new pattern or proposing alternative solutions.	21	30

KENDRIYA VIDYALAYA SANGATHAN, JABALPUR REGION

CLASS- XII

CHEMISTRY (043)

CHAPTER NAME : SOLUTIONS

PREPARED BY: GROUP I MEMBERS

IMPORTANT POINTS/ NOTES ON TIP:

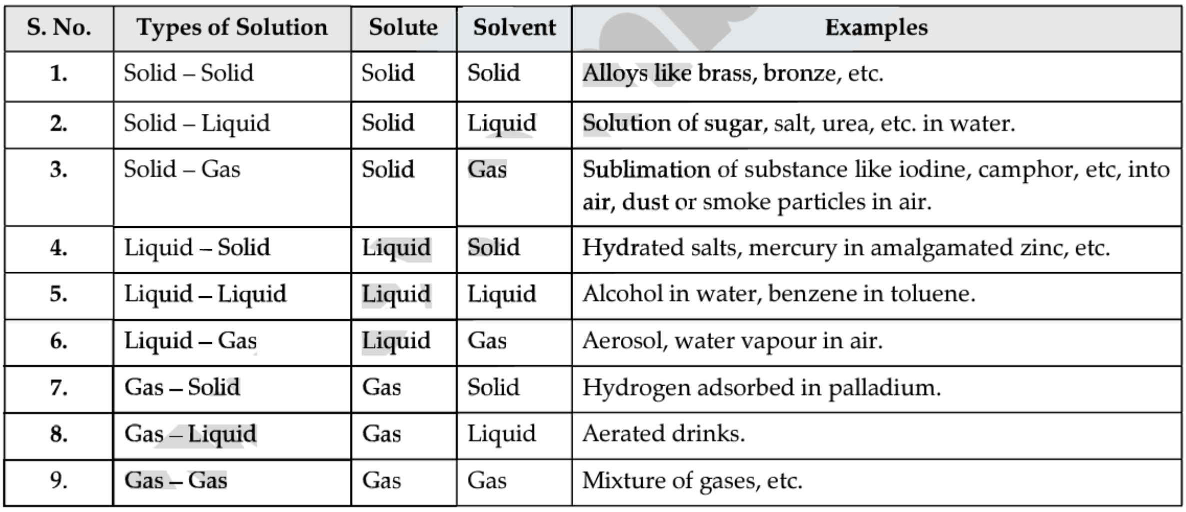
SOLUTIONS

- Solution is a homogeneous mixture of two or more pure substances.
- Constituents of a solution:

(i) Solute = Dissolved in smaller quantity. e.g., sugar, salt, etc.

(ii) Solvent = Dissolved in larger quantity. e.g., water, milk, etc.

- Types of solutions:



S. No.	Types of Solution	Solute	Solvent	Examples
1.	Solid – Solid	Solid	Solid	Alloys like brass, bronze, etc.
2.	Solid – Liquid	Solid	Liquid	Solution of sugar, salt, urea, etc. in water.
3.	Solid – Gas	Solid	Gas	Sublimation of substance like iodine, camphor, etc, into air, dust or smoke particles in air.
4.	Liquid – Solid	Liquid	Solid	Hydrated salts, mercury in amalgamated zinc, etc.
5.	Liquid – Liquid	Liquid	Liquid	Alcohol in water, benzene in toluene.
6.	Liquid – Gas	Liquid	Gas	Aerosol, water vapour in air.
7.	Gas – Solid	Gas	Solid	Hydrogen adsorbed in palladium.
8.	Gas – Liquid	Gas	Liquid	Aerated drinks.
9.	Gas – Gas	Gas	Gas	Mixture of gases, etc.

- Solubility is the maximum amount of solute that can be dissolved in 100 g solvent to form a saturated solution at a given temperature.
- Causes: Interionic attraction in the solute molecules, intermolecular attraction between solvent molecules, solvation and temperature.
- Factors affecting solubility: Nature of solute and solvent, temperature, hydration energy and pressure.
-

$$\textbf{Mass percentage}\left(\frac{w}{W}\right)=\frac{\text{Mass of solute present in the solution}}{\text{Total mass of the solution}}\times 100$$

$$\textbf{Volume percentage}\left(\frac{v}{V}\right)=\frac{\text{Volume of solute}}{\text{Total volume of the solution}}\times 100$$

$$\textbf{Mass by volume percentage of solute}\left(\frac{w}{V}\right)=\frac{\text{Mass of solute}}{\text{Volume of solution}}\times 100$$

-

$$\textbf{Parts per million (ppm)}=\frac{\text{Number of parts of component (A)}}{\text{Total number of parts of all components of the solution}}\times 10^6$$

-

Mole fraction:

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

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

$$\chi_A+\chi_B=1$$

- Molarity (M): Number of moles of solute per litre of solution.
-

$$M=\frac{\text{Number of moles of solute}}{\text{Volume of solution (in Litre)}}=\frac{W_B\times 1000}{M_B\times V}=\frac{n_B}{V}$$

where WB is weight of solute, V is volume of solution, MB is molar mass of solute and nB is number of moles of solute.

Unit: mol L–1 or M (molar).

-

$$\textbf{Molality }(m)=\frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}=\frac{W_B\times 1000}{W\times W_A}=\frac{n}{W}$$

where W_A is weight of solvent, W_B is quantity of solute, W is molar mass of solute.

- **Unit:** mol kg^{-1} or m (molal)

$$\textbf{Normality (N)}=\frac{\text{Number of gram equivalent of solute}}{\text{Volume of solution in Litre}}=\frac{W_B\times 1000}{E_B\times V}$$

where W_B is mass of solute, E_B is equivalent weight of solute and V is volume of solution.

- **Unit:** eq/L or N.

Relationship between Molarity (M) and Molality (*m*):

$$m = \frac{1000\,\mathrm{M}}{1000\mathrm{d} - \mathrm{M} \times \mathrm{M_B}}$$

Relationship between mole fraction of solute (χ_B) and molality (*m*):

$$m = \frac{\chi_B \times 1000}{\chi_A \times M_A}$$

Relationship between molarity and density:

$$\text{Molarity (M)} = \frac{\%\ \text{Strength} \times \text{Density} \times 10}{\mathrm{M_B}}$$

Relationship between normality and density:

$$\text{Normality (N)} = \frac{\%\ \text{Strength} \times \text{Density} \times 10}{\text{Equivalent mass of solute}}$$

- Henry's law: "The mass of a gas dissolved in a given volume of the liquid at a constant temperature depends upon the pressure applied."

  $p = k_H\, x$, where k_H = Henry's constant.

- Vapour pressure is the pressure exerted by vapours of a liquid at equilibrium state at constant temperature.
- Raoult's law for non-volatile solute states that relative lowering of vapour pressure for a solution is equal to the mole fraction of solute.

$$\chi_B = \frac{p^\circ_A - p_A}{p^\circ_A}$$

- Raoult's law for non-volatile solute states that relative lowering of vapour pressure for a solution is equal to the mole fraction of solute.

$$\chi_B = \frac{p^\circ_A - p_A}{p^\circ_A}$$

- Ideal solutions obey Raoult's law.

(i) $p_A = p_A{}^0 x_A$; $p_B = p_B{}^0 x_B$

(ii) $\Delta_{mix}H = 0$

(iii) $\Delta_{mix}V = 0$

(iv) The force of attraction between A–A and B–B is nearly equal to A–B. Ex. n hexane and n heptane, bromoethane and chloroethane, benzene and toluene

- Non-ideal solutions do not obey Raoult's law.

(i) $p_A \neq p_A{}^0 x_A$; $p_B \neq p_B{}^0 x_B$

(ii) $\Delta_{mix}H \neq 0$

(iii)$\Delta_{mix}V \neq 0$

(iv) The force of attraction between A–A and B–B is not equal to A–B.

- Positive deviation from Raoult's law: A–B interactions are weaker than the interactions between A–A or B–B leading to an increase in vapour pressure. Ex. ethanol and acetone, carbon disulphide and acetone.
- Negative deviation from Raoult's law: A–B interactions are stronger than the interactions between A–A or B–B leading to decrease in vapour pressure. Ex. phenol and aniline, chloroform and acetone.
- Azeotropes are liquid mixtures which distil over without change in composition.

(i) Maximum boiling azeotropes : Large negative deviation from Raoult's law. Ex. ethanol-water mixture.

(ii) Minimum boiling azeotropes : Large positive deviation from Raoult's law. Ex. 68% nitric acid and 32% water by mass.

- Colligative properties Number of particles in the the solute (molecule or ions) in definite volume of the solvent.

Relative lowering of vapour pressure:

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

-

Elevation of boiling point:

$$\Delta T_b = K_b \times m$$

or, $$\Delta T_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

or, $$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$

-

Depression of freezing point:

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

or, $$\Delta T_f = K_f \times \frac{W_{\text{solute}}}{M_{\text{solute}}} \times \frac{1000}{W_{\text{solvent}}}$$

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

-

Osmotic pressure:

$$\pi = CRT$$

or, $$\pi = \frac{\text{Number of moles of solute}}{\text{Volume of solution}} \times R \times T$$

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

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

- Osmosis is the process in which, there is net flow of solvent from the solution of lower concentration to the higher concentration by a semipermeable membrane.
- Osmotic pressure is the extra pressure that is applied to just stop the flow of solvent to solution across a semipermeable membrane.
- Abnormal molecular mass: Molecular mass calculated with the help of colligative property which is different from theoretical molecular mass.

$$\text{van't Hoff factor } (i) = \frac{\text{Observed (experimental) value of a colligative property}}{\text{Normal (calculated) value of the same colligative property}}$$

$$i = \frac{\Delta_{obs}}{\Delta_{cal}} \qquad i = \frac{M_{cal}}{M_{obs}}$$

Degree of association, $$\alpha = \frac{i-1}{1-\frac{1}{n}}$$

where i is van't Hoff factor and n is number of ions produced per formula of the compound.

Degree of dissociation, $$\alpha = \frac{i-1}{n-1}$$

where i is van't Hoff factor and n is number of ions produced per formula of the compound.

QUESTION BANK

SECTION-A The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.		
1	***1.What is the mole fraction of ethylene glycol in a solution containing 20g by mass?*** ***(a) 0.022 (b) 0.054 (c) 0.068 (d) 0.090***	[1]
2	***Which of the following is useful in relating concentration of solution with its vapour pressure?*** ***(a) Mole fraction (b) Parts per million*** ***(c) Mass percentage (d) Molality***	[1]
3	***Low concentration of oxygen in the blood and tissues of people living at high altitude is due to*** ***(a) low temperature*** ***(b) low atmospheric pressure*** ***(c) high atmospheric pressure*** ***(d) both low temperature and high atmospheric pressure***	[1]
4	***Which of the following statement is false?*** ***(a) Two different solutions of sucrose of same molality-prepared in different solvents will have the same depression in freezing point.*** ***(b) The osmotic pressure of a solution is given by the equation 3.14(pi) = CRT (where C is the molarity of the solution).*** ***(c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of barium chloride, potassium chloride, acetic acid and sucrose is*** ***BaCl2> KCl > CH2COOH > sucrose*** ***(d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.***	[1]

5	***The value of Henry's constant KH 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***	**[1]**
6	**What is the molarity of 20% (w/v) H2SO4 solution?** **a) 0.51 M** **b) 1.02 M** **c) 4.08 M** **d) 2.04 M**	**[1]**
7	**If a mixture of A and B boils at a temperature lower than the boiling point of either of the components, what kind of deviation does the mixture show?** **a) No deviation** **b) Maximum and minimum deviation from Raoult's law** **c) Negative deviation from Raoult's law** **d) Positive deviation from Raoult's law**	**[1]**
8	**What deviation is shown by a mixture of equimolar phenol and aniline?** **a) Negative deviation** **b) Positive deviation** **c) No deviation** **d) Alternating positive and negative**	**[1]**
9	**What are colligative properties useful for?** **a) Determining boiling and melting temperature** **b) Determining molar mass** **c) Determining equivalent weight** **d) Determining van't Hoff factor**	**[1]**
10	**What is a necessary condition for osmosis to take place?** **a) Semi-permeable membrane**	**[1]**

	b) Same concentration of solvent **c) High temperature** **d) Pressure greater than osmotic pressure**	
	In the following questions (Q. No. 11 - 20) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	Assertion (A): Molarity of a solution in liquid state changes with temperature. Reason (R): The volume of a solution changes with change in temperature.	**[1]**
12	Assertion: The concentration of pollutants in water or atmosphere is often expressed in terms of ppm Reason :Concentration in parts per million can be expressed as mass to mass, volume of volume and mass to volume .	**[1]**
13	Assertion: One molar aqueous solution is more concentrated than that of 1 molal aqueous solution . Reason : Molarity is a function of temperature as volume depends on temperature.	**[1]**
14	Assertion:Pressure does not have any effect on solubility of solids in liquids. Reason : Solids and liquids are highly incompressible	**[1]**
15	Assertion:In an ideal solution , ΔmixH is zero Reason :In an ideal solution , A-B interactions are lower than A-A and B-B interactions.	**[1]**
16	Assertion: A solution of phenol and aniline will show negative deviations from Raoult's law Reason : In case of negative deviations from Raoult's law , A-B forces are stronger than A-A and B-B forces .	**[1]**
17	Assertion:Osmosis does not take place in two isotonic solutions separated by semipermeable membrane. Reason : Isotonic solutions have same osmotic pressure	**[1]**

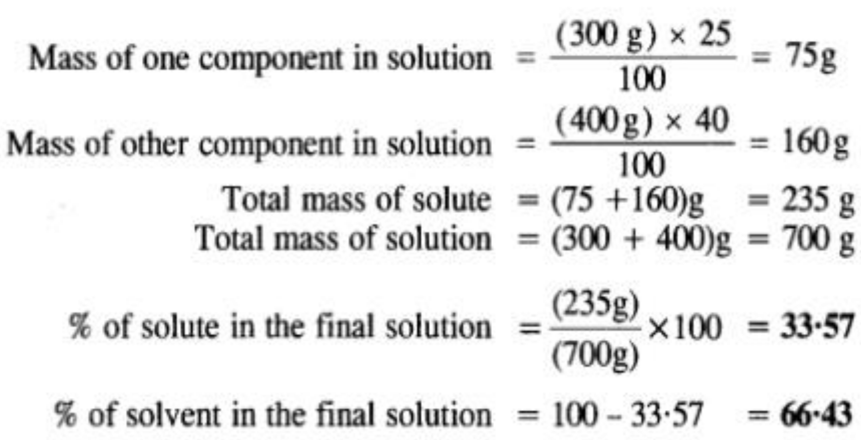
18	Assertion: 1 M solution of KCl has greater osmotic pressure than 1 M solution of glucose at the same temperature Reason :In solution KCl dissociates to produce more number of particles .	**[1]**
19	Assertion:Molecular mass of KCl calculated on the basis of colligative properties will be lower than the normal molecular mass. Reason : Experimentally determined molar mass of always lower than the true value.	**[1]**
20	Assertion:Amalgam of mercury with sodium is an example of solid solutions . Reason:Mercury is solvent and sodium is solute in the solution	**[1]**

ANSWER KEY:

1	**c**	**2**	**a**	**3**	**B**	**4**	**a**	**5**	**b**
6	**d**	**7**	**d**	**8**	**A**	**9**	**b**	**10**	**a**
11	**a**	**12**	**b**	**13**	**B**	**14**	**a**	**15**	**c**
16	**a**	**17**	**a**	**18**	**A**	**19**	**c**	**20**	**c**

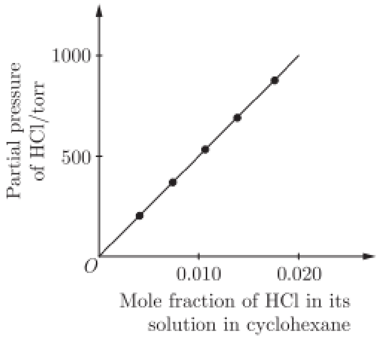
	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	***Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.***	**[2]**
ANS.	***NaCl is a non-volatile solute, therefore, addition of NaCl to water lowers the vapour pressure of water. As a result boiling point of water increases. On the other hand, methyl alcohol is more volatile than water, therefore its addition increases the total vapour pressure over the solution. As a result, boiling point of water decreases.***	
22	***Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride***	**[2]**
ANS.	***30% by mass of C6H6 in CCl4 = 30 g C6H6 in 100 g solution***	

	∴ no. of moles of C6H6 = 30/78 = 0.385 $(\text{molar mass of } C_6H_6 = 78\text{g})$ no. of moles of $CCl_4\ (n_{CCl_4}) = \frac{70}{154} = 0.455$ $\cdot\ x_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{CCl_4}}$ $= \frac{0.385}{0.385 + 0.455} = \frac{0.385}{0.84} = 0.458$ $x_{CCl_4} = 1 - 0.458 = 0.542$	
23	(a)***.Why are aquatic species more comfortable in cold water in comparison to warm water?*** (b)***How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Explain the phenomenon involved in the process.***	**[2]**
ANS.	(a) ***At a given pressure the solubility of oxygen in water increases with decrease in temperature. Thus presence of more oxygen at lower temperature makes the aquatic species more comfortable in cold water.*** (b)***When salt is spread over snow covered roads, it lowers the freezing point of water to such an extent that water does not freeze to form ice. As a result, the snow starts melting.***	
24	***Why is it not possible to obtain pure ethanol by fractional distillation? What general name is given to binary mixtures which show deviation from Raoult's law and whose components cannot be separated by fractional distillation? How many types of such mixtures are there?***	**[2]**
ANS.	***The solution or mixture having the same composition in liquid as well as in vapour phase and boils at a constant temperature is known as azeotropes. Due to constant composition it cannot be separated by fractional distillation. There are two types of azeotropes*** ***(i) Minimum boiling azeotropes: Solution which shows large positive deviation from Raoult's law form minimum boiling azeotropes at a specific composition, e.g., ethanol-water mixture*** ***(ii) Maximum boiling azeotropes: Solutions which show large negative deviation from Raoult's law form maximum boiling azeotropes, e.g., solution having composition 68% HN03 and 32% water by mass.***	

25	**Define the following terms:** **(i) Mole fraction** **(ii) Molality**	**[2]**
ANS.	**(i) Mole fraction:** It is defined as the ratio of the number of moles of the solute to the total number of moles in the solution. **(ii) Molality:** It is defined as the number of moles of a solute present in 1000g (1kg) of a solvent.	
	SECTION C The following questions are short answer type and carry 3 marks each.	
26	***Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 g of a 25% and 400 g of a 40% solution by mass.***	**[3]**
ANS.	 Mass of one component in solution $= \frac{(300\text{ g}) \times 25}{100} = 75\text{g}$ Mass of other component in solution $= \frac{(400\text{g}) \times 40}{100} = 160\text{g}$ Total mass of solute $= (75 + 160)\text{g} = 235\text{ g}$ Total mass of solution $= (300 + 400)\text{g} = 700\text{ g}$ % of solute in the final solution $= \frac{(235\text{g})}{(700\text{g})} \times 100 = \mathbf{33{\cdot}57}$ % of solvent in the final solution $= 100 - 33{\cdot}57 = \mathbf{66{\cdot}43}$	
27	***A 4% solution (w/w) of sucrose (M = 342 g mol–1) in water has a freezing of*** ***271.15 K. Calculate the freezing point of 5% glucose (M = 108 g mol–1) in*** ***water.***	**[3]**
ANS.	***(Given: Freezing point of pure water = 273.15 K)*** ***Mass of sucrose (WB)=4 g*** ***Mass of water (WA)=100−4=96g*** ***MB=342*** ***ΔTf=273.15−271.5=2K*** ***Kf= ΔTf×MB×WA/WB×1000*** ***Kf=2×342× 96/4×1000=16.41*** ***Now, for solution of glucose***	

	Mass of glucose (WB)= 5g ***Mass of water (WA) =100 -5 =95g*** ***MB=180gmol-1*** $\Delta Tf = Kf \times WB \times 1000/MB \times WA = 16.416 \times 5 \times 1000/180 \times 95 = 4.8K$ $\Delta Tf = T^{\circ}f - Tf = 4.8 = 273.15 - Tf$ $Tf = 273.15 - 4.8 = 268.35K$	
28	***Calculate the freezing point of a solution containing 60gms of glucose in 250gms of water Kf for water=1.86Kkgmol-1***	**[3]**
ANS.	***The number of moles of glucose = Mass of glucose/Molecular weight of glucose*** ***= 60 /180*** ***=0.333 mol*** ***The molality of glucose solution = Number of moles of glucose / Mass of solvent (in kg)*** ***= 0.333 molx1000 /250*** ***=1.333 mol/kg*** ***The depression in the freezing point of glucose solution :ΔT f= Kfm*** ***=1.86K kg /mol×1.333 mol/kg=2.48 K*** ***The freezing point of pure water is 273.15K*** ***The freezing point of glucose solution = Tof - ΔT f*** ***=273.15−2.48*** ***=270.67 K***	
29	(a) Explain the following phenomena with the help of Henry’s law. (i) A painful condition known as bends. (ii) Feeling of weakness and discomfort in breathing at high altitude. (b) Why soda water bottle kept at room temperature fizzes on opening?	**[3]**
ANS.	(i) Bends is a condition that occurs to sea drivers or scuba drivers. They have to breathe air under high pressure underwater. Nitrogen gas is not soluble at normal pressure. In underwaters, they dissolve in the blood. Once the divers come up to the surface, the gases escape the blood by forming bubbles of N2 in blood. These bubbles can block capillaries and obstruct the flow of O2, which forms the painful condition of bends.	

	(ii) At higher altitudes, atmospheric pressure is low and it reduces the solubility of oxygen in blood and tissues of people travelling or living at high altitudes. The lack of oxygen causes weakness and unable to think properly, a condition known as anoxia. (iii) When a soda water bottle is opened at room temperature and normal pressure conditions, the pressure inside the bottle reduces and solubility of CO2 reduces, thus causing the gas bubbles to escape and soda water fizzing.	
30.	**An aqueous solution of 2 percent non-volatile solute exerts a pressure of 1·004 bar at the boiling point of the solvent. What is the molecular mass of the solute ?**	
ANS.	According to Raoult's Law, $\frac{P_A^\circ - P_S}{P_S} = \frac{n_B}{n_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$ P_A° (for water) $= 1{\cdot}013$ bar ; $P_S = 1{\cdot}004$ bar ; $W_B = 2\text{g}$; $W_A = 100 - 2 = 98\text{ g}$; $M_A = 18\text{ g mol}^{-1}$. $\frac{(1{\cdot}013 - 1{\cdot}004)\text{ bar}}{(1{\cdot}004\text{ bar})} = \frac{(2\text{ g}) \times (18\text{ g mol}^{-1})}{M_B \times (98\text{ g})}$ $\therefore \quad M_B = \frac{(2\text{ g}) \times (18\text{ g mol}^{-1}) \times (1{\cdot}004\text{ bar})}{(0{\cdot}009\text{ bar}) \times (98\text{ g})} = \mathbf{41{\cdot}0\text{ g mol}^{-1}}$	
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	Solution which obey's Raoult's law at every range of concentration are called ideal solution which do not show any deviation while those solution which do not obey's Raoult's law are called non-ideal solution. Non-ideal solution show two types of deviation from Raoult's law called positive and negative deviation. Azeotropes are the mixture of liquids which boils at constant temperature like a pure liquid and possess same composition of components in liquid as well as in vapour phase. Azeotropes arises due to very large deviation from Rault's law.	**[4]**
31.1	Azeotropic mixture distils without any change in composition. Why ?	
ANS.	Azeotropic mixtures are constant boiling mixture and cannot distils without any Change in composition.	
31.2	(ii) Give two examples of non-ideal solution showing negative deviation.	

ANS.	(a) Chloroform and acetone. (b) Chloroform and benzene.	
31.3	(iii) Two liquid ‘P’ and ‘Q’ are mixed and the resulting solution becomes colder. What do you conclude about deviation from Raoult’s law ? (iv) Give mathematical expression of Raoult’s law for non-volatile solute in volatile solvent	
ANS.	The solution show positive deviation from Raoult’s law. $\frac{P^o{}_A - P_s}{P^o{}_A} = x_B$	
	OR	
31.3	Write the expression for the pressure of non ideal solution with positive and negative deviations.	
ANS.	$Ps > x_A P_A^\circ + x_B P_B^\circ$ Positive deviations $Ps < x_A P_A^\circ + x_B P_B^\circ$ Negative deviations.	
32	Many gases dissolve in water, Oxygen dissolves only to small extent which sustains all aquatic life. NH3 and HCl are highly soluble in water. Solubility of gases increases with increase in pressure and decreases with increase in temperature.  Henry’s law states “The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas in the solution. p Kx = H .” Where, KH is Henry’s law constant. If we draw a graph between partial pressure of the gas versus mole fraction of gas in solution, then we will get straight line as shown in graph. Different gases have different KH values of the same temperature. This suggests, KH is a function of nature of gas. Answer the following questions :	**[4]**
32.1	**What is significance of K_H ?**	
ANS.	**Higher the value of KH , lower will be solubility of gas**	
32.2	**What is slope of the line given in the graph?**	
ANS.	**Slope of line = K_H (Henry’s law constant).**	

32.3	**(i) Why does solubility of gas in liquid decreases with increase solution in cyclohexane in temperature? (ii) Why are cold drinks filled with CO2 at high pressure?**	
ANS.	**(i) K_H increases with increase in temperature, therefore, solubility decreases. (ii) It is because solubility of CO_2 in cold drink increases with increase in pressure.**	
	OR	
32.3	**(i) What is cause of anoxia at high altitude? (ii) Why do scuba divers take air diluted with helium?**	
ANS.	**(i) Low concentration of oxygen in blood and tissues at higher altitude causes people weak and unable to think clearly due to anoxia. (ii) To avoid bends (pains) as well as the toxic effect of high concentration of N_2 in blood as N_2 is more soluble in blood than Helium.**	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	**19.5g of CH2FCOOH is dissolved in 500g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van's Hoff factor and dissociation constant of fluoroacetic acid.**	**[5]**
ANS.	Given, w1 = 500 g = 0.5 kg, w2 = 19.5 g, Kf = 1.86 K kg mol-1, ΔTf = 1 K Molar mass of CH2FCOOH (M2) = 2 × 12 + 3 × 1 + 1 × 19 + 2 × 16 = 24 + 3 + 19 + 32 = 78 g mol-1 ΔTf = i Kf m	

$$i = \frac{\Delta T_f}{K_f m} \quad \text{...(i)}$$

$$m = \frac{w_2}{M_2 \times w_1}$$

$$= \frac{19.5\text{ g}}{(78\text{ g mol}^{-1}) \times (0.5\text{ kg})}$$

$$= 0.5\ \text{mol kg}^{-1} \quad \text{...(ii)}$$

From eq. (i), we get

$$i = \frac{1}{(1.86\text{ K kg mol}^{-1}) \times (0.5\text{ mol kg}^{-1})}$$

$$= 1.0753$$

Calculation of dissociation constant, K_a

Let α be the degree of dissociation of CH_2FCOOH then

$$CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$$

	CH_2FCOOH	CH_2FCOO^-	H^+
Initial conc.	C mol L^{-1}	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Total = $C(1+\alpha)$

$$\therefore \quad i = \frac{C(1+\alpha)}{C}$$

$$\Rightarrow \quad i = 1 + \alpha$$

$$\Rightarrow \quad \alpha = i - 1$$

$$= 1.0753 - 1$$

$$= 0.0753$$

Now, $$K_a = \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]}$$

$$= \frac{C\alpha . C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha}$$

	Taking the volume of the solution as 500 mL, we have the concentration : $C = \frac{\frac{19.5}{78}}{500} \times 1000\ \text{M}$ $= 0.5\ \text{M}$ Therefore, $K_a = \frac{C\alpha^2}{1-\alpha}$ $= \frac{0.5 \times (0.0753)^2}{1 - 0.0753}$ $= \frac{0.5 \times 0.00567}{0.9247}$ $= 0.00307$ $= 3.07 \times 10^{-3}$	
34	**(a)State Henry's law and mention some of its important applications.** **(b)Henry's law constant for the solubility of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.**	**[5]**
ANS.	**(a)The partial pressure of a gas in vapour phase is proportional to the mole fraction of the gas (x) in the solution. $p = K_H x$** **Applications of Henry's law :** **(i) In order to increase the solubility of CO2 gas in soft drinks and soda water, the bottles are normally sealed under high pressure. Increase in pressure increases the solubility of a gas in a solvent according to Henry's Law.** **(ii) As the partial pressure of oxygen in air is high, in lungs it combines with haemoglobin to form oxyhaemoglobin. In tissues, the partial pressure of oxygen is comparatively low. Therefore, oxyhaemoglobin releases oxygen in order to carry out cellular activities.** **(b)** Here, p = 760 mm Hg, $K_H = 4.27 \times 10^5$ mm Hg (at 298 K) According to Henry's law, $p = K_H \chi$ $\chi = \frac{p}{k_H}$ $= \frac{760\ \text{mmHg}}{4.27 \times 10^5\ \text{mmHg}}$ $= 177.99 \times 10^{-5}$ $= 178 \times 10^{-5}$ Hence, the mole fraction of methane in benzene is 178×10^{-5}.	

35	**Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80g of benzene is mixed with 100g of toluene.**	**[5]**
ANS.	Molar mass of benzene (C_6H_6) = 6 × 12 + 6 × 1 = 78g mol^{-1} Molar mass of toluene ($C_6H_5CH_3$) = 7 × 12 + 8 × 1 = 92 g mol^{-1} No. of moles present in 80 g of benzene = $\frac{80}{78}$ mol = 1.026 mol No. of moles present in 100 g of toluene = $\frac{100}{92}$ mol = 1.087 mol Mole fraction of benzene, x_{C6H6}, = $\frac{1.026}{1.026+1.087}$ = 0.486 ∴ Mole fraction of toluene,$x_{C6H5CH3}$5013 = 1 − 0.486 = 0.514 It is given that vapour pressure of pure benzene, $p^0_{C_6H_6}$ = 50.71 mm Hg Vapour pressure of pure toluene, $p^0_{C_6H_5CH_3}$ = 32.06 mm Hg Therefore, partial vapour pressure of benzene, $P_{total} = x_{C6H6} \times p^0_{C_6H_6}$ = 0.486 × 50.71 = 24.645 mm Hg Partial vapour pressure of toluene, $P_{C6H5CH3} = x_{C6H5CH3} \times P^0_{C_6H_5CH_3}$ = 0.514 × 32.06 = 16.479 mm Hg Total vapour pressure of solution (p) = 24.645 + 16.479 = 41.124 mm Hg Mole fraction of benzene in vapour phase = $\frac{x_{C_6H_6} \times p^0_{C_6H_6}}{p_{total}}$ = $\frac{0.486 \times (50.71)mm}{(41.124)mm}$ = 0.599 ≅ 0.6	

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KENDRIYA VIDYALAYA SANGATHAN, JABALPUR REGION

CLASS- XII / XI

CHEMISTRY (043)

CHAPTER NAME: ELECTROCHEMISTRY

PREPARED BY: GROUP II MEMBERS

IMPORTANT POINTS/ NOTES ON TIP:

- **(IN FORM OF SHORT NOTES KINDLY INCLUDE GRAPHS, FORMULAS, FLOW CHARTS, DIAGRAM ALSO AS PER REQUIREMENTS OF CHAPTER)**
- Electrode For the electric current to pass through an electrolytic conductor, the two rods or plates called electrodes are always needed. These plates are connected to the terminals of the battery to form a cell. The electrode through which the electric current flows into the electrolytic solution is called the anode, also called the positive electrode, and anions are oxidised here.

An electrode through which the electric current flows out of the electrolytic solution is called the cathode, also called the negative electrode, and cations are reduced there.

Electrolysis - Electrolysis is the process of chemical deposition of the electrolyte by passing an electric current. Electrolysis takes place in an electrolytic cell. This cell will convert the electrical energy to chemical energy.

The product of electrolysis will depend on the following factors:

(i) The nature of the electrolyte

(ii) The nature of the electrodes

(iii) The concentration of the ions in the substance

(iv) The amount of current passed

Faraday's laws of electrolysis – First law

The amount of ion oxidised or reduced at either electrode during the passage of current is proportional to the quantity of electricity passed.

$w \propto Q$ or $w \propto (I \times t)$

$w = ZIt$

Where, w is the mass of the material deposited on the electrode or liberated

Q is the amount of charge utilised t is the time for which current was passed through the electrolyte I is the strength of the current in amperes Z is the electrochemical equivalent

Faraday's laws of electrolysis – Second law

During electrolysis, when the same quantity of electricity passes through the electrolytic solution, a number of different substances liberated are proportional to their chemical equivalent weights (Equivalent weight is defined as the ratio of the atomic mass of metal and the number of electrons required for reducing the cation).

$W \propto E$

$W/E = F$ (constant) $F = 96500$ C per mole = Faraday constant

Application of electrolysis

(a) In the preparation of chemicals (b) In the extraction of metals

(c) Preparation of organic compounds (d) Corrosion and their prevention

Arrhenius Theory of Electrolytic Dissociation

The properties of the electrolytic solutions were explained by the Arrhenius theory of electrolytic solution. The important points of the theory are as follows:

- When the electrolyte is dissolved in water, it will break into positive charges and negative charges. These charged particles are called ions. The negatively charged ions are called anions, and the positively charged ions are called cations.
- Ionisation is the process by which the molecules are split into ions in an electrolyte.
- The degree of dissociation or degree of ionisation is given by the equation,

α = Number of molecules dissociated into ions/Total number of molecules

- When electricity is passed through the electrolytic solution, the cations will move towards the cathode, and the anions move towards the anode.
- The ions are constantly reuniting to form molecules; hence, there is a dynamic equilibrium between the ionised and non-ionised states.
- The electrolytic solution will always have a neutral charge.

- The properties of the electrolytic solutions will be the properties of the ions present in the solution.
- The conductivity of the electrolytic solution will depend on the number of ions and their nature.

Electrolytic Conductance

The conductance is the property of the conductor which permits the flow of electricity through it. It is equal to the reciprocal of the resistance.

Conductance = 1/Resistance = 1/R

(a) Ohm's law: According to this law, the current flowing through a conductor at a given standard temperature is directly proportional to the potential difference (V) and inversely proportional to the resistance (R). $I = V/R$

(b) Specific resistance (ρ): The resistance between two opposite faces of one cm cube of metal is called the specific resistance. It is also called resistivity. $\rho = R.a/l$

The unit of specific resistance is the ohm. cm

(c) Specific conductance or conductivity (k): It is the reciprocal of specific resistance. It is called specific conductance. $K = 1/\rho$

(d) Electrical conductivity (C) :

It is the reciprocal of resistance which is expressed as ohm^{-1} or mho

$C = 1/R$ The unit of electrical conductivity is siemens.

(e) Equivalent conductivity

The conducting power of all the ions furnished by one equivalent of an electrolyte in any solution is called equivalent conductivity The equivalent conductivity is expressed as

Equivalent conductivity (Λ_{eq}) = Conductivity (K)/Concentration in equivalents per unit volume (C_{eq}).

(d) Molar conductivity

The conducting power of all the ions furnished by one mole of an electrolyte in any solution is called molar conductivity.m$\Lambda_m = K/C_m$

Relation between molar conductivity and equivalent conductivity

According to the definition,

$\Lambda_m = K/C_m$ ———(1)

And $\Lambda_{eq} = K/C_{eq}$ ———(2)

Using equations (1) and (2), we get

$C_m/C_{eq} = \Lambda_{eq} /\Lambda_m$

$\Lambda_{eq} / \Lambda_m = 1/z$

$\Lambda_m = z \times \Lambda_{eq}$

Where z can have values equal to 1,2,3,…..

Kohlrausch's Law - Kohlrausch's law states that at infinite dilution, the conductivity of an electrolyte solution is equal to the addition of the conductivity of both ions (which are in the given electrolyte).

Cell - A combination of two electrodes is called the cell.

Types of Cells

Cells are divided into the following two types:

Electrolytic cells: In this type of cell, electrical energy is converted into chemical energy.

Electrochemical cells: In this type of cell, chemical energy is converted into electrical energy.

Electrochemical Cell

It is a device that produces electricity as a result of a chemical reaction.

The cells work on oxidation-reduction reaction.

Anode -The electrode of negative polarity at which the oxidation occurs.

Cathode -The electrode of positive polarity at which the reduction occurs.

Salt Bridge -The salt bridge completes the circuit of an electrochemical cell, thereby allowing the flow of current through it. It also helps maintain the overall electrical neutrality of the cell. Generally, a U-tube containing a solution of KCl or NH_4NO_3 sets the Agar Agar powder in the form of a jelly-like structure

Electrode Potential

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential. For example, if a zinc plate is placed in a solution containing Zn^{2+} ions, it will become negatively charged with respect to the solution. This will create a potential difference between the plate and the solution. This is called the electric potential of zinc.

Oxidation potential: When the electrode is charged negatively with respect to the solution, i.e., when the electrode acts as an anode, oxidation occurs.

$M \rightarrow M^{n+} + ne^-$

Reduction potential: When the electrode is charged positively with respect to the solution, i.e., when the electrode acts as a cathode, reduction occurs.

$M^{n+} + ne^- \rightarrow M$

EMF of the cell -The EMF of the cell is equal to the sum of the potential on the two electrodes. It is the sum of the oxidation potential of the anode and the reduction potential of the cathode.

Standard Electrode Potential

The potential difference developed between a metal electrode and the solution of its ion of unit molarity (1M) at 25^0 C is called the standard electrode potential.

Electrochemical Series

By measuring the potential of various electrodes versus hydrogen electrodes (SHE), a series of standard electrode potentials has been established.

When the electrode is in contact with its ions, it is arranged on the basis of the values of their standard reduction potentials or standard oxidation potentials. The resulting series is called the electrochemical or electromotive, or activity series of the elements.

Characteristics of Electrochemical Series

(a) A negative sign of standard reduction potential indicates that an electrode, when joined with SHE, acts as an anode, and oxidation occurs on this electrode. Similarly, the positive sign of SRP indicates that an electrode, when joined with SHE, acts as the cathode, and reduction occurs on this electrode.

(b) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series.

(c) The substances which are stronger oxidising agents than H^+ ions are placed below hydrogen in the series.

(d) The metals on top are called active metals, and activity decreases from top to bottom.

Application of Electrochemical Series

(i) Reactivity of metals

(a) Alkali metals and alkaline earth metals have high negative values of SRP, which are chemically active. These metals react with cold water and evolve hydrogen, and readily dissolve in acids.

(b) Metals like Fe, Pb, Sn, Ni etc., do not react with cold water but react with steam to evolve hydrogen.

(c) Metals U, Cu, Ag, Au etc., which lie between hydrogen, are less reactive and do not evolve hydrogen from water.

(ii) The electropositive character of metals

The electropositive character of metals decreases from top to bottom.

(iii) Displacement reactions

To predict whether a given metal will displace another from its salt solution, the metal having low SRP will displace the metals from its salt solution, which has a higher value of SRP.

(iv) Reducing power of metals

Reducing nature decreases from top to bottom in the electrochemical series.

(v) Oxidising nature of non-metals

Oxidising nature increases from top to bottom in the electrochemical series.

(vi) Thermal stability of metallic oxides

The thermal stability of metal oxide decreases from top to bottom.

(vii) Products of electrolysis

The ion, which is a stronger oxidising agent, is discharged first at the cathode.

K^+, Ca^{2+}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}

Increasing order of deposition

(viii) Corrosion of metals

Corrosion is defined as the deterioration of a substance because of its reaction with its environment. The corrosion tendency decreases from top to bottom.

(ix) Extraction of metals

Ag and Au are extracted by the cyanide process.

Nernst Equation - Nernst equation is an equation relating the cell potential to the standard potential and to the activities of the electrically active species. The standard cell potential is related to the effective concentrations of the components.

Relation between Gibbs Free Energy and EMF - The Gibbs free energy can be calculated by multiplying the total charge driven through the cell and the potential difference. Thus,

$-\Delta G$ = Total charge x EMF of the cell

$-\Delta G = nF \times E_{cell}$

The negative sign shows a decrease in free energy. As the EMF of the cell becomes more and more positive, the Gibbs free energy will become more and more positive.

Points to remember

- Electrochemistry is the branch of Chemistry that deals with the changes caused in matter by passing an electric current and converting chemical energy to electrical energy and vice versa.
- Substances whose aqueous solutions allow the conductance of electric current and are chemically decomposed are called electrolytes.

- For the electric current to pass through an electrolytic conductor, the two rods or plates called electrodes are always needed.
- Electrolysis is the process of chemical deposition of the electrolyte by passing an electric current.
- Faraday established the relation between the amount of material deposited at the electrode or liberated and the amount of current passed through the electrolyte.
- The properties of the electrolytic solutions were explained by the Arrhenius theory of electrolytic solution.
- The reciprocal of specific resistance is called specific conductance.
- Kohlrausch's law states that at infinite dilution, the conductivity of an electrolyte solution is equal to the addition of the conductivity of both ions.
- An electrochemical cell is a device that produces electricity as a result of a chemical reaction.
- The potential difference between the electrode and the electrolytic solution is called the electric potential.
- The standard cell potential is related to the effective concentrations of the components by the Nernst equation.

