



DELHI PRIVATE SCHOOL SHARJAH

SUBJECT: CHEMISTRY

CLASS XII 2023 - 24



ACADEMIC WINDOW

A NOTE FROM THE HOD

Chemistry has been called the science of what things are. Its intent is the exploration of the nature of the materials that fabricate our physical environment, why they hold the different properties that depict them, how their atomic structure may be fathomed, how they may be manipulated and changed. Chemistry is the main incentive for the life that we live today; it has provided modern society with facilities that make our day to day lives easier.

Some students seem naturally enthusiastic about learning, but many need or expect their instructors to inspire, challenge, and stimulate them. There is no single magical formula for motivating students. Students learn by doing, making, writing, designing, creating, solving. So we should ensure opportunities by assigning tasks that are neither too easy nor too difficult.

This academic window is planned as a skill-based questionnaire that emphasis on thinking skills, experimental skills and application skills and it consist of the following units– Index, Exam wise syllabus, Chapter names and sample papers for Formative and summative assessments. Synopsis given in the beginning of each chapter includes summary of the relevant chapter. Based on the updated Question