QUESTION BANK

SECTION-A The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.		
1	Which of the following statements about galvanic cell is incorrect (a) anode is positive (b) oxidation occurs at the electrode with lower reduction potential (c) cathode is positive (d) reduction occurs at cathode	**[1]**
2	Which device converts chemical energy of a spontaneous redox reaction into electrical energy? (a) Galvanic cell (b) Electrolytic cell (c) Daniell cell (d) Both (a) and (c)	**[1]**
3	The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called _________. (a) Cell potentials (b) Cell emf (c) Potential difference (d) Cell voltage	**[1]**

4	The reference electrode is made by using (a) ZnCl2 (b) CuSO4 (c) HgCl2 (d) Hg2Cl2	**[1]**
5	The standard hydrogen electrode potential is zero, because (a) hydrogen oxidized easily (b) electrode potential is considered as zero (c) hydrogen atom has only one electron (d) hydrogen is a very light element	**[1]**
6	Which of the following statement is not correct about an inert electrode in a cell ? (a) It does not participate in the cell reaction. (b) It provides surface either for oxidation or for reduction reaction. (c) It provides surface for conduction of electrons. (d) It provides surface for redox reaction.	**[1]**
7	The unit of equivalent conductivity is (a) ohm cm (b) ohm–1 cm2 (g equivalent)–1 (c) ohm cm2 (g equivalent) (d) S cm–2	**[1]**
8	The unit of specific conductivity is (a) ohm cm–1 (b) ohm cm–2 (c) ohm–1 cm (d) ohm–1 cm–1	**[1]**
9	Kohlrausch's law states that at (a) finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte. (b) infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte. (c) infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte. (d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.	**[1]**
10	On which of the following magnitude of conductivity doe not depends? (a) Nature of material (b) Temperature(c) Pressure (d) Mass of the material	**[1]**
	In the following questions (Q. No. 11 - 20) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	A: Cu is less reactive than hydrogen. R : $E^0_{Cu2+/Cu}$ is negative.	**[1]**
12	A: E_{cell} should have a positive value for the cell to function. R: $E_{cathode} < E_{anode}$	**[1]**
13	A: Conductivity of all electrolytes decreases on dilution. Reason : On dilution number of ions per unit volume decreases.	**[1]**
14	Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted. R: For weak electrolytes degree of dissociation increases with dilution of solution.	**[1]**
15	A: Mercury cell does not give steady potential. R: In the cell reaction, ions are not involved in solution.	**[1]**
16	A: For the cell reaction, Zn(s) + Cu2 (+ Zn2 (+aq) + Cuts) voltmeter gives zero reading at equilibrium. R : At the equilibrium, there is no change in concentration of Cu2 + and Zn2+ ions.	**[1]**
17	**A:** For concentration cell, zn(s) Zn 11 For spontaneous cell reaction, Cl < C2 RT C2 R : For concentration cell, Ecell —log For spontaneous reaction, Ecell = +ve so, C2 > Cl.	**[1]**
18	A:The Nernst equation gives the concentration dependence of emf of the cell. R : In a cell, current flows from cathode to anode. osition of an electron can be determined exactly with the help of an electron microscope.	**[1]**
19	**A :** Electrode potential for the electrode Mn*/Mn with concentration is given by the expression under STP conditions. R : STP conditions require the temperature to be 273 K.	**[1]**
20	**A :** Increase in the concentration of copper half cell in a cell, increases the emf ofthe cell. R : as per Nearnst Equation	**[1]**
ANSWER KEY:		

1	**(a)**	**2**	**(d)**	**3**	**(b)**	**4**	**(d)**	**5**	**(b)**
6	**(d)**	**7**	**(b)**	**8**	**(d)**	**9**	**(d)**	**10**	**(d)**
11	**(c)**	**12**	**(a)**	**13**	**(c)**	**14**	**(a)**	**15**	**(c)**
16	**(a)**	**17**	**(c)**	**18**	**(b)**	**19**	**(a)**	**20**	**(a)**

	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	**Under what conditions is $E^0_{cell} = 0$ and $\Delta_rG^0 = 0$?**	**[2]**
ANS.	At the condition of equilibrium, $E^0_{cell} = 0$ and $\Delta_rG^0 = 0$	
22	**What is electrode potential ?**	**[2]**
ANS.	Electrode potential appears at the interface between an electrode and electrolyte due to the transfer of charged species across the interface.	
23	**Why is alternating current used for measuring resistance of an electrolytic solution?**	**[2]**
ANS.	Alternate current is used for measuring the resistance of an electrolytic solution because direct current will cause the electrolysis of the electrolyte. As a result Concentration of the ions in the solution will change.	
24	**In an aqueous solution how does specific conductivity of electrolytes change with addition of water?**	**[2]**
ANS.	The specific conductivity or conductivity (κ) of electrolytes decreases with the addition of water or upon dilution because the number of ions per unit volume decrease.	
25	**Which reference electrode is used to measure the electrode potential of other electrodes ?**	**[2]**
ANS.	Standard hydrogen electrode (SHE) is used as reference electrode to measure the electrode potential of other electrodes. Its electrode potential is assumed as zero. The electrode potential of any electrode as measured with respect to a standard hydrogen electrode is known as its standard electrode potential (E).	
	SECTION C The following questions are short answer type and carry 3 marks each.	
26	**Consider a cell given below** **$Cu\ |Cu^{2}+\ ||\ Cl-\ |\ Cl_2$, Pt** **Write the reactions that occur at anode and cathode.**	**[3]**
ANS.	The reaction taking place at the two electrodes are:	

	At anode : Cu(s) → Cu^{2+}(aq) + $2e^-$ At cathode: Cl_2 (g) + $2e^-$ → 2 Cl^-	
27	**Write the Nernst equation for the cell reaction in the Daniell cell. How will the E_{cell} be affected when concentration of Zn^{2+} ions is increased ?**	**[3]**
ANS.	Daniell cell involves the redox reaction : Zn(s) + $CuSO_4$(aq) → $ZnSO_4$ (aq) + Cu(s) Thus in the cell Zn(s) is oxidised to Zn^{2}+ (aq) ions in the oxidation half cell while Cu^{2}+ (aq) ions are reduced to Cu(s) in the reduction half cell. According to Nernst equation, $E_{cell} = E^0_{cell} - (0.059/2) \{\log[Zn^{2+}(aq)] / [Cu^{2+}(aq)]$ Hence E_{cell} decreases as the [Zn^{2+}(aq)] increases.	
28	**What advantage do the fuel cells have over primary and secondary batteries?**	**[3]**
ANS.	Primary batteries or cells contain a limited amount of reactants and are discharged when the reactants are consumed. Secondary batteries or cells can be recharged but the process takes a long time. Fuel cells work continuously as long the reactants (i.e. fuel) are supplied.	
29	**Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually?**	**[3]**
ANS.	CH_3COOH is a weak electrolyte and is dissociated to small extent. With dilution, its degree of dissociation increases i.e. more ions are released in solution. Therefore, Λ_m of CH_3COOH increases drastically. On the other hand, CH_3COONa is a strong electrolyte and is almost completely dissociated in aqueous solution. With dilution, only interionic forces of attraction increase resulting in only small increase in the value of Λ_m .	
30.	**Write the cell reaction of a lead storage battery when it is discharged. How does the density of the electrolyte change when the battery is discharged?**	
ANS.	The cell reaction of a lead storage battery when it is discharged, may be given as: Pb(s) + $4H^+$(aq) + $2SO_4^{2-}$ (aq) → PbO_2(s) + 2PbSO4 (s) + $2H_2O$(l) Density of the electrolyte i.e. conc.H_2SO_4 solution decreases because of the dilution of electrolyte taking place since water is formed as one of the products.	
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	

31	PASSAGE:- Metallic conductance involves movement of electrons where as electrolytic conductance involves movement of ions. Specific conductance increases with increase in concentration where as Λm (molar conductivity) decreases with increasein concentration. Electrochemical cell convertschemical energy of redox reaction into electricity.Mercury cell, Dry cells are primary cells where asNi—Cd cell, lead storage battery are secondarycells. Electrochemical series is arrangement ofelements in increasing order of their reductionpotential. Electrolytic cell converts electrical energyinto chemical energy which is used in electrolysis.Amount of products formed are decided with thehelp of Faraday’s laws of Electrolysis. Kohlrauschlaw helps to determine limiting molar conductivityof weak electrolyte, their degree of ionisation(a) and their dissociation constants. Corrosion iselectrochemical phenomenon. Metal undergoingcorrosion acts as anode, loses electrons to formions which combine with substances present inatmosphere to form surface compounds. Morereactive metals are coated over less reactive metalsto prevent corrosions. H_2 —O_2 fuel cell was used inapollo space programme.	**[4]**
31.1	Out of 0.5 M, 0.01 M, 0.1 M and 1.0 M whichsolution of KCl will have highest value of specific conductance? Why?	
ANS.	1.0 M KCl solution because it will have morenumber of ions per unit volume of solution.	
31.2	Write the product of electrolysis of aq. NaClon cathode. Why?	
ANS.	$2H^+ + 2e^- \rightarrow H_2$ [$E°H^+/H_2 = 0$, is higher than $E° Na^+/Na = -2.71$ V]	
31.3	When does electrochemical cell behaves likeelectrolytic cell?	
ANS.	When E external > E° cell	
	OR	
31.3	For an electrochemical cell Mg(s) + 2Ag+\(aq) → 2Ag(s) + Mg2+ .Give the cell representationand write Nernst equation.	
ANS.	Mg(s) | Mg2+ (aq) | | Ag+(aq) | Ag(s) Ecell = E°cell – 0.059/2 log [Mg2+]/[Ag +]^2	
32	PASSAGE:- Electrochemistry plays a very important part inour daily life. Primary cells like dry cell is used intorches, wall clock, mercury cell is used in hearingaids, watches. Secondary cells Ni–Cd cell is used incordless phones, lithium battery is used in mobiles,lead storage battery is used in vehicle and inverter.Fuel cells like H_2—O_2 cell was used in apollo spaceprogramme. A 38% solution of sulphuric and isused in lead storage battery. Its density is 1.30 gmL^{-1}. The battery holds 3.5 L of the acid. Duringthe discharge of the battery, the	**[4]**

	density of H_2SO_4 falls to 1.14 g mL –1(20% solution by mass) (Molarmass of $H_2SO_4$is 98 g mol $^{-1}$)	
32.1	Write the chemical reaction taking place at anode when lead storage battery is in use.	
ANS.	$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$ (At anode)	
32.2	How much electricity in Faraday is required to carry out the reduction of one mole of PbO_2?	
ANS.	$PbO_2 + 4H^+ + 2e^- + SO_4^{2-} \rightarrow PbSO_4 + 2H_2O$ 2 Faraday is required.	
32.3	What is molarity of sulphuric acid beforedischarge?	
ANS.	M =percentage Molar mass by mass× ×10 *d* =.9838 1 30 10× × =98494 = 5.041 M	
	OR	
32.3	What is mass of sulphuric acid in solution afterdischarge?	
ANS.	Mass of solution after discharge = 3500 mL ×1.14 g mL^{-1} = 3990 g Mass of H_2SO_4 present in solution (20%) =10020× 3990 g = 798 g	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	**State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for reduction of 1 mole of Cu^{2+} ions to Cu?**	**[5]**
ANS.	When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte. If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation: $W \propto Q$ A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs, Q = current in amperes x time in seconds Q = I x t $W \propto I \times t$ W = Z x I x t where, Z is a constant, known as electrochemical equivalent, and is characteristic of the substance deposited.	

	When a current of one ampere is passed for one second,i.e one coulomb ($Q = 1$), then $W = Z$ The electrode reaction is $Cu^{2+} + 2e^{-} \rightarrow Cu$ ∴ quantity of charge required for reduction of 1 mole of Cu2+ =2F Cu^{2+}=2F =2×96500=193000C	
34	**State Kohlrausch's law. How does the law help in calculating Λ^{0}_{∞} CH_3COOH ?**	**[5]**
ANS.	At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i. e. anions and cations. $\Lambda_{\infty} = \lambda_a + \lambda_c$ The λ_a and λ_c are called the ionic conductances of cation and a anion at infinite dilution respectively. The molar conductivity of an strong electrolyte at infinite dilution is the sum of the ionic conductivity of the cations and anions. In case of weak electrolytes, it is not possible to determine the value of limiting molar conductance at infinite dilution. However this can be determine by using Kohlrausch's law. Example CH3COOH is a weak electrolyte. Λ^{∞}_{m} (CH3COOH) = λ_m^{∞} (CH3COO-) + λ_m^{∞} (H^+) =[λ_m^{∞} (CH3COO-) + λ_m^{∞} (Na^+)] + [λ_m^{∞} (H^+) + λ_m^{∞} (Cl^-)] – [λ_m^{∞} (Na^+) + λ_m^{∞} (Cl^-)] = Λ^{∞}_{m} (CH3COONa) + Λ^{∞}_{m} (HCl) – Λ^{∞}_{m} (NaCl)	
35	**What is the relationship between Gibbs free energy of the cell reaction in a galvanic cell and the emf or E_{cell} ? When will the maximum work be obtained from a galvanic cell ?**	**[5]**
ANS.	the relation may be given as : $\Delta G = -nF E_{cell}$ If the redox reaction is under standard conditions, then $\Delta G^{\circ} = -nFE_{cell}$ Here nF is the quantity of charge passed. In case we want to obtain maximum work from the galvanic charge has to be passed reversibly. As pointed above, the reversible work done by the galvanic cell is equal decrease in its Gibbs free energy.	

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KENDRIYA VIDYALAYA SANGATHAN, JABALPUR REGION

CLASS- XII

CHEMISTRY (043)

CHAPTER NAME: CHEMICAL KINETICS

PREPARED BY: GROUP III MEMBERS

IMPORTANT POINTS/ NOTES ON TIP:

Chemical Kinetics : The branch of physical chemistry which deals with the study of rate of reaction and factors affecting rate.

Rate of chemical reaction: The change in concentration of any reactant or product per unit time is called rate of reaction.

Types of Rate of Reaction :

1. Average rate of reaction : The rate of reaction measured over the long time interval is called average rate of reaction.

2. Instantaneous rate of reaction : The rate of reaction measured at a particular time is called instantaneous rate of reaction.

(Rate)*i* = (Instantaneous rate) $dx/dt = -d[R]/dt = +d[P]/dt$

Factors affecting Rate of Reaction

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant

5. Presence of catalyst

6. Radiation in photochemical reaction

Rate constant (k) : It is equal to the rate of reaction when molar concentration of reactant is at unity.

Rate law : The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to the equal to no of moles actually participating in the reaction.

For a reaction, aA + bB ---------> cC + Dd

Rate law = k[A]*p*[B]*q*

where powers *p* and *q* are determined experimentally.

Molecularity : Molecularity of a simple reaction is defined as the total number of molecules of reactants which collide simultaneously to bring a chemical reaction. Let a reaction A^a $+B^b$ -------->Products + $ So, Molecularity = a+ b.

Order of reaction : The sum of powers to which the concentration terms are raised in a rate law expression is called order of reaction.

Orders of reaction is determined experimentally.

Half-life period : The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

Activation energy : The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

Activation energy = Threshold energy – Kinetic energy

Temperature coefficient : The ratio of rate constant at two temperatures having difference of 10ºC is called temperature coefficient.

Temperature coefficient = Rate constant at T + 10ºC/Rate constant at TºC

Arhenius Equation :

$K = Ae\ {-}^{Ea/RT}$

where, K = Rate constant

A = Arrhenius energy (Frequency factor or pre-exponential factor)

Ea = Activation energy R = Rate constant T = Temperature

$e^{-Ea/RT}$ = Fraction of molecules having energy equal to or more than activation energy

Integrated rate law equation for zero order reaction is given as below :

(a) *k* = [R0] −[Rt]

Where k is rate constant and [R]0 is initial molar concentration.

(b) $t_{1/2}$ = [R]/2k

2. Integrated rate law equation for first order reaction :

(a) *k* = 0 2.303 log [R0]/ [Rt]*t*

(b) Half-life period (*t*1/2) for first order reaction :

*t*½ = 0.693/*k*

Pseudo chemical reaction : The chemical reaction which looks like higher order

reaction but in real it follows lower order reaction.

$CH3COOC2H5 + H2O \rightarrow CH3COOH + C2H5OH$

Rate = k[CH3COOC2H5]1

COLLISION THEORY OF REACTION RATES According to collision theory, the rate of a reaction depends upon the collision frequency ( )z and the fraction of effective collisions f . So, Rate of reaction ∞ z f (a) With the increase in temperature, the kinetic energy of molecules increases and this leads to an increase in collision frequency ( )z , as the average kinetic energy of the molecules is directly proportional to absolute temperature. (b) For effective collision, the colliding molecules must have more than or equal to certain minimum amount of energy called threshold energy Ec and proper orientation. On increasing the temperature, the fraction of effective collisions f increases due to which rate of reaction increases.

QUESTION BANK

SECTION-A The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.		
1	What effect does temperature have on the half-life of a first-order reaction? a) It increases b) It decreases c) It remains the same d) Both increases as well as decrease	**[1]**
2	Only a simple homogeneous reaction requires which of the following methods? a) Integration method b) Half-life period method	**[1]**

	c) Graphical method d) Ostwald's isolation method	
3	In 30 minutes, a first-order reaction is 50% complete. Calculate the amount of time it took to complete 87.5 percent of the reaction. a) 30 minutes b) 60 minutes c) 90 minutes d) 120 minutes	**[1]**
4	For a reaction P + Q → 2 R + S , the incorrect statement is (a) Rate of disappearance of P = Rate of appearance of S (b) Rate of disappearance of Q = 2 x Rate of appearance of R (c) Rate of disappearance of Q = Rate of disappearance of P (d) Rate of disappearance of Q = 1⁄2 x Rate of appearance of R	**[1]**
5	In a reaction, 2X → Y, the concentration of X decreases from 0.50 M to 0.38 M in 10 min. Whatis the rate of reaction in Ms^{-1} during this interval? (a) 2×10^{-4} (b) 4×10^{-2} (c) 2×10^{-2} (d) 1×10^{-2}	**[1]**
6	Order of reaction is decided by (a) temperature (b) mechanism of reaction as well as relative concentration of reactants (c) molecularity (d) pressure	**[1]**
7	What will be the fraction of molecules having energy equal to or greater than activation energy, Ea? (a) K (b) A (c) $Ae^{-Ea/Rt}$ (d) $e^{-Ea/Rt}$	**[1]**
8	In the formation of S02 by contact process; $2SO_2 + O_2 \rightarrow 2SO_3$, the rate of reaction was measured as −d[O2]/dt = 2.5×10^{-4} mol L^{-1}s^{-1}. at The rate of formation of of S03 will be	**[1]**

	(a) -5.0×10^{-4} mol $L^{-1}s^{-1}$ (b) -1.25×10^{-4} mol $L^{-1}s^{-1}$ (c) 3.75×10^{-4} mol $L^{-1}s^{-1}$ (d) 5.00×10^{-4} mol $L^{-1}s^{-1}$	
9	**In the reaction $2A + B \rightarrow A_2B$, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will** (a) increase 2 times (b) increase 4 times (C) decrease 2 times (d) remain the same	**[1]**
10	**Consider a first order gas phase decomposition reaction given below :** **$A(g) \rightarrow B(g) + C(g)$** **The initial pressure of the system before decomposition of A was pi. After lapse of time 't', total pressure of the system increased by x units and became 'pt The rate constant k for the reaction is given as _________.** **(a) k = 2.303/t log Pi/Pi-x** **(b)) k = 2.303/t log Pi/2Pi-Pt** **(c)) k = 2.303/t log Pi/2Pi-2Pt** **(d)) k = 2.303/t log Pi/Pi+x**	**[1]**
	In the following questions (Q. No. 11 - 20) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	**Assertion:** Activation complex for the forward reaction will have lower energy than that for the backward reaction in an exothermic reaction. **Reason:** Reactants have greater energy than products for an exothermic reaction.	**[1]**
12	**Assertion:** Increase in temperature increases the rate of reaction. **Reason:** More colliding molecules will have energy greater than threshold energy.	**[1]**

13	**Assertion:** The unit of the rate constant is independent of the order of the reaction. **Reason:** The power of concentration terms in the rate equation keeps changing with change in order.	**[1]**
14	**Assertion:** Increase in concentration of reactant will not change the rate for a zero-order reaction. **Reason:** Rate constant for a zero-order reaction is a constant for a particular initial concentration.	**[1]**
15	Assertion: the rate of reaction is accelerated by the presence of catalyst. Reason: The presence of catalyst makes the value of $\Delta G°$ more negative	**[1]**
16	**Assertion: The rate constant of a zero order reaction has same unit as that of the rate of the reaction** **Reason : The concentration of reactants is taken to be unity while determining rate Constant**	**[1]**
17	**Assertion: Increase in temperature increases rate of a chemical reaction.** **Reason: increase in temperature decreases activation energy of the reaction**	**[1]**
18	**(A) : The rate of reaction always depend on concentration of reactant** **(R) : For zero order reactions concentration of reactant does not affect rate**	**[1]**
19	**Assertion: The order of a reaction may be fractional but molecularity is never** **Reason: The order of reaction is experimental but molecularity depends on stoichiometric co-efficient of the reactants in the balanced chemical equation.**	**[1]**
20	**Assertion : A catalyst increases rate of reaction** **Reason: A catalyst decreases activation energy of the reaction**	**[1]**

ANSWER KEY:

1	**B**	**2**	**a**	**3**	**c**	**4**	**b**	**5**	**a**
6	**B**	**7**	**d**	**8**	**d**	**9**	**a**	**10**	**b**
11	**D**	**12**	**a**	**13**	**d**	**14**	**b**	**15**	**c**
16	**C**	**17**	**a**	**18**	**d**	**19**	**a**	**20**	**a**

	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y ?	**[2]**
ANS.	If [X] is increased to 3 times, then the new rate is (1) rate’ = $k[3X]^2$ rate’ = $9\ k\ [X]^2$ = 9 rate Thus, rate of reaction becomes 9 times and hence rate of formation of Y increases 9-times.	
22	**(a) Write down any four differences between order of reaction and molecularity of reaction.**	**[2]**
ANS.	**Order** 1. It is the sum of the powers of concentration terms in the rate law expression. 2. It is determined experimentally. 3. Order of reaction need not to be a whole number. 4. Order of reaction can be zero. **Molecularity** 1.It is the number of reacting species undergoing simultaneously collision ina reaction. 2. It is a theoretical concept. 3. It is whole number only. 4. It can’t be zero or fractional	
23	**A first order reaction has a rate constant 1.15 X $10^{-3}s^{-1}$. How long will 5 g of this reactant take to reduce to 3g?**	**[2]**
ANS.	t=2.302/k log [A]0/[A]=2.032/1.15x10^{-3}log 5/3 =2 x 10^{-3}x 0.2219 =443.8 s	
24	Find the two-third life, $t_{2/3}$, of a first order reaction in which; k = 5.4 x 10^{-14} s^{-1}	**[2]**
ANS.	Formula; $t_{2/3}$ = (2.303 / k) log (a / a- x) Here, x = 2a / 3 and k = 5.4 x 10^{-14} s^{-1} Thus, $t_{2/3}$ = [2.303 / 5.4 x 10^{-14} s^{-1}] (log [a /(a - 2a / 3)] $t_{2/3}$ = [2.303 / 5.4 x 10^{-14}] log3	

$= 0.4264\ (0.4771)\ (10^{14})\ s$

$= 0.2034 \times 10^{14}\ s$

25 Can a reaction have a) zero activation energy b) negative activation energy? **[2]**

ANS. a) No; if Ea is zero all collisions will lead to product formation, which is not possible.

b) If Ea is negative than K>>A which is not possible

SECTION C

The following questions are short answer type and carry 3 marks each.

26 The following results have been obtained during the kinetic study of the reaction: **[3]**

$$2A + B \text{ ----> } C + D$$

Expt.	[A] mol L^{-1}	[B] molL^{-1}	Initial rate of formation of D, molL^{-1} min^{-1}
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.4×10^{-2}

Determine the rate law.

ANS. rate $=k[A]^{\alpha}[B]^{\beta}$

1. $6.0 \times 10^{-3} = k\,[0.1]^{\alpha}\,[0.1]^{\beta}$
2. $7.2 \times 10^{-2} = k\,[0.3]^{\alpha}[0.2]^{\beta}$
3. $2.88 \times 10^{-1} = k\,[0.3]^{\alpha}\,[0.4]^{\beta}$
4. $2.4 \times 10^{-2} = k\,[0.4]^{\alpha}[0.1]^{\beta}$

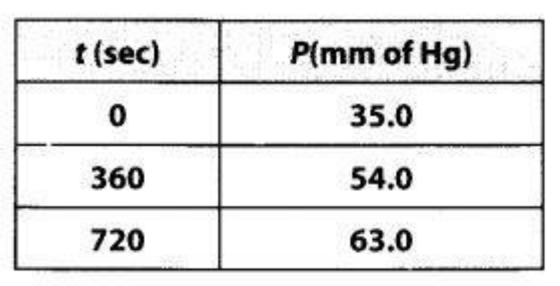
⇒ dividing (2) by (3)

$7.2 \times 10^{-2}/2.88 \times 10^{-1} = k[0.3]^{\alpha}[0.2]^{\beta} / k\,[0.3]^{\alpha}[0.4]^{\beta}$

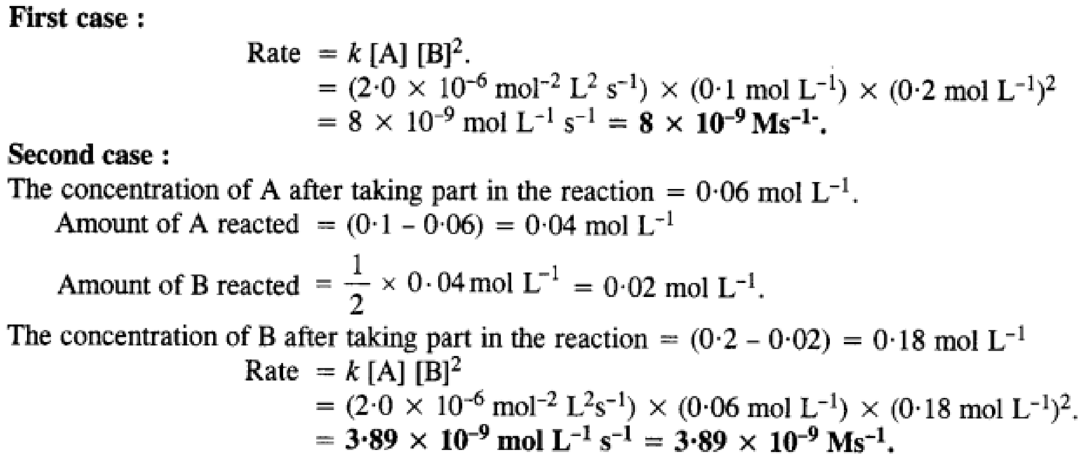
$[1/4] = [1/2]^{\beta}$ $[1/2]^{2} = [1/2]^{\beta}$

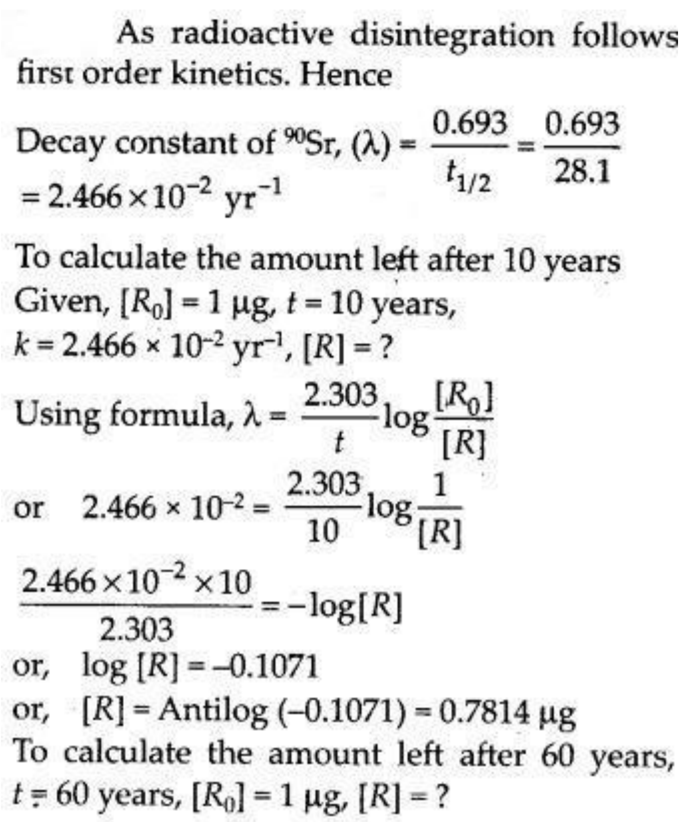
- = 2 ⇒ dividing (1) by (4)

$6.0 \times 10^{-3} / 2.40 \times 10^{-2} = k\,[0.1]^{\alpha}[0.1]^{\beta} / k[0.4]^{\alpha}[0.1]^{\beta}$

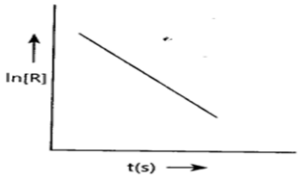
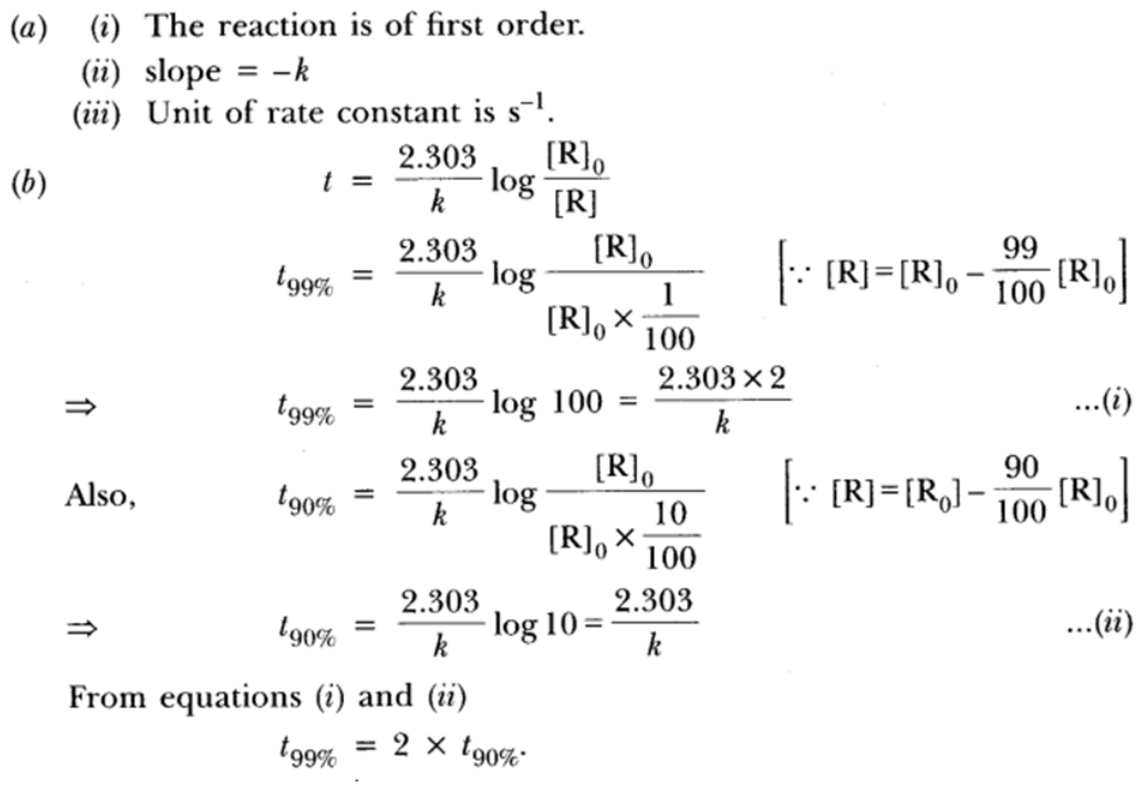
<table>
<tr><td></td><td>[1/4] = $[1/4]^{\alpha}$
$\alpha = 1$,
hence rate law : rate =k $[A]^1[B]^2$</td><td></td></tr>
<tr><td>27</td><td>If half-life period for a first order reaction in A is 2 minutes, how long will it take [A]0 to reach 10% of its initial concentration ?</td><td>[3]</td></tr>
<tr><td>ANS.</td><td>$\mathrm{k} = \frac{0.693}{t_{\frac{1}{2}}}$
$= \frac{0.693}{2\ min}$
$0.3465 min^{-1}$
$\mathrm{t} = \frac{2.303}{K} \log \frac{[A]_0}{[A]}$
$= \frac{2.303}{0.3465} \log \frac{100}{10}$
$\mathrm{t} = \frac{2.303}{0.3465\ min^{-1}} \times \log 10$
$= \frac{2.303}{0.3465} \times 1$
$= 6.6\ \mathrm{min}$</td><td></td></tr>
<tr><td>28</td><td><table><tr><th><i>t</i> (sec)</th><th><i>P</i>(mm of Hg)</th></tr><tr><td>0</td><td>35.0</td></tr><tr><td>360</td><td>54.0</td></tr><tr><td>720</td><td>63.0</td></tr></table>Calculate the rate constant</td><td>[3]</td></tr>
<tr><td>ANS.</td><td>For the decomposition of azo isopropane to hexane and nitrogen at 543 K, the following data are obtained.</td><td></td></tr>
</table>

	$(CH_3)_2CHN{=}NCH(CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6H_{14(g)}$ Azoisopropane Hexane Initial pressure P_0 0 0 Pressure after time t $P_0 - p$ p p Total pressure after time t (P_t) $= (P_0 - p) + p + p = P_0 + p$ or $p = P_t - P_0$ $[R]_0 \propto P_0$ and $[R] \propto P_0 - p$ On substituting the value of p, $[R] \propto P_0 - (P_t - P_0)$, *i.e.* $[R] \propto 2P_0 - P_t$ As decomposition of azoisopropane is a first order reaction $\therefore \quad k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$ When $t = 360$ sec, $k = \frac{2.303}{360}\log\frac{35.0}{2\times35.0-54.0} = \frac{2.303}{360}\log\frac{35.0}{16}$ $= 2.175\times10^{-3}\ s^{-1}$ When $t = 720$ sec, $k = \frac{2.303}{720}\log\frac{35.0}{2\times35.0-63} = \frac{2.303}{720}\log 5$ $= 2.235\times10^{-3}\ s^{-1}$ $\therefore$ Average value of k $= \frac{2.175+2.235}{2}\times10^{-3}\ s^{-1}$ $= 2.20\times10^{-3}\ s^{-1}$	
29	Radioactive decay follows first order kinetics. The rate constant for the decomposition of a hydrocarbon is 2·418 x 10^{-5} s^{-1} at 546 K. If the energy of activation is 179·9 kJ mol^{-1}, what will be the value of pre-exponential factor?	**[3]**
ANS.	According to Arrhenius equation, $\log K = \log A - \frac{E_a}{2{\cdot}303RT}$ $k = 2{\cdot}418\times10^{-5}s^{-1};\ E_a = 179900\ J\ mol^{-1};\ R = 8{\cdot}314\ J\ K^{-1}\ mol^{-1};\ T = 546\ K$ $\log A = \log K + \frac{E_a}{2{\cdot}303RT}$ $= \log(2{\cdot}418\times10^{-5}s^{-1}) + \frac{(179900\ J\ mol^{-1})}{2{\cdot}303\times(8{\cdot}314\ J\ K^{-1}\ mol^{-1})\times546K}$ $= -4{\cdot}6184 + 17{\cdot}21 = 12{\cdot}5916$ $A = \text{Antilog}\ 12{\cdot}5916 = \mathbf{3{\cdot}9\times10^{12}\,s^{-1}}.$	
30.	For the reaction ; 2A + B → A2B, the reaction rate = k [A][B]2 with k = 2·0 x 10-6 mol-2 L2 s-1. Calculate the initial rate of the reaction when [A] = 0·1 mol L-1; [B] = 0·2 mol L-1. Also calculate the reaction rate when [A] is reduced to 0·06 mol L-1.	

ANS.	 **First case :** Rate $= k\,[A]\,[B]^2$. $= (2{\cdot}0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}) \times (0{\cdot}1\ \text{mol L}^{-1}) \times (0{\cdot}2\ \text{mol L}^{-1})^2$ $= 8 \times 10^{-9}\ \text{mol L}^{-1}\ \text{s}^{-1} = \mathbf{8 \times 10^{-9}\ Ms^{-1}}$. **Second case :** The concentration of A after taking part in the reaction $= 0{\cdot}06\ \text{mol L}^{-1}$. Amount of A reacted $= (0{\cdot}1 - 0{\cdot}06) = 0{\cdot}04\ \text{mol L}^{-1}$ Amount of B reacted $= \frac{1}{2} \times 0{\cdot}04\ \text{mol L}^{-1} = 0{\cdot}02\ \text{mol L}^{-1}$. The concentration of B after taking part in the reaction $= (0{\cdot}2 - 0{\cdot}02) = 0{\cdot}18\ \text{mol L}^{-1}$ Rate $= k\,[A]\,[B]^2$ $= (2{\cdot}0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\text{s}^{-1}) \times (0{\cdot}06\ \text{mol L}^{-1}) \times (0{\cdot}18\ \text{mol L}^{-1})^2$. $= \mathbf{3{\cdot}89 \times 10^{-9}\ mol\ L^{-1}\ s^{-1} = 3{\cdot}89 \times 10^{-9}\ Ms^{-1}}$.	
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time.It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time.A number of factors such as temperature ,concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law : Rate = $k[A]^x[B]^y$,x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of x+y gives the overall order of a reaction. When a sequence of elementary reactions gives us the product, the reactions are called complex reactions. Molecularity and order of an elementary reaction are same. Zero order reactions are relatively uncommon but they occur under special conditions. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. c. How order and molecularity are different for complex reactions?	**[4]**
31.1	What is the effect of temperature on the rate constant of a reaction?	
ANS.	It will increase	
31.2	. For a reaction A+B ---> product The rate law is given by Rate = $k[A]^2[B]^{1/2}$. what is the order of the reaction?	
ANS.	2.5	

31.3	A first order reaction has a rate constant $2x10^{-3}s^{-}$. How long will 6g ofthis reactant take to reduce to 2g?	
ANS.	t= 2.303log3/$2x10^{-2}$ =2399sec	
	OR	
31.3	During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 µg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?	
ANS.	 As radioactive disintegration follows first order kinetics. Hence Decay constant of ^{90}Sr, $(\lambda) = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$ $= 2.466 \times 10^{-2}\ yr^{-1}$ To calculate the amount left after 10 years Given, $[R_0] = 1\ \mu g$, $t = 10$ years, $k = 2.466 \times 10^{-2}\ yr^{-1}$, $[R] = ?$ Using formula, $\lambda = \frac{2.303}{t}\log\frac{[R_0]}{[R]}$ or $2.466 \times 10^{-2} = \frac{2.303}{10}\log\frac{1}{[R]}$ $\frac{2.466 \times 10^{-2} \times 10}{2.303} = -\log[R]$ or, $\log[R] = -0.1071$ or, $[R] = \text{Antilog}(-0.1071) = 0.7814\ \mu g$ To calculate the amount left after 60 years, $t = 60$ years, $[R_0] = 1\ \mu g$, $[R] = ?$	
32	Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occurs on metal surfaces are a few examples of zero order reactions. The decompositions which occurs on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure. 2NH3(g)−−−−−→N2(g)+3H2(g) Rate=k[NH3]0=k In this reaction, Pt acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making the rate of the reaction independent of its concentration.	**[4]**

32.1	What are zero order reactions?	
ANS.	**Those reaction in which the rate is not dependent on any concentration term are called zero order reaction.**	
32.2	**Which of the unit of rate constant for first order reaction is similar to**	
ANS.	**Frequency**	
32.3	**Why is the decomposition of NH3 on Pt surface a zero order reaction?**	
ANS.	**In this reaction, Pt acts as a catalyst. At high temperature, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of platinum catalyst. Thus the reaction remains independent of its concentration.**	
	OR	
32.3	**A zero order reaction in A has a rate constant of 0.003 molL^{-1}sec^{-1}. How long will it take for A's initial concentration to fall from 0.10 M to 0.075 M?**	
ANS.	**According to zero order reaction** **$[A] = [A_O]-kt$** **Where [A] is the concentration at time, t** **$[A_O]$ is the concentration at time = 0** **k is the rate constant** **Given: $[A] = 0.075$ M, $[A_O] = 0.10$ M , $k = 0.003$ molL^{-1}sec^{-1}** **Time,t=?** **Substitute the values in the formula of zero order reaction** **$0.075 = 0.10 - 0.003t$** **t= 8.33 s**	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	i) The rate constant of a first order reaction increases from 2 x10^{-2}s^{-1} to 8 x 10^{-2} s^{-1} when the temperature changes from 300 K to 320 K. Calculate the energy of activation (E_a) (log 2 = 0.301 , log 3 = 0.4771, log4 = 0.6021) ii) A reaction is of first order in reactant A and of second order in reactant B. How is the rate of this reaction affected when?	**[5]**

	(A)the concentration of B alone is increased to three times. (B) The concentrations of A as well as B are doubled?	
ANS.	. i) Correct Formula , Substitution and calculation, E_a = 55.33 KJ/mol. ii) a) 9 times (b) 8 times	
34	(a) For a chemical reaction R —» P, the variation in the concentration, ln[R] vs. time (s) plot given as (i) Predict the order of the reaction. (ii) What is the slope of the line? (iii) Write the unit of rate constant for this reaction. (b) Show that the time required for 99% completion is double of the time required for the completion of 90% reaction. 	**[5]**
ANS.	(*a*) (*i*) The reaction is of first order. (*ii*) slope = $-k$ (*iii*) Unit of rate constant is s^{-1}. (*b*) $t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$ $t_{99\%} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0\times\frac{1}{100}}$ $\left[\because [R]=[R]_0-\frac{99}{100}[R]_0\right]$ $\Rightarrow$ $t_{99\%} = \frac{2.303}{k}\log 100 = \frac{2.303\times 2}{k}$ ...(*i*) Also, $t_{90\%} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0\times\frac{10}{100}}$ $\left[\because [R]=[R_0]-\frac{90}{100}[R]_0\right]$ $\Rightarrow$ $t_{90\%} = \frac{2.303}{k}\log 10 = \frac{2.303}{k}$ ...(*ii*) From equations (*i*) and (*ii*) $t_{99\%} = 2\times t_{90\%}$.	

35	What are threshold and activation energy? The rate constant of a first order reaction becomes 5 times when the temprature is raised from 350 K TO 400K. Calculate the activation energy of the reaction	**[5]**
ANS.	. Activation energy is the minimum energy which must supplied to the reactant molecule so that the collision between the reactant molecules is effective and can produce the chemical change. And threshold energy is the total energy that a reactant must have to convert into products From Arrhenius equation $\mathrm{Log}\,k_2/k_1 = E_a/2.303\,R[1/T_1-1/T_2]$ Log of $5x/x = E_a/(2.303 \times 8.314) \times [1/350-1/400]$ $\mathrm{Log}5 = E_a/(2.303 \times 8.314)[50/350 \times 400]$ $E_a = (\log 5 \times 2.303 \times 8.314 \times 350 \times 400)/50$ = 37480 j/mol =37.480Kj/mol	

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CLASS- XII

CHEMISTRY (043)

CHAPTER NAME: The d- and f- Block elements

PREPARED BY: GROUP IV MEMBERS

SHORT NOTES OF d- & f block elements •

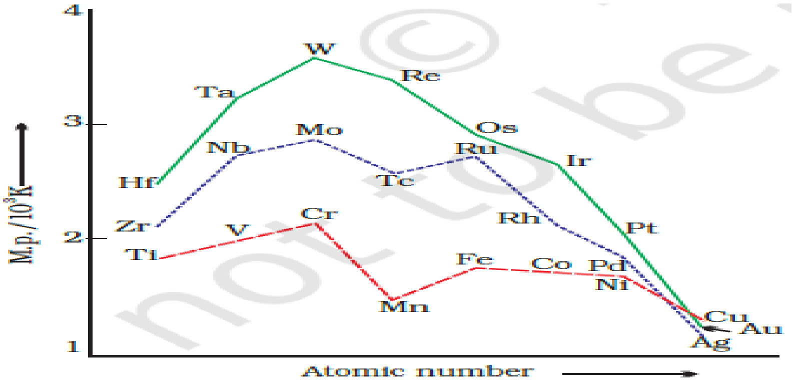
- The elements of group 3-12 which have incompletely filled d-orbitals in the ground state are called d- block elements. •
- They are also called transitional elements as their properties are in between those of s and p block elements. •
- The electronic configuration is given as $(n-1)\ d^{1-10}\ ns^{1-2}$.

Ist Transition series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	2	2
3d	1	2	3	4	5	6	7	8	10	10
2nd Transition series	y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	3	4	5	6	7	8	9	10
3rd Transition series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	8	10	10
4th Transition series	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

General properties •

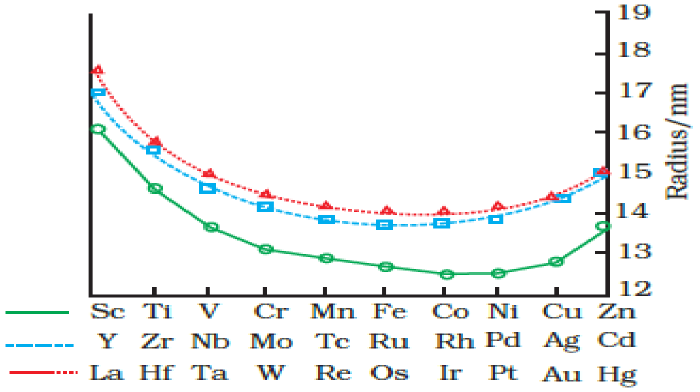
- Physical Properties They are all metals, malleable and ductile(except Hg) .
- They display high tensile strength, high thermal and electrical conductivity

- **Variation in melting points**



The Melting of Mn is low due to presence of extra stable d^5 electronic congigration.

- **Variation in atomic and ionic sizes**
  - With increasing atomic number, ions of the same charge in given series experience decrease in radius as when a new electron enters a d orbital, the nuclear charge increases by unity.
  - 4f orbitals must be filled before 5d orbitals which leads to a regular decrease in atomic radii known as Lanthanoid contraction which is responsible for decreasing atomic sizes with increasing atomic number.



- • **Ionisation Enthalpy**
  - The ionization enthalpy in a group decreases from 3d to 4d series and increases from 4d to 5d series because of Lanthanoid contraction.
  - Mn^+ has $3d^5 4s^1$ configuration and configuration of Cr^+ is d^5, therefore, ionisation enthalpy of Mn^+ is lower than Cr^+. In the same way, Fe^{2+} has d^6 configuration and Mn^{2+} has $3d^5$ configuration. Hence, ionisation enthalpy of Fe^{2+} is lower than the Mn^{2+}.In other words, we can say that the third ionisation enthalpy of Fe is lower than that of Mn.
- **Oxidation states**
  - Transition elements show a great variety of oxidation states in the compounds due to incomplete d-orbitals.
  - Elements in the middle of the group have the maximum number of oxidation states, example: Manganese exhibits oxidation states from +2 to +7.
  - Transition elements show higher oxidation in oxide because oxygen is divalent use as bridge atom.

- **Trends in the M^{2+}/M Standard Electrode Potentials**
    - No regular trend is shown in E° values as ionization and sublimation enthalpy have no regular trend.
    - $E^0_{Cu^{2+}/Cu} = +0.34$ Volt because ionisation enthalpies does not compensate by $\Delta_{hyd}H^0$
- **Magnetic Properties**
    - The two types of elements are diamagnetic and paramagnetic.
    - Diamagnetic substances have paired electrons only like Zn whereas paramagnetic substances have atleast one unpaired electron.
    - The magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,$\mu = \sqrt{n}(n + 2)$ Bohr magneton (BM)

where n is the number of unpaired electrons

- **Colored compound formation**
    - The transition elements form colored ions as they have unpaired d-electrons. When light is absorbed in the visible region, it causes excitation of unpaired d-electrons after return of electron in ground state which causesformation of colored compounds. Which is also called d-d transition.

- **Alloy Formation**
    - d- block elements form alloy due to: Availability of d-orbitals for bond formation high ionic charges, Similar sizes of the metal ions.
    - Some of the alloys are Steel and Brass.

- **Chemical Reactivity**
    - Transition metals differ in chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids while few of them stay unaffected by simple acids.
- **Catalytic Properties**
    - Many of the transition metals and their compounds acts as catalyst, especially oxides.
    - Some of the commonly used catalysts are Iron, Nickel, Cobalt, Platinum and their compounds.
    - Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).
- **Interstitial Compound Formation**
    - These are the compounds formed when small atoms (H, C, and N) get trapped inside the crystal lattices of metals. Example: TiC, Fe_3H, Mn_4N.
    - They are chemically inert, have a good metallic conductivity and are extremely hard.
- **Compounds of Transition Elements**

  Potassium dichromate ($K_2Cr_2O_7$)
    - It is a crystalline solid orange in colour.
    - It is prepared from the chromate ore using the following reactions:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

- The sodium chromate solution (yellow colour) is acidified with sulphuric acid
  $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$
- The $Na_2Cr_2O_7$ solution (Orange Colour solution) is treated with potassium chloride formed $K_2Cr_2O_7$ (orange coloured crystal)
  $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$
- It is used in preparation of azo compounds and in leather industry.

Potassium Permanganate ($KMnO_4$)

- It is a crystalline solid dark purple in color.
- It is prepared commercially as

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

- It is used in titration, bleaching of silk and in organic synthesis.

❖ f block elements

- The f block elements comprises of two series of elements called Lanthanoids and Actinoids.
- The general electronic configuration for f block elements is $(n-2)\, f^{1-14}\, (n-1)^{d-1}\, ns^2$.

n=6 for Lanthanoid and n=7 for Actinoids

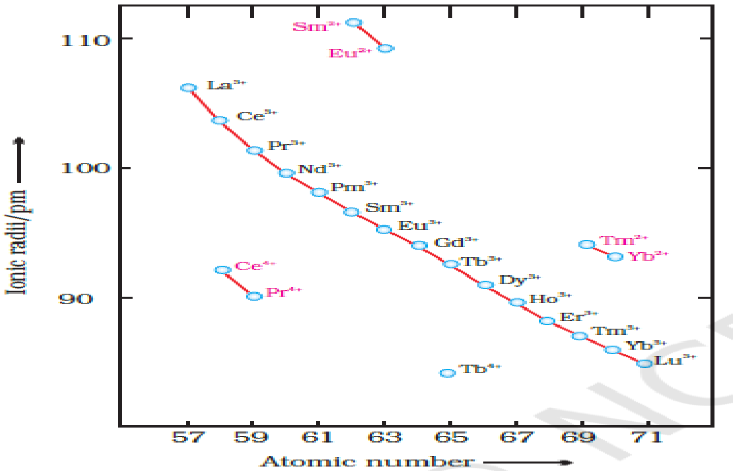
- **Lanthanoids**

General Properties

- They are soft metals silvery white in colour.
- They are good conductors of electricity.

Atomic and ionic sizes

- There is an overall decrease in atomic and ionic radii from La to Lu (with increasing atomic number) due to Lanthanoid Contraction.



Oxidation States

- Some of the elements exhibit +2 and +4 oxidation states but mainly they show +3 oxidation state.

- **Actinoids**

General Properties

- Actinoids are radioactive elements.

- They have high melting point and are highly electropositive.

Atomic and ionic radii

- With increasing atomic number, the electrons are added to the 5f shell resulting in increase in nuclear charge causing the shell to shrink which is known as actinoid contraction. Due to actinoid contraction, atomic and ionic radii decrease with increasing atomic number

Oxidation States

- They generally exhibit +3 oxidation state but the distribution in oxidation states is uneven. They exhibit higher oxidation states of +4, +5, +6, +7.

- **Comparison of Lanthanoids with Actinoids**

Lanthanoids	Actinoids
They are less reactive than actinoids.	They are highly reactive metals.
4f orbital is progressively filled.	5f orbital is progressively filled.
hey show limited oxidation state +2, +3, +4	A variety of oxidation states is shown. +3, +4, +5, +6, +7
They are non-radioactive except promethium.	They are radioactive elements.

QUESTION BANK

SECTION-A The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.		
1	Which one of the following is diamagnetic ion? (a) Co^{2+} (b)Ni^{2+} (c) Cu^{2+} (d)Zn^{2+}	**[1]**
2	The number of unpaired electrons in gaseous species of Mn^{3+}, Cl^{3+} and V^{3+} respectively areand the most stable species is (a) 4, 3 and 2; V^{3+} (b) 3, 3 and 2; Cr^{3+} (c) 4, 3 and 2; Cr^{3+} (d)3, 3 and 3; Mn^{3+}	**[1]**
3	Fe^{3+} ion is more stable than Fe^{2+} ion because (a) more the charge on the atom, more is its stability (b) configuration of Fe^{2+} is $3d^6$ while Fe^{3+} is $3d^5$ (c) Fe^{2+} has a larger size than Fe^{3+} (d) d)Fe^{3+} ions are coloured hence more stable	**[1]**
4	Colour of transition metal ions are due to absorption of some wavelength. This results in	**[1]**

	(a) p-p transition (b) f-f transition (c)s-p transition (d) d-d transition	
5	What happens when potassium iodide reacts with acidic solution of potassium dichromate? (a) It liberates iodine (b)Potassium sulphate is formed (c) Chromium sulphate is formed (d)All the above products are formed	**[1]**
6	The melting point of copper is higher than that of zinc because (a) copper has a bcc structure (b)the atomic volume of copper is higher (c) the electrons of copper are involved in metallic bonding (d) the 's' as well as 'd' electrons of copper are involved in metallic bonding	**[1]**
7	Which of the following statements is not correct? (a) La(OH)$_3$ is less basic than Lu(OH)$_3$ (b) La is actually an element of transition series rather than Lanthanoids (c) Atomic radius of Zr and Hf is same (d) In Lanthanoid series, the ionic radius of Lu^{3+} is smallest	**[1]**
8	Interstitial compounds are formed when small atoms are trapped inside the crystal lattice ofmetals. Which of the following is not the characteristic property of interstitial compounds? (a)They have high melting points in comparison to pure metals. (b)They are very hard (c) They retain metallic conductivity. (d)They are chemically very reactive	**[1]**
9	Cerium (Z=58) is an important member of lanthanoids. Which of the following statementsabout cerium is incorrect (a) The common oxidation state of cerium are +3 and +4. (b)The +3 oxidation state of cerium is more stable than +4 oxidation state. (c)The +4 oxidation state of cerium is not known solutions. (d) Cerium(IV) acts as an oxidizing agent.	**[1]**
10	Which of the following element is used in treatment of cancer? (a) Th (b) U (c) Pu (d) Np	**[1]**
	In the following questions (Q. No. 11 - 20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (b) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	**Assertion** : Reactivity of transition elements decreases almost regularly from Sc to Cu.	**[1]**

	Reason : There is regular increase in I. E. across the series.	
12	**Assertion** : KMnO4 acts as an oxidising agent in acidic, basic or neutral medium. **Reason** : It oxidises ferrous sulphate to ferric sulphate.	**[1]**
13	**Assertion** : Cu^+ ion is not stable in aqueous solution. **Reason** :Large value of I.E. of Cu is compensated by much more negative hydration energy ofCu^{2+} (aq).	**[1]**
14	**Assertion** : Actinoid contraction is greater than lanthanoid contraction. **Re**ason : In Actinoids 5f subshell is present with very poor shielding of electrons.	**[1]**
15	**Assertion** : Transition metal Fe is used as catalyst in ammonia production. **Reason** : Fe is consumed in the reaction to produce good yield of products.	**[1]**
16	Assertion : Zinc is not regarded as a transition element. Reason : In Zn, 3d orbitals are completely filled in its ground as well as in its oxidised state.	**[1]**
17	Assertion : Manganese has an exceptionally low melting point in 3d series. Reason : Manganese has weak metallic bond due to inter electronic repulsion. .	**[1]**
18	Assertion : Transition metal show very low degree of paramagnetism. Reason : Transition metal atoms has large number of unpaired electron.. .	**[1]**
19	Assertion : Actinoids shows more variety of oxidation state. Reason : Actinoids are comparatively larger size than lanthanoids. .	**[1]**
20	Assertion : The higher oxidation state of transition metals usually seen in oxide and oxoanions Reason : oxygen is capable to form multiple bond with transition metals. .	**[1]**

ANSWER KEY:

1	**d**	**2**	**c**	**3**	**B**	**4**	**d**	**5**	**d**
6	**c**	**7**	**a**	**8**	**D**	**9**	**c**	**10**	**a**
11	**a**	**12**	**b**	**13**	**A**	**14**	**a**	**15**	**c**
16	**a**	**17**	**c**	**18**	**D**	**19**	**b**	**20**	**a**

	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	Explain the following: (a) The enthalpies of atomization of transition metals are quite high. (b) The transition metals and many of their compounds act as good catalysts	**[2]**
ANS.	(a) In transition elements, there are large number of unpaired electrons in their atoms, thus they have a stronger inter atomic interaction and thereby stronger bonding between the atoms. Due to this they have high enthalpies of atomization. (b) Because they provide surface and utilised electron of d-orbitals for binding, they can easily form intermediate products	

<table>
<tr><td>22</td><td>How would you account for the following?
(i) The highest oxidation state of a transition metal is usually exhibited in its oxide.
(ii) The oxidising power of the following three oxoions in the series follows the order
$VO^{+2} < Cr_2O_7^{-2} < MnO^{-}_4$</td><td>[2]</td></tr>
<tr><td>ANS.</td><td>(i) because oxygen is divalent and use as bridge atom.
(ii) As oxidation number of metal atom in metal oxide increases, oxidising power increases</td><td></td></tr>
<tr><td>23</td><td>Describe the general trends in the following properties of the first series (3d) of the transition elements:
(i) Number of oxidation states exhibited
(ii) Formation of oxometal ions</td><td>[2]</td></tr>
<tr><td>ANS.</td><td>(i) The number of oxidation states increases upto middle of series i.e. unto +7 and then decreases.
(ii) Oxometal ions are polyatomic ions with oxygen. Example : VO^{2+}, VO^{+2}, TiO^{2+}</td><td></td></tr>
<tr><td>24</td><td>Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (i) iodine (ii) H_2S.</td><td>[2]</td></tr>
<tr><td>ANS.</td><td>$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
Cr_2O_7 2– + 8H+ + $3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O$</td><td></td></tr>
<tr><td>25</td><td>What is Mischmetal and write its composition. Also write its uses.</td><td>[2]</td></tr>
<tr><td>ANS.</td><td>Mischmetal is an alloy of lanthanum. Composition: Lanthanoid metal (95%), Iron (5%) and traces of C, S, Ca and Al.
It is used in Mg based alloy to produce bullets, shell and lighter flint.</td><td></td></tr>
<tr><td></td><td>SECTION C
The following questions are short answer type and carry 3 marks each.</td><td></td></tr>
<tr><td>26</td><td>When MnO2 is fused with KOH in the presence of KNO3 as an oxidizing agent, it gives a dark green compound (A). Compound (A) disproportionate in acidic solution to give purple compound (B). An alkaline solution of compound (B) oxidises KI to compound (C) whereas an acidified solution of compound (B) oxidises KI to (D). Identify (A), (B), (C), and (D).</td><td>[3]</td></tr>
<tr><td>ANS.</td><td>A = K_2MnO_4 / MnO_4^{2-}
B = $KMnO_4$ / MnO_4^{--}
C = IO_3^- or KIO_3
D = I_2</td><td></td></tr>
<tr><td>27</td><td><table>
<tr><td></td><td>Cr</td><td>Mn</td><td>Fe</td><td>Co</td><td>Ni</td><td>Cu</td><td>Zn</td></tr>
<tr><td>$E^0{}_{M^{2+}/M}$</td><td>-0.91</td><td>-1.18</td><td>-0.44</td><td>-0.28</td><td>-.025</td><td>+0.34</td><td>-0.76</td></tr>
</table>
From the given E^o values of the first row transition elements, answer the following questions
(i) Why is E^o $Mn^{2+/}Mn$ value highly negative as compared to other elements ?
(ii) What is the reason for the irregularity in the above E^o values ?
(iii) Why is E^o $Cu^{2+/}Cu$ value exceptionally positive ?</td><td>[3]</td></tr>
</table>

ANS.	(i) Because of the stable half-filled $3d^5$ configuration in Mn^{2+}. (ii) Because of the irregular sum of ΔiH_1 and ΔiH_2 values. (iii) Because of ΔaH^o, sum of ΔiH_1 and ΔiH_2 values do not compensate by $\Delta_{hyd}H^o$.	
28	What is meant by the term lanthanoid contraction? and what are its consequences.	**[3]**
ANS.	Lanthanoid contraction: Steady decrease in the size of the lanthanoids with increase in the atomic number across the period. The electrons of 4f orbitals offer imperfect / poor shielding effect in the same subshell. Consequences: i) Due to this 5d series elements have nearly same radii as that of 4d series. ii) Decrease in the basic strength from La(OH)3 to Lu(OH)3. iii) Due to similar atomic size there is difficulty in separation of lanthanides.	
29	How would you account for the following? (i) With the same d-orbital configuration (d^4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidizing agent. (ii) The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series. (iii) Actinoids show wide range of oxidation states.	**[3]**
ANS.	(i) Cr^{2+} has the configuration $3d^4$ which easily changes to d3due to stable half filled t_2g orbitals. Therefore Cr^{2+} is reducing agent. While Mn^{2+} has stable half filled d^5configuration. Hence Mn^{3+} easily changes to Mn^{2+} and acts as oxidising agent. (ii) Due to comparable energies of 5f 6d and 7s orbitals of actinoids, these show larger number of oxidation states than corresponding members of lanthanoids (iii) Due to comparable energies of 5f ,6d and 7s orbitals / levels.	
30.	(i) Silver atom has completely filled d-orbitals in its ground state, it is still considered to be a transition element. Justify the statement. (ii) Why are E^o values of Mn and Zn more negative than expected ? (iii) Why do transition metals form alloys ?	
ANS.	(i) Silver has incompletely filled d-orbitals but d9 configuration in +2 oxidation state. (ii) Mn^{2+} and Zn^{2+} has stable half-filled and fully filled configurations / relatively less sublimation enthalpy of Mn and Zn. (iii) Because of similar atomic radii.	
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula (n-1)*d*10n*s*2. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements. The *d* orbitals of the transition elements protrude to the periphery of an atom more than the other orbitals (i.e., *s* and *p*), hence, they are more influenced by the surroundings as well as affect the atoms or molecules surrounding them. In some respects, ions of a given d^n configuration (n = 1 – 9) have similar magnetic and electronic properties. With partly	**[4]**

	filled *d* orbitals these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. All these characteristics have been discussed in detail later in this Unit. There are greater similarities in the properties of the transition elements of a horizontal row in contrast to the non-transition elements. However, some group similarities also exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3*d* row) and then consider some group similarities.	
31.1	On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not?	
ANS.	On the basis of incompletely filled 3*d* orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled *d* orbitals ($3d^{10}$) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.	
31.2	Which element in 3d series has lowest enthalpy of atomisation?	
ANS.	Zn	
31.3	Calculate the spin-only moment of Co^{2+} (Z = 27) by writing the electronic configuration of Co and Co^{2+}.	
ANS.	Co = $[Ar]4s^2\ 3d^7$, Co^{+2} = $[Ar]\ 3d^7$ $\mu = \sqrt{n(n+2)}$,$\mu = \sqrt{3(3+2)}$, $\mu = \sqrt{15}$ BM	
	OR	
31.3	Which of the following cations are coloured in aqueous solutions and why? Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+}. (Atomic Number Sc-21, Ti-22, V-23, Mn-25)	
ANS.	$Sc^{3+} = 3d^0 4s^0$ = no unpaired electron $V^{3+} = 3d^1 4s^0$ = unpaired electron $Ti^{4+} = 3d^0 4s^0$ = no unpaired electron $Mn^{2+} = 3d^5 4s^0$ = 5 unpaired electron Thus V^{3+} and Mn^{2+} are coloured in their aqueous solution due to presence of unpaired electron.	
32	The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many *d* electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no *d* electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the *s* and *d* electrons upto manganese ($Ti^{IV}O_2$, $V^{V}O_2^{+}$,$Cr^{V1}O_4^{2-}$, $Mn^{VII}O_4^{-}$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}. The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d* orbitals in such a way that their oxidation states differ from each other	**[4]**

	by unity, e.g., V^{II}, V^{III},V^{IV}, V^{V}. This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two. An interesting feature in the variability of oxidation states of the *d*–block elements is notice among the groups (groups 4 through 10). Although in the *p*–block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of *d*-block. For example, in group 6, $Mo^{(VI)}$ and $W^{(VI)}$ are found to be more stable than $Cr^{(VI)}$. Thus Cr($^{VI)}$ in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not. Low oxidation states are found when a complex compound has ligands capable of p-acceptor character in addition to the s-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel andiron is zero.	
32.1	Name a first series transition element which does not exhibit variable oxidation states.	
ANS.	Scandium (*Z* = 21) does not exhibit variable oxidation states.	
32.2	Which of the 3*d* series of the transition metals exhibits the largest number of oxidation states and why?	
ANS.	Manganese (Z = 25), as its atom has the maximum number of unpaired electrons.	
32.3	What is meant by 'disproportionation' of an oxidation state? Give an example.	
ANS.	When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution $3\ Mn^{VI}O_4^{2-} + 4\ H^+ \longrightarrow 2\ MnV^{II}O_4^- + Mn^{IV}O_2 + 2H_2O$	
	OR	
32.3	Explain why Cu^+ ion is not stable in aqueous solutions?	
ANS.	Cu+ in aqueous solution undergoes disproportionation, i.e., $2Cu^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$ The E^0 value for this is favourable.	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	(a) Describe the preparation of potassium dichromate from chromite ore. What is the effect of change of pH on dichromate ion? (b) How is the variability in oxidation states of transition elements different from that of non-transition elements? Illustrate with examples.	**[5]**
ANS.	**a) Potassium dichromate is prepared from chromate by reacting chromite ore with Na_2CO_3** $4\ FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$. The yellow solution of sodium chromate is filtered off and acidified with H_2SO_4 to give orange sodium dichromate $2Na_2CrO_4 + 2H+ \rightarrow Na_2Cr_2O_7 + H_2O + 2Na$ Sodium dichromate is then treated with KCl to give potassium dichromate as orange crystals. $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O7^{2-} + H_2O$ $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$	

	(b) In transition elements, the successive oxidation state differs by unity, e.g, Mn shows all the oxidation states from +2 to +7. On the other hand, non-transition metals exhibit variable oxidation states which differ by two units, e.g. $Pb^{(II),}$ $Pb^{(IV)}$, $Sn^{(II)}$, $Sn^{(IV)}$ etc	
34	(a) Actinoid contraction is greater from element to element than lanthanoid contraction. Why?. (b) Why do transition metals exhibit higher enthalpies of atomization ? (c) Name an element of lanthanoid series which is well known to shown +4 oxidation state. Is it a strong oxidising agent or reducing agent ? (d) Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why ? (e) Write the ionic equation showing the oxidation of Fe(II) salt by acidified dichromate solution.	**[5]**
ANS.	a) The 5*f* electrons are more effectively shielded from nuclear charge. In other words the 5*f* electrons themselves provide poor shielding from element to element in the series b) Because of strong interatomic interactions / Strong metallic bonding between atoms. c) Cerium / Terbium ; Oxidising agent. d) Cr^{2+} is stronger reducing agent than Fe^{2+} Reason: d^4 —> d^3 occurs in case of Cr^{2+} to Cr^{3+} But d^6 —> d^5 occurs in case of Fe^{2+} to Fe^{3+} e) $Cr_2O_7^{2-} + 14 H^+ + 6 Fe^{2+} \rightarrow 2 Cr^{3+} + 6 Fe^{3+} + 7$ H2O	
35	Assign reasons for the following: a) The enthalpies of atomization of transition elements are high. b) Zr and Hf are of almost identical atomic radii. c) E°$M^{2+/}$M values are not regular for first-row transition metals (3d series). d) Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF4, whereas the highest oxide is Mn_20_7 e) Zn, Cd and Hg are non-transition elements.	**[5]**
ANS.	(a) This is because transition elements have strong metallic bonds as they have large number of unpaired electrons, therefore they have greater inter atomic overlap (b) Because of lanthanoid contraction / poor shielding effect of 4f orbitals. (c) E°(M^{2+}/M) values are not regular in the first transition series metals because of irregular variation of ionization enthalpies (IE1 + IE2) and the sublimation energies. (d)) Among transition elements, the bonds formed in +2 and +3 oxidation states are mostly ionic. The compounds formed in higher oxidation states are generally formed by sharing of d-electrons. Therefore, Mn can form MnO4- which has multiple bonds also, while fluorine cannot form multiple bonds. (e) Zn, Cd and Hg have completely filled d-orbitals in its ground state as well as in its oxidised state.	**(5)**

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CLASS- XII

CHEMISTRY (043)

CHAPTER NAME:COORDINATION CHEMISTRY

PREPARED BY: MEMBERS OF GROUP V

IMPORTANT POINTS/ NOTES ON TIP:

- **(IN FORM OF SHORT NOTES KINDLY INCLUDE GRAPHS, FORMULAS, FLOW CHARTS, DIAGRAM ALSO AS PER REQUIREMENTS OF CHAPTER)**

Introduction

- Complex compounds or coordination compounds are those molecular compounds which retain their identity in solid as well as in solution are known as complexcompounds.

Ligands

The ions or molecules bound to the central atom/ion in the coordination entity arecalled ligands.

Types of Ligands

(i) Unidentate, a ligand which is bound to a metal ion through a single donor atom.

e.g., H2O, NH3, CO, $_{2}$Cl$^{⍰}$, NH $^{⍰}$ etc.

(ii) Didentate, a ligand which is bound to a metal ion through a two donor atoms.


Oxalate ion

ethylene diamine

(iii) Polydentate, a ligand which is bound to a metal ion through a several donor atoms.

e.g., ethylene diamine tetraacetate ion $[EDTA]^{4-}$

(iv) Ambidentate ligands, which can ligate through two different atoms.

e.g. NO^{2-}, ONO^{-},

Chelate ligands, these may be a di- or polydentate ligand which form closed ring with central metal ion. Closed ring is known as chelate ring. Number of more chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity.

Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups *e.g.,* $Co(NH3)6]^{3+}$ are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups *e.g.,* $[Co(NH3)4Cl2]^{+}$, are known as heteroleptic.

Nomenclature of Coordination Compounds

Cationic Complex

[Cr(NH3)3(H2O)3]Cl2

triamminetriaquachromium (III) chloride

(iv) Prefixes mono, di, tri, etc. are used to indicate the number of the individualligands and ligands are named in an alphabetical order.

(v) Central metal atom and oxidation state indicated by Roman numeral inparenthesis.

(vi) Name of ionisable anion.

Anionic Complex

K3[Fe(CN)6]

Potassium hexacyanoferrate (III)

(i) Name of ionisable metal and oxidation state

(ii) Name of ligand in an alphabetical order

(iii)Central metal atom + ate and oxidation

state

Neutral Complex

[Pt(NH3)2Cl(NO2)]

Diammine chloronitrito-N-platinum (II)

(i) Name of ligands in an alphabetical order

(ii) Central metal atom and oxidation state

Isomerism in Coordination Compounds

Stereo isomerism and structural isomerism are the two principal types of isomerismswhich are known among coordination compounds.

Stereo Isomerism

It occurs due to different arrangements of ligands around central metal atom. It is oftwo types : geometrical isomerism and optical isomerism.

Geometrical Isomerism

It arises in heteroleptic complexes due to different possible geometric arrangementsof the ligands. Important examples of this behavior are found in square planar and octahedral complexes.

Optical Isomerism

- It arises when mirror images cannot be superimposed on one another. These mirror images are called as enantiomers. The two forms are called *dextro* (*d*) and *laevo* (*l*).
- Optical isomerism is common in octahedral complexes but at least one didentateligand should be present.

  e.g., $[Co(en)3]^{3+}$, $[PtCl2(en)2]^{2+}$ etc.

Structural Isomerism

(i) **Linkage isomerism,** arises in a coordination compound containing ambidentateligand.

e.g., [Co(NH3)5(NO2)]Cl2 →[Co(NH3)5(ONO)]Cl2

(ii) **Coordination isomerism,** arises from the interchange of ligands betweencationic and anionic entities of different metal ions present in a complex.

e.g., [Co(NH3)6][Cr(CN)6] and [Cr(NH3)6][Co(CN)6]

(iii) **Ionisation isomerism,** when the ionisable anion exchange with anion ligand.

e.g., [CO(NH3)5SO4]Br and [Co(NH3)5Br]SO4

(iv) **Solvate isomerism,** is also known as 'hydrate isomerism'. In this case water isinvolved as a solvent.

e.g., [Cr(H2O)6]Cl3 , [Cr(H2O)5Cl2.H2O and [Cr(H2O)4Cl2]Cl.2H2O

Bonding in Coordination Compounds

Werner’s Theory

(i) In complex compounds, metal atom exhibit two types of valencies – primary valency and secondary valency.

(ii) Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.

(iii) Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decidedby secondary valencies.

Valence Bond Theory

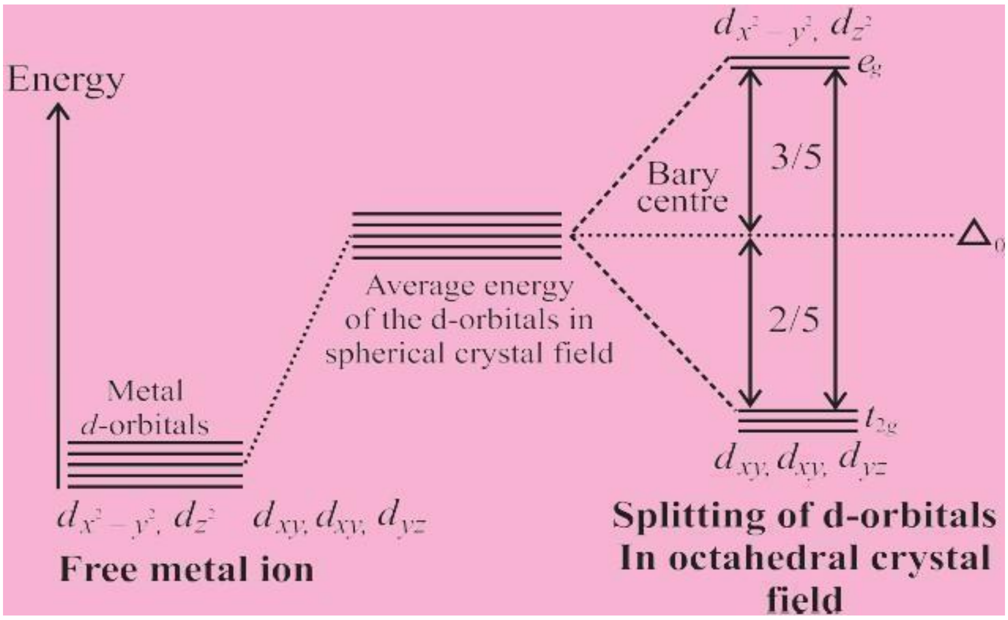
According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlapwith ligand orbitals that can donate electron pairs for bonding.

Crystal Field Theory

The five *d*-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field theory.

Colour in Coordination Compounds

- In complex compounds *d*-orbitals split in two sets *t2g* and *eg*. These have differentenergies. The difference in energies lies in visible region and electron jump from groundstate *t2g* level to higher state *eg* level. This is known as *d-d* transition and it is responsiblefor colour of coordination compounds.
- *d-d* transition takes place in d^1 to d^9 ions, so the ions having d^1 to d^9 configurationare coloured. On the other hand, the ions d^0 and d^{10} configuration



do not show *d-d* transition.

Importance and Applications of Coordination Compounds

2 - Hardness of water is estimated by simple titration with Na EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.
- Some important extraction processes of metals, like those of silver and gold make use of complex formation.
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to [Ni(CO)4], which is decomposed to yield pure nickel.
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, [(Ph3P)3RhCl], a Wilkinson catalyst, is used for the hydrogenation of alkenes.

QUESTION BANK

SECTION-A

The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.

1	The sum of primary valancy and secondary valancy of the metal M in the complex $[M(en)_2(Ox)]Cl$ is a) 3 b) 6 c) -3 d) 9	**[1]**
2	A complex has a molecular formula $MSO_4Cl.6H_2O$ .The aqueous solution of it gives white precipitate with Barium chloride solution and no precipitate is obtained when it is treated with silver nitrate solution. If the secondary valency of the metal is six, which one of the following correctly represents the complex? a) $[M(H_2O)_4Cl]SO_4.2H_2O$ b) $[M(H_2O)_6]SO_4$ c) $[M(H_2O)_5Cl]SO_4.H_2O$ d) $[M(H_2O)_3Cl]SO_4.3H_2O$	**[1]**

3	Oxidation state of Iron and the charge on the ligand NO in [Fe ($H_2O)_5$ NO] SO_4 are a) +2 and 0 respectively b) +3 and 0 respectively c) +3 and -1 respectively d) +1 and +1 respectively	**[1]**
4	Trunbull'sblue is (a) Ferricyanide (b) Ferrous ferricyanide (c) Ferrous cyanide (d) $Fe_3[Fe(CN)_6]_4$	**[1]**
5	Fac-mer isomerism is associated with which one of the following complexes? (a) $[M(AA)_2]$ (b) $[MA_3B_3]$ (c) $[M(AA)_3]$ (d) $[MA_4B_2]$	**[1]**
6	Which of the following is a hexadentate ligand? (a) $EDTA^{4-}$ (b) $(COO)_2^{2-}$ (c) en (d) NH_3	**[1]**
7	Which of the following has square planar structure? (a) $[NiCl_4]^{2-}$ (b) $[Ni(CO)_4]$ (c) $[Ni(CN)_4]^{2-}$ (d) None of these	**[1]**
8	The complex ions $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ are called (a) Ionization isomers (b) Linkage isomers (c) Co-ordination isomers (d) Geometrical isomers	**[1]**

9	Which type of isomerism is shown by the complex compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ (a) Ionisation (b) Optical (c) Linkage (d) Coordination	**[1]**
10	EDTA is used for the estimation of (a) Na^+ and K^+ ions (b) Cl^- and Br^- ions (c) Cu^{2+} and Cs^+ ions (d) Ca^{2+} and Mg^{2+} ions	**[1]**
	In the following questions (Q. No. 11 - 20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (c) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	**Assertion:** Linkage isomerism arises in coordination compounds because of ambidentate ligand. **Reason:** Ambidentate ligand like NO^{2-} has two different donor atoms i.e., N and O	**[1]**
12	**Assertion:** $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colorless. **Reason:** d-d transition is not possible in $[Sc(H_2O)_6]^{3+}$.	**[1]**
13	**Assertion:** Tetrahedral complexes can show geometrical isomerism. **Reason:** This is because all the four ligands lie at the same distance from the Central metal atom in a tetrahedral geometry.	**[1]**

14	**Assertion:** Optical isomerism is not shown by square planar complexes. Reason (R): Square planar complexes do not have chiral structure.	**[1]**
15	**Assertion:** Toxic metal ions are removed by the chelating ligands. **Reason:** Chelate complexes tend to be more stable.	**[1]**
16	**Assertion:** $[Ni(CN)_4]^{2-}$ is square planar and diamagnetic **Reason:** It has no unpaired electrons due to the presence of a strong ligand.	**[1]**
17	**Assertion:** Oxalate ion is a bidentate ligand. **Reason:** Oxalate ion has two donor atoms	**[1]**
18	**Assertion:** $[FeF_6]^{3-}$ is a low spin complex. **Reason:** Low spin complexes have a lesser number of unpaired electrons.	**[1]**
19	**Assertion:** Geometrical isomerism is also called cis-trans isomerism. **Reason:** Tetrahedral complexes show geometrical isomerism.	**[1]**
20	**Assertion:** $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic. **Reason:** $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.	**[1]**

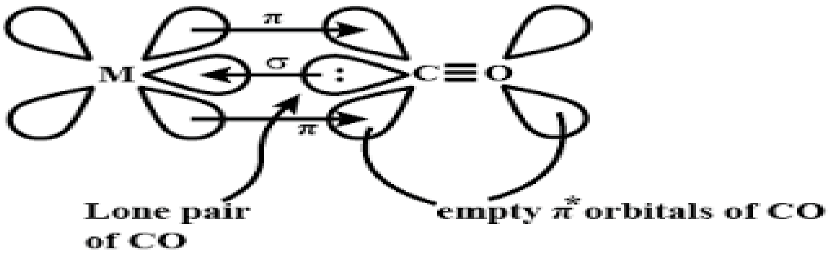
ANSWER KEY:

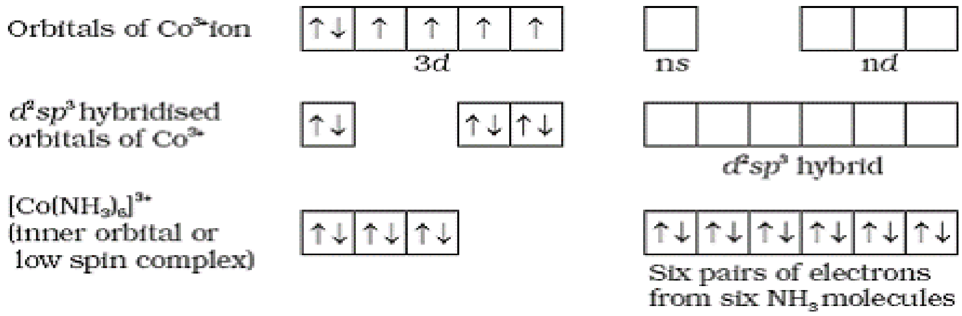
1	**d**	**2**	**c**	**3**	**d**	**4**	**B**	**5**	**b**
6	**a**	**7**	**c**	**8**	**b**	**9**	**a**	**10**	**d**
11	**a**	**12**	**a**	**13**	**d**	**14**	**a**	**15**	**a**
16	**a**	**17**	**a**	**18**	**d**	**19**	**c**	**20**	**b**

	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	Why are tetrahedral complexes high spin?	**[2]**
ANS.	It is because of small splitting energy gap, electrons are not forced to pair, therefore, there are large number of unpaired electrons, i.e. high spin.	
22	Write the IUPAC name of the complex $[Cr(NH_3)_4 Cl_2]^+$. What type of isomerism does it exhibit?	**[2]**
ANS.	IUPAC name : Tetraamine dichlorido chromium (III) ion. It exhibits geometrical isomerism.	
23	When a co-ordination compound $CrCl_3 .6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write i) Structural formula of the complex.	**[2]**

	(ii) IUPAC name of the complex.	
ANS.	i) The complex formed on mixing a coordination compound $CrCl_3 .6H_2 O$ with $AgNO_3$ is as follows $CrCl_3 .6H_2O + AgNO_3 \rightarrow [Cr(H_2O)_5Cl]Cl_2 . H_2O$ (ii) Pentaaquachloridochromium (III) chloride monohydrate	
24	Give evidence that $[Co (NH_3)_5Cl] SO_4$ and $[Co (NH_3)_5(SO_4)] Cl$ are ionization isomers.	**[2]**
ANS.	$[Co (NH_3)_5Cl] SO_4 + BaCl_2 \rightarrow BaSO_4$ (white ppt) $[Co (NH_3)_5(SO_4)] Cl + AgNO_3$ -→AgCl (white ppt)	
25	Indicate the types of isomerism exhibited by the following complexes. (i) $K [Cr (H_2O)_2(C_2O_4)_2$ (ii) $[Co(en)_3]Cl_3$ (iii) $[Co (NH_3)_5(NO_2)](NO_3)_2$ (iv) $[Pt(NH_3)(H_2O)Cl_2]$	**[2]**
ANS.	(i) Both geometrical (cis and trans) and optical isomers for cis. (ii) Two optical isomers (iii) Geometrical, ionization and linkage isomers. (iv) Geometrical (cis and trans)	
	SECTION C The following questions are short answer type and carry 3 marks each.	
26	Explain why $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex. (At. no. Co = 27, Ni = 28)	**[3]**
ANS.	In $[Co(NH_3]^{3+}$ $d^2 sp^3$, the d-electrons of Co^{3+} ([Ar]$3d^6$ get paired leaving behind two empty d-orbital and undergo hybridization and hence inner orbital complex, while in $[Ni(NH3)_6]^{2+}$ the d-electrons of Ni^{2+} ([Ar]$3d^8$ do not pair up and use outer 4d subshell hence outer orbital complex.	
27	Give the name, the stereochemistry and the magnetic behaviour of the following complexes: (i) $[CO(NH_3)_5] Cl] Cl_2$	**[3]**

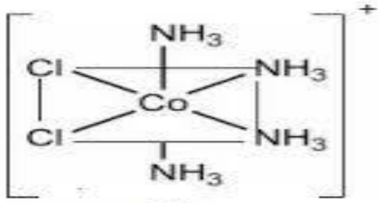
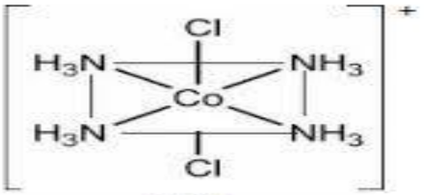
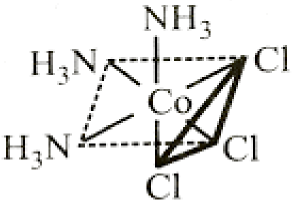
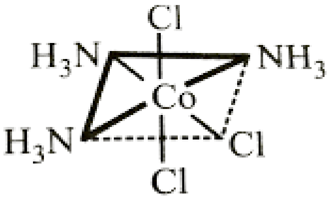
	(ii) K_2 [Ni(CN)$_4$	
ANS.	(i)Pentaammine chloridocobalt (III)chloride. It is octahedral (d^2sp^3) and diamagnetic. (ii)Potassium tetracyanido nickelate(II). It is square planar (dsp^2 hybridised) and diamagnetic	
28	(i) What type of isomerism is shown by $[CO(NH_3)_5 ONO]Cl_2$? (ii) On the basis of crystal field theory, write the electronic configuration for d^4 ion if Δ 0 < P. (iii) Write the hybridization and shape of $[Fe(CN)_6]^{3-}$. (Atomic number of Fe is 26)	**[3]**
ANS.	(i) Linkage isomerism (ii) t_2g^3 eg^1 (iii) d^2sp^3, octahedral shape.	
29	(a) Predict the number of unpaired electrons in hexaaquamanganese(II) ion. [Atomic number of Mn = 25] (b) Write the chemical formula and shape of hexaamminecobalt(III) sulphate. (c) A $CuSO_4$ solution is mixed with $(NH_4)_2SO_4$ solution in the ratio of 1 : 4 does not give test for Cu^{2+} ion, Why?	**[3]**
ANS.	(a) It has 5 unpaired electrons. (b) $[Co(NH_3)_6]_2(SO_4)_3$, octahedral. (c) $[Cu(NH_3)_4]SO_4$ is formed which does not have free Cu2+ ions.	
30.	State a reason for each of the following situations: (i) Co^{2+} is easily oxidised to Co^{3+} in presence of a strong ligand. (ii) CO is a stronger complexing reagent than NH_3 . (iii) The molecular shape of $Ni(CO)_4$ is not the same as that of $[Ni(CN)_4]^{2-}$.	**3**
ANS.	(i) Strong ligands provide energy which overcomes 3rd ionisation enthalpy and Co^{2+} gets oxidised to Co^{3+}. (ii) CO can form a sigma as well as pi bond, therefore, it is stronger ligand than NH3 which can form only a sigma bond. (iii) $Ni(CO)_4$ has sp^3 hybridization, tetrahedral shape, whereas $[Ni(CN)_4]^{2-}$ has dsp^2 hybridization, therefore, it has a square planar shape	
	SECTION D	

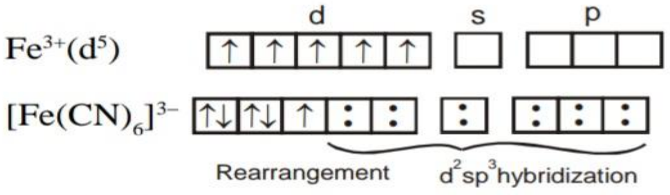
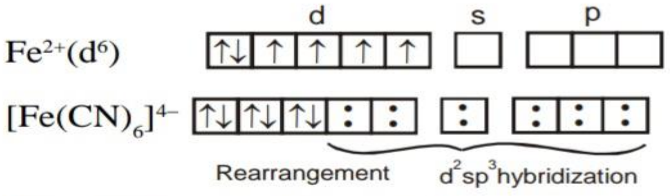
	The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.	
31	PASSAGE: **Read the passage given below and answer the following questions:** For understanding the structure and bonding in transition metal complexes, the magnetic properties are very helpful. Low spin complexes are generally diamagnetic because of pairing of electrons, whereas high spin complexes are usually paramagnetic because of presence of unpaired electrons. Larger the number of unpaired electrons, stronger will be the para magnetism. However magnetic behaviour of a complex can be confirmed from magnetic moment measurement Magnetic moment $\mu=\sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons. Greater the number of unpaired electrons more will be the magnetic moment. Metal carbonyl is an example of coordination compounds in which carbon monoxide (CO) acts as ligand. These are also called homoleptic carbonyls. These compounds contain both σ and π character. Some carbonyls have metal-metal bonds. The reactivity of metal carbonyls is due to (i) the metal centre and (ii) the CO ligands. CO is capable of accepting an appreciable amount of electron density from the metal atom into their empty π or π* orbitals. These types of ligands are called π-accepter or π-acid ligands. These interactions increase the Δo value...	
31.1	a).What is the oxidation state of metal in [$Mn_2(CO)_{10}$]?	**1**
ANS.	Zero	
31.2	b).Give two examples of ambidentate ligands.	**1**
ANS.	CN^- and NO_2^-	
31.3	c).Explain synergic bonding in carbonyl compounds	**2**
ANS.	The metal-carbon bond in a metal carbonyl is characterized by both σ and π. The synergic action of the metal-ligand link strengthens the binding between the carbonyl molecule and the metal. A lone pair of electrons on the carbonyl carbon must be donated into a vacant orbital of metal to form the M-C sigma bond. In contrast, to form the M-C π bond, a lone pair of electrons must be donated from a filled d orbital of metal to the vacant antibonding π∗ orbital of carbon monoxide. Synergic bonding describes this back bonding ability that helps to stabilise the metal ligand contact 	

	OR	
31.3	Discuss with the help of VBT the Magnetic nature and hybridisation in $[Co(NH_3)_6]^{+3}$	**2**
ANS.		
32	PASSAGE: 1.Below is the table given showing complexes formed from Cobalt(III) chloride and ammonia by Alfred Werner. Observe the table carefully and answer the questions that follow :	**[4]**

Compound	Colour	Moles of AgCl formed from 1 mole of compound	Total no. of ions produced
(A) $CoCl_3.4NH_3$	Violet	1	2
(B) $CoCl3.5NH_3$	Rose	2	3
(C) $CoCl_3.3NH_3$	Blue Green	0	0

32.1	Write the formula & IUPAC name of compound B	
ANS.	**$[Co(NH_3)_5Cl]Cl_2$**	
32.2	How many is the primary and secondary valences of cobalt in compound	
ANS.	**primary valency= 3 , Secondary valency= 6**	
32.3	**Draw geometrical isomers of compound A.**	
ANS.	**A = cis$[Co(NH_3)_4Cl_2]Cl$, trans$[Co(NH_3)_4Cl_2]Cl$**	

	 Cis  Trans	
	OR	
32.3	**Draw geometrical isomers of compound C.**	
ANS.	 *fac-*  *mer-*	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	.(i).$FeSO_4$ solution mixed with $(NH4)_2SO_4$ solution in 1: 1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why? (ii).Predict the number of unpaired electrons and magnetic moment in the square planar $[Pt(CN)_4]^{2-}$ ion. (iii).Although both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ have sp^3 hybridisation yet $[NiCl_4]^{2-}$ is paramagnetic and $[Ni(CO)_4]$ is diamagnetic. Give reason. (Atomic no. of Ni = 28) (iv).Write the electronic configuration of Fe (III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (a) strong field ligand, and (b) weak field ligand. (Atomic no. of Fe = 26) (v).$[Fe(CN)_6]^{3-}$ is weakly paramagnetic whereas $[Fe(CN)_6]^{4-}$ is diamagnetic. Give reason to support this statement. [Atomic no.: Fe = 26]	**[5]**

ANS.	(i) Ferrous sulphate and ammonium sulphate forms a double salt, that is Mohr's salt which is responsible for giving the Fe^{2+} . Whereas Copper forms complex with ammonia. Free cupric ions are not present in solution. The complex salt does not ionize to give $Cu^{2+,}$ hence failing the test. $FeSO_4+(NH_4)_2SO_4+6H_2O \rightarrow FeSO_4(NH_4)2SO_4.6H_2O$(Mohr's salt) $CuSO_4+4NH_3+5H_2O \rightarrow [Cu(NH_3)_4SO_4]5H_2O$ (ii) No. of unpaired electron = 0 ; Magnetic Momentum = 0 ; diamagnetic (iii) This is due to difference in the nature of ligands. Cl^- is weak field ligand and it does not cause the pairing of unpaired 3d electron. Hence $[NiCl_4]^{-2}$ is paramagnetic. In $[Ni(CO)_4]$ Ni is in zero oxidation state i.e. it has a configuration of $3d^8\ 4s^2$. But CO is strong field ligand. Therefore, it causes the pairing of unpaired 3d electron. Also it causes the 4s electrons to shift to the 3d orbital thereby giving rise to sp^3 hybridization. Since no unpaired electrons are present in this Case $[Ni(CO)_4]$ is diamagnetic . (iv) In strong filed $t_2g^5\ e\ g^0$ In weak field $t_2g^3\ e\ g^2$ v)  One d-orbital is singly occupied, hence it is weakly paramagnetic in nature. $[Fe(CN)_6]^{4-}$ involves also d^2sp^3 hybridization but it has Fe^{2+} ion as central io  All orbitals are doubly occupied, hence it is diamagnetic in nature.	
34	.(i).Arrange the following complex ions in increasing order of their crystal field splitting energy (Δ_o) : $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$	[5]

	(ii).Write the hybridization and magnetic character of the complex $[Ni(CO)_4]$ on the basis of valence bond theory. (At. No.: Ni= 28) (iii).Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is: a) More stable? b) The high spin complex? (iv).What is the difference between an ambidentate ligand and bidentate ligand? (v).Write the electronic configuration of d5 in terms of t_{2g} and e_g in an octahedral filed when: (a) $\Delta o > P$, and (b) $\Delta o < P$	
ANS.	(i) CFSE is higher when the complex contains strong field ligand. Thus, crystal field splitting energy increases in the order $[Cr(Cl)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$ Because according to spectrochemical series the order of field strength is $Cl^- < NH_3 < CN^-$ (ii)sp^3 and diamagnetic (iii) a. $[Co(C_2O_4)_3]^{3-}$ b. $[CoF_6]^{3-}$ (iv) A bidentate ligand is one in which a single molecule has two donor sites or atoms and it can bind with two coordinate bonds with a metal at a same time, whereas an ambident ligand has two donor sites or atoms but at a same time only one can bind with metal. Example CN^-, where C and N any one atom can bind as cyano or isocyano with the metal. while $C_2O_4^{2-}$ is a Bidentate it can bind with metal by two O atoms at a same time. (v) (i) $t_{2g}^5 e_g^0$ (ii) $t_{2g} e_g^3$	
35	For the complex $[Fe(en)_2 Cl_2]Cl$, identify the following: (i) Oxidation number of iron. (ii) Hybridisation and shape of the complex. (iii) Magnetic behaviour of the complex. (v) Number of its geometrical isomers. Whether there may be optical isomer also. (vi) Name of the complex.	**[5]**
ANS.	(i) +3 (III) (ii) d^2sp^3, octahedral	

	(iii) paramagnetic (iv) Two geometrical isomers , Yes, there may be optical isomer also due to presence of polydentate ligand. (v) Dichlorido bis-(ethane 1, 2-diamine) Iron (III)	

……

तत् त्वं पूषन् अपावृणु
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CLASS- XII

CHEMISTRY (043)

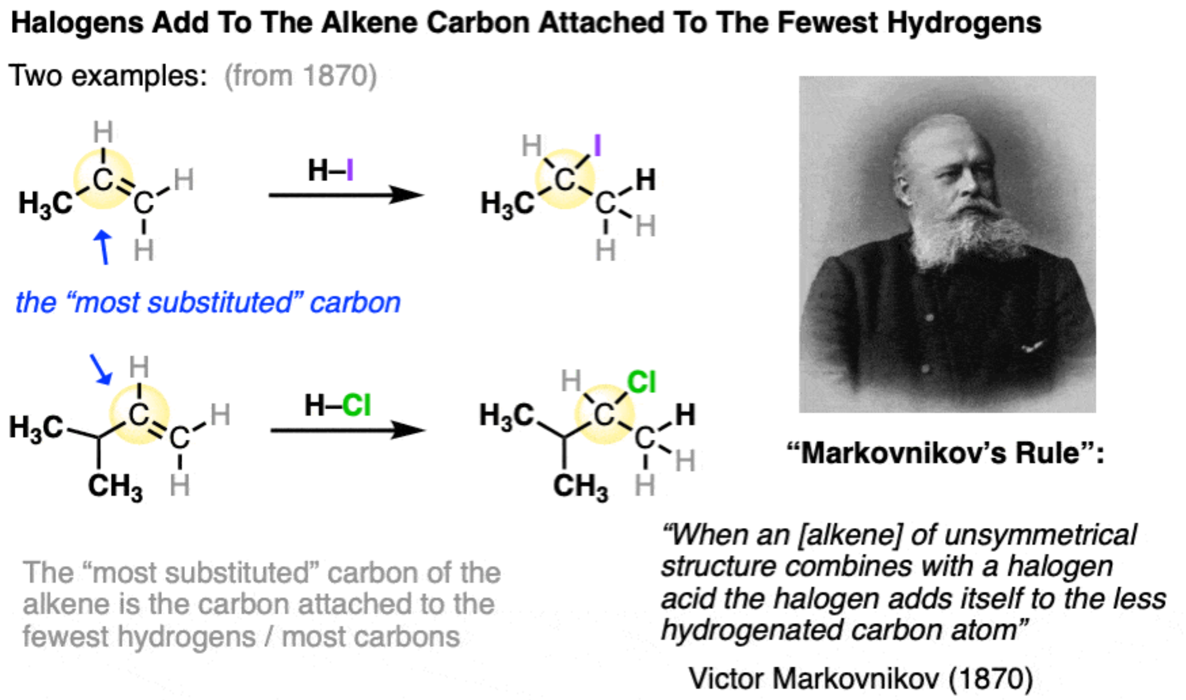
CHAPTER NAME: HALOALKANE AND HALOARENE

PREPARED BY: MEMBERS OF GROUP VI

IMPORTANT POINTS/ NOTES ON TIP:

- **(IN FORM OF SHORT NOTES KINDLY INCLUDE GRAPHS, FORMULAS, FLOW CHARTS, DIAGRAM ALSO AS PER REQUIREMENTS OF CHAPTER)**
- .Nomenclature &Classification
  The various other different rules that are used in the naming compounds are…
- The longest chain of the carbon atoms that contains the halogen atom must be selected.
- Chain must be numbered as per the minimum number of carbon carrying halogen atoms.
- If more than one bond is present i.e double or triple bonds (multiple bonds),then it must be given the preference in numbering the carbon chain.
- In the IUPAC naming system these alkyl halides and Aryl Halide are commonly called the haloalkanes and Haloarene.
- Haloalkanes and haloarenes may be classified as follows: These may be classified as mono, di, or polyhalogen (tri-,tetra-, etc.) compounds depending on whether they contain one, two or more halogen atoms in their structures.

- .Preparation methods of haloalkanes
  (from alcohols , halogen Exchange finkelsteinswarts, from alkenes (markovnikov's rule) addition of halogens
  The most convenient method of preparation of haloalkane is from alcohols. R-OH when reacts with suitable reagents, the reaction results in the formation of R − X. The suitable reagents that help in the reaction are
- Concentrated halogen acids (HX)
- Phosphorus halides (PX_5 or PX_3)
- Thionyl chloride ($SOCl_2$)
- The Finkelstein reaction is used to make alkyl halides and haloalkanes. The Finkelstein reaction is often referred to as the halogen exchange reaction or the halex reaction. The Finkelstein reaction has the following formula: Alkyl iodides are formed when bromide, NaI, alkyl chloride, and dry acetone combine.
  n an early study of this reaction, Russian chemist Victor Markovnikov published the observation that the halogen tended to add to the carbon of the alkene which was bonded to the least number of hydrogens.
- This has come to be known as "Markovnikov's Rule".



Halogens Add To The Alkene Carbon Attached To The Fewest Hydrogens

Two examples: (from 1870)

The "most substituted" carbon of the alkene is the carbon attached to the fewest hydrogens / most carbons

"Markovnikov's Rule":

"When an [alkene] of unsymmetrical structure combines with a halogen acid the halogen adds itself to the less hydrogenated carbon atom"

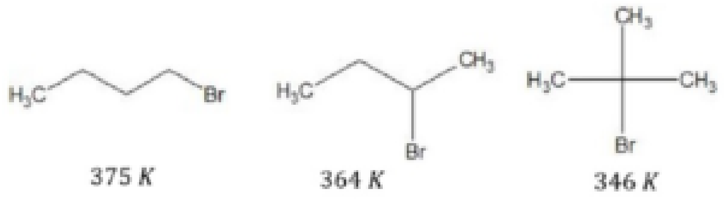
Victor Markovnikov (1870)

- Preparation method of haloarenes (sandmeyer's reaction, electrophilic substitution)
  Sandmeyer Reaction
- i) Radical halogenation

- Formation of alkyl bromide and alkyl chloride is possible by radical halogenation reaction. However, radicals are inherently very non-selective. In addition, radicals are non-specific and highly reactive intermediates that form a mixture of products.
-
- For example, bromination or chlorination of free radicals leads to the formation of various haloalkanes. This makes it difficult to separate a single product. Therefore, it is not the preferred method for preparing haloalkanes.
- CH3CH2CH2CH3−→−−−Cl2/HvCH3CH2CH2CH2Cl+CH3CH2CH(Cl)CH3CH3CH2CH2CH3 →Cl2/HvCH3CH2CH2CH2Cl+CH3CH2CH(Cl)CH3
-
- ii) Electrophilic Substitution Reaction
- This method is useful for the preparation of haloarenes such as aryl bromide and aryl chloride. Electrophilic substitution uses halogens such as chlorine and bromine in the presence of Lewis acid to form aryl bromide and aryl chloride. However, the reaction must follow certain conditions to produce the appropriate electrophile.
-
- For example, the reaction should be carried out in the presence of Lewis acid. In addition, the reaction must take place in the dark. The reaction to obtain an electrophile is as follows:
- C6H5−CH3+X2−→−−−−Fe/DarkCH3−C6H5−X(para)+CH3−C6H5−X(ortho)C6H5−CH3+X2 →Fe/DarkCH3−C6H5−X(para)+CH3−C6H5−X(ortho)
-
- Preparation:
- The electrophiles for the above reaction are Cl^+ and Br^+, and HCl and HBr are by-products of the reaction. Therefore, the electrophilic substitution mechanism is used for producing aryl bromide and aryl chloride.
-
- Sandmeyer Reaction Mechanism
- It is two-step method of Diazonium salt formation and Diazonium salt reaction with a cuprous halide (Cu_2X_2)
-
- Primary aromatic amines react with sodium nitrite in the presence of cold mineral acids to form diazonium salts. In this case, HNO_2 is produced in the reaction by treating sodium nitrite with HX at a temperature of 273 to 278 K.

- C6H5−NH2−→−−−−−−−0.5∘CNaNO2+HClN+2Cl−−C6H5−→−−−−−CuCl/HClC6H5−ClC6H5−NH2→0.5∘CNaNO2+HClN2+Cl−−C6H5→CuCl/HClC6H5−Cl
-
- Haloalkanes and Haloarenes from Alkenes
- Haloalkanes and haloarenes can be prepared by adding halogen (X_2) to the double bond of the alkene. It is also possible to add hydrogen halide (HX). This halogen can be chlorine, bromine, or iodine.
- The addition of HX:
- Alkenes can be converted to haloalkanes by electrophilic addition reaction. Alkenes react with HX to form R-X.
- The order of reactivity of halides with alkenes follows the order of
- HI > HBr > HCl > HF.
- The reaction, in this case, is an example of a regioselective reaction. With this type of reaction, the quantity of the product grows steadily. In addition, the reaction determines the major product by addition to the entire alkene double bond according to Markovnikov's addition rules.
- According to Markovnikov's law, in the addition reaction of asymmetric alkenes, the negative part of the reagent or halogen binds to the carbon-containing fewer hydrogen atoms.
- For example, prop-1-ene reacts with hydrogen bromide to form 2-bromopropane as the main product.
-
- .Physical properties (melting and boiling points, solubility & density)
  1) Physical State
- Alkyl halides are colourless in nature in its pure state. However, bromides and iodides develop colour on exposure to light. The reason for the development of colour is the decomposition of halogens in presence of light. The reaction representing the phenomenon is
- $2R{-}I \dashrightarrow \rightarrow R{-}R + I_2$
- Many of the halogen compounds having volatile nature have a sweet smell. Haloarenes are also colourless liquids or crystalline solids that have a characteristic smell.
- 2) Boiling Point

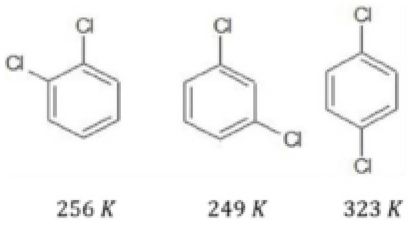
- We know there is a large difference in electronegativity between the carbon and halogen atom of any given compound resulting in the development of highly polarized molecules. The polarity of the C-X bond and higher molecular mass in comparison to the actual hydrocarbon results in the development of very strong intermolecular forces of attraction in the derivatives of halogen.
- The stronger intermolecular forces of attraction are due to dipole-dipole and van der Waals interaction. The boiling point of haloalkanes and haloarenes depends upon the intermolecular forces of attraction. Hence, the boiling points of derivatives of chlorides, bromides, and iodides are comparatively higher the hydrocarbons of the similar molecular mass.
- The size and molecular mass of halogen members increase when we move down the group in the homologous series thereby forming stronger forces of attraction. Hence the boiling point increases as we move down the group in the homologous series.
- The order of the boiling point of alkyl halides are RI > RBr > RCl > RF
- Additionally, the boiling point also increases for isomeric haloalkanes. However, the boiling point decreases with the branching of the compound. This is because branching of haloalkanes results in the lesser surface area, thus decreasing the van der Waal’s forces interaction.
- Moreover, as the branching increases the molecule forms sort of a spherical shape resulting in the decrease in the area of contact and forming weaker intermolecular forces. Derivatives such as methyl chloride, ethyl chloride, methyl bromide and few chlorofluoromethanes are gases at room temperature. However, the higher members of the group are usually solids or liquids.
- Boiling points of haloarenes follow the order: Iodoarene > Bromoarene > Chloroarene. Moreover, the boiling point of isomeric dihaloarenes is almost similar.



Difference in the Boiling Point of Haloalkanes

- 3) Melting Point
- The melting point is based on the strength of the lattice structure of a compound. Isomeric dihalobenzenes have almost similar boiling points but the difference can be seen in the melting points. Para-isomer have a higher melting point in comparison to ortho-isomer and meta-isomer of the same compound.

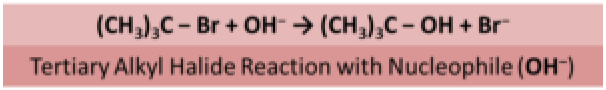
- It is because para-isomers have highly compact crystal lattice in comparison to ortho-isomer and meta-isomer. Therefore, higher numbers of molecules are packed compactly in the crystal lattice. Hence, higher energy is required to break the lattice structure thereby increasing the melting point temperature of the compound.



- Difference in the Melting Point of Haloarenes
- 4) Density
- Density is directly proportional to the mass of any compound. Therefore, as the mass increases down the homologous series, the density increases. Thus, the derivatives of fluorine are less dense than derivatives of chlorine and derivatives of chlorine are less dense than derivatives of bromine.
- Additionally, density increases with the increase in the number of carbon and halogen atoms. Furthermore, it depends upon the atomic mass of the halogen atom. For example, refer to the below diagram

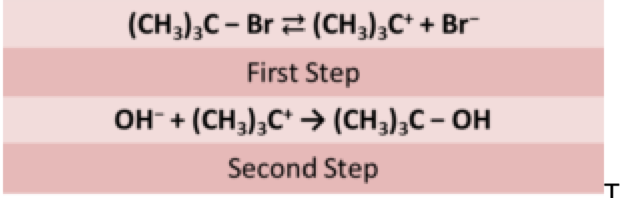
$$n - C_3H_7Cl < n - C_3H_7Br < n - C_3H_7I$$

- $0.89\ g/mL \qquad 1.33\ g/mL \qquad 1.75\ g/mL$
- In the above example, the number of carbon atoms remains same but the mass of halogen atoms is different from one another. This, in turn, increases the density of the derivatives. Therefore, the arrangement of relative densities are
- RI > RBr > RCl
- 5) Solubility
- Alkyl halides are slightly soluble in water. Even though haloalkanes and haloarenes are polar compounds, they are immiscible with water. Relatively larger amount of energy is required for dissolution of a compound and to break the attractive forces between halogen and the carbon atom.
- However, less energy is released when a bond is formed after dissolution ion and water. Moreover, the stability of R-X bond is very low in comparison to the bond formed in water molecules polarity difference.
- Thus, haloalkanes and haloarenes neither develop new H-bond nor it breaks the old H-bonds. Hence, the solubility of R-X is low. However, these compounds are soluble in organic solvents because of the low polarity of organic solvents such as ether, benzene etc.

- Therefore, the strength of the intermolecular forces between organic solvents and carbon-halogen compounds is similar to carbon-halogen molecules and solvent molecules. In the case of haloarenes, para-isomer is less soluble than ortho-isomer.
-
- .Chemical reactions (1. Nucleophilic substitution optical rotation mechanism of substitution reactions (sn1) & (sn2) 2. Elimination reactions (saytzeff) 3. Reaction with metals (grignard reagents &wurtz reaction)
  Reactions of Haloalkanes – Nucleophilic Substitution Reactions
- There are generally two types of nucleophilic substitution reaction.
- SN^1
- SN^2
- Substitution Nucleophilic Unimolecular (SN^1)
- In this section, we will study about SN^1 chemical reaction and what conditions haloalkanes require for undergoing this reaction. The meaning of SN^1 reaction lies in the name itself “substitution, nucleophilic, and unimolecular.” Therefore, this reaction will follow the first order kinetics. In another term, we can say that the rate determining step in this reaction is unimolecular.
- Moreover, the rate of reaction will depend upon the concentration of the one species which in this case is haloalkane or alkyl halide. For instance, if a tertiary alkyl halide and reacts with a nucleophile result in the formation of tertiary alcohol and halide ion.
- 

  $(CH_3)_3C-Br + OH^- \rightarrow (CH_3)_3C-OH + Br^-$

  Tertiary Alkyl Halide Reaction with Nucleophile (OH^-)
- From the reaction, we can decipher that SN^1 reaction is a two-step process and it leads to the formation of carbocation intermediates.
- The First Step: Polarization and cleaving of C-X bond occur to form carbocation intermediates. The first step is the reversible process. It is also the rate determining step of the reaction.
- The Second Step: Nucleophile attacks the carbocation to form the respective product.

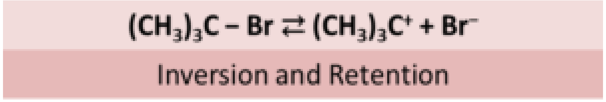
  $(CH_3)_3C-Br \rightleftarrows (CH_3)_3C^+ + Br^-$

  First Step

  $OH^- + (CH_3)_3C^+ \rightarrow (CH_3)_3C-OH$

  Second Step

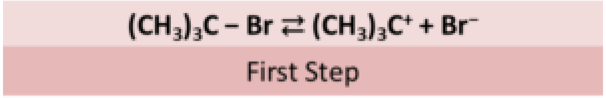
  The planar nature of carbocation results in both inversion and retention configuration.

- 

  $(CH_3)_3C-Br \rightleftarrows (CH_3)_3C^+ + Br^-$

  Inversion and Retention

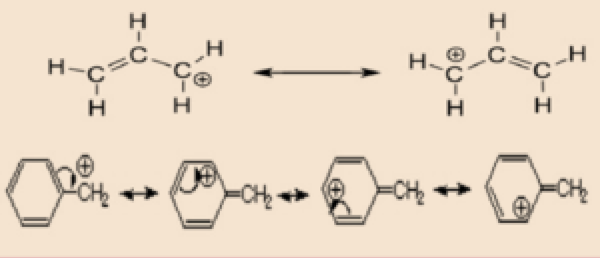
- Conditions of SN^1 Reaction
- The rate of the reaction will depend on the concentration of the alkyl halide and it will not depend upon the nucleophile. This is because the rate always depends on the slowest step which in this case is the breakdown of the C-Br bond in order to form a carbocation. Therefore, the reaction will be a first-order reaction. The breakdown energy for breaking the bond is obtained from solvation of the leaving group.
- Water and alcohol are types of polar protic solvent. These solvents have the capacity to attract the halogen group thereby facilitating the breakdown of C-X bond in the reaction. This will result in the formation of carbocation intermediate. Additionally, the stabilization of leaving the group is possible with the help of the protic solvents through hydrogen bonding. Hence, the first step is



$$(CH_3)_3C - Br \rightleftarrows (CH_3)_3C^+ + Br^-$$

First Step

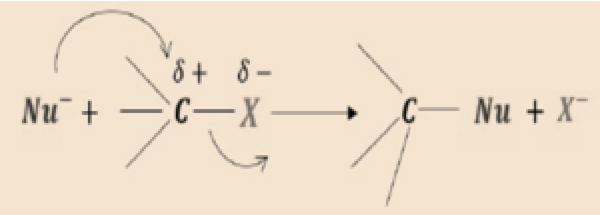
- The stability of carbocation will determine the speed of the rate of reaction (more the stability faster the reaction). Therefore the more easily the leaving group (X^-) can leave the compound the more easily the nucleophile can attack the compound and leads to substitution process.
- Order of Reactivity
- Therefore, the reactivity of halides towards S_N1 reaction is R – I > R – Br > R – Cl > R – F. We know that C-I bond of the alkyl iodides can be easily broken and it is easy to release I^- or the leaving group. Therefore, it becomes easy for the nucleophile to attack the alkyl halides and result in the substitution. On the other hand, it is tough to break C-F bond because it is very strong and in turn, it is difficult for the nucleophile to attack.
- The reactivity order of alkyl halides in the case of S_N1 reaction is- $3^0 > 2^0 > 1^0$ > methyl. The same reason is responsible for more reactivity of compounds such as benzylic halide and allylic halides towards S_N1 reaction because it leads to the formation of highly stable resonance structures of carbocation intermediates.



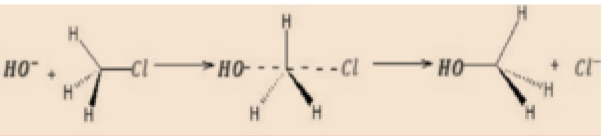
Resonance Structures in S_N1 reaction

- Substitution Nucleophilic Bimolecular (SN^2)
- SN^2 chemical reactions follow second order kinetics. The rate determining step depends on both the concentration of alkyl halides (R-X) and the nucleophile present

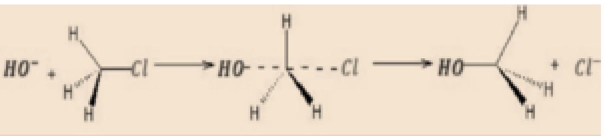
in the reaction. The SN^2 reaction is a one-step process and there is no formation of intermediates. The basic mechanism of the reaction is

- 

  S$_N$2 Reaction

- Mechanism of SN^2 Reaction
- We will study the mechanism of SN^2 chemical reactions with the help of an example. Let's take an example of CH_3Cl haloalkane reacting with the nucleophile OH^-.
- 

  Example of S$_N$2 Reaction

  Example of S$_N$2 Reaction

- This reaction is a one-step process, unlike SN^1 reaction. In this reaction, there is no formation of intermediates. The reaction undergoes a transition state where the nucleophiles are attached to the alkyl halides. Hence it is very clear the rate determining step is dependent on the concentration as well as the nucleophile.
- The order of reactivity of the halides are R − I > R − Br > R − Cl > R − F
- Conditions of the SN^2 Chemical Reactions
- There is a requirement of the strong nucleophile to undergo SN^2 reaction. The reaction takes place in the presence of solvents that are polar aprotic such as DMSO, DMF. The SN^2 reaction does not occur in presence of polar protic solvent because these types of solvent deactivate the charged nucleophile during the bond formation of polar protic solvent with the strong nucleophile.
- Elimination reaction occurs when an alkyl halide reacts with alcoholic KOH solution under heating conditions. The elimination takes place of hydrogen from β –carbon and the elimination of halogen member occur from α –carbon. The reaction will result in the formation of alkene as the final product.
  The Grignard Reaction is the addition of an organomagnesium halide (Grignard reagent) to a ketone or aldehyde, to form a tertiary or secondary alcohol, respectively. The reaction with formaldehyde leads to a primary alcohol.

Wurtz Reaction Equation

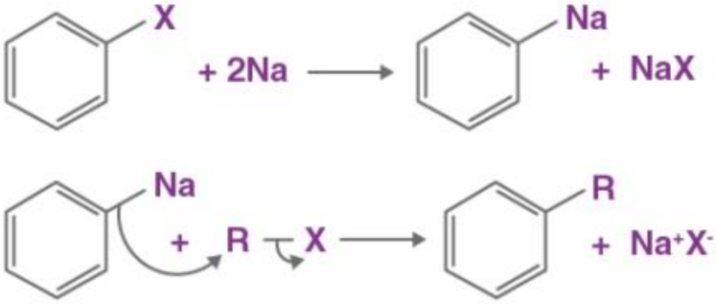
- The general form of the Wurtz reaction equation can be written as follows:
- $2R\text{-}X + 2Na \rightarrow R\text{-}R + 2Na^{+} X^{-}$
- It can be observed from this equation that the two R groups are joined, yielding an alkane with a longer chain along with NaX, where X is a Halogen.

- .Reactions of haloarenes (Nucleophilic substitution, Electrophilic substitution reactions Reaction with metals Wurtz-Fittig reaction &Fittig reaction)

  Nucleophilic Substitution Reactions of HaloarenesThe hydroxyl group acts as a substitute: The halogen atom is replaced by a hydroxyl group when a haloarene is heated to 623K under 300 atmosphere with an aqueous sodium hydroxide solution, generating phenoxide.14 Mar 2022

The replacement of an atom or group of atoms by an electrophile in a molecule is called an electrophilic substitution reaction. Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reaction

When the aryl halide is reacted with sodium metal, an intermediate organo-alkali compound is formed, which is followed by a nucleophilic attack of the alkyl halide as shown below. Thus, the required alkyl-aryl is formed.



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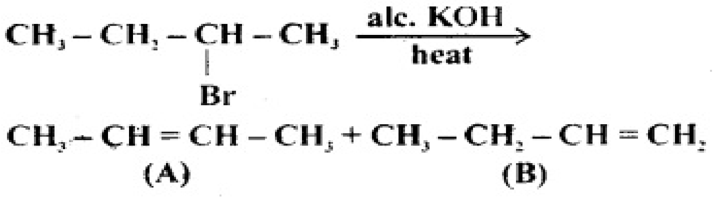
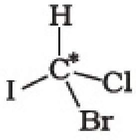
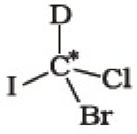
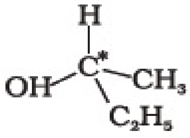
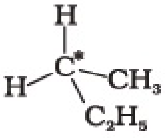
A Fittig reaction is a chemical reaction where two aryl halides react in the presence of Sodium and dry ether. The product formed by the Fittig reaction consists of two aryl groups joined by a single bond.

QUESTION BANK

SECTION-A The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.		
1	Which of the following is correct for the reaction  $CH_3-CH_2-\underset{\mathrm{Br}}{CH}-CH_3 \xrightarrow[\text{heat}]{\text{alc. KOH}}$ $\underset{(A)}{CH_3-CH=CH-CH_3} + \underset{(B)}{CH_3-CH_2-CH=CH_2}$ a) A is major product and B is minor product b) B is major product and A is minor product c) Only A will be obtained as a product d) Only B will be obtained as a product	**[1]**
2	Fluorobenzene can be synthesized in laboratory (A) by heating phenol with HF and KF (B) by heating the benzene diazonium salt with HBF4 (C) by direct fluorination of benzene with F2 gas (D) by heating 1-Bromobenzene with NaF solution	**[1]**
3	. In the solvolysis of 3-Methyl-3 chloro hexane, which of the following statement is not correct? (A) It involves carbocation intermediate (B) the intermediate involves sp2hybridised carbon (C) it involves inversion of configuration (D) the rate of reaction depends on 3-Methyl-3 chlorohexane concentration	**[1]**
4	Tertiary alkyl halides are practically inert to substitution by SN2 mechanism because of (A) steric hindrance (B) inductive effect (C) instability (D) insolubility	**[1]**
5	When ethyl chloride reacts with ethanolic sodium nitrite, products formed are (A) Ethyl nitrite (B) Nitroethane (C) Ethanol (D) Diethyl ether	**[1]**

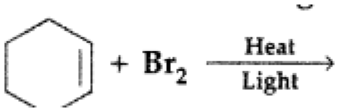
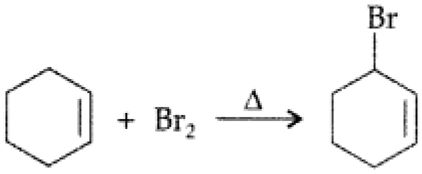
6	In which of the following molecules carbon atom marked with asterisk (*) is asymmetric?  (a)  (b)  (c)  (d) (A) (a), (b), (c), (d) (B) (a), (b), (c) (C) (b), (c), (d) (D) (a), (c), (d)	**[1]**
7	Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction ? (A) Cl^- (B) Cl^+ (C) $AlCl_3$ (D) $[AlCl_4]^-$	**[1]**
8	Benzal chloride on hydrolysis gives (A) Benzyl alcohol (B) Benzoic acid (C) Benzaldehyde (D) Benzo tri alcohol	**[1]**
9	For the reaction (2º) (major) R – Br R – O – N = O →, the suitable reagent is (A) NaNO2 + HCl (B) HNO2 (C) AgNO2 (D) KNO2	**[1]**
10	Which of the following statements is incorrect? (A) An SN1 reaction proceeds completely with inversion of configuration (B) An SN2 reaction proceeds with stereo chemical inversion (C) An SN2 reaction follows second-order kinetics (D) E2 reactions are generally stereoselective	**[1]**
	In the following questions (Q. No. 11 - 20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (d) 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 the correct statement but reason is wrong statement.	

	(d) Assertion is wrong statement but reason is correct statement.	
11	**Assertion: Presence of –NO2 group facilitates the nucleophilic substitution reactions in aryl halides.** **Reason: the intermediate carbanion is stabiliised due to the presence of –NO2 group.**	**[1]**
12	Assertion: Nucleophilic substitution is more difficult to carry out on vinyl chloride than ethyl chloride. Reason : vinyl group is an electron donating group.	**[1]**
13	. Assertion: 2-bromopentane gives pent-2-ene as the major product when heated with alcoholic KOH. Reason : In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.	**[1]**
14	. Assertion : It is difficult to replace chlorine by –OH in chlorobenzene in comparison to that in chloroethane. Reason : Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance	**[1]**
15	Assertion: The C–Cl bond length in chlorobenzene is shorter than that in CH_3–Cl. Reason: In haloarenes Cl is attached to sp^2 hyridised carbon which is more electronegative than sp^3 hybridised carbon.	**[1]**
16	Assertion: Chlorobenzene is less reactive than benzene towards the electrophilic substitution reaction. Reason: Resonance destabilises the carbo cation	**[1]**
17	**. Assertion :** Alkyl benzene is not prepared by Friedel-Crafts alkylation of benzene. ***Reason :*** Alkyl halides are less reactive than acyl halides.	**[1]**
18	Assertion : Haloalkanes are immiscible in water. Reason : halogen of haloalkane form hydrogen bond with water	**[1]**
19	**Assertion: Chloroform is generally stored in dark coloured bottles filled to the brim.** **Reason: Chloroform reacts with glass in the presence of sun light.**	**[1]**
20	**Assertion: Molecules that are not super imposable on their mirror images are chiral.** **Reason: All chiral molecules has chiral centres.**	**[1]**

ANSWER KEY:

1	**A**	**2**	**B**	**3**	**D**	**4**	**A**	**5**	**A**

6	**B**	**7**	**B**	**8**	**C**	**9**	**D**	**10**	**A**
11	**A**	**12**	**C**	**13**		**14**	**B**	**15**	**A**
16	**A**	**17**	**C**	**18**	**A**	**19**	**B**	**20**	**C**

	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	Draw the structure of major mono halogen product in the following reaction : (Comptt. Delhi 2012)  	**[2]**
ANS.	Answer:  	
22	What happens when ethyl chloride is treated with aqueous KOH?	**[2]**
ANS.	$\underset{\text{Chloroethane}}{C_2H_5Cl} + \text{aq. KOH} \xrightarrow{\Delta} \underset{\text{Ethanol}}{C_2H_5OH} + KCl$	
23	Which of the products will be a major product in the reaction given below? Explain. $CH_3CH=CH_2 + HI \rightarrow$	**[2]**
ANS.	**Answer:** According to Markovnikov's Rule, (B) will be the major product. The electronegative part of the reagent is added to the carbon of the double bond with the least number of hydrogens. As a result of the reaction, compound B will be generated as a primary product. Also, according to the Markonikov rule, 2-Iodopropane is the most important product. When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the reagent is connected to the unsaturated C atom with the least number of hydrogen atoms, according to Markovnikov's rule.	
24	Cyanide ion acts as an ambident nucleophile. From which end does it act as a stronger nucleophile in an aqueous medium? Give reason for your answer.	**[2]**

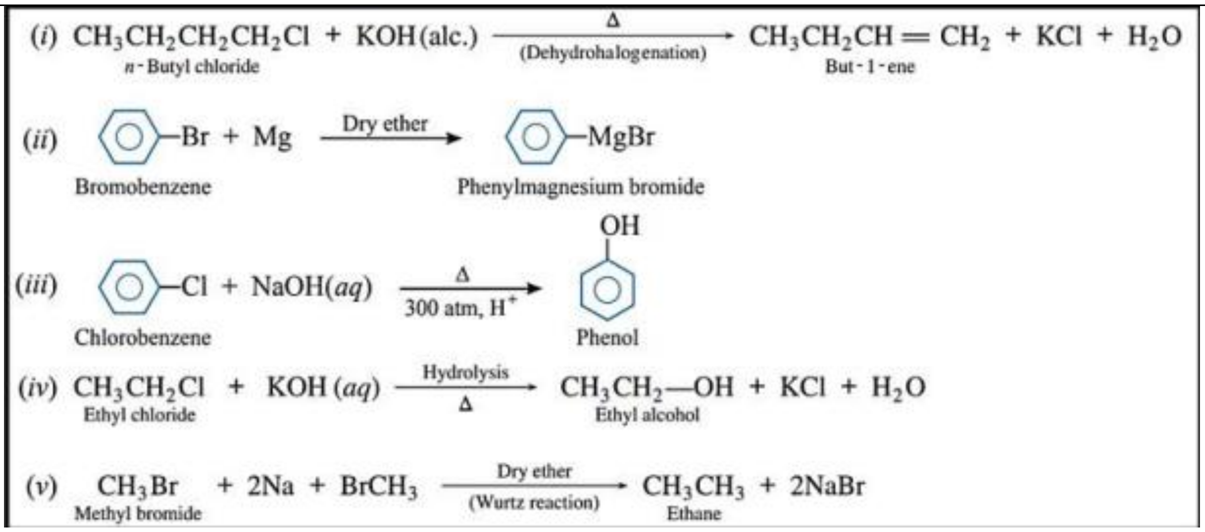
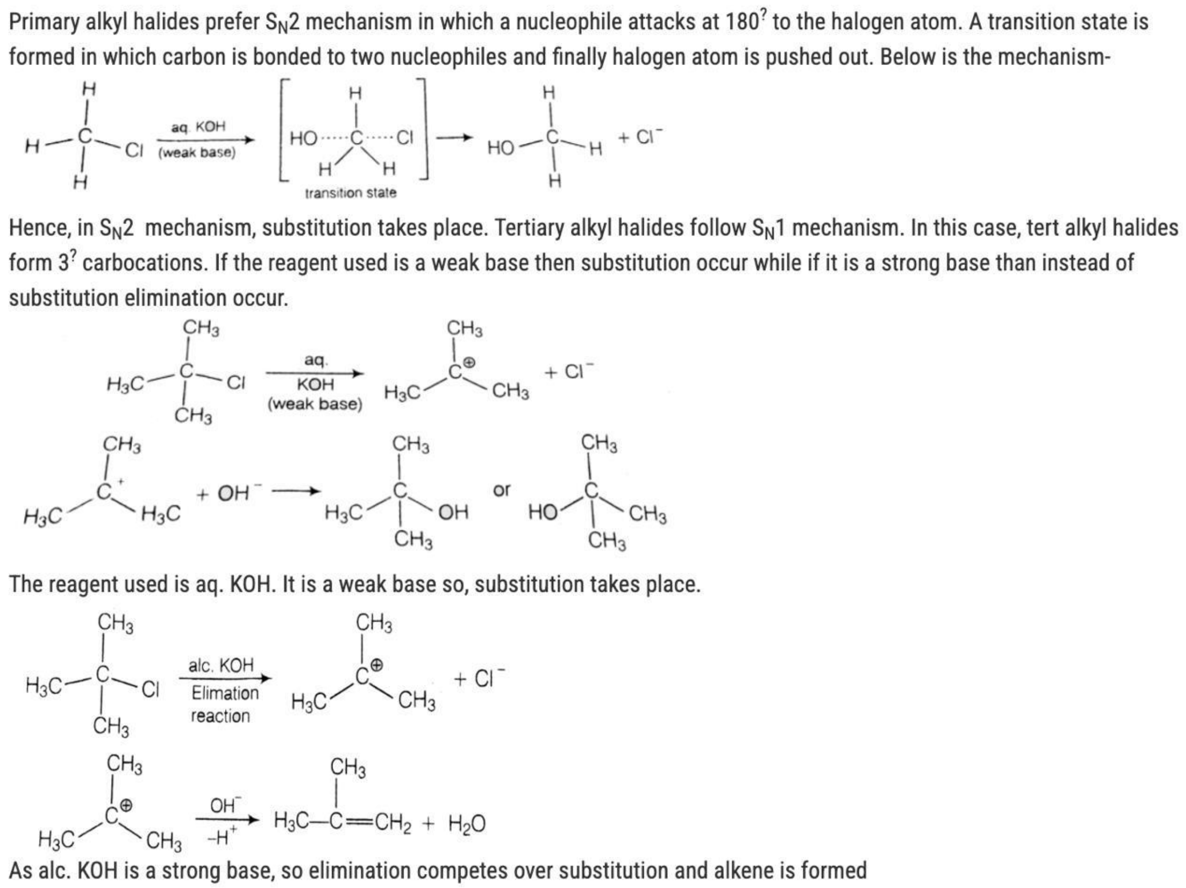
ANS.	**Answer:** It acts as a stronger nucleophile from the carbon end because it will lead to the formation of C-C bond which is more stable than C- N bond. Cyanide ion (C= N) is an ambident nucleophile because it can react either through nitrogen. Since, C-C bond is stronger than C-N bond so, cyanide ion carbon or will mainly attack through carbon to form alkyl cyanide	
25	**(a) Why does p-dichlorobenzene have a higher m.p. than its o- and m-isomers?** **(b) Why is (±)-Butan-2-ol optically inactive?**	**[2]**
ANS.	a. p-isomers are comparatively more symmetrical and fit closely in the crystal lattice, thus requiring more heat to break these strong forces of attraction. Therefore, higher melting point than o- and m-isomers. b. (±)-Butan-2-ol is optically inactive because in the racemic mix one type of rotation is cancelled by the other.	
	SECTION C The following questions are short answer type and carry 3 marks each.	
26	**Ques. Answer the following:** i. **Haloalkanes easily dissolve in organic solvents, why?** ii. **What is known as a racemic mixture? Give an example.** iii. **Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in SN_1 substitution reaction and why?**	**[3]**
ANS.	**Ans.** i. Because the new forces of attraction set up between haloalkanes and solvent molecules are of the same strength as the forces of attraction being broken. ii. A mixture that contains the equal proportions of two enantiomers of a compound in equal proportions is called a racemic mixture Example: (±) butan-2-ol iii. Since the reactivity of SN1 reactions increases as the stability of intermediate carbocation increases. Of the two 2° bromides, the carbocation intermediate derived from C_6H-$CH(C_6H_5)Br$ i.e. $C_6H_5CHC_6H_5$ is more stable as compared to the carbocation $C_6H+5CHCH_3$ obtained from $C_6H_5CH(CH_3)Br$ because it is stabilized by two phenyl groups due to resonance.	

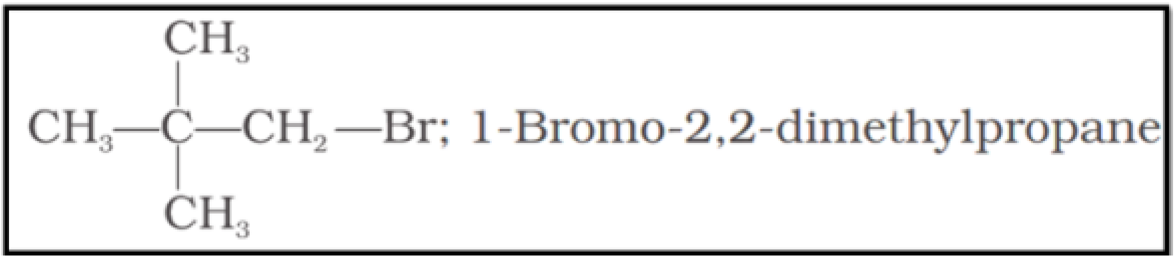
27	**Q10. Describe the reactions mentioned below and give a example:** **(A) Swarts reaction.** **(B) Finkelstein reaction.** **(C) Wurtz reaction.**	**[3]**
ANS.	**Ans. (A) Swarts reaction.** Alkyl fluorides from alkyl chlorides or alkyl bromides are formed by using the Swarts reaction. This can be achieved by heating the alkyl chloride/ bromide in the existence of fluoride in specific heavy metals. The reaction is as follows: $CH3–Br + AgF \rightarrow CH3F + AgBr$ **(B) Finkelstein reaction.** When an alkyl bromide or alkyl chloride is changed into an alkyl iodide, which is further treated with a sodium iodide solution present in an acetone. The reaction is as follows: $CH3CH2Br + NaI \rightarrow CH3CH2I + NaBr$ **(C) Wurtz reaction.** When alkyl halides come in contact with sodium metal in a dry ethereal (moisture-free) solution form higher alkanes. It can also be applied to produce higher alkanes with an equal number of carbon atoms. The reaction is as follows: $2RX + 2Na \longrightarrow RR + 2NaX$	
28	i. **State one use each of DDT and iodoform.** ii. **Which compound in the following couples will react faster in SN2 displacement and why?** **(a) 1-bromopentane or 2-bromopentane** **(b) l-bromo-2-methylbutane or 2-bromo-2-methylbutane.**	**[3]**
ANS.	i. Use of DDT (Dichorodiphenyl Trichloroethane): As a powerful insecticide, it is widely used for sugarcane and fodder crops to kill mosquitoes and lice which carry pathogens. Use of iodoform (CHI_3): It is used as an antiseptic for dressing wounds. Its antiseptic	

	action is due to the liberation of iodine when iodoform comes in contact with skin but not due to iodoform itself. ii. In SN_2 reactions, reactivity depends upon steric hindrance (a) 1-Bromopentane (1° halogen) has less steric hindrance, therefore, is more reactive than 2-Bromopentane hence undergoes SN_2 reactions faster. (b) 1-Bromo-2-methylbutane having less steric hindrance, is thus more reactive towards SN_2 reaction than 2-bromo-2-methyl butane (more steric hindrance).	
29	Compound 'A' with the molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both. (i) Write down the structural formula of both compounds 'A' and 'B'. (ii) Out of these two compounds, which one will be converted to the product with inverted configuration?	**[3]**
ANS.	Alkyl halides on treatment with aq. KOH gives alcohol as the major product. $C_4H_9Br + KOH (aq) \rightarrow C_4H_9OH + KBr$ In the case of compound .A. rate of reaction depends upon the concentration of .A. only, the reaction proceeds through the SN mechanism. Since the SN1 mechanism is favoured by 3° alkyl halides. A should be In the case of compound .B. which is an optically active isomer of .A., rate of reaction depends upon the concentration of .B. as well as KOH. Therefore, the reaction occurs by SN mechanism which is favoured by 1∘ and 2∘ alkyl halides. The compound B is	
30.	Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of ZnCl2?	
ANS.	There is partial double bond character between oxygen and SP2 hybridised carbon of benzene ring. In case of alkyl halide, formation of carbocation takes place which ultimately reacts with the HCl to give a alkyl halide. However, for aryl halide formation of phenyl carbocation should take place which is not possible because it is highly unstable. Hence aryl halide is not formed.	

		
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	Chlorofluorocarbons (CFCs) described as 'miracle chemicals' have no natural resources. They were first manufactured in the 1930s and industries soon found variety of applications for them due to their chemical non-reactivity and heat absorbing properties. CFCs have been used as refrigerants in air conditioners and refrigerators, in aerosol spray cans, in manufacturing foams and as cleansing agents in the manufacture of electronics. These chemicals have been given the tradename 'Freons' and the term since became a household name.	**[4]**
31.1	What is 'Freon – 12'?	
ANS.	Dichlorodifluoromethane, CF2Cl2	
31.2	Draw its molecular structure.	
ANS.	Tetrahedral Structure Diagram	
31.3	State any two harmful effects of CFCs on the environment.	
ANS.	i. Depletion of Ozone layer in the Stratosphere. ii. Green- House Effect and global warming	
	OR	
31.3	State any two ways to reduce the harmful effect of CFCs.	
ANS.	i. Buy air-conditioning and refrigeration equipment that does not use CFCs ii. Buy aerosol products that do not use CFCs as propellants iii. Conduct regular inspection and maintenance of AC and refrigeration appliance to prevent leakage.	
32	PASSAGE: The substitution reaction of alkyl halides occurs in SN1 and SN2 mechanism, whatever mechanism alkyl halide follow for substitution reaction to occur, the polarity of the carbon halogen bond is responsible for the substitution reaction. The rate of SN1 reactions is governed by the stability of carbocation whereas for SN2 reactions steric factor is a deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by	**[4]**

	alkyl halide.	
32.1	Among 1-bromopropane and 2-methyl-2-bromo propane, which will follow SN1 mechanism?	
ANS.	2-methyl-2-bromo propane	
32.2	Among the following in which inversion of configuration will occur on reaction with aq alkali 1-bromo propane, and 2-methyl-2-bromo butane?	
ANS.	1-bromo propane	
32.3	What is the role of polar protic solvent in SN1 reaction?	
ANS.	Polar protic solvents help to stabilize both the carbocation and the anion and that solvation of both cations and anions helps the SN1 mechanism proceed. So that's why polar protic solvent will favor an SN1 mechanism.	
	OR	
32.3	How will a protic solvent system affect the SN2 reaction?	
ANS.	For SN2 reactions involving anions as the nucleophile, protic solvents act to decrease the nucleophilicity of that anion by solvation through hydrogen bonding. The anion acquires a “coating” of solvent molecules thus inhibiting the ability of the anion to approach the substrate.	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	What happens when (i) n-butyl chloride is treated with alcoholic KOH, (ii) bromobenzene is treated with Mg in the presence of dry ether, (iii) chlorobenzene is subjected to hydrolysis, (iv) ethyl chloride is treated with aqueous KOH, (v) methyl bromide is treated with sodium in the presence of dry ether	**[5]**

ANS.	 (i) $CH_3CH_2CH_2CH_2Cl + KOH(alc.) \xrightarrow[\text{(Dehydrohalogenation)}]{\Delta} CH_3CH_2CH=CH_2 + KCl + H_2O$ n-Butyl chloride But-1-ene (ii) Bromobenzene Phenylmagnesium bromide (iii) Chlorobenzene Phenol (iv) $CH_3CH_2Cl + KOH(aq) \xrightarrow[\Delta]{\text{Hydrolysis}} CH_3CH_2\text{—}OH + KCl + H_2O$ Ethyl chloride Ethyl alcohol (v) $CH_3Br + 2Na + BrCH_3 \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} CH_3CH_3 + 2NaBr$ Methyl bromide Ethane	
34	Some alkyl halides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.	**[5]**
ANS.	 Primary alkyl halides prefer S_N2 mechanism in which a nucleophile attacks at $180^?$ to the halogen atom. A transition state is formed in which carbon is bonded to two nucleophiles and finally halogen atom is pushed out. Below is the mechanism- Hence, in S_N2 mechanism, substitution takes place. Tertiary alkyl halides follow S_N1 mechanism. In this case, tert alkyl halides form $3^?$ carbocations. If the reagent used is a weak base then substitution occur while if it is a strong base than instead of substitution elimination occur. The reagent used is aq. KOH. It is a weak base so, substitution takes place. As alc. KOH is a strong base, so elimination competes over substitution and alkene is formed	
35	I) Write down the structure and IUPAC name for neo-pentyl bromide. [2] II) Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of ZnCl2? [3]	**[5]**

ANS.	I)  $CH_3-C(CH_3)_2-CH_2-Br$; 1-Bromo-2,2-dimethylpropane II) C—O bond in phenols is more stable due to resonance effect and it has double bond character, hence breaking of this bond is difficult.	

……

तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन
Kendriya Vidyalaya Sangathan

KENDRIYA VIDYALAYA SANGATHAN, JABALPUR REGION

CLASS- XII

CHEMISTRY (043)

CHAPTER NAME: ALCOHOLS, PHENOLS & ETHERS

PREPARED BY: MEMBERS OF GROUP VII

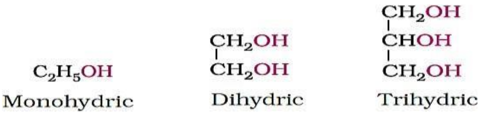
IMPORTANT POINTS/ NOTES ON TIP:

Quick Revision Points: -

Alcohols	Phenols	Ethers
$RH \xrightarrow[+OH]{-H} ROH$	$ArH \xrightarrow[+OH]{-H} ArOH$	$RH \xrightarrow[+O\text{-}R]{-H} RO\text{-}R$ $RH \xrightarrow[+O\text{-}Ar]{-H} RO\text{-}Ar$

Classification of Alcohols and Phenols

- Alcohols and phenols may be classified as mono–, di–, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively

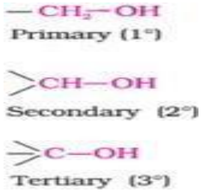
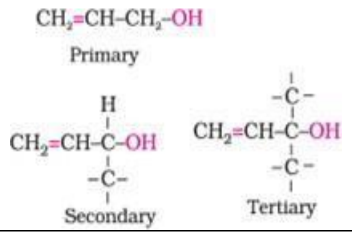
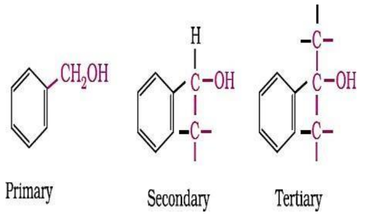

C_2H_5OH Monohydric
CH_2OH-CH_2OH Dihydric
$CH_2OH-CHOH-CH_2OH$ Trihydric


Monohydric Dihydric Trihydric

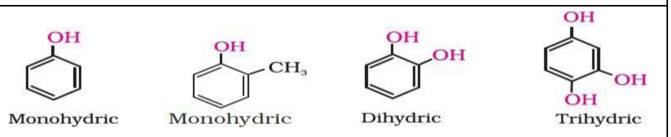
Classification of Monohydric alcohols

according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

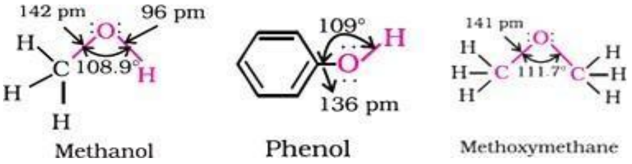
(i) **Compounds containing $C_{sp^3} - OH$ bond:**

(a) Alkyl alcohols	(b) Allylic alcohols	(c) Benzylic alcohols
–OH group is attached to an sp^3 hybridised carbon atom of an alkyl group.	—OH group is attached to a sp^3hybridised carbon adjacent tothe carbon-carbon doublebond, that is to an allylic carbon	—OH group is attached to a sp^3— hybridised carbon atom next to anaromatic ring.
		

(ii) **Compounds containing $C_{sp^2} - OH$ bond:**

(a)Vinylic alcohol	(b) Aryl alcohols or Phenols
—OH group bonded to a carbon-carbon double bond, i.e., to a vinylic carbon	—OH group bonded to the sp^2-hybridised carbon atom ofan aromatic ring
$CH_2 = CH - OH$	

Classification of Ethers

(a) simple or symmetrical ether- if the alkyl or aryl groups attached to the oxygen atom are the same. Diethyl ether, $C_2H_5OC_2H_5$	**Structures of Functional Groups** 
(b)mixed or unsymmetrical ether- if the two groups are different. $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$	

Isomerism in Alcohols: Alcohols exhibit four types of isomerism

(i) Chain isomerism: $C_4H_{10}O$ Butan-1-ol, 2-methylpropan-1-ol

(ii)Position isomerism: C_3H_8O Propan-1-ol,propan-2-ol

(iii)Functional isomerism: C_2H_6O Ethanol, methoxy methane (iv) Optical isomerism: Monohydric alcohols containing chiral carbon atoms exhibit optical isomerism. E.g. Butan-2-ol, Pentan-2-ol

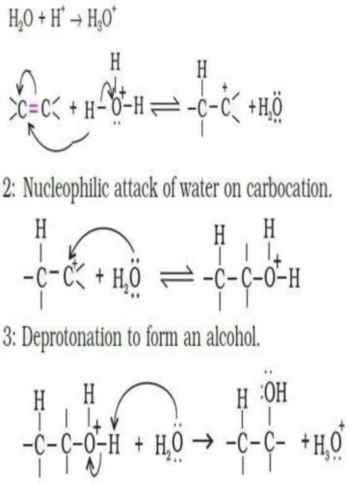
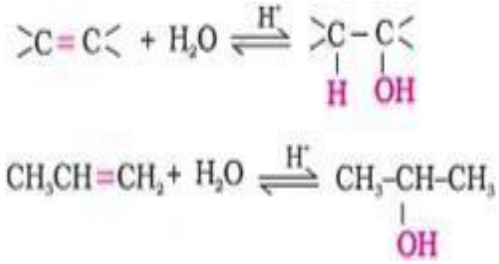
Nomenclature of Alcohols : According to IUPAC system, 'e' of the parent alkane is replaced with the suffix 'ol'. For naming polyhydric alcohols, the 'e' of alkane is retained and the ending 'ol' is added.

Nomenclature of Phenols: - The simplest hydroxy derivative of benzene is phenol. It isits common name and IUPAC name. For disubstituted compounds the terms *ortho* (1,2- disubstituted), *meta* (1,3 disubstituted) and *para* (1,4-disubstituted) are often used in the common names.

Nomenclature of Ethers:- The larger (R) group is chosen as the parent hydrocarbon and smaller group is written as alkoxy or phenoxy

Preparation of Alcohols

(1) From alkenes

(i)***By acid catalysed hydration:*** Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule	**Mechanism** Step 1: Protonation of alkene to form carbocationby electrophilic attack of **H_3O^+ or H^+** 
	

(ii) *By hydroboration–oxidation*:

Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodiumhydroxide

$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow (CH_3-CH_2-CH_2)_3B \xrightarrow{3H_2O_2,\ \bar{O}H} \underset{\text{Propan-1-ol}}{3CH_3-CH_2-CH_2-OH} + B(OH)_3$$

(2). From carbonyl compounds

By reduction of aldehydes and ketones:

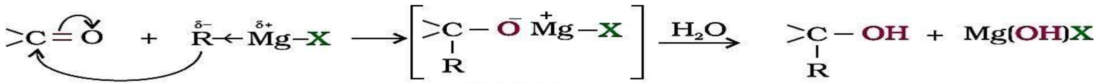
Reducing agents : **H_2** with catalyst, sodium borohydride ($NaBH_4$) or $LiAlH_4$.Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH \qquad RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{\underset{|}{CH}}-R'$$

(3) By reduction of carboxylic acids and esters:

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH \qquad RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

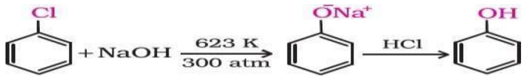
(4) From Grignard reagents:



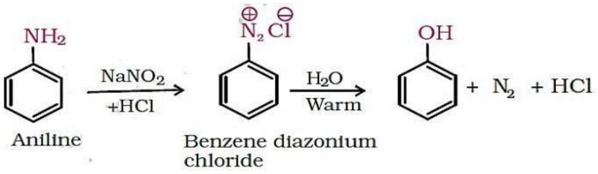
Methanal→ primary alcohol, Other aldehyde → secondary alcohol, Ketones → tertiaryalcoho

Preparation of Phenols

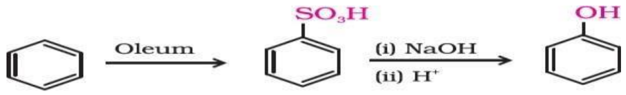
(1) From haloarenes



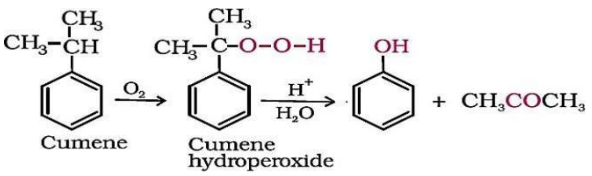
(2) From diazonium salts



(3). From benzenesulphonic acid



4. From cumene



Physical Properties of Alcohols and Phenols Boiling Points

- Increase with increase in the number of carbon atoms (increase in van der Waal's forces).
- In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waal's forces with decrease in surface area).
- Due to the presence of intermolecular hydrogen bonding, boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses.

Solubility

- Soluble in water due to their ability to form hydrogen bonds with water molecules.
- The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.
- Several of the lower molecular mass alcohols are miscible with water in all proportions.

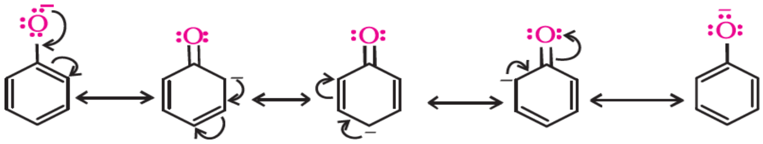
Chemical Reactions of Alcohols and Phenols

(i) **Reactions involving cleavage of O – H Bond**

(a) Acidity of alcohols and phenols:

$R-OH + 2Na \rightarrow 2R-ONa + H_2$ $C_6H_5-OH + 2Na \rightarrow 2C_6H_5-ONa + H_2$

Alcohols are weaker acids than water due to (+I effect) group present in alcohols, which decreases the polarity of -O-H bond. Acid strength of alcohols: 1° > 2° > 3° Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond. Order of acidity is: $RCOOH > H_2CO_3 > C_6H_5OH > H_2O > ROH$. Phenol is more acidic than alcohols due to stabilization of phenoxide ion through resonance.



Presence of electron withdrawing groups ($-NO_2$, -CN, -X) increases the acidity of phenol by stabilizing phenoxide ion while presence of electron releasing groups (-R, -NH_2, -OR) decreases the acidity of phenol by destabilizing phenoxide ion. Thus, increasing acidic strength is o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4, 6 Trinitrophenol (picric acid) Higher K_a and lower pK_a value correspond to the stronger acid.

***(b)** Esterification*

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

$$Ar/ROH + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

The introduction of acetyl (CH_3CO-) group in phenols is known as acetylation.

(ii) Reactions involving cleavage of carbon – oxygen (C–O) bond in Alcohols

1. Reaction with hydrogen halides:

- Alcohols react with hydrogen halides to form alkyl halides.

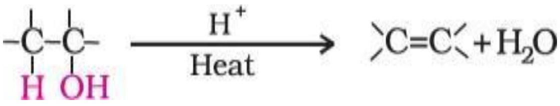
$$ROH + HX \rightarrow R-X + H_2O$$

- Reactivity of Alcohols: Tertiary > Secondary > Primary
- Lucas Test: - Used to distinguish primary, secondary and tertiary alcohols
  - Lucas reagent (conc. HCl and $ZnCl_2$)
  - Alcohols are soluble in Lucas reagent while Alkyl halides (RX) are immiscible and produce turbidity in solution.
  - tertiary alcohols- Immediate turbidity
  - Secondary alcohols- Turbidity appears After 5 minutes
  - Primary alcohols- No turbidity at room temperature.

2. Reaction with phosphorus trihalides:

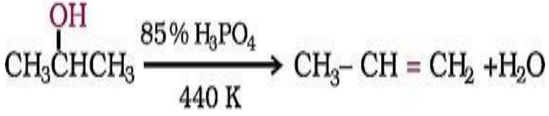
$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3 \quad (X = Cl, Br) \qquad R-OH \xrightarrow[X_2=Br_2,I_2]{red\ P/X_2} R-X$$

3. Dehydration:

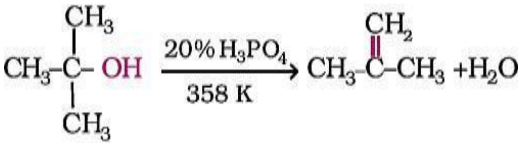


$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Secondary and tertiary alcohols are dehydrated under milder conditions. For example



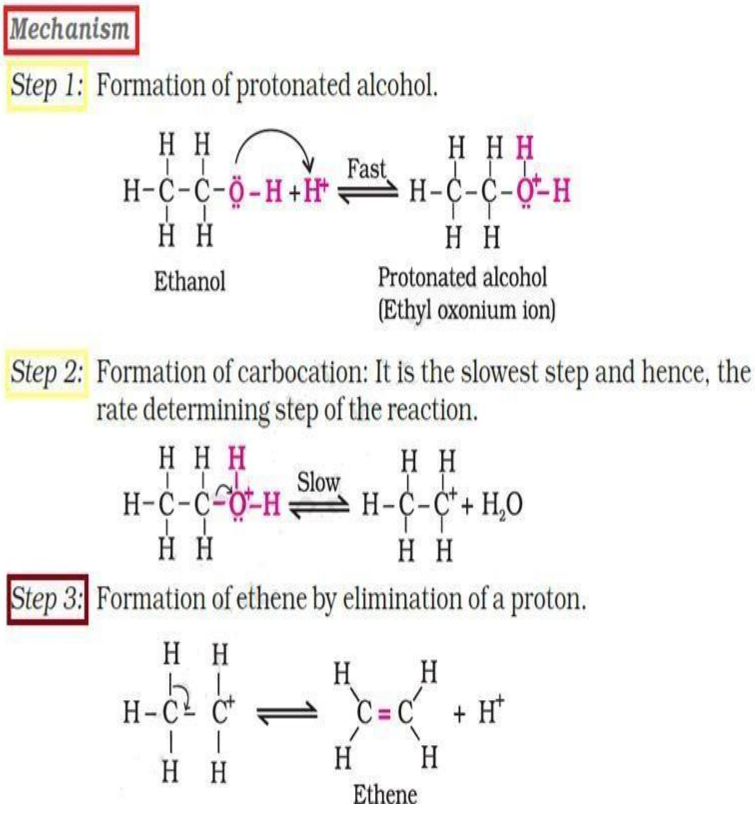
$$CH_3CH(OH)CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$



$$(CH_3)_3C-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-C(=CH_2)-CH_3 + H_2O$$

the relative ease of dehydration of alcohols

Tertiary > Secondary > Primary



Mechanism

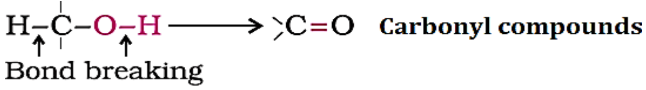
Step 1: Formation of protonated alcohol.

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

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

4. **Oxidation:**

- Oxidation of alcohols involves the formation of a carbon oxygen double bond with cleavage of an O-H and C-H bonds.



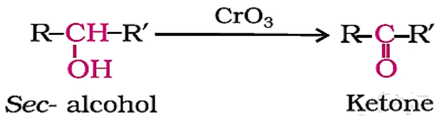
- also known as catalytic dehydrogenation reactions as it involves loss of dihydrogenfrom an alcohol molecule
- Primary alcohol → Aldehyde → Carboxylic acid
- Primary alcohol → Carboxylic acid (strong oxidizing agent, acidified $KMnO_4$)
- Secondary alcohol → Ketone
- CrO_3 (Chromic anhydride)in anhydrous medium is used as the oxidising agent for

  the isolation of aldehydes. $RCH_2OH \xrightarrow{CrO_3} RCHO$

- A better Oxidizing agent: pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl. (PCC retains C=C bond, if present)

$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

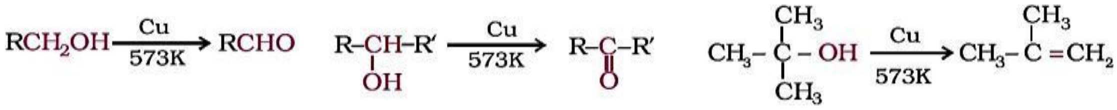
- Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).



$$\underset{\textit{Sec-}\text{ alcohol}}{R-\underset{OH}{\underset{|}{CH}}-R'} \xrightarrow{CrO_3} \underset{\text{Ketone}}{R-\underset{O}{\underset{\|}{C}}-R'}$$

- Tertiary alcohols do not undergo oxidation reaction.
- When the vapours of a primary or a secondary alcohol are passed overheated copper at 573 K, dehydrogenation takes place and an aldehyde or a

  ketone is formed while tertiary alcohols undergo dehydration.

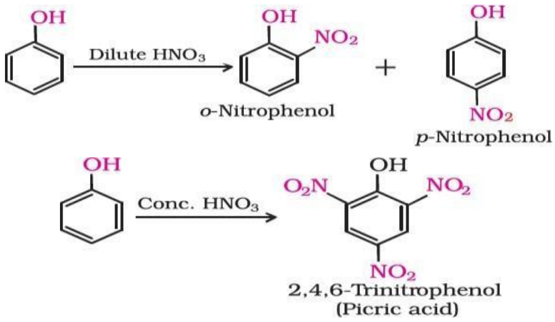


$$RCH_2OH \xrightarrow[573K]{Cu} RCHO \qquad R-\underset{OH}{\underset{|}{CH}}-R' \xrightarrow[573K]{Cu} R-\underset{O}{\underset{\|}{C}}-R' \qquad CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$$

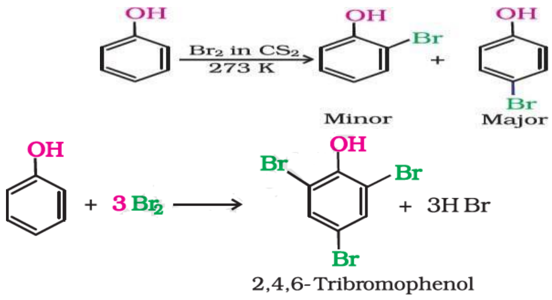
Chemical Reactions of Phenols

1. Electrophilic aromatic substitution on aromatic ring of Phenol
   -OH group is activating and ortho and para directing.
   Due to resonance electron density is more at o- and p- position

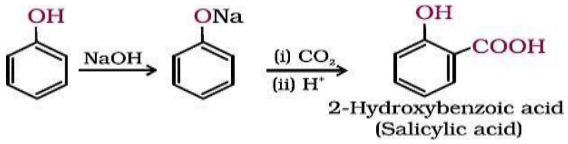
Nitration



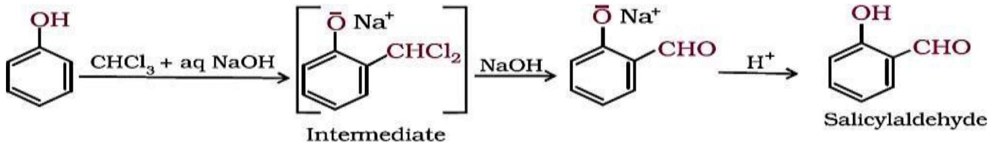
Halogenation (Bromination)



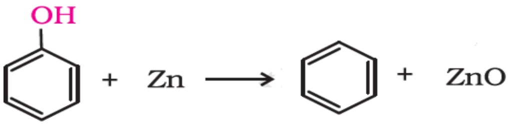
2. Kolbe's reaction



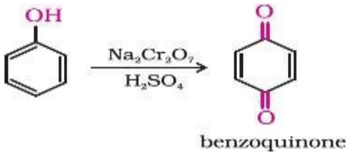
3. Reimer-Tiemann reaction



4. Reaction of phenol with zinc dust

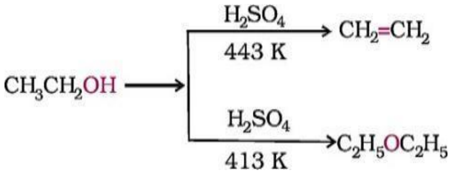


5. Oxidation



Preparation of Ethers

1. By dehydration of alcohols

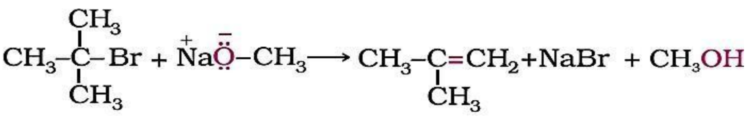


2. Williamson synthesis

- an alkyl halide is reacted with sodium alkoxide.

$$R{-}X + R'{-}\ddot{\underset{..}{\bar{O}}}\ \overset{+}{Na} \longrightarrow R{-}\ddot{\underset{..}{O}}{-}R' + Na\ X$$

- Better results are obtained if the alkyl halide is primary (as tert. halide under goes elimination reaction)

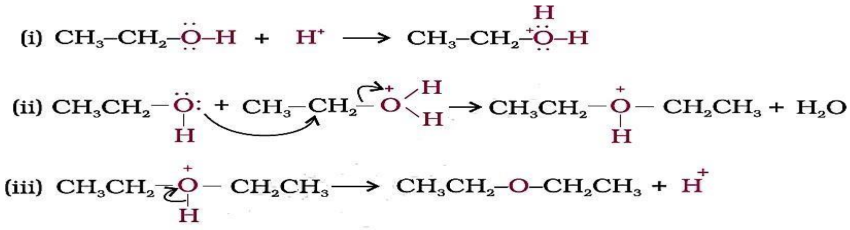


$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Br + \overset{+}{Na}\ddot{\bar{O}}{-}CH_3 \longrightarrow CH_3{-}\underset{CH_3}{C}{=}CH_2 + NaBr + CH_3OH$$

2-Methylpropene

Mechanism of Dehydration of Alcohol to Ether

The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol



It is not appropriate for the preparation of mixed ether like ethylmethyl ether.

Chemical Reactions of Ethers

1. Reactions involving Cleavage of C–O bond in ethers

$$R{-}O{-}R + HX \longrightarrow RX + R{-}OH$$

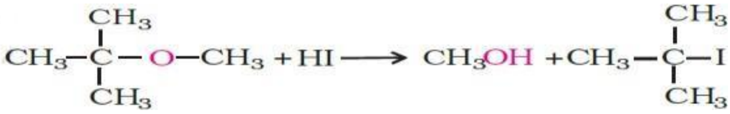
$$R{-}OH + HX \longrightarrow R{-}X + H_2O$$

Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide

When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

$$CH_3{-}\ddot{O}{-}CH_2CH_3 + H{-}I \longrightarrow CH_3{-}I + CH_3CH_2{-}OH$$

- when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide(S_N1 reaction).

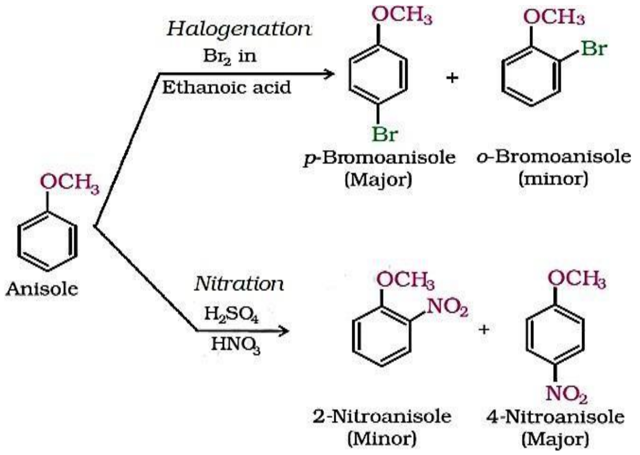


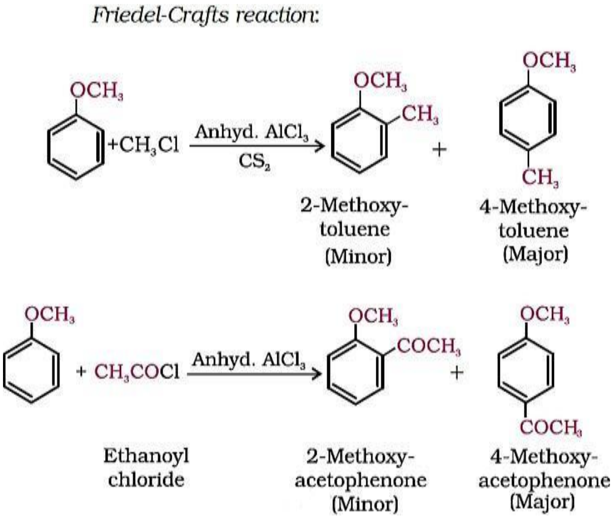
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O{-}CH_3 + HI \longrightarrow CH_3OH + CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}I$$

-

2. Electrophilic substitution

The alkoxy group (-OR) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution





QUESTION BANK

SECTION-A

The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.

1	Arrange the given compound on the basis of the increasing boiling point Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol. (a) Methanol < ethanol < propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol. (b) Ethanol < methanol < propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol. (c) Propan-1-ol < Methanol < ethanol < butan-2-ol < butan-1-ol < pentan-1-ol. (d) Methanol < ethanol < butan-2-ol < butan-1-ol < propan-1-ol < pentan-1-ol.	**[1]**
2	Phenol reacts with Br_2 in CS_2 at low temperature to give (a) o-Bromophenol (b) o-and p-promophenols (c) p-Bromophenol (d) 2, 4, 6Tribromophenol	**[1]**
3	The major organic product in the reaction, CH3-O-C(CH3)3 + HI → Product is (a) CH3I + (CH3)3COH (b) CH3OH + (CH3)3CI (c) ICH2OC(CH3)3 (d) CH3OC$(CH3)_2$I	**[1]**
4	Which of the following alcohols gives 2-butenc on dehydration by conc. H2SO4? (a) 2-methyl propene-2-ol (b) 2-methyl 1 -propanol (c) Butane-2-ol (d) Butane 1-ol	**[1]**
5	One mole of ethyl acetate on treatment with an excess of LiAlH4 in dry ether and subsequent acidification produces (a) 1 mole acetic acid + 1 mole ethyl alcohol (b) 1 mole ethyl alcohol + 1 mole methyl alcohol (c) 2 moles of ethyl alcohol (d) 1 mole of 2-butanol	**[1]**
6	. Which of the following reagents cannot, be used to oxidise primary alcohols to aldehydes? (a) CrO3 in anhydrous medium (b) KMnO4 in acidic medium	**[1]**

	(c) Pyridinium chlorochromate (d) Heat in the presence of Cu at 573 K	
7	1-Phenylethanol can be prepared by the reaction of benzaldehyde with (a) methyl bromide (b) ethyl iodide and magnesium (c) methyl iodide and magnesium (d) methyl bromide and aluminium bromide	**[1]**
8	Which of the following alcohols will give the most stable carbocation during dehydration? (a) 2-methyl-1-propanol (b) 2-methyl-2-propanol (c) 1-Butanol (d) 2-Butanol	**[1]**
9	A compound X with the molecular formula C2H8O can be oxidised to another compound Y whose molecular formulae is C3H6O2. The compound X may be (a) CH3CH2OCH3 (b) CH3CH2CHO (c) CH3CH2CH2OH (d) CH3CHOHCH3	**[1]**
10	Order of esterification of alcohols are (a) 3° > 1° > 2° (b) 2°> 3° > 1° (c) 1 ° > 2° > 3° (d) None of these	**[1]**
	In the following questions (Q. No. 11 - 20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (e) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	Assertion : Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol Reason : Addition of water in acidic medium proceeds through the formation of primary carbocation.	**[1]**
12	Assertion : p-nitrophenol is more acidic than phenol. Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negativechargedue to resonance.	**[1]**
13	Assertion : Phenols give o- and p-nitrophenol on nitration with conc. HNO3 and H2SO4mixture. Reason : —OH group in phenol is o–, p– directing	**[1]**
14	Assertion: Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol Reason: Addition of water in acidic medium proceeds through the formation of primary carbocation.	**[1]**
15	Assertion: p-nitrophenol is more acidic than phenol. Reason: Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.	**[1]**
16	Assertion: IUPAC name of the compound is 2-Ethoxy-2-methylethane. Reason: In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by -OR or -OAr group [where R = alkyl group and Ar = aryl group]	**[1]**

17	Assertion: Bond angle in ethers is slightly less than the tetrahedral angle. Reason: There is a repulsion between the two bulky (-R) groups.	**[1]**
18	.Assertion: Boiling points of alcohols are greater than ethers of same molar mass. Reason: Ethers can form intermolecular hydrogen-bonding with each other.	**[1]**
19	Assertion: Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid. Reason: Lewis acid polarises the bromine molecule.	**[1]**
20	Assertion: o-Nitrophenol is less soluble in water than the m- and p-isomers. Reason: m- and p- Nitrophenols exist as associated molecules.	**[1]**

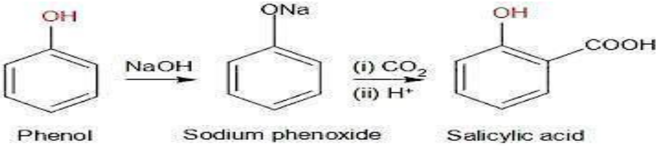
ANSWER KEY:

1	**a**	**2**	**b**	**3**	**b**	**4**	**c**	**5**	**c**
6	**d**	**7**	**c**	**8**	**b**	**9**	**c**	**10**	**c**
11	**b**	**12**	**a**	**13**	**d**	**14**	**b**	**15**	**a**
16	**d**	**17**	**d**	**18**	**a**	**19**	**d**	**20**	**b**

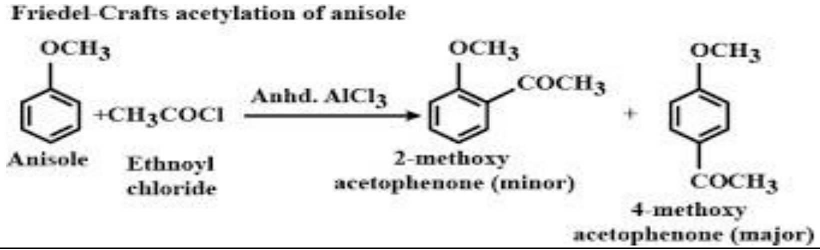
	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	Anisole on reaction with HI gives Phenol and CH3I as main products and not iodo benzeneand CH3OH. Why?	**[2]**
ANS.	Answer: Anisole reacts with HI to give phenol and methyl iodide and not iodo benzene and methyl alcohol because I^- ion prefers to combine with the smaller group in order to minimize the	
22	Account for the following: (a) Boiling of the C2H5OH is more than that of C2H5Cl. (b)The solubility of alcohols in water decreases with increase in molecular masses.	**[2]**
ANS.	Answer: (a) due more extensive hydrogen bonding in C_2H_5OH as compared to C_2H_5Cl. (b) with increase in molecular masses the non-polar alkyl group becomes more predominan	
23	Explain the following behaviours: (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses. (ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.	**[2]**
ANS.	(i) Alcohols can form H-bonds with water and break the H-bonds already existing between water molecules. So they are soluble in water. On the other hand, hydrocarbons cannot form H-bonds with water and hence are insoluble in water. (ii) Due to strong – R and -1 effect of the – NO2 group, electron density in the – OH bond decreases and hence the loss of a proton becomes easier. Moreover O-nitrophenoxide ion is stabilized by resonance, thereby making O-nitrophenol a stronger acid. In O-methoxyphenol, due to + R effect of the – OCH3 group the electron density in the O – H bond increases thereby making the loss of proton difficult. Furthermore, the omethoxyphenoxide ion left after the loss of a proton is destabilized by resonance because the two	

<table>
<tr><td></td><td>negative charges repel each other. So O-methoxyphenol is a weaker acid.</td><td></td></tr>
<tr><td>24</td><td>Write the equations involved in the following reactions:
(i) Reimer-Tiemann reaction
(ii) Williamson’s ether Synthesis.</td><td>[2]</td></tr>
<tr><td>ANS.</td><td>see in book
(i) Reimer-Tiemann reaction : Treatment of phenol with CHCl3 in presence of aqueous NaOH at 340K followed by hydrolysis gives salicylaldehyde.
(ii) Williamson’s ether synthesis : The reaction involves the nucleophilic substitution of the halide ion from the alkyl halide by the alkoxide ion by SN2 mechanism. [see reaction in book]
Example :</td><td></td></tr>
<tr><td>25</td><td>Write the chemical equations involved in the following reactions:
(i) Kolbe’s reaction (ii) Friedal Crafts acetylation of anisole.</td><td>[2]</td></tr>
<tr><td>ANS.</td><td>

(i)



(ii)



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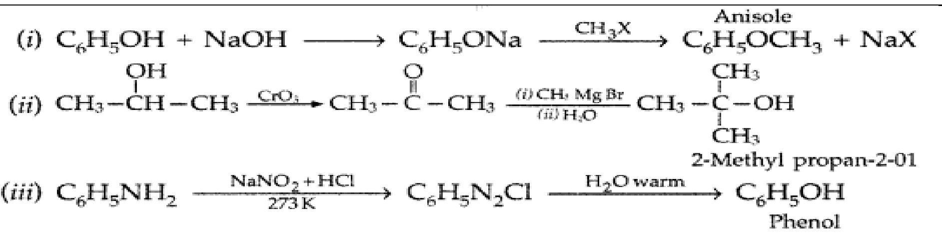
SECTION C

The following questions are short answer type and carry 3 marks each.

</td><td></td></tr>
<tr><td>26</td><td>How do you convert the following :
(i) Phenol to anisole
(ii) Propan-2-ol to 2-methylpropan-2-ol
(iii) Aniline to phenol</td><td>[3]</td></tr>
<tr><td>ANS.</td><td>



$$(i)\ C_6H_5OH + NaOH \longrightarrow C_6H_5ONa \xrightarrow{CH_3X} \overset{\text{Anisole}}{C_6H_5OCH_3} + NaX$$

$$(ii)\ CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow{CrO_3} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(ii)\,H_2O]{(i)\,CH_3MgBr} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

2-Methyl propan-2-01

$$(iii)\ C_6H_5NH_2 \xrightarrow[273\,K]{NaNO_2+HCl} C_6H_5N_2Cl \xrightarrow{H_2O\ \text{warm}} \underset{\text{Phenol}}{C_6H_5OH}$$

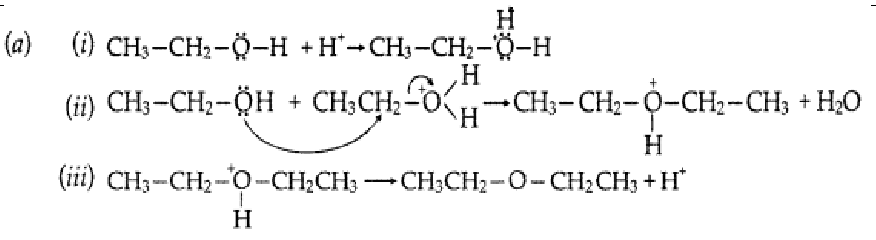
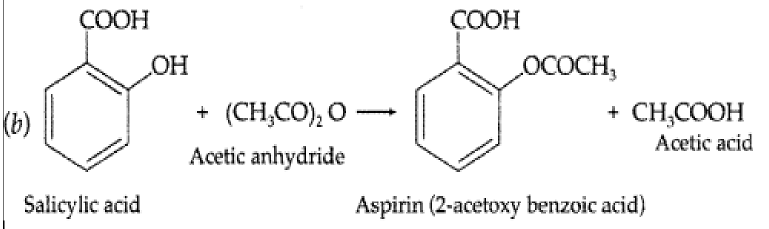
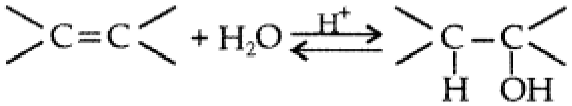
</td><td></td></tr>
<tr><td>27</td><td>

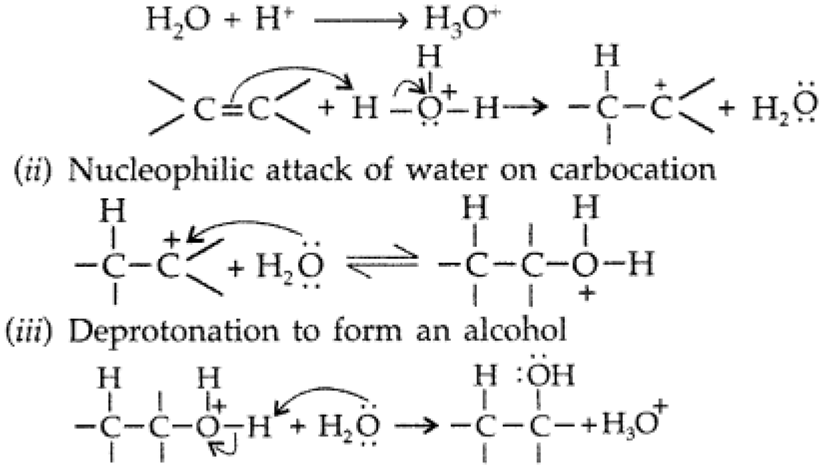
(a) Write the mechanism of the following reaction

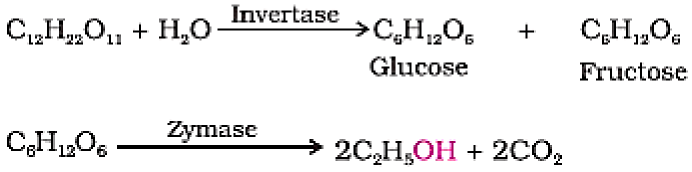
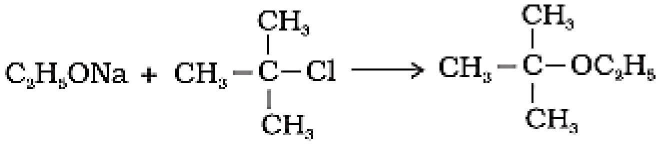
$$2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2\text{-}O\text{-}CH_2CH_3$$

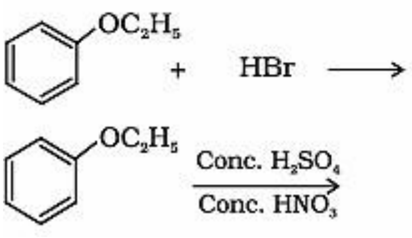
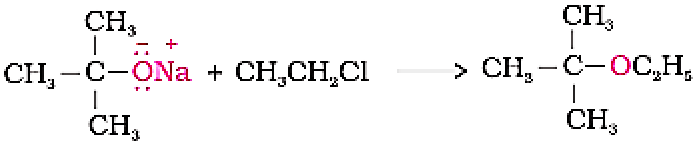
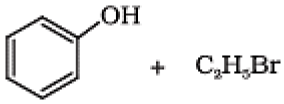
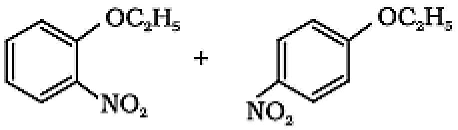
(b) Write the equation involved in the acetylation of Salicylic acidAnswer :

</td><td>[3]</td></tr>
</table>

ANS.	(a)  (i) $CH_3-CH_2-\ddot{O}-H + H^+ \rightarrow CH_3-CH_2-\overset{H}{\overset{+}{\ddot{O}}}-H$ (ii) $CH_3-CH_2-\ddot{O}H + CH_3CH_2-\overset{+}{O}\langle^{H}_{H} \rightarrow CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 + H_2O$ (iii) $CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2CH_3 \rightarrow CH_3CH_2-O-CH_2CH_3 + H^+$ (b) 	
28	Explain the following observations: (i) The boiling point of ethanol is higher than that of methoxymethane. (ii) Phenol is more acidic than ethanol. (iii) o- and p-nitrophenols are more acidic than phenol.	**[3]**
ANS.	(i) Due to presence of intermolecular H-bonding, associated molecules are formed, hence ethanol has high boiling point while methoxymethane does not have intermolecular H-bonding. (ii) Phenol on losing H+ ion forms phenoxide ion, and ethanol on losing H+ ion forms ethoxide ion. Phenoxide ion is more stable than ethoxide ion as phenoxide ion exists in resonance structure. Due to this phenol is more acidic than ethanol. (iii) Both o- and p-nitrophenols contain the NO2 group which is an electron withdrawing group. Due to -R and -I effect of the -NO2 group, electron density in the OH bond of substituted phenol decreases and hence the loss of proton becomes easy and therefore more acidic.	
29	i) Name the factors responsible for the solubility of alcohols in water. ii) What is denatured alcohol? iii) Out of 2-chloroethanol and ethanol which is more acidic and why?	**[3]**
ANS.	i) a) Hydrogen bonding b) Size of alkyl/aryl group. ii) Alcohol is made unfit for drinking by mixing some copper sulphate and pyridine in it. This is called denatured alcohol. iii) 2-Chloroethanol, due to –I effect of chlorine atom.	
30.	Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol-	
ANS.	Answer: Acid catalysed hydration : Alkenes react with water in the presence of acid as catalyst to form alcohols  $>C=C< + H_2O \xrightleftharpoons{H^+} >\underset{H}{C}-\underset{OH}{C}<$ Mechanism : It involves three steps :	

	(i) Protonation of alkene to form carbocation by electrophilic attack of H_3O^+  $H_2O + H^+ \longrightarrow H_3O^+$ (ii) Nucleophilic attack of water on carbocation (iii) Deprotonation to form an alcohol	
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	**CASE STUDY BASED QUESTIONS** Read the passage given below and answer the following questions. Each question carries one mark each. Once Raman visited a chemical store accidently. New stock (chemical compound) had been delivered to shop keeper. Shop keeper was asked to talk about the chemical received. He said that this compound (X) containing C, Hand O is unreactive towards sodium. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. The following questions are multiple choice questions. Choose the most appropriate answer. If Raman was a chemistry student, what the answers would be for the following questions?	**[4]**
31.1	i)Which functional group is (X) ?	
ANS.	**Ether**	
31.2	ii) The IUPAC name of the carboxylic acid formed is ?	
ANS.	**ethanoic acid**	
31.3	iii) Compound (Y) is ?	
ANS.	**Ethyl iodide**	
	OR	
31.3	iv) Compound (X) on treatment with excess of Cl2 in presence of light gives?	
ANS.	**perchloro diethyl ether**	
	SECTION E	

	The following questions are long answer type and carry 5 marks each.	
32	**Name the reagents used in the following reactions: (1+1+1+1+1)5 marks** (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) Benzyl alcohol to benzoic acid. (v) Dehydration of propan-2-ol to propene.	**[5]**
ANS.	: i) Acidified potassium dichromate or any suitable reagent ii) pyridinium chlorochromate (PCC) or suitable reagent. iii) Aqueous bromine or Br2/H2O iv) acidified or alkaline potassium permanganate followed by hydrolysis $v)$ H_2SO_4 at 440 K	
33	**Answer the following questions. (2+1+2) 5 marks** i) Krishna took four isomeric alcohols which have similar molar masses i.e. 74. How will hearrange these alcohols in increasing order of their boiling points and write the structures of these compounds. ii) Why do alcohols soluble in water? iii) Name the enzymes and write the reactions involved in the preparation of ethanol fromsucrose by fermentation.	**[5]**
ANS.	i) n – butanol > isobutyl alcohol> butan – 2 – ol > ter-butyl alcohol (write the structures) ii) alcohols form hydrogen bond with water iii) Enzyme name – Invertase  $C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$ $C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$	
34	**Answer the following questions given. (2+2+1) 5 marks** i) The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.  $C_2H_5ONa + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OC_2H_5$ a) What would be the major product of this reaction ? b) Write a suitable reaction for the preparation of t-butylethyl ether. ii) Predict the products of the following reactions:	**[5]**

	 (iii) Which is more acidic ethanol or water. Why?	
ANS.	**Answers:** (i) (a) The major product of the given reaction is 2-methylprop-1-ene (b)  (ii)  And  (iii) Water because +I effect of ethyl group reduces acidic strength.	

KENDRIYA VIDYALAYA SANGATHAN, JABALPUR REGION

CLASS- XII

CHEMISTRY (043)

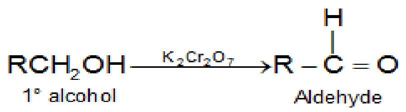
CHAPTER NAME: Aldehydes, Ketones and carboxylic acids

PREPARED BY: MEMBERS OF GROUP VIII

IMPORTANT POINTS/ NOTES ON TIP:

.Preparation of Aldehydes

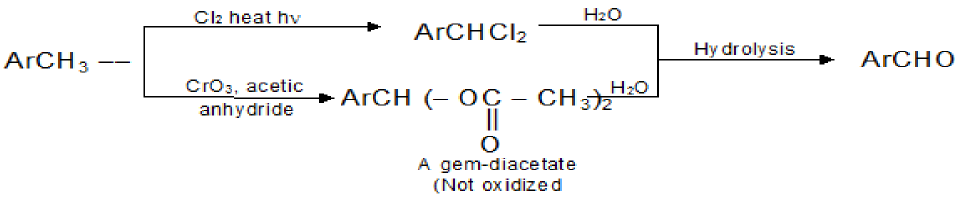
a. Oxidation of primary alcohols



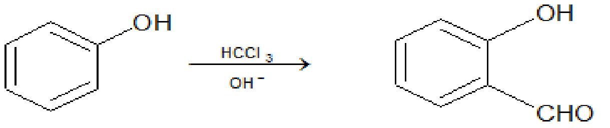
$RCH_2OH \xrightarrow{K_2Cr_2O_7} R-\overset{H}{\overset{|}{C}}=O$ (By special distillation method)

$RCH_2OH \xrightarrow[CH_2Cl]{P.C.C.} R-CHO$

b. Oxidation of methyl benzenes



c. Reimer – Tiemann synthesis of phenolic aldehydes



The electrophile is the dichlorocarbene, :CCl_2, formation of carbene is an example of α-elimination. $\overline{O}H + HCCl_3 \xrightarrow{-HCl} \ddot{C}Cl_2$

d. Reduction of acid chlorides

Poisoned with quinoline-S (trace)

Rosenmund's reaction

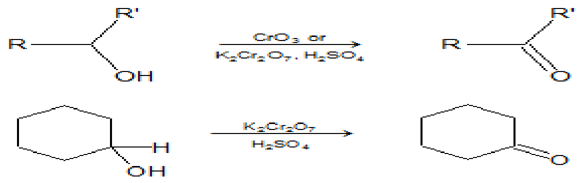
e. Stephen's Method

$R-C\equiv N \xrightarrow[HCl,\ 2.\ H_2O]{1.\ SnCl_2} RCHO$

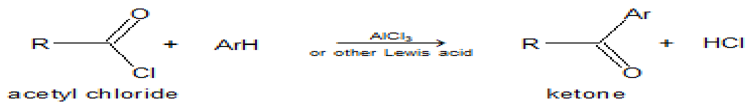
H_2O (Hydrolysis of intermediate) $RCH = NH$ to $RCHO$ and NH_3

Preparation of Ketones:

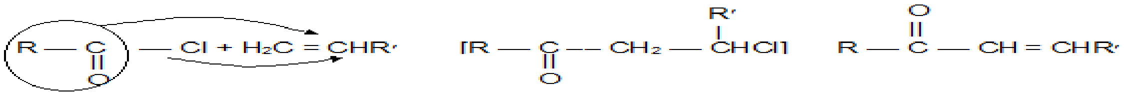
a) Oxidation of Secondary alcohols:



b) Friedel – Crafts acylation

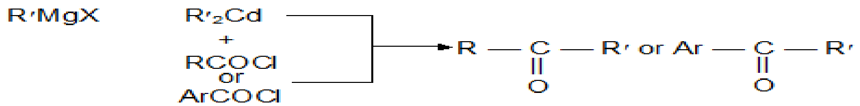


c) Acylation of Alkenes



This is Markovnikov addition initiated by $R-\overset{+}{C}=\ddot{O}:$, an acylium cation.

d) With Organometallics

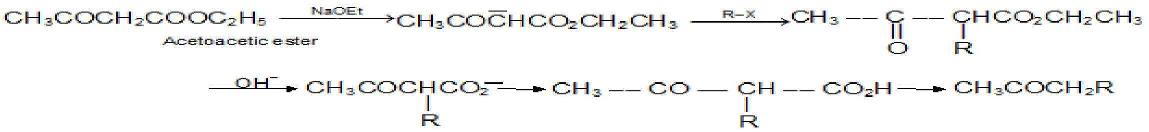


R′ must by aryl or primary alkyl

e) By heating the calcium salt of any monocarboxylic acid other than formic acid

$$(RCO_2)_2Ca + \Delta \rightarrow R_2CO + CaCO_3$$

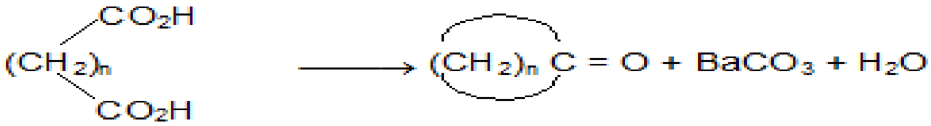
f) Acetoacetic ester synthesis of ketones



$$CH_3COCH_2COOC_2H_5 \xrightarrow{NaOEt} CH_3CO\bar{C}HCO_2CH_2CH_3 \xrightarrow{R-X} CH_3-\underset{\underset{O}{\|}}{C}-\underset{R}{\underset{|}{C}}HCO_2CH_2CH_3$$

$$\xrightarrow{OH^-} CH_3CO\underset{R}{\underset{|}{C}}HCO_2^- \longrightarrow CH_3-CO-\underset{R}{\underset{|}{C}}H-CO_2H \longrightarrow CH_3COCH_2R$$

g) Ring Ketones from Dicarboxylic acids and their Derivaties:



n = 4 and 5

Cyclopentanone or cyclohexanone

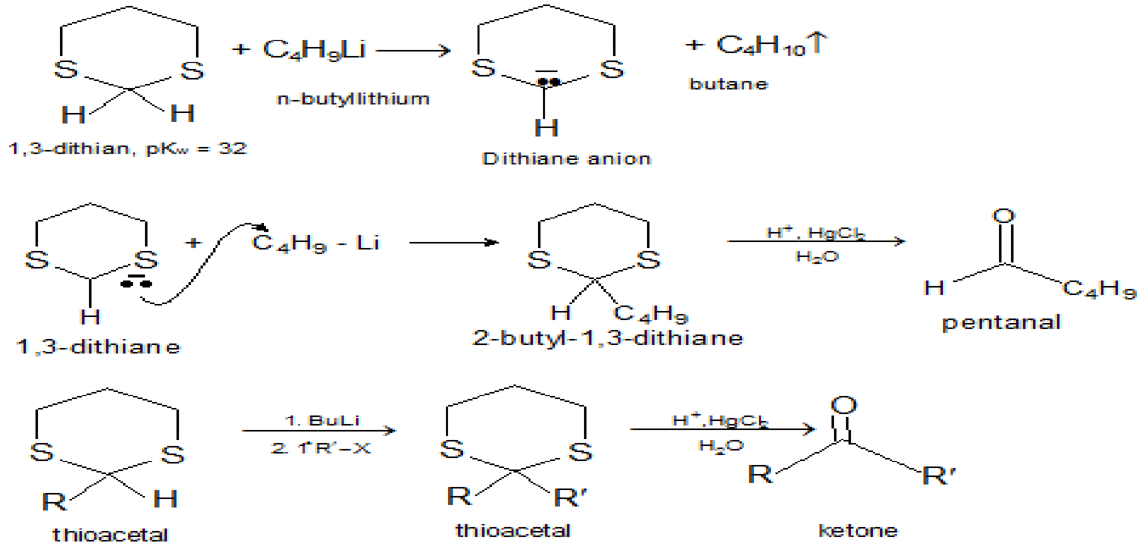
h) Synthesis of Ketones and Aldehydes Using 1,3-Dithianes:

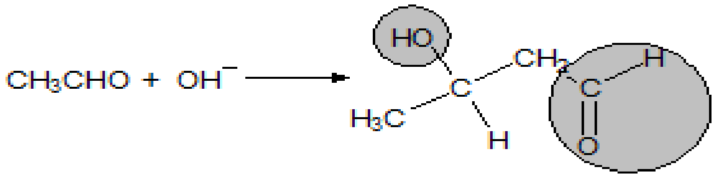
Reactions of Aldehydes and Ketones:

a) Aldol condensation

Aldehydes and ketones having alpha hydrogen atom:

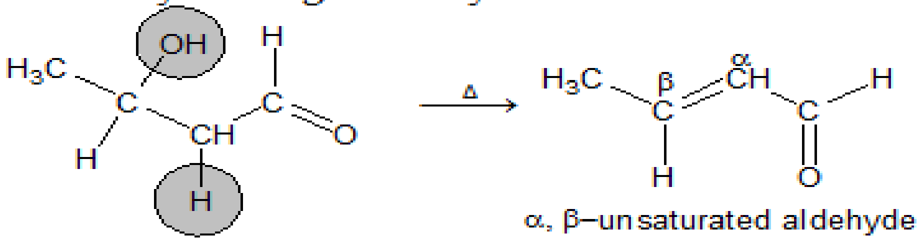
Reactions of Aldehydes and Ketones:





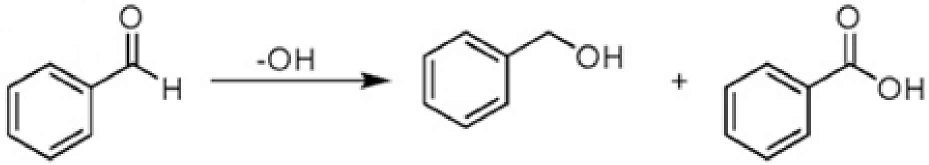
(Since it contains two functional groups aldehydes and alcohol)

Aldol easily undergoes dehydration

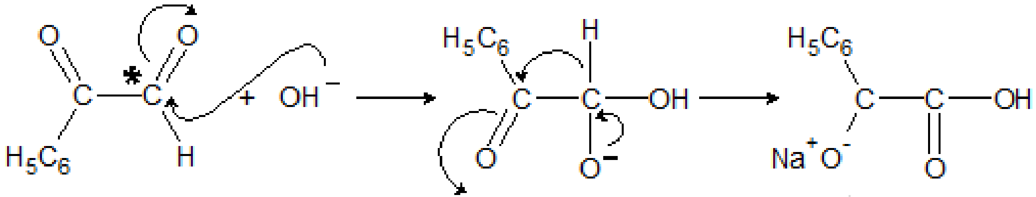


b) Cannizzaro reaction:

Aldehydes and ketones having no alpha hydrogen atom:



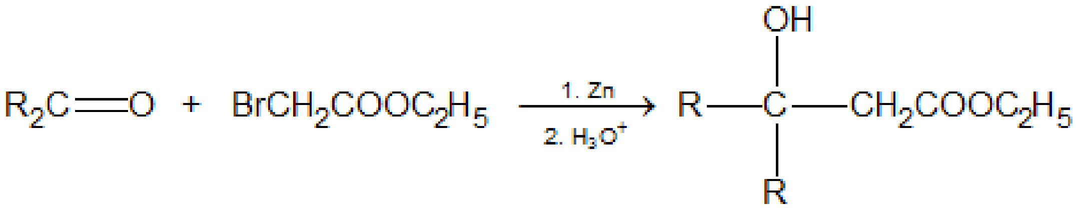
When two carbonyl groups are present within a molecule,think of intramolecular reaction.OH- will attack more positively charged carbon. In this case, it is right >c=0 group.



Sodium salt of Mandelic acid

c) Reformatsky Reaction

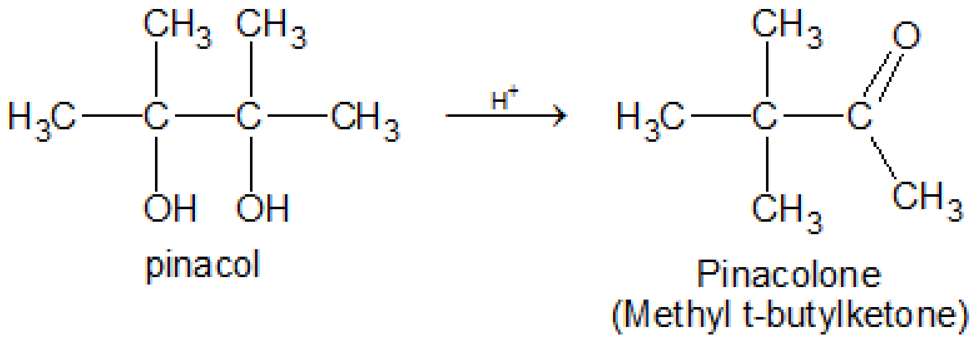
This is the reaction of a-haloester, usually an a-bromoester with an aldehyde or ketone in the presence of Zinc metal to produce b-hydroxyester



$$R_2C{=}O + BrCH_2COOC_2H_5 \xrightarrow[2.\ H_3O^+]{1.\ Zn} R{-}\overset{OH}{\underset{R}{C}}{-}CH_2COOC_2H_5$$

e) Pinacol-pinacolone Rearrangement

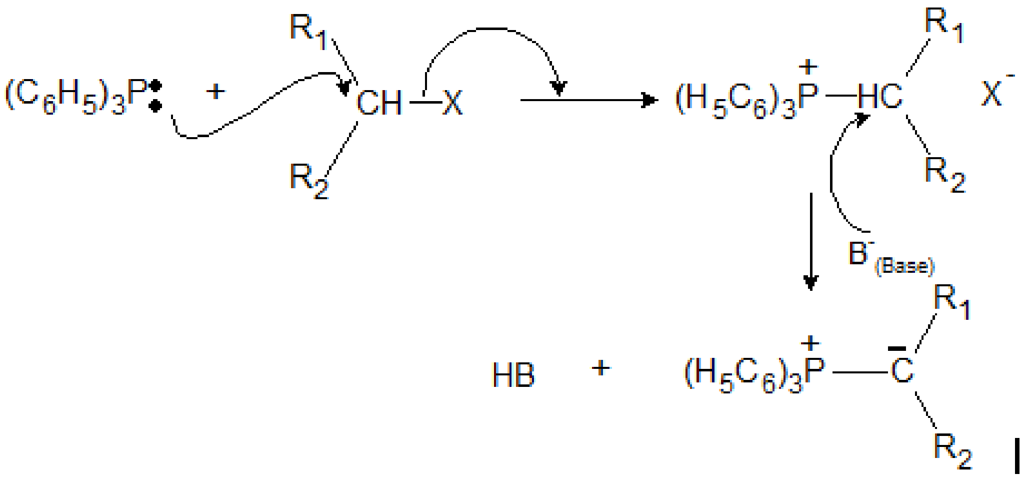
The acid catalysed rearrangement of 1,2 diols (Vicinal diols) to aldehydes or ketones with the elimination of water is known as pinacol pinacolone rearrangement.



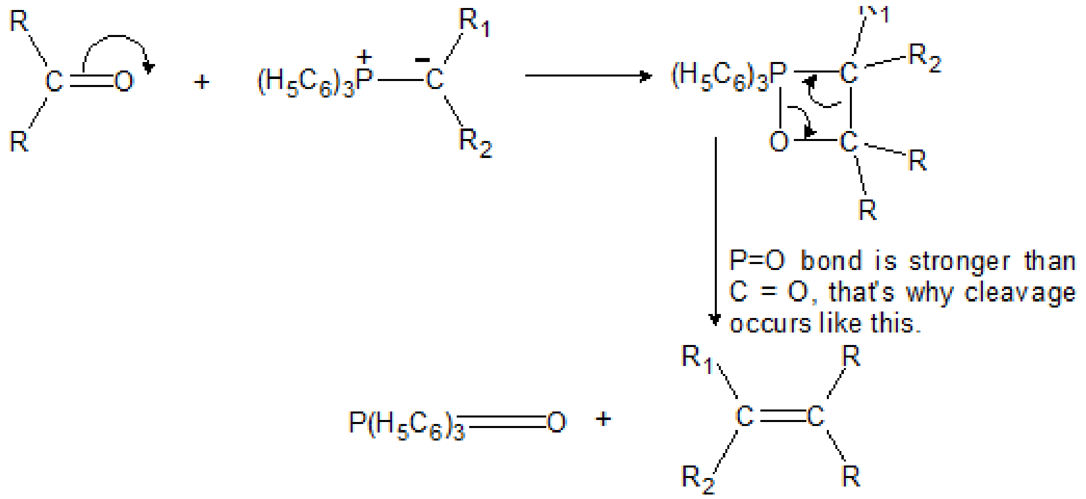
a) Wittig-Ylide Reaction

Aldehydes and Ketones react with phosphorus Ylides to yield alkenes and triphenyl phosphine oxide. An Ylide is a neutral molecule having a negative carbon adjacent to a positive hetero atom. Phosphorus ylides are also called phosphoranes.

Preparation of Ylides

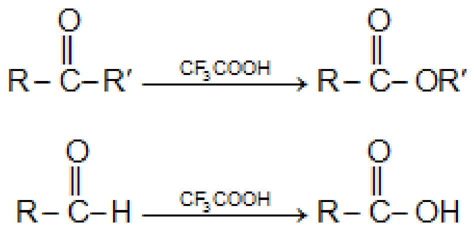


Reaction of Ylide with >C=O



P=O bond is stronger than C = O, that's why cleavage occurs like this.

d) Baeyer-Villiger Oxidation

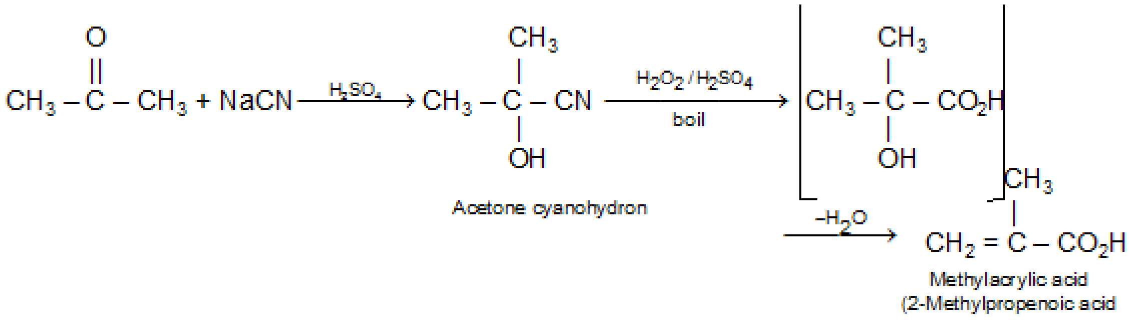


$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{CF_3COOH} R-\overset{\overset{O}{\|}}{C}-OR'$$

$$R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{CF_3COOH} R-\overset{\overset{O}{\|}}{C}-OH$$

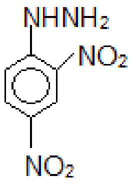
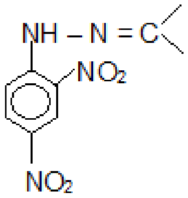
Above things happens in BVO (Bayer Villiger oxidation). Reagents are either per acetic acid or perbenzoic acid or pertrifluoroacetic acid or permonosulphuric acid.

e) Addition of cyanide

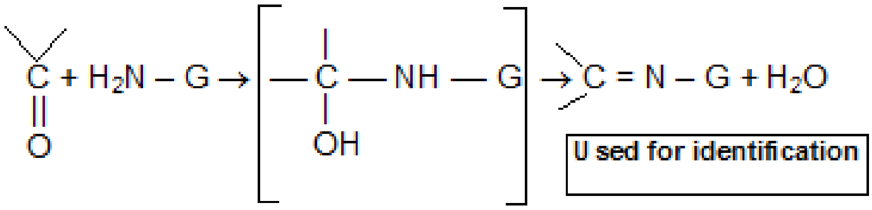


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + NaCN \xrightarrow{H_2SO_4} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CN \xrightarrow[\text{boil}]{H_2O_2/H_2SO_4} \left[CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO_2H\right] \xrightarrow{-H_2O} CH_2=\overset{\overset{CH_3}{|}}{C}-CO_2H$$

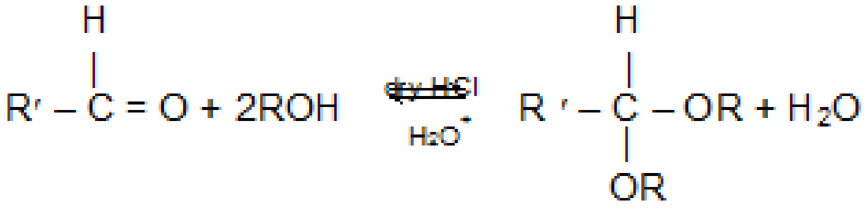
f) Addition of bisulfite:

	$H_2N - G$	Product	
H_2NOH	Hydroxylamine	$> C = N - OH$	Oxime
$H_2N - NH_2$	Hydrazine	$> C = N - NH_2$	Hydrazone
$H_2N - NH - C_6H_5$	Phenylhydrazine	$> C = N - NHC_6H_5$	Phenylhydrazone
$H_2N - NH - CO - NH_2$	Semicarbazide	$> C = N - NHCONH_2$	Semicarbazone
	2, 4-Dinitrophenyl hydrazine		2, 4-dinitrophenylhydrazone (bright orange or yellow precipitate used for identifying aldehydes and ketones

g) Addition of derivative of ammonia



h) Addition of Alcohols; Acetal Formation

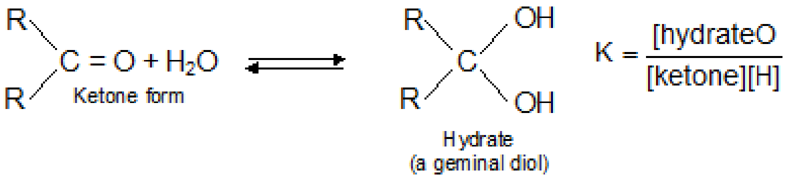


$$R' - \overset{H}{\overset{|}{C}} = O + 2ROH \underset{H_2O}{\overset{\text{~~dry HCl~~}}{\rightleftharpoons}} R' - \underset{OR}{\overset{H}{C}} - OR + H_2O$$

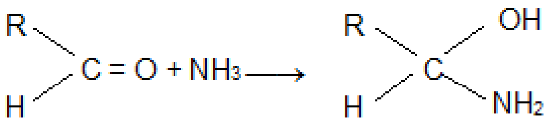
An acetal (gem-diether)

In H3O+, RCHO is regenerated because acetals undergo acid catalyzed cleavage much more easily than do ethers. Since acetals are stable in neutral or basic media, they are used to protect the – CH = O group.

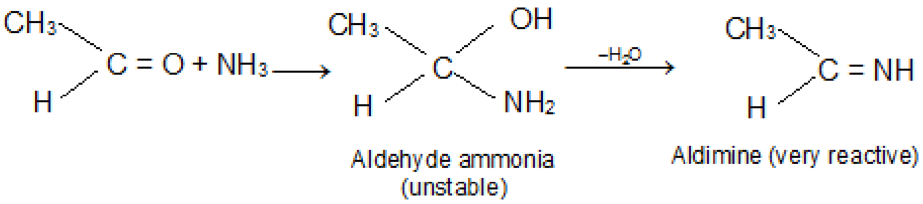
i) Addition of Water



j) Addition of Ammonia:

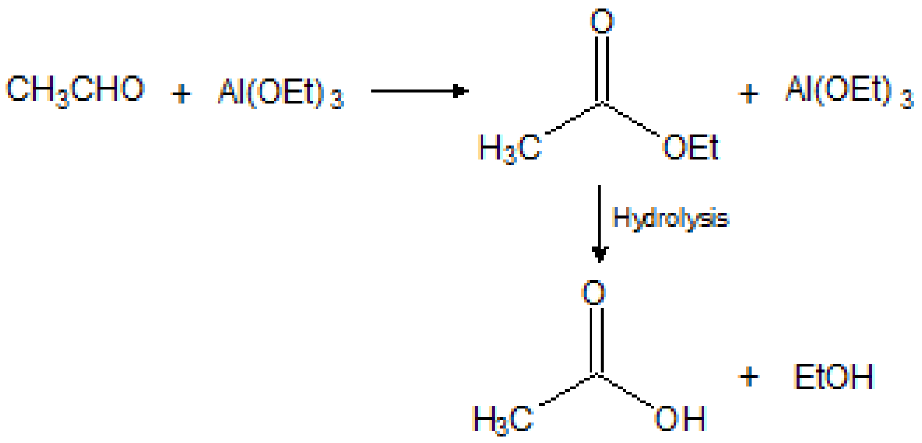


Aldehy de ammonia



k) Tischenko reaction:

All aldehydes can be made to undergo the Cannizzaro reaction by treatment with aluminium ethoxide. Under these conditions the acids and alcohols are combined as the ester, and the reaction is then known as the Tischenko reaction; eg, acetaldehyde gives ethyl acetate, and propionaldehyde gives propyl propionate.



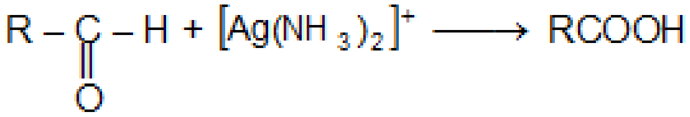
Oxidation of Aldehydes and Ketone

a)

$$RCH=O/ArCH=O \xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7/H^+} R-CO_2H/ArCO_2H$$

b) Tollen's Reagent

A specific oxidant for RCHO is $[Ag(NH_3)_2]^+$

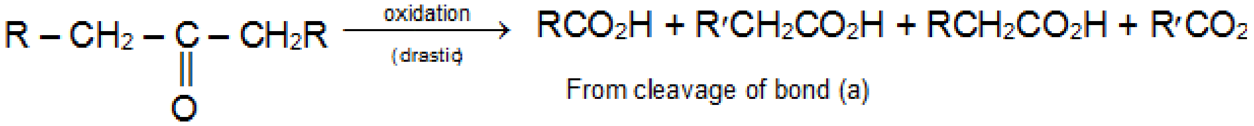


$$R-\underset{\underset{O}{\|}}{C}-H + [Ag(NH_3)_2]^+ \longrightarrow RCOOH$$

Tollen's test chiefly used for the detection of aldehydes.

Tollen's reagent doesnot attack carbon-carbon double bonds.

c) Strong Oxidants: Ketones resist mild oxidation, but with strong oxidants at high temperature they undergo cleavage of C – C bonds on either sides of the carbonyl group



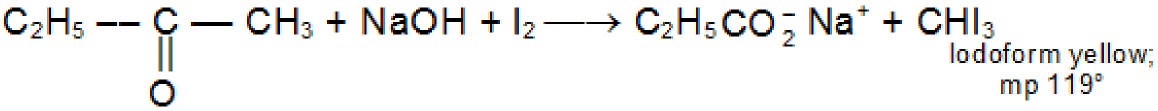
$$R-CH_2-\underset{\underset{O}{\|}}{C}-CH_2R \xrightarrow[\text{(drastic)}]{\text{oxidation}} RCO_2H + R'CH_2CO_2H + RCH_2CO_2H + R'CO_2$$

From cleavage of bond (a)

d) Haloform Reaction

CH3COR are readily oxidised by NaOI (NaOH + I2) to iodoform, CHI3, and RCO2Na

Example:

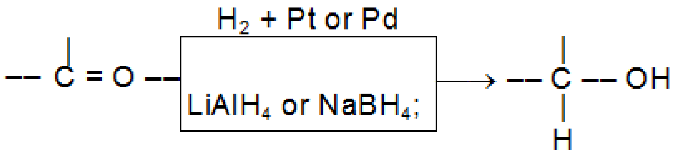


$$C_2H_5-\underset{\underset{O}{\|}}{C}-CH_3 + NaOH + I_2 \longrightarrow C_2H_5CO_2^- Na^+ + CHI_3$$

Iodoform yellow;
mp 119°

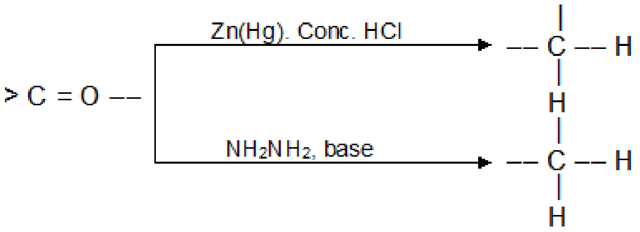
Reduction:

a) Reduction to alcohols



Aldehydes → 1° alcohols; Ketones → 2°alcohols

b) Reduction to hydrocarbons



Clemmensen reduction for compounds sensitive to base

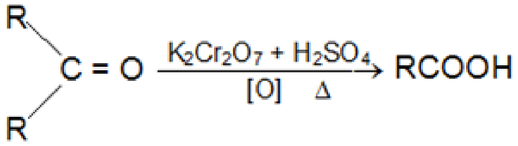
Wolff-Kishner reduction for compounds sensitive to acids

Methods of Preparations of Carboxylic Acids

a. Oxidation of Aldehydes & Ketones

$$R-CH_2OH \xrightarrow[{[O]}]{K_2Cr_2O_7 + H_2SO_4} RCHO \xrightarrow[{[O]}]{K_2Cr_2O_7 + H_2SO_4} RCOOH$$

$$R-CHO \xrightarrow[2.\ H_3O^+]{1.\ Ag_2O \text{ or } Ag(NH_3)_2^+} RCO_2H$$



b. Oxidation of Alkanes:

$$RCH = CHR' \xrightarrow[2.\ Heat,\ H_2O]{1.\ KMnO_4,\ OH^-} RCO_2H + R'CO_2H$$

c. Hydrolysis of Nitriles (Cyanides)

$$R-C \equiv N \xrightarrow[H^+,\ HOH]{\text{Acid hydrolysis}} R.COOH + NH_3$$

d. Carbonation of Grignard Reagents

$$R-X + Mg \xrightarrow{\text{Diethyl ether}} RMgX \xrightarrow{CO_2} RCO_2MgX \xrightarrow{H_3O^+} RCO_2H$$

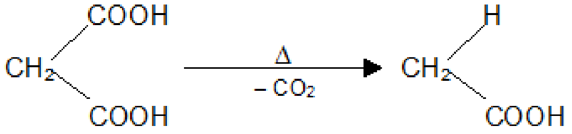
$$\text{or } Ar-Br + Mg \xrightarrow{\text{Diethyl ether}} ArMgBr \xrightarrow{CO_2} ArCO_2MgBr \xrightarrow{H_3O^+} ArCO_2H$$

e. Koch Reaction:

An olefin is heated with carbon monoxide and steam under pressure at 300-400° in the presence of a catalyst, e.g. phosphoric acid.

$$CH_2 = CH_2 + CO + H_2O \xrightarrow[\text{steam } 300\text{–}400^\circ C]{H_3PO_4} CH_3 - CH_2 - COOH$$

f. Heating Gem Dicarboxylic Acids:



Acetic acid

Chemical Reactions of Carboxylic Acids

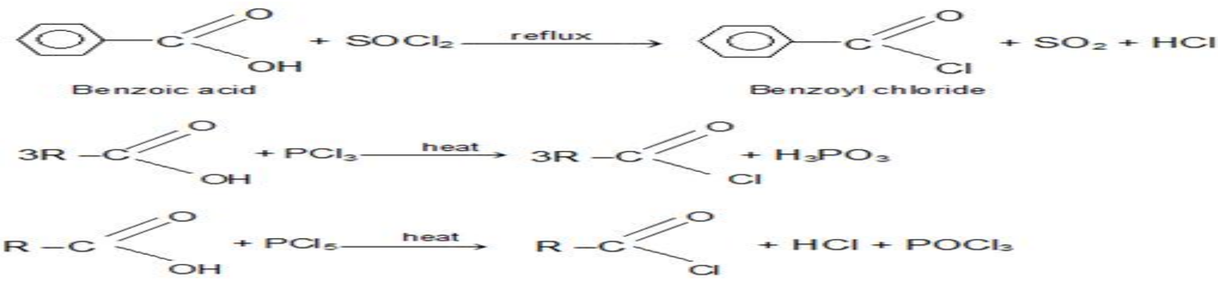
a. Salt formation:

2CH3COOH + 2Na → 2CH3COO–Na+ + H2

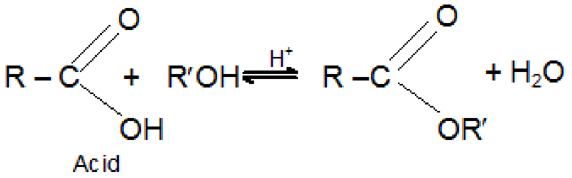
CH3COOH + NaOH → CH3COO–Na+ + H2O

CH3COOH + NaHCO3 → CH3COO–Na+ + H2O + CO2

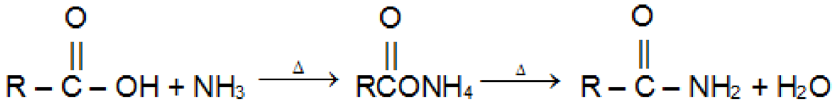
b. Conversion into Acid Chlorides:



c. Conversion into Esters (Esterification)



d. Conversion into Amides



$$R - \overset{\overset{O}{\parallel}}{C} - OH + NH_3 \xrightarrow{\Delta} \overset{\overset{O}{\parallel}}{RCONH_4} \xrightarrow{\Delta} R - \overset{\overset{O}{\parallel}}{C} - NH_2 + H_2O$$

e. Conversion into Anhydrides

$$2CH_3COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CO)_2O + H_2O$$

f. Reduction:

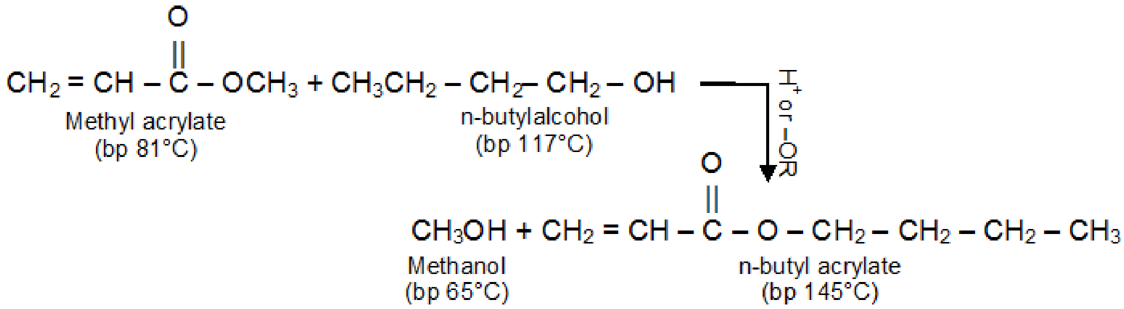
$$4R\text{–}COOH + 3LiAlH_4 \longrightarrow 4H_2 + 2LiAlO_2 + (RCH_2O)_4\,AlLi \xrightarrow{H_2O} RCH_2OH$$

g. Halogenation:

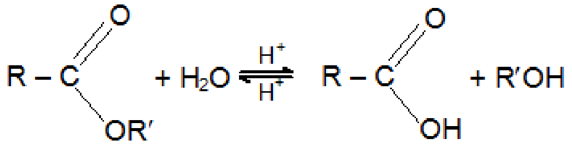
$$CH_3 - COOH \xrightarrow{Cl_2,P} Cl - CH_2 - COOH \xrightarrow{Cl_2,P} Cl_2CH - COOH \xrightarrow{Cl_2,\ P} Cl_3CCOOH$$

Esters

a) Transesterification :



b) Hydrolysis:



c) Reduction:

$$CH_3-(CH_2)_{10}-COOCH_3 \xrightarrow[150^\circ\text{ High pressure}]{H_2,\ CuO,\ CuCr_2O_4} CH_3(CH_2)_{10}CH_2OH + CH_3OH$$

Methyl laurate — Lauryl alcohol

$$CH_3-(CH_2)_{14}-COOC_2H_5 \xrightarrow{LiAlH_4} \xrightarrow{H^+} CH_3-(CH_2)_{14}-CH_2-OH$$

Ethyl palmitate — 1–Hexadodecanol

Acid Chlorides:

a) Acetylation

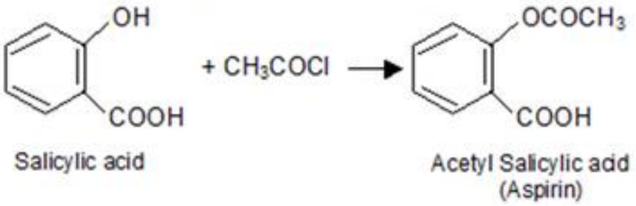
$$CH_3COCl + HOH \longrightarrow CH_3COOH + HCl$$

$$CH_3COCl + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$$

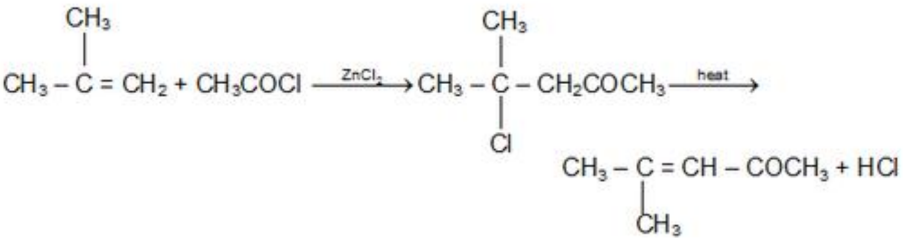
Acetyl chloride — Ethyl acetate

$$CH_3COCl + H_2NC_6H_5 \longrightarrow C_6H_5NHCOCH_3 + HCl$$

Aniline — Acetanilide



b) Reaction with Olefins:



QUESTION BANK

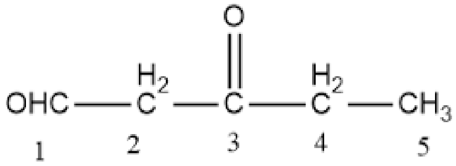
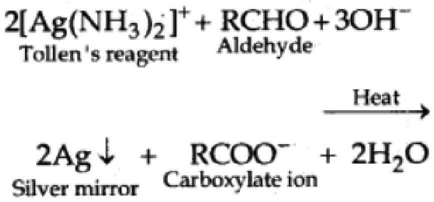
SECTION-A The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.		
1	1. When benzaldehyde and formaldehyde are heated in an aqueous $NaOH$ solution, they produce A) Sodium formate + benzyl alcohol B) Methanol + sodium benzoate C) Methanol + benzyl alcohol D) Sodium formate + sodium benzoate	**[1]**
2	The Rosenmund reaction can produce which of the following carbonyl compounds? a) Methanal b) Benzaldehyde c) Butanone d) Acetone	**[1]**
3	Reactions occur between aldehydes and ketones. a) nucleophilic addition b) electrophilic substitution c) electrophilic addition d) nucleophilic substitution	**[1]**
4	Which of the following reactions to a nucleophilic assault is the least reactive? a) Acetaldehyde b) Di Tert-Butyl ketone c) Diisopropyl ketone d) Butanone	**[1]**
5	Acetone combines with ethylene glycol in dry HCl gas to generate _________ a) hemiacetals b) cyclic ketals c) cyclic acetals d) acetals	**[1]**
6	Which of the following is not a formaldehyde application? a) Preservation of biological specimens b) Preparation of acetic acid c) Silvering of mirrors d) Manufacturing of bakelite	**[1]**
7	Which of the following compounds is formed when benzyl alcohol is oxidised with $KMnO4$? a) $CO2$ and $H2O$ b) Benzoic acid c) Benzaldehyde d) Benzophenone	**[1]**
8	At 287K, which of the following is a gas? a) Propanal b) Acetaldehyde c) Formaldehyde d) Acetone	**[1]**
9	Which of the following substances is the least water-soluble? a) Methanal b) Pentanal c) Propanone d) Ethanal	**[1]**
10	Which of these has the least unpleasant odour? a) Methanal b) Butanal c) Propanal d) Ethanal	**[1]**

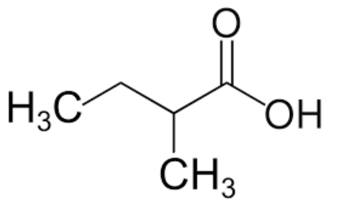
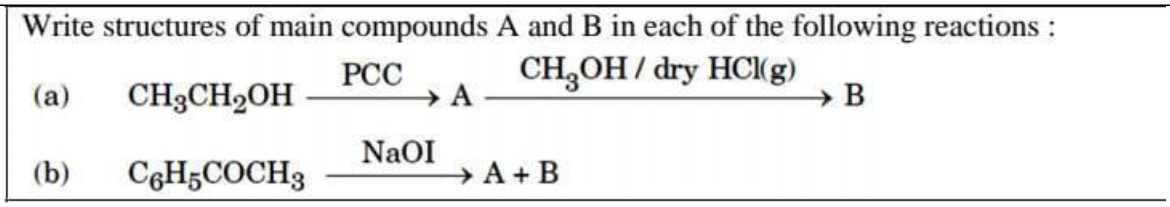
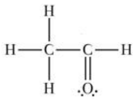
	In the following questions (Q. No. 11 - 20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (f) Assertion and reason both are correct statements and reason is correct explanation for assertion. (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion. (c) Assertion is the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	Assertion:The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. Reason: There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.	**[1]**
12	Assertion: the compounds containing -CHO group are easity oxidised to corresponding carboxylic acids Reason: carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$	**[1]**
13	Assertion: fomaldehyde is a planer molecule Reason: it contains sp^2 hybridised carbon atom	**[1]**
14	Assertion: aldehydes and ketones react with Tollen's reagent to form silver mirror Reason: both aldehydes and kitones contain a carbonyl group	**[1]**
15	Assertion: carboxylic acids have higher boiling points than alkanes Reason: carboxilic acids are resonance hybrids	**[1]**
16	Assertion: acetic acid is stronger acid than CH_3CH_2COOH Reason: acetic acid is resonance stabilized	**[1]**
17	Assertion: aromatic carbixylic acids do not undergo Friedel-Crafts reaction Reason: the carboxyl group is deactivating	**[1]**
18	Assertion: formic acid reduces Tollen's reagent Reason: formic acid has aldehydic group	**[1]**
19	Assertion: the compounds containing methyl ketone responds to iodoform test Reason: ethyl alcohol also responds iodoform test	**[1]**

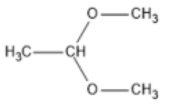
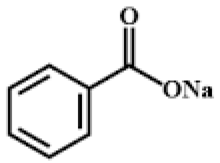
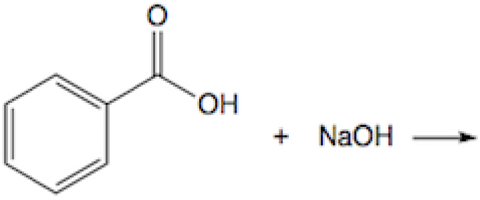
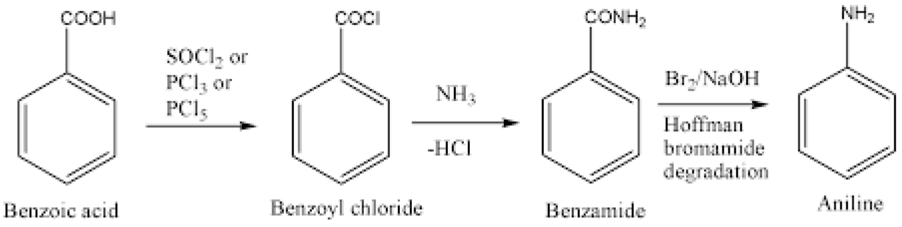
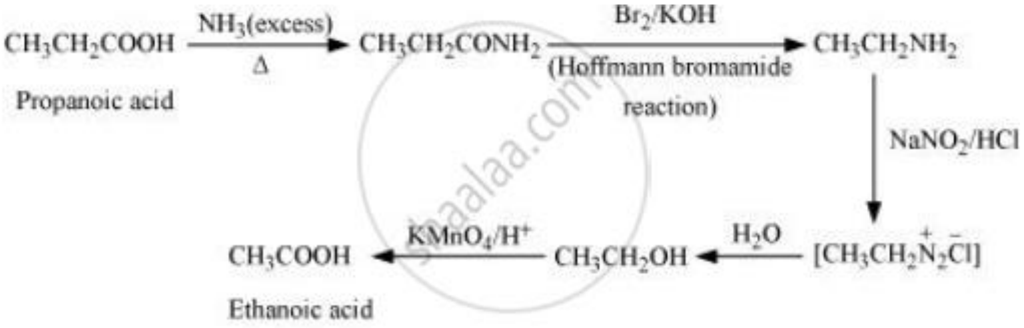
20	Assertion: the pka of aceetic acid is lower than that of phenol Reason: phenoxide ion is more resonance stabilized than acetate ion	**[1]**

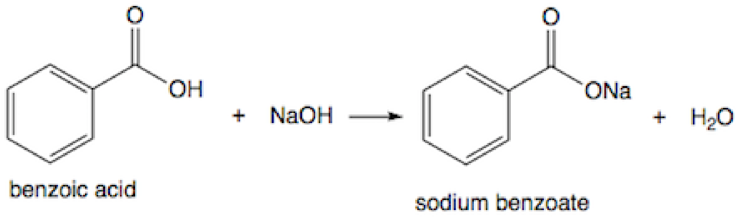
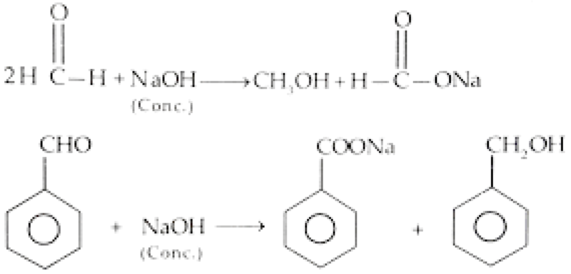
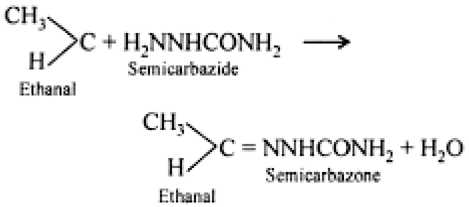
ANSWER KEY:

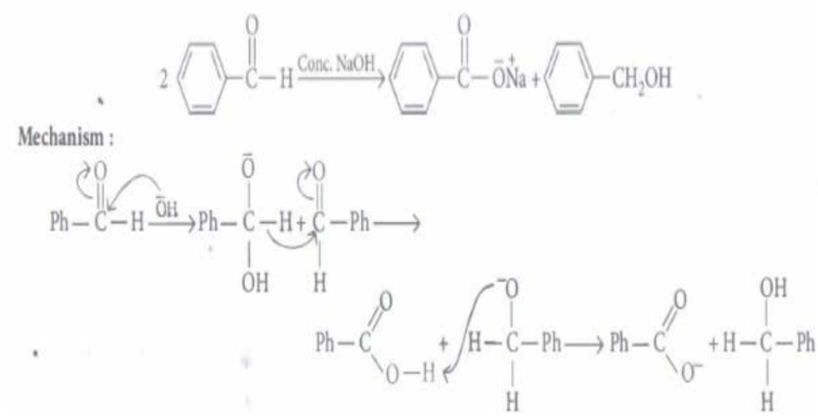
1	**a**	**2**	**b**	**3**	**A**	**4**	**b**	**5**	**b**
6	**b**	**7**	**b**	**8**	**C**	**9**	**b**	**10**	**b**
11	**a**	**12**	**b**	**13**	**A**	**14**	**b**	**15**	**b**
16	**c**	**17**	**a**	**18**	**A**	**19**	**a**	**20**	**c**

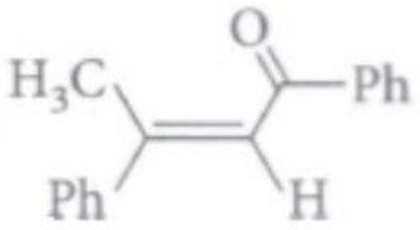
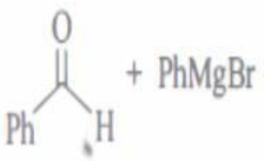
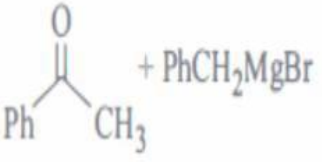
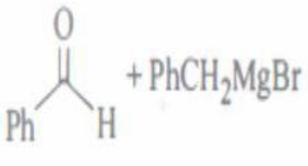
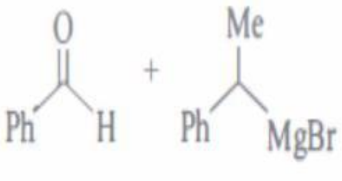
	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	Write the structure of 3-oxopentanal	**[2]**
ANS.	 3-oxopentanal	
22	What is Tollen's reagent? Write one usefulness of this reagent.	**[2]**
ANS.	Ammonical silver nitrate solution is called Tollen's reagent. Uses : it is used to test aldehydes. Both aliphatic and aromatic aldehydes reduce Tollen's reagent to shining silver mirror. It is also used to distuingish aldehydes from ketones  $\underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + \underset{\text{Aldehyde}}{RCHO} + 3OH^- \xrightarrow{\text{Heat}} \underset{\text{Silver mirror}}{2Ag\downarrow} + \underset{\text{Carboxylate ion}}{RCOO^-} + 2H_2O$	
23	Arrange the following in an increasing order of their reactivity in nucleophilic addition reaction Butanone, ethanal, propanone, propanal	**[2]**
ANS.	Butanone<propanone<propanal<ethanal.	
24	Write the IUPAC name of	**[2]**

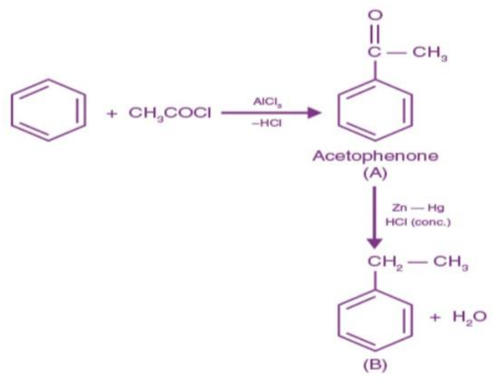
	 :	
ANS.	2-methylbutanoic acid	
25	Give a chemical test to distinguish between ethanal and propanal	**[2]**
ANS.	Ethanal on heating with I2 and NaOH gives a yellow ppt of iodoform but propanal does not respond to this test.	
	SECTION C The following questions are short answer type and carry 3 marks each.	
26	Give reasons: (a) Benzoic acid is a stronger acid than acetic acid (b) Methanal is more reactive towards nucleophilic reaction addition than ethanal (c) Give a simple chemical test to distinguish between propanal and propanone	**[3]**
ANS.	(a)Benzoic acid itself is a somewhat stronger acid than acetic acid. The carboxyl group of benzoic acid is attached to an sp2-hybridized carbon which is more electronegative and electron-withdrawing than the sp3-hybridized carbon attached to the carboxyl group of acetic acid (b)Methanal is more reactive than ethanal towards Nucleophilic addition reaction due to steric and electronic reasons. Presence of methyl group in ethanal hinders the approach of nucleophile to carbonyl carbon than in methanal. (c)propanal is an aldehyde, it reduces Tollen's reagent. However, because propanone is a ketone, Tollen's reagent is not reduced	
27	 Write structures of main compounds A and B in each of the following reactions : (a) $CH_3CH_2OH \xrightarrow{PCC} A \xrightarrow{CH_3OH\ /\ dry\ HCl(g)} B$ (b) $C_6H_5COCH_3 \xrightarrow{NaOI} A + B$	**[3]**
ANS.	(a)A  B	

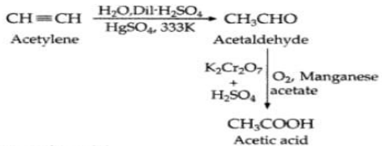
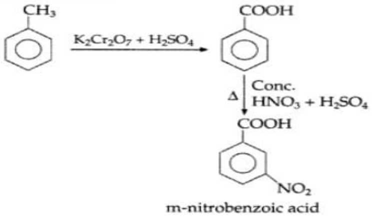
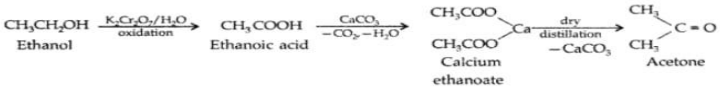
	 1,1-dimethoxyethane Molecular formula: $C_4H_{10}O_2$ Molecular mass: 90 L (b)A B  CHI_3 **Iodoform**	
28	Carry out the following reactions: (a) Benzoic acid to aniline (b) Propanoic acid to ethanoic acid (c) Write major product in the following  benzoic acid	**[3]**
ANS.	(a)  (b) 	

	 (c	
29	Account for the following (a) aromatic carboxylic acids donot undergo friedal craft reaction (b) pka value of 4nitrobenzoic acid is lower than that of benzoic acid	**[3]**
ANS.	(a) Because –COOH group present in aromatic carboxylic acids is an electron withdrawing group causing deactivation of benzene ring. This results in the bonding of anhydrous AlCl3 with carboxyl group. Hence electrophillic substitution i.e. Friedel-Crafts reaction does not occur in aromatic carboxylic acids. (b) As 4-nitrobenzoic acid contains –NO2 group which is an electron withdrawing group resulting in higher acidity than benzoic acid. Greater is the acidic character lower is the pKa value. Thus pKa value of 4-nitrobenzoic acid is lower than that of benzoic acid.	
30.	(a) Write the chemical equation for the reaction involved in cannnizzaro reaction. (b) Draw the structure of the semicarbazone of ethanal.	
ANS.	(a)  (b) 	
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	PASSAGE: When an aldehyde with no a-hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to carboxylic acid salt and other half is converted to	**[4]**

	an alcohol. In other words, half of the reactant is oxidized and other half is reduced. This reaction is known as Cannizzaro reaction. 	
31.1	i) A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives (a)benzyl alcohol and sodium formate (b) sodium benzoate and methyl alcohol (c) sodium benzoate and sodium formate (d) benzyl alcohol and methyl alcohol.	
ANS.	(a)	
31.2	Which of the following compounds will undergo Cannizzaro reaction? (a) CH3CHO (b) CH3COCH3 (c) C6H5CHO (d) C6H5CH2CHO	
ANS.	(c)	
31.3	Trichloroacetaldehyde is subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compounds is (a) 2, 2, 2-trichloroethanol (b) trichloromethanol (c) 2, 2, 2-trichloropropanol (d) chloroform	
ANS.	(a)	
	OR	

31.3	Which of the following reaction will not result in the formation of carbon-carbon bonds? (a) Cannizzaro reaction (b) Wurtz reaction (c) Reimer- Tiemann reaction (d) Friedel-Crafts acylation	
ANS.	(a)	
32	PASSAGE: A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on reaction with KOH gives only M. M = 	**[4]**
32.1	Compound H is formed by the reaction of (a)  (b)  (c)  (d) 	
ANS.	(b)	
	The structures of compound J, Kand L, respectively, are (a) PhCOCH3 , PhCH2COCH3 and PhCH2COO-K+ (b) PhCHO, PhCH2CHO and PhCOO-K+ (c) PhCOCH3, PhCH2CHO and CH3 (d)PhCHO,PhCOCH3, PhCOO-K+	

ANS.	(d)	
32.3	When (J) is treated with acetic anhydride, in the presence of corresponding salt of an acid, the product obtained is (a) cinnamic acid (b) crotonic acid (c) maleic acid (d) benzylic acid	
ANS.	(a)	
	OR	
32.3	The oxidation of toluene to benzaldehyde by chromyl chlorite is called	
ANS.	Etard’s Reaction	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	Why are carboxylic acids more acidic than alcohols or phenols, although they all have hydrogen atoms attached to an oxygen atom (-0-H)?	**[5]**
ANS.	Carboxylic acids are more acidic than alcohols or phenols. However, they all have a hydrogen atom attached to an oxygen atom (—O—H) because the conjugate base of carboxylic acids or the carboxylate ion is stabilised by resonance. Due to the resonance in carboxylic acids, the negative charge is at the more electronegative atom (oxygen atom). In alcohols or phenols, the negative charge is on the less electronegative atoms. Thus, carboxylic acids can release protons easier than alcohols or phenols.	
34	Ethylbenzene is generally prepared by acetylation of benzene followed by reduction and not by direct alkylation. Think of a possible reason.	**[5]**
ANS.	Preparation of ethylbenzene from acylation of benzene and reduction is shown as:  	

	Direct alkylation is not performed because a poly substituted product is formed. Due to the disadvantage of poly substitution, Friedel-Craft's alkylation reaction is not used to prepare alkylbenzenes. Instead of Friedel-Craft's acylation is used.	
35	(a) How will you carry out the following conversions? (i) Acetylene to Acetic acid (ii) Toluene to m-nitrobenzoic acid (iii) Ethanol to Acetone (b) Give reasons : (i) Chloroacetic acid is stronger than acetic acid. (ii) pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds.	**[5]**
ANS.	(a)(i)Acetylene to Acetic acid  (ii) Toluene to m-nitrobenzoic acid  (iii) Ethanol to acetone :  (b) (i) Because – I effect of Cl decreases the electron density in the O-H bond thereby making the releaseof a proton easier. (ii) In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium OH- will attack carbonyl group.	

■■

तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन
Kendriya Vidyalaya Sangathan

KENDRIYA VIDYALAYA SANGATHAN, JABALPUR REGION

CLASS- XII / XI

CHEMISTRY (043)

CHAPTER NAME: AMINES

PREPARED BY: Members of GROUP 9

IMPORTANT POINTS/ NOTES ON TIP:

Aliphatic And Aromatic Amines

Aliphatic amines have at least one alkyl group bonded to the nitrogen. The lone pair of electrons on the nitrogen. The lone pair of electrons on the nitrogen means that aliphatic amines behave similarly to ammonia:

- they act as nucleophiles and take part in reaction involving donation of the lone pair
- they act as Bronsted-Lowry bases (H^+ acceptors).

Aromatic amines contain a benzene ring directly attached to the NH2 group.
The delocalized system of the benzene group is able to incorporate the lone pair of electrons from the nitrogen atom, meaning that aromatic amines have different properties to aliphatic amines.

Nomenclature Of Amines

- In common system, an aliphatic amine is named by prefixing alkyl group to amine, i.e., alkylamine as one word (e.g. methylamine).
- In secondary and tertiary amines, when two or more group are the same, the prefix di or tri is appended before the name of alkyl group.
- In IUPAC system amines are named as alkanamines, derived by replacement of ‘e’ of alkane by the word amine. For example, CH_3NH_2 is named as methanamine. In case, more than one amino group is present at different positions in the parent chair, their positions are

specified by giving numbers to the carbon atoms bearing $–NH_2$ groups and suitable prefix such as di, tri, etc. is attached to the amine. The letter ‘e’ of the suffix of the hydrocarbon part is retained.

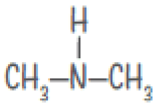
- For example, $H_2N–CH_2–CH_2–NH_2$ is named as ethane -1, 2-diamine.
- In arylamines, $–NH_2$ group is directly attached to the benzene ring. $C_6H_5NH_2$ is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name.
- While naming arylamines according to IUPAC system, suffix ‘e’ of arene is replaced by ‘amine’. Thus in IUPAC system, $C_6H_5–NH_2$ is named as benzenamine.

Structure And Classification Of Amines

Amines are classified as 1°, 2°, or 3° depending on the number of carbon groups bonded to nitrogen.

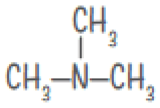
- **Aliphatic amine:** All carbons bonded to nitrogen are derived from alkyl groups.
  $CH_3–NH_2$ (Methylamine (a 1° amine))

$CH_3–NH_2$ (Methylamine (a 1° amine))



$CH_3-\overset{\overset{H}{|}}{N}-CH_3$

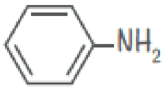
Dimethymine (a 2° amine)



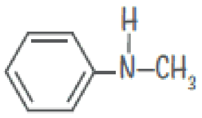
$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$

Trimethylamine (a 3° amine)

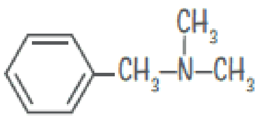
- **Aromatic amine:** One or more of the group bonded to nitrogen are aryl groups.



Aniline (a 1° aromatic amine)



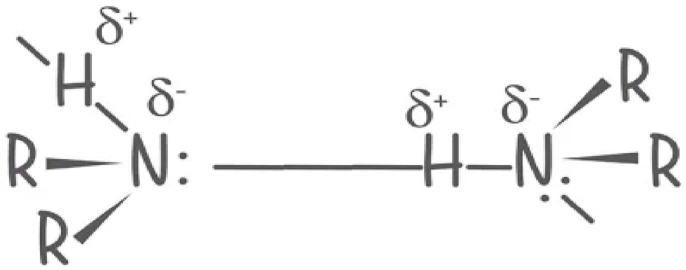
N-Methylaniline
(a 2° aromatic amine)



Benzyldimethylamine
(a 3° aliphatic amine)

Physical Properties Of Amines

- They have unpleasant odors (rotting fish like ammonia).
- They are polar compounds.
  Difference in electronegativity between N–H (3.0 – 2.1 = 0.9)
- 1° and 2° amines have hydrogen bonds (N–H). Weaker than alcohols (O–H)
  3° amines do not form hydrogen bonds (no H atom).
- Boiling points : Hydrocarbons < Amines < Alcohols
- Almost soluble in water (hydrogen bonding).

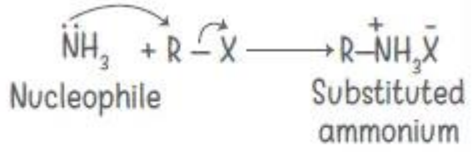


Preparation Of Amines

Reduction of Nitro Compounds

Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.

Ammonolysis of Nitro Compounds

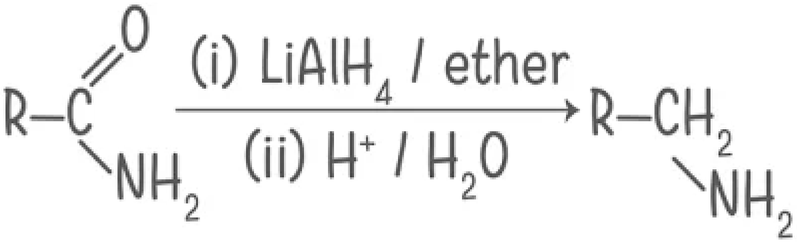


$$RX \xrightarrow{NH_3} \underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3NH} \xrightarrow{RX} \underset{(4^\circ)}{R_4N^\ominus}$$

RX→NH3RNH2(1°)→RXR2NH(2°)→RXR3NH(3°)→RXR4N(4°)⊖*RXNH*3(1°)*RNH*2*RX* (2°)*R*2*NHRX*(3°)*R*3*NHRX*(4°)*R*4*N*⊖

Reduction of Amides

The amides on reduction with lithium aluminium hydride amines.



Nitriles on reduction with lithium aluminium hydride (LiAlH4) or catalytic hydrogenation produce primary amines. This reaction is used ascent of amine series. i.e., for preparation of amines containing one carbon atom more than the starting amine.
R–C≡N:Nitrile→[R]R–CH2N¨H2NitrileNitrile*R–C≡N*:[*R*]Nitrile*R–CH*2*N¨H*2

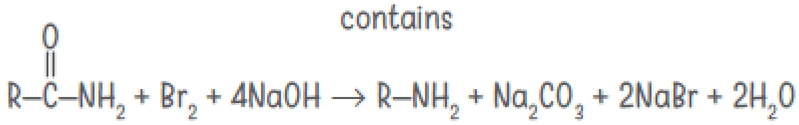
Hoffmann Bromamide Degradation Reaction

$$\underset{\text{Nitrile}}{R\text{–}C \equiv N:} \xrightarrow{[R]} \underset{\text{Nitrile}}{R\text{–}CH_2\ddot{N}H_2}$$

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reactinon, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains

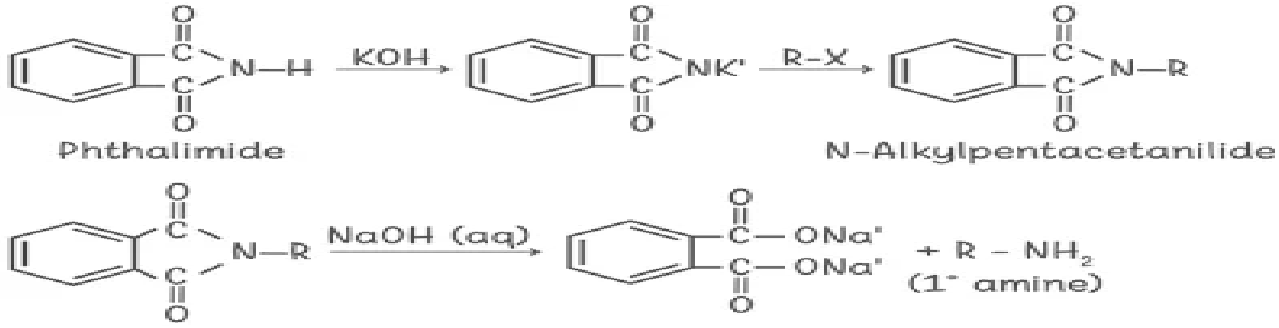
Gabriel Phthalimide S ynthesis

contains



$$R\text{–}\overset{\overset{\Large O}{\|}}{C}\text{–}NH_2 + Br_2 + 4NaOH \rightarrow R\text{–}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the



Identification Of Amines

Hinsberg’s reagent (benzene sulphonylchloride) reacts with primary, secondary and tertiary amines in a different manner. This is used for the distinction of three types of amines.

- Primary amines react with benzene sulphonyl chloride to produce N-alkyl benzene sulphonamide. Hydrogen attached to nitrogen in the product is acidic so it soluble in alkali.
- A secondary amine reacts with Hinsberg’s reagent to from N.N-dialkyl benzene sulphonamide which remains insoluble in alkali.
- A tertiary amine does not react with benzene sulphonyl chloride.

Chemical Properties Of Amines

Addition of Water Acid catalysed addition of water gives alkyl formaldehyde derivative.

$CHOH \rightarrow RNHCHO$

RNC + H_2O → RN = CHOH → RNHCHO

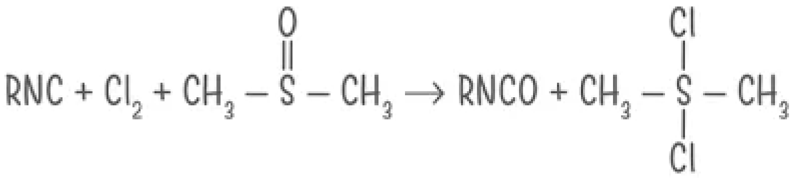
Reduction with LAH

RNC → $RNHCH_3$

Reduced to N-methyl amines.

RNC → $RNHCH_3$

On reaction with HgO or with ozone as well as with halogen and dimethylsulphoxide, oxidised to isocyanates.



$$RNC + Cl_2 + CH_3 - \overset{\overset{\displaystyle O}{\|}}{S} - CH_3 \rightarrow RNCO + CH_3 - \underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{S}} - CH_3$$

Salt Formation : Since amines are weak bases, they react with strong acids to form ammonium salts. Methylamine for example reactes with strong acid yielding the corresponding methylammonium salt.

$$\underset{\text{Methylaminemolecule}}{CH_3NH_2(g)} + \underset{\text{Hydrogenchloridemolecule}}{HCl(g)} \longrightarrow \underset{\text{Methylaminemolecule}}{CH_3N + H_3Cl-}$$

CH3NH2(g)Methylaminemolecule +HCl(g)Hydrogenchloridemolecule → CH3N+H3Cl–MethylaminemoleculeMethylaminemolecule*CH*3*NH*2(*g*) +Hydrogenchloridemolecule*HCl*(*g*) Methylaminemolecule*CH*3*N*+*H*3*Cl*–

Acylation

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation. This reaction is considered as the replacement of hydrogen atom of –NH2 or > N–H group by the acyl group.

Carbylamine R eaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide forms isocyanides or carbylamines which are foul smelling substances.

Uses Of Amines

- Aromatic amines are mainly used as a starting material for the production of azo dyes.
- Many drugs are designed to interfere with the action of natural amines.
- Amines are used in making artificial fibers.
- Aromatic amines are used in detergent production.

QUESTION BANK

SECTION-A The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.		
1	1. Which of the following is a 3° amine? (i) 1-methylcyclohexylamine (ii) Triethylamine (iii) tert-butylamine (iv) N- methyl aniline	**[1]**
2	The correct IUPAC name for CH2=CHCH2NHCH3 is (i) Allylmethylamine (ii) (ii) 2-amino-4-pentene (iii) (iii) 4-aminopent-1-ene (iv) (iv) N-methylprop-2-en-1-amine	**[1]**
3	. Amongst the following, the strongest base in aqueous medium is ___________. (i) CH3NH2 (ii) NCCH2NH2 (iii) (CH3)2NH (iv) C6H5NHCH3	**[1]**
4	4. Which of the following is the weakest Brönsted base? (i) Benzamine (ii) Ethanamine (Iii) 11dimethyl amine (iv) 1,1,1teimethyl amine	**[1]**
5	. Which of the following alkyl halides is best suited for this reaction through SN1 mechanism? (i) CH3Br (ii) C6H5Br (iii) C6H5CH2Br (iv) C2H5 Br	**[1]**
6	Which of the following not be a good choice for reducing an aryl nitro compound to an amine? (i) H2 (excess)/Pt (ii) LiAlH4 in ether (iii) Fe and HCl (iv) Sn and HCl	**[1]**
7	To prepare a 1° amine from an alkyl halide with simultaneous addition of one CH2 group in the carbon chain, the reagent used as a source of nitrogen is ___________. (i) Sodium amide, NaNH2 (ii) Sodium azide, NaN3 (iii) Potassium cyanide, KCN (iv) Potassium phthalimide, C6H4(CO)2N–K+	**[1]**

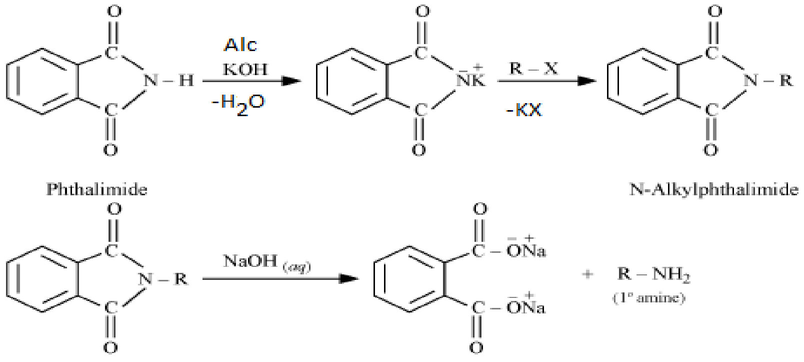
8	. The source of nitrogen in Gabriel synthesis of amines is _____________. (i) Sodium azide, NaN3 (ii) Sodium nitrite, NaNO2 (iii) Potassium cyanide, KCN (iv) Potassium phthalimide, C6H4(CO)2N–K+	**[1]**
9	Amongst the given set of reactants, the most appropriate for preparing 2° amine is _____. (i) 1° R—NH2 + RCHO followed by H2/Pt (ii) 2° R—Br + NaCN followed by H2/Pt (iii) 2° R—Br + NH3 (iv) 1° R—Br (2 mol) + potassium phthalimide followed by H3O+/heat	**[1]**
10	The best reagent for converting 2–phenylpropanamide into 2-phenylpropanolamine is _____. (i) excess H2 (ii) Br2 in aqueous NaOH (iii) I2 inpresence of red P (iv) LiAlH4 in ether	**[1]**
	In the following questions (Q. No. 11 - 20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (g) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	**. Assertion :** Aromatic 1°amines can be prepared by Gabriel phthalimide synthesis. **Reason :** Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.	**[1]**
12	**Assertion :** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam. **Reason :** $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.	**[1]**
13	**Assertion :** Amines are basic in nature. **Reason :** Amines have lone pair of electrons on nitrogen atom.	**[1]**

14	**. Assertion :** Acetanilide is less basic than aniline. **Reason :** Acetylation of aniline results in decrease of electron density on nitrogen.	**[1]**
15	**Assertion :** Nitration of aniline can be conveniently done by protecting the amino group by acetylation. **Reason :** Acetylation increases the electron-density in the benzene ring.	**[1]**
16	**Assertion :** Aniline does not undergo Friedel-Crafts reaction. **Reason :** –NH2 group of aniline reacts with AlCl3 (Lewis acid) to give acid-base reaction.	**[1]**
17	**Assertion :** Acylation of amines gives a monosubstituted product whereas alkylation of amines gives poly-substituted product. **Reason :** Acyl group sterically hinders the approach of further acyl group	**[1]**
18	**Assertion :** Nitrating mixture used for carrying out nitration of benzene consists of conc. HNO_3+ conc. H_2SO_4 **Reason :** In presence of H_2SO_4, HNO_3 acts as a base and produces NO_2^+ ions.	**[1]**
19	**Assertion(A):** Hoffmann's bromamide reaction is given by amides. **Reason(R):** Primary amines are more basic than secondary amines.	**[1]**
20	**Assertion(A):** Acylation of amine gives a monosubstituted product whereas alkylation of amines gives polysubstituted product. **Reason(R):** Acyl group sterically hinders the approach of further acyl group.	**[1]**

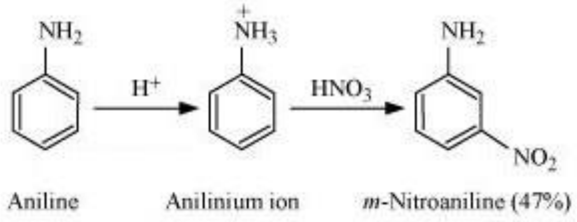
ANSWER KEY:

1	**B**	**2**	**D**	**3**	**C**	**4**	**A**	**5**	**B**
6	**B**	**7**	**C**	**8**	**D**	**9**	**C**	**10**	**D**
11	**A**	**12**	**D**	**13**	**A**	**14**	**D**	**15**	**C**
16	**A**	**17**	**C**	**18**	**A**	**19**	**C**	**20**	**A**

	SECTION B **The following questions are very short answer type and carry 2 marks each.**	
21	**1)** (i) Arrange the following compounds in an increasing order of basic strength: $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2 (ii) Arrange the following compounds in a decreasing order of pK_b values: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$	**[2]**

ANS.	(a) In aqueous solution, basic strength decreases in the order. (C2H5)NH>(C2H5)3N>C2H5NH2>NH3 (b) In gaseous phase, (basic strength decreases in the order. (C2H5)3N>(C2H5)2NH>C2H5NH2>NH3. (ii)Decreasing order of pKb value_ C6H5NH2, C6H5NHCH3,(C2H5)2NH2,C2H5NH2	
22	**2)** Give reasons: (i) Aniline is a weaker base than cyclohexyl amine. (ii) It is difficult to prepare primary amines by ammonolysis of alkyl halides	**[2]**
ANS.	i) Cyclohexylamine is more basic than aniline because aniline is a resonance hybrid of various resonance structures. As a result, in aniline the electron donating capacity of nitrogen for protonation is considerably decreased. (ii) Ammonolysis of alkyl halides does not give single amine but gives a mixture of primary, secondary and tertiary amines.	
23	Write equations for (i) Gabriel phthalimide reaction (ii) Hofmann bromamide reaction	**[2]**
ANS.	Gabriel phthalimide synthesis: Phthalimide reacts with ethanolic KOH to give potassium salt of phthalimide. It is then heated with alkyl halide to give N-alkyl phthalimide. On alkaline hydrolysis, a primary amine is obtained.  Hoffman bromamide degradation reaction_ RCONH2+Br2+4KOH_>$RNH2 + 2KBr + K2CO3 + H2O$	

24	Give a chemical test to distinguish between each of the following pairs of: (i) Ethylamine and aniline. (ii) compounds Aniline and benzylamine.	**[2]**
ANS.	Azo dye test. Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphthol (in alkaline solution) forms brilliant orange or red dye. Ethylamine will not form dye. It will give brisk effervescence (due to liberation of nitrogen gas) but solution remains clear. (ii) Aniline and benzylamine : Azo dye test. Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphthol (in alkaline solution) forms brilliant orange or red dye. Benzylamine will not give such test.	
25	**5 (i)**Write IUPAC name of(CH3)2NCH2CH3 (ii) Which of the two is more basic and why C6H5NH2 and C6H5CH3NH2	**[2]**
ANS.	(i) N,N dimethyl ethanmine (ii) C6H5CH3C6H5NH2 Is more basic because of +I Effect	
	SECTION C The following questions are short answer type and carry 3 marks each.	
26	**1)** Give reason: (i) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines. (ii) Aniline does not give Friedel-Crafts reaction. (iii) Although $-NH_2$ group is o/p directing in electrophilic substitution reactions, yet aniline on nitration gives good yield of m-nitroaniline. (ii)Aniline does not undergo Friedel craft's reactions because the reagent AlCl3 (the Lewis acid which is used as a catalyst in friedel crafts reaction), being electron deficient acts as a Lewis base. and attacks on the lone pair of nitrogen present in aniline to form an insoluble complex which precipitates out and the reaction does not proceed. (iii)Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).	**[3]**

ANS.		
27	(i) Aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis. (ii) Aliphatic amines are stronger bases than ammonia.	**[3]**
ANS.	Ans: (1) Aeromatic primary amines can not be prepared by this method by this method because aryl halide do not undergo nucleophilic substitution with the anion formed by pthalamide. (ii) Aliphatic amines are stronger bases than ammonia die to +I effect of alkyl groups leading to high electron density on the nitrogen atom.	
28	State reasons for the following: (i) pK_b value of aniline is more than that of methylamine. (ii) Ethylamine is soluble in water, whereas aniline is not soluble in water. Primary amines have higher boiling points than tertiary amines.	**[3]**
ANS.	(i) pKb of aniline is more than that of methylamine. In aniline, the lone pair of electrons on N atom is in resonance with benzene ring. Hence, it cannot be easily donated to an acid. This decreases its basicity. In methyl amine, the +I effect of methyl group increases the electron density on N atom so that the lone pair of electrons on N atom can be easily donated to an acid. Hence, methylamine is more basic than aniline. Higher is the basicity, lower is the pKb and vice versa. Ethylamine is soluble in water whereas aniline is not. With increase in the molecular weight, the solubility decreases. Aniline has higher molecular weight than ethylamine. Primary amines have high melting point than tertiary amine due to formation of hydrogen bonding .	
29	An organic compound (A) with molecular formula C_3H_7NO on heating with Br_2 and KOH forms a compound (B). Compound (B) on heating with $CHCl_3$ and alcoholic KOH produces a foul smelling compound (C) and on reacting with $C_6H_5SO_2Cl$ forms a compound (D) which is soluble in alkali. Write the structures of (A), (B), (C) and (D).	**[3]**
ANS.	The given organic compound (a) with the molecular formula C3H7NO can undergo a series of reactions to form different compounds. Here are the structures and reactions involved:	

(a) Compound A: CH3CH2CH2NH2

(b) Compound B: CH3CH2CH2NBr2

(c) Compound C: CH3CH2CH2NHBr

(d) Compound D: CH3CH2CH2NHC6H5SO2

Now, let's look at the reactions:

1. Compound A reacts with Br2 and KOH to form Compound B. This is **bromination** where Br2 is added across the double bond:

CH3CH2CH2NH2 + Br2 + KOH → CH3CH2CH2NBr2 + KBr + H2O

2. Compound B reacts with CHCl3 and alcoholic KOH to form Compound C. This is the **Hofmann bromamide reaction:**

CH3CH2CH2NBr2 + CHCl3 + KOH → CH3CH2CH2NHBr + KBr + CHCl2 + H2O

3. Compound B also reacts with C6H5SO2Cl to form Compound D. This is the reaction of **amine with aryl sulfonyl chloride:**

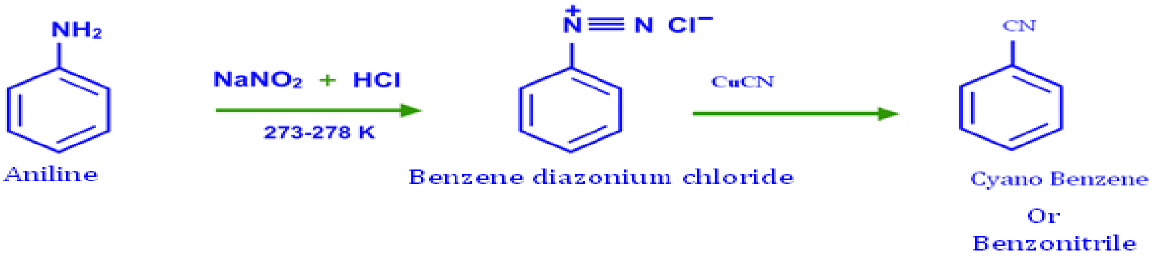
CH3CH2CH2NBr2 + C6H5SO2Cl → CH3CH2CH2NHC6H5SO2 + HBr

Compound D is soluble in alkali due to the presence of the amine group.

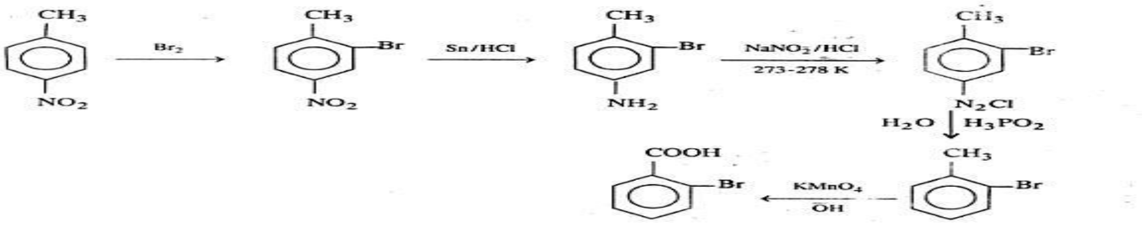
30. How will you convert

(i) Aniline into benzonitrile
(ii) Chloroethane to propane 1 amine
(iii) 4 nitrotoluene to 2 bromobenzoic acid

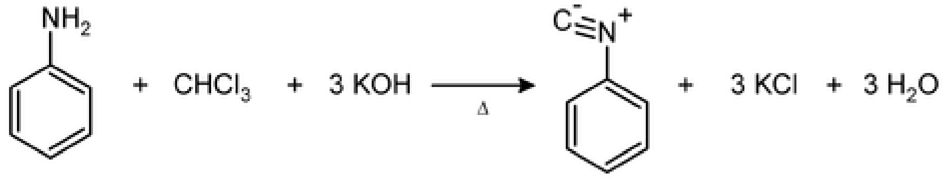
ANS.

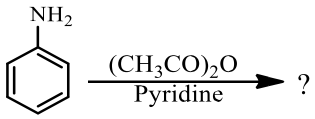
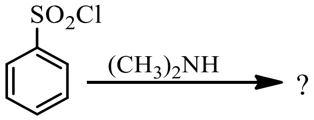
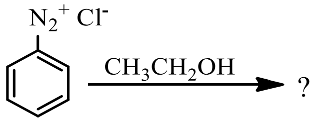


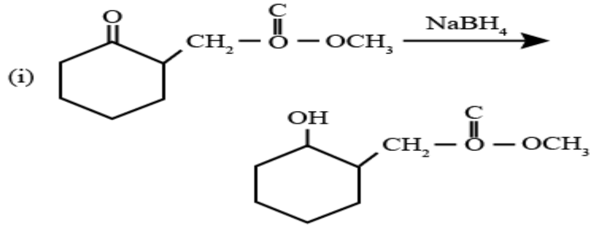
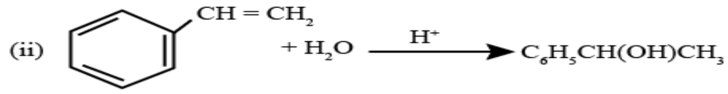
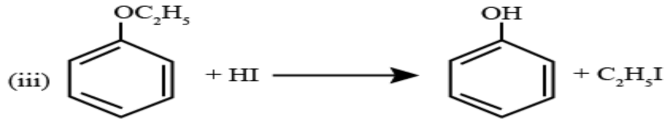
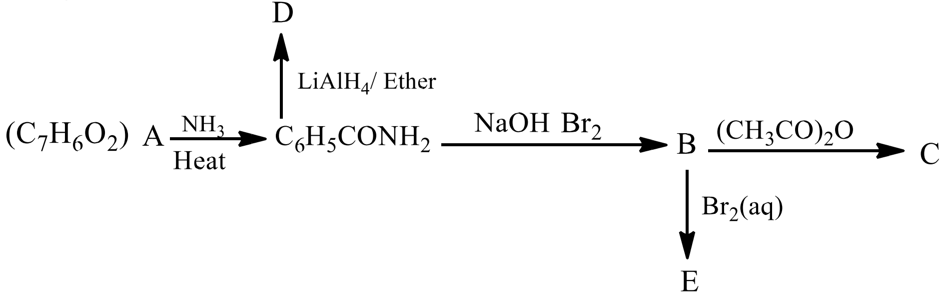
(ii)CH3CH2Cl+KCN→CH3CH2CN
CH3CH2CN+LiAlH4→CH3CH2CH2NH2

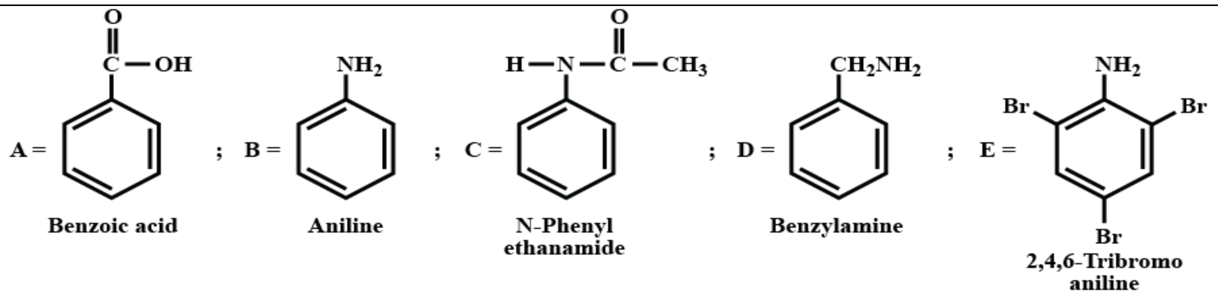
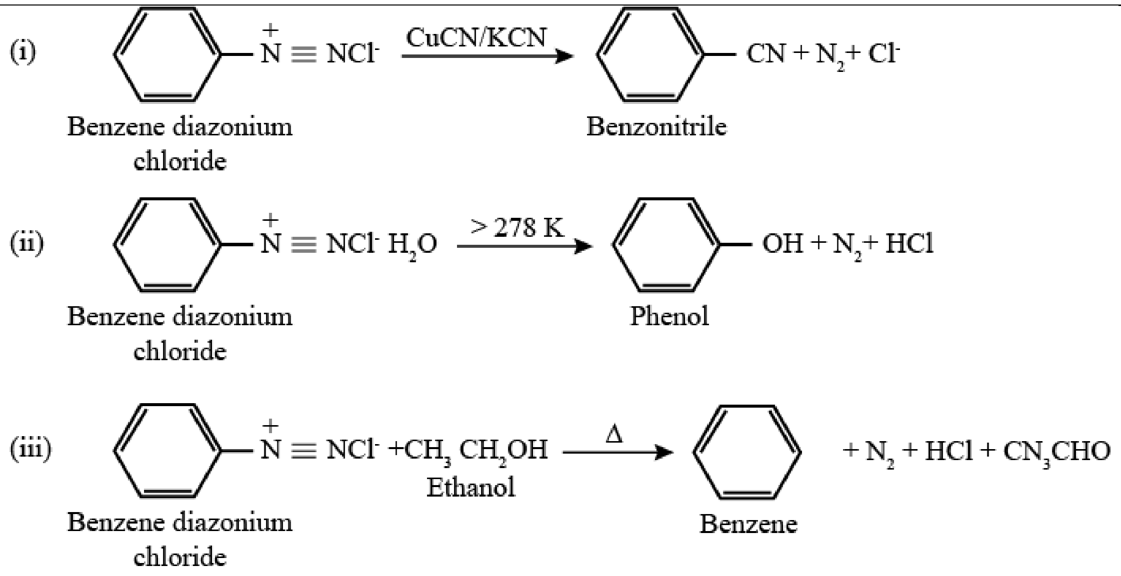


(iii)

	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	PASSAGE: When the mixture contains the three amine salts (1°, 2° and 3°) along with quaternary salt, it is distilled with KOH solution. The three amines distill, leaving the quaternary salt unchanged in the solution. Then the mixture of amines is separated by fractional distillation, Hinsbergs method and Hoffmann's method.	**[4]**
31.1	(i)What is Hinsberg reagent ?	
ANS.	**aromatic sulphonyl chloride**	
31.2	(ii) What will be the product of Primary amine with Hinsberg's reagent ?	
ANS.	**N-alkyl benzene sulphonamide soluble in KOH solution**	
31.3	Give distinguishing test between a) aniline and N,N Dimethylbenzamine. N,N Dimethylbenzamine and N-methylbenzamine .	
ANS.	A) Carbylamine B) Hinsberg reagent	
	OR	
31.3	Give carbylamine test for aniline.	
ANS.		
32	PASSAGE: Read the passage given below and answer the following questions: A mixture of two aromatic compounds (A) and (B) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound (A), when heated with alcoholic solution of KOH produce $C7H5N$ (C) associated with unpleasant odour. Answer the following questions.	**[4]**
32.1	(i) What is compound 'A'?	
ANS.	.(i) Aniline	
32.2	(i) Name the reaction of (A) with alcoholic solution of KOH to produce	

	compound (C) of unpleasant odour ?	
ANS.	Carbylamine reaction or Isocyanide Test	
32.3	(i) The alkaline aqueous layer (B) when heated with chloroform and then acidified give a mixture of isomeric compounds of molecular formula $C_7H_6O_2$. (B) is (a) C_6H_5CHO (b) C_6H_5COOH (c) $C_6H_5CH_3$ (d) C_6H_5OH	
ANS.	(ii) Phenol	
	OR	
32.3	(i) Why direct nitration of an aromatic compound (A) is not feasible ?	
ANS.	Nitric acid being strong oxidizing agent oxidises it to give oxidized products and gives mixture of ortho ,para and meta nitro aniline	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	i) Identify the products: a)  b)  c)  ii) Give a simple chemical test to distinguish between aniline and N, N- Dimethylaniline. iii) Arrange the following in the increasing order of their pK_b values :	**[5]**

ANS.	   Aliphatic or aromatic primary amines on heating with chloroform and alcoholic KOH give foul smelling alkyl isocyanides or carbylamines. Secondary or tertiary amines do not give this test. C6H5−NH2+CHCl3+3KOHΔ−→C6H5−NC+3KCl+3H2O N, N-dimethylaniline is a tertiary amine and do not give this test.. The increasing order for pKb values is C2H5NH2(3.29)<C6H5NHCH3(9.30)<C6H5NH2(9.38). The numbers in bracket indicates pKb. Higher is the pKb value, lower is the basic strength of amine Thus, the increasing order for pKb values indicates decreasing order of the basic strength of amine. Aniline is least basic and ethanamine is most basic. Aniline is least basic as unshared pair of electrons on N atom is involved in resonance with benzene ring and cannot be easily donated. When an alkyl group such as methyl or ethyl is present, the electron releasing inductive effect (+I effect) of alkyl group increases the electron density on N atom and unshared pair of electrons on N atom can be easily donated	
34	An aromatic compound ‘A’ of molecular formula $C_7H_6O_2$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions. 	**[5]**

ANS.		
35	(i) Write the structures of main products when benzene diazonium chloride reacts with the following reagents: a) $H_3PO_2 + H_2O$ b) CuCN/KCN c) H_2O (ii) Arrange the following in the increasing order of their basic character in an aqueous solution: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ (iii) Give a simple chemical test to distinguish between the following pair of compounds: $C_6H_5–NH_2$ and $C_6H_5–NH–CH_3$	**[5]**
ANS.	(a)  (b) (ii) $(CH3)3N<C2H5NH2<C2H5OH$ (c) Aniline on diazotization (ice cold nitrous acid solution) followed by coupling with 2-naphtol (in alkaline solution) forms brilliant orange or red dye. Benzylamine will not give such test	

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तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन
Kendriya Vidyalaya Sangathan

KENDRIYA VIDYALAYA SANGATHAN, JABALPUR REGION

CLASS- XII

CHEMISTRY (043)

CHAPTER NAME: BIOMOLECULES

PREPARED BY: MEMBERS OF GROUP X

IMPORTANT POINTS/ NOTES ON TIP:

- (IN FORM OF SHORT NOTES KINDLY INCLUDE GRAPHS, FORMULAS, FLOW CHARTS, DIAGRAM ALSO AS PER REQUIREMENTS OF CHAPTER)
- .Monosaccharides-Cannot be hydrolyzed further .eg- glucose, fructose, ribose
- .Disaccharides- Sucrose (α-D- glucose + β-D-fructose) , Maltose(α-D- glucose + α-D- glucose) Lactose(β-D-galactose + β-D-glucose)
- .Polysaccharides- Starch (two components—Amylose and Amylopectin) polymer of α-D- glucose
- .Amylose Water soluble , 15-20% of starch., unbranched chain , C1– C4 glycosidic linkage
- Amylopectin Water insoluble , 80-85% of starch., branched chain polymer, C1–C4 & C1–C6 glycosidic linkage

- Cellulose Straight chain polysaccharide of β -D-glucose units/ joined by C1-C4glycosidic linkage (β-link), not digestible by human / constituent of cell wall of plant cells
- Glycogen Highly branched polymer of α-D- glucose .found in liver, muscles and brain.
- reducing sugars Aldehydic/ ketonic groups free so reduce Fehling's/ Tollens solution and. Egmaltose and lactose Non reducing sugars Aldehydic/ ketonic groups are bonded so can not reduce Fehling's solution and Tollens' reagent. Eg- Sucrose
- .Anomers. The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called anomeric carbon Such isomers, i.e., α –form and β -form, are called anomers.
- .Invert sugar Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is named as invert sugar
- .Glycosidic linkage-Linkage between two mono saccharide
- Importance of Carbohydrates-Major portion of our food. / used as storage molecules as starch in plants and glycogen in animals/. Cell wall of bacteria and plants is made up of cellulose./wood and cloth are cellulose / provide raw materials for many important industries like textiles, paper, lacquers and breweries
- essential amino acids which cannot be synthesised in the body and must be obtained through diet, egValine, Leucine Nonessential amino acids which can be synthesised in the body, eg - Glycine, Alanine
- zwitter ion- In aqueous solution, amino acids exist as a dipolar ion known as zwitter ion
- peptide linkage- peptide linkage is an amide formed between –COOH group and –NH2 group of two successive amino acids in peptide chain.
- Tertiary structure of proteins: further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular.
- Denaturation of Proteins- When a protein is subjected to physical change like

change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. (During denaturation 2° and 3° structures are destroyed but 1º structure remains intact.) eg- The coagulation of egg white on boiling, curdling of milk

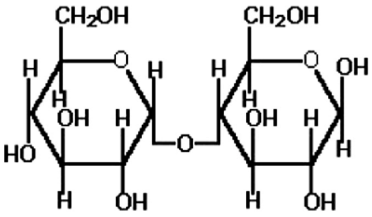
- Enzymes Enzymes are essential biological catalysts which are required to catalyse biological reactions, e.g., maltose, lactose, invertase, etc. Almost all the enzymes are globular proteins.
- Fat soluble vitamins -These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues Water soluble vit B, C. these vitamins must be supplied regularly in diet because they are readily excreted in urine
- Vitamins –(sources/ Deficiency diseases) Vit- A (Fish liver oil, carrots)- Night blindness / Vitamin B1 (Yeast, milk,)- Beri beri Vit-B2 (Milk, eggwhite)- Cheilosis / Vit- B6 (Yeast, milk,)- Convulsions / Vit- B12 (Meat, fish,)- anaemia Vit C(Citrus fruits)- Scurvy, / Vit D(Exposure to sunlight, fish and egg yolk)- Rickets, osteomalacia Vit E(wheat oil, sunflower oil)- fragility of RBCs / Vit K(leafy vegetables)- Increased blood clotting time
- DNA pentose sugar (D-2-deoxyribose) + phosphoric acid + nitrogenious bases (A , G , C, T) RNA pentose sugar (ribose) + phosphoric acid + nitrogenious bases (A , G , C, U)
- Nucleoside / tides- i) Nucleoside → sugar + base ii) Nucleotides → sugar + base + phosphate
- Phosphodiester **link Linkage between two nucleotides in polynucleotides**
- **Functions of Nucleic Acids DNA reserve genetic information, maintain the identity of different species e is capable of self duplication during cell division, synthesizes protein in the cell.**

QUESTION BANK

SECTION-A

The following questions are multiple -choice questions with one correct answer. Each question carries 1 mark.

1	Amino acids are a) Acidic b) basic c) amphoteric d) neutral	**[1]**
2	Proteins are found to have two different types of secondary structures viz. α-helix and β-pleated sheet structure. α-helix structure of protein is stabilisedby : (a) Peptide bonds (b) van der Waals forces (c) Hydrogen bonds (d) Dipole-dipole interactions	**[1]**
3	Which of the following acids is a vitamin? (a) Aspartic acid (b) Ascorbic acid (c) Adipic acid (d) Saccharic acid	**[1]**
4	Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present? (a) 5′ and 3′ (b) 1′ and 5′ (c) 5′ and 5′ (d) 3′ and 3′	**[1]**
5	Which of the following reactions of glucose can be explained only by its cyclic structure? (a) Glucose forms pentaacetate. (b) Glucose reacts with hydroxylamine to form an oxime. (c) Pentaacetate of glucose does not react with hydroxylamine. (d) Glucose is oxidized by nitric acid to gluconic acid.	**[1]**
6	Lysin is a __________________ a) α-Amino acid (b) Basic amino acid (c) Amino acid synthesised in body (d) β-Amino acid	**[1]**
7	The change in optical rotation of freshly prepared solution of glucose is known as (a) racemisation (b) specific rotation (c) mutarotation (d) tautomerism	**[1]**
8	The α- and β-glucose are (a) isomers of D(+) glucose and L(–) glucose respectively. (b) diastereomers of glucose (c) anomers of glucose (d) isomers which differ in the configuration of C-2.	**[1]**

9	Which of the following is correct about H-bonding in DNA? (a) A – T, G – C (b) A – G, T – G(c) G – T, A – C (d) A – A, T – T	**[1]**
10	ADP and ATP differ in number of (a) phosphate units (b) ribose units (c) adenine units (d) nitrogen atoms	**[1]**
	In the following questions (Q. No. 11 - 20) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (h) 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 the correct statement but reason is wrong statement. (d) Assertion is wrong statement but reason is correct statement.	
11	Assertion: Glycine must be taken through diet. Reason: It is a non-essential amino acid.	**[1]**
12	. Assertion : β-glycosidic linkage is present in maltose.  Reason : Maltose is composed of two glucose units in which C–1 of one glucose unit is linked to C–4 of another glucose unit.	**[1]**
13	Assertion: Vitamin D can be stored in our body Reason: Vitamin D is fat soluble vitamin.	**[1]**
14	Assertion : Tertiary amines are more basic than corresponding secondary and primary amines in gaseous state. Reason (R): Tertiary amines have three alkyl groups which cause +I effect.	**[1]**

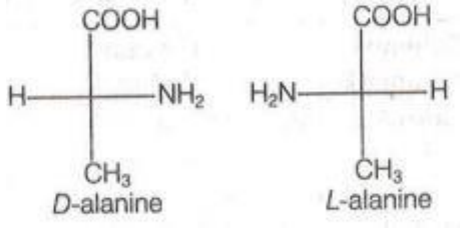
15	Assertion : Proteins are found to have two different types of secondary structures viz alpha-helix and beta pleated sheet structure. Reason (R): The secondary structure of proteins is stabilized by hydrogen bonding.	**[1]**
16	Assertion : Maltose and lactose are examples of reducing sugars. Reason : Maltose and lactose reduce Fehling’s solution and Tollens’ reagent.	**[1]**
17	Assertion : Glucose reacts with phenyl hydrazine and Fehling's solution but not with NaHSO3. Reason: NaHSO3 cannot break the ring structure.	**[1]**
18	Assertion (A) In presence of enzyme, substrate molecule can be attacked by the reagent effectively. Reason (R) Active sites of enzymes hold the substrate molecule in a suitable position.	**[1]**
19	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.	**[1]**
20	Assertion : Polysaccharides are called non-sugars. Reason : Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides.	**[1]**

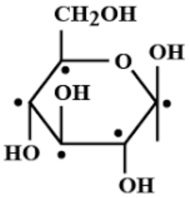
ANSWER KEY:

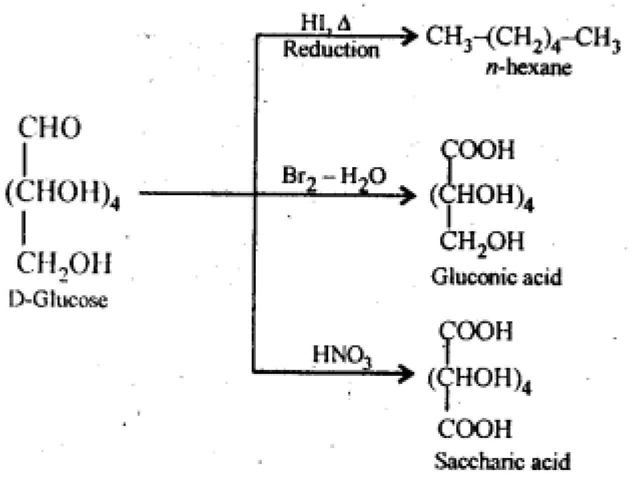
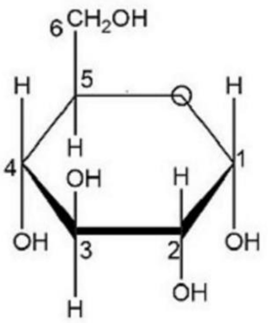
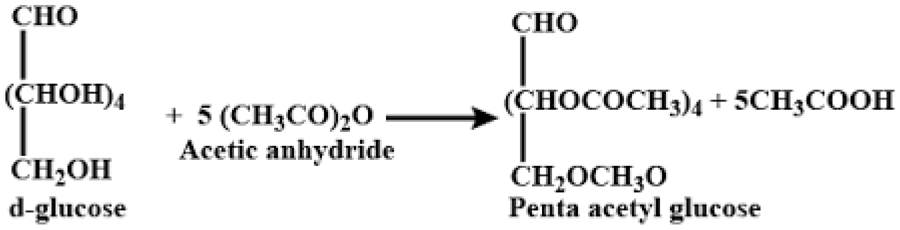
1	**C**	**2**	**C**	**3**	**A**	**4**	**A**	**5**	**C**
6	**A**	**7**	**C**	**8**	**C**	**9**	**A**	**10**	**A**
11	**D**	**12**	**D**	**13**	**A**	**14**	**A**	**15**	**B**
16	**A**	**17**	**A**	**18**	**A**	**19**	**C**	**20**	**B**

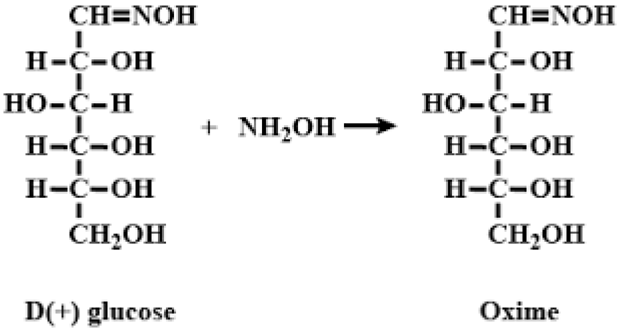
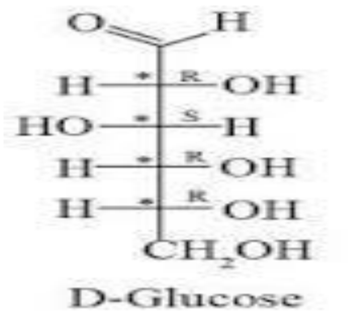
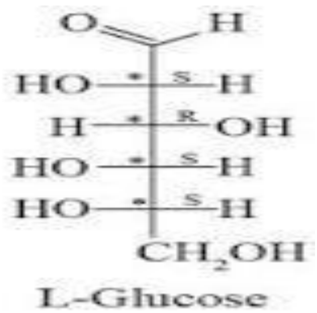
SECTION B

The following questions are very short answer type and carry 2 marks each.

21	Name the sugar present in milk. How many monosaccharide units are present in it? What are such oligosaccharides called?	**[2]**
ANS.	Sugar present in milk (i.e., milk sugar) is called lactose. Two monosaccharide units (i.e., glucose and galactose) are present in it. Such oligosaccharides are called disaccharides.	
22	Sucrose is dextrorotatory but the mixture obtained after hydrolysis is laevorotatory. Explain.	**[2]**
ANS.	Sucrose is dextrorotatory but on hydrolysis igt gives dextrorotatary glucose and laevo rotatory fructose. Since the laevorotation of fructose (−92.4°) is more than dextrorotation of glucose (+52.5°), the mixture is laevorotatory.	
23	How do enzymes help a substrate to be attacked by the reagent effectively?	**[2]**
ANS.	At the surface of enzyme, active sites are present. These active sites of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively. This reduces the magnitude of activation energy. Enzymes contains cavities of characteristics shape and possessing active groups known as active centre on the surface. The molecules of the reactant (substrate) having complementary shape, fit into these cavities. On account of these active groups, an activated complex is formed which then decomposes to yield the products.	
24	Describe the term D- and L- configuration used for amino acids with examples.	**[2]**
ANS.	All naturally occurring α–amino acids (except glycine) are optically active due to the presence of chiral carbon atom. These have either D- or L-configuration. D-form means that, the amino (−NH2) group is present towards the right hand side. L-form shows the presence of (−NH2) group on the left hand side.  *D*-alanine *L*-alanine	
25	Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.	**[2]**

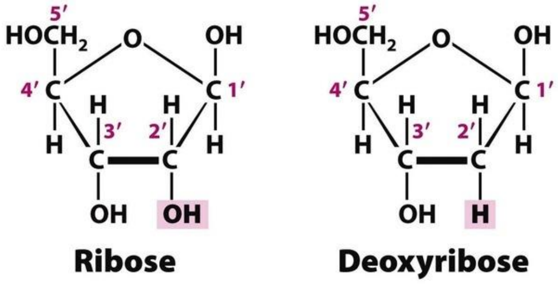
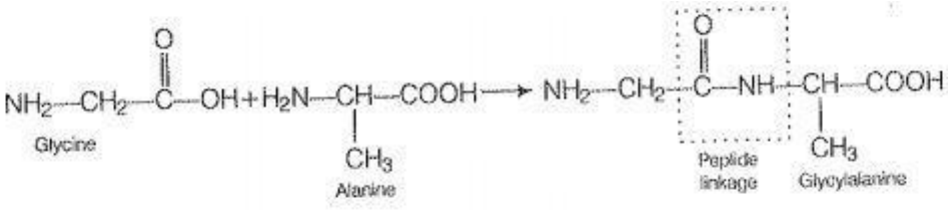
ANS.	As a result of boiling ,soluble forms of proteins such as globular proteins undergo coagulation or precipitation to give fibrous proteins which are insoluble in water. This coagulation also results in loss of biological activity of the proteins and this loss in biological activity, is called denaturation. During denaturation, 2° and 3° structures of proteins are destroyed but 1° structure remains intact.	
	SECTION C The following questions are short answer type and carry 3 marks each.	
26	(i)How many chiral carbon atoms are present in D (+) glucose? (ii) Write the name of the enantiomer of D-glucose. (iii) What is the meaning of the (+) sign in the name D (+) glucose?	**[3]**
ANS.	i) 4 chiral  ii) As the l-isomer of glucose, it is the enantiomer of the more common d-glucose. with formula $C_6H_{12}O_6$ or $O{=}CH[CH(OH)]_5H$ iii) The term D represents the configuration, whereas the sign '(+)' represents the dextrorotatory nature of the glucose molecule.	
27	(i) Which one of the following is a disaccharide: Starch, Maltose, Fructose, Glucose? (ii) What is the difference between fibrous protein and globular protein? (iii) Write the name of vitamin whose deficiency causes bone deformities in children.	**[3]**
ANS.	i) Maltose, ii) Fibrous proteins are long, strand-like proteins that are insoluble in water, weak acids, and weak bases, whereas globular proteins have a spherical shape and are soluble in water, acids, and bases. iii) Vitamin D	
28	What happens when D-glucose is treated with i) HI (ii) Bromine water (iii) HNO3 .	**[3]**

ANS.		
29	What is essentially the difference between α-glucose and β-glucose? What is meant by pyranose structure of glucose?	**[3]**
ANS.	i)The sole chemical difference between alpha and beta glucose is the orientation of the -OH (hydroxyl) and -H (hydrogen) group on carbon 1. Unlike beta glucose, which has its -OH group attached above the ring, alpha glucose has its -OH group linked below the ring. ii) The ring is made up of six members that contains 5 carbon and 1 Oxygen atom The pyranose ring of glucose is formed by reacting the hydroxyl group positioned on the fifth Carbon of glucose with the aldehyde group attached to the first position of the Carbon atom of the same glucose molecule. α-D-glucose 	
30.	Write the chemical reaction equations for the reactions of glucose with (i) acetic anhydride, (ii) NH2OH. Also draw Fischer projections of D-glucose and L-glucose.	
ANS.		

	  D-Glucose  L-Glucose	
	SECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.**	
31	PASSAGE: **Read the passage given below and answer the following questions:** When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. The denaturation causes change in secondary and tertiary structures but primary structures remains intact. Examples of denaturation of protein are coagulation of egg white on boiling, curdling of milk, formation of cheese when an acid is added to milk.	**[4]**
31.1	**Mark the wrong statement about denaturation of proteins** (a) The primary structure of the protein does not change (b) Globular proteins are converted into fibrous proteins. (c) Fibrous proteins are converted into globular proteins. (d) The biological activity of the protein is destroyed.	
ANS.	(c) Fibrous proteins are converted into globular proteins.	
31.2	**Which structure(s) of proteins remains(s) intact during denaturation process?**	

	(a) Both secondary and tertiary structures (b) Primary structure only (c) Secondary structure only (d) Tertiary structure only	
ANS.	b) Primary structure only	
31.3	**Cheese is a** (a) globular protein (b) conjugated protein (c) denatured protein (d) derived protein	
ANS.	(c) denatured protein	
	OR	
31.3	**Secondary structure of protein refers to** (a) mainly denatured proteins and structure of prosthetic groups (b) three-dimensional structure, especially the bond between amino acid residues that are distant from each other in the polypeptide chain (c) linear sequence of amino acid residues in the polypeptide chain (d) regular folding patterns of continuous portions of the polypeptide chain	
ANS.	(d) regular folding patterns of continuous portions of the polypeptide chain	
32	PASSAGE: Read the passage given below and answer the following questions:(1×4= 4) The sequence of bases in m-RNA are read in a serial order in groups of three at a time. Each triplet of nucleotides (having a specific sequence of bases) is known as codon. Each codon specifies one amino acid. Many amino acids have more than one codons. The amino acids are brought to the mRNA by another type of RNA and called t-RNA. Each amino acid has atleast one corresponding t-RNA. At one end of the t-RNA molecule is a trinucleotide base sequence that is complementary to some trinucleotide base sequence on m-RNA.	**[4]**
32.1	Which of the following nitrogen bases is not present in RNA? (A) Thymine (B) Adenine (C) Guanine (D) Cytosine	
ANS.	A) Thymine	
32.2	Each triplet of nucleotides is called: (A) Anticodon (B) Codon (C) m-RNA (D) t-RNA	
ANS.	(A) Anticodon	
32.3	The amino acids are brought to the mRNA by: (A) r-RNA (B) DNA (C) t-RNA (D) None of these.	
ANS.	(C) t-RNA	

	OR	
32.3	In mRNA, the complementary bases of AAT is: (A) CCG (B) UUA (C) AUU (D) UUU	
ANS.	(D) UUU	
	SECTION E **The following questions are long answer type and carry 5 marks each.**	
33	1. The Two strands in DNA are not identical but complementary. Explain. 2. What are enzymes? Give one example. 3. Where are the DNA printing used? 4. What product would be formed when a nucleotide from DNA containing thymine is hydrolysed? 5. Glucose or sucrose are soluble in water but cyclohexane or benzene are insoluble in water. Explain.	**[5]**
ANS.	1) Because each strand can be used to make the other strand. the strands are said to be complementary. Before a cell divides, it duplicates its DNA in a copying process called replication. 2) Enzymes are pritein that catalyse biological reactions. They are very specific in nature and catalyse only a particular reaction for a particular substrate. Eg lipase 3) DNA fingerprinting is a chemical test that shows the genetic makeup of a person or other living things. It's used as evidence in courts, to identify bodies, track down blood relatives, and to look for cures for disease. 4) When a nucleotide from the DNA containing thymine is hydrolyzed thymine β-D-2deoxyribose and phosphoric acid are obtained as products. 5) Glucose contains five and sucrose contains eight −OH group. These −OH groups form H-bonds with water. As a result of this extensive intermolecular H-bonding, glucose and sucrose are soluble in water. on the other hand, benzene and cyclohexane do not contain −OH bonds and hence do not form H-bonds with water.	
34	1. Aldopentoses named as ribose and 2-deoxyribose are found in nucleic acids. What is their relative configuration? 2. Structures of glycine and alanine are given below. Show the peptide linkage in glycylalanine. H2N−CH2−COOH (Glycince) H2N-CH-CH3COOH (Alanine) 3. How are vitamins classified? 4. Why glucose is given to patients under exhaustion?	**[5]**

	5. What is phosphodiester linkage?	
ANS.	1)  2)  3) On the basis of their solubility in water or fat, vitamins are classified into two groups. **(i) <u>Fat-soluble vitamins:</u>** Vitamins that are soluble in fat and oils, but not in water, belong to this group. For example: Vitamins A, D, E, and K **(ii) <u>Water-soluble vitamins:</u>** Vitamins that are soluble in water belong to this group. For example: B group vitamins (B_1, B_2, B_6, B_{12}, etc.) and vitamin C However, biotin or vitamin H is neither soluble in water nor in fat. 4) It provides instant energy to the body to carry out all the necessary functions efficiently. 5) The phosphate-hydroxyl linkage between two nucleotides where the phosphate attached to the hydroxyl group at the 5' carbon of pentose sugar is in turn bonded to the hydroxyl group of the 3' carbon of the pentose sugar of the next nucleotide is known as a phosphodiester bond.	
35	1. Amino acids show amphoteric behaviour .Why ? 2. The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain. 3. Mention any one important function of nucleic acid? 4. What is meant by tertiary structure of proteins?	**[5]**

	5. Write the difference between hormones and vitamins.	
ANS.	1. An amino acid has a carboxyl group (-COOH) and an amino group (-NH_2). The carboxyl can give up a proton, and the amino can accept a proton. Thus an amino acid acts as both acid and a base, i.e. amphoteric. 2. The amino acids exist as zwitterions, $H_3{}^{+}N{-}CHR{-}COO^{-}$. Due to this dipolar salt like character they have strong dipole-dipole attractions or elecrostatic. Therefore, their melting points are higher than haloacids which do not have salt like character. 3. Nucleic acids, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), carry genetic information which is read in cells to make the RNA and proteins by which living things function. The well-known structure of the DNA double helix allows this information to be copied and passed on to the next generation. 4. It refers to the unique three-dimensional conformations that globular proteins assume as a consequence of the interactions between the side chains in their primary structure. 5. Vitamins are the organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism. Hormones are proteins secreted by the ductless glands of the body.	

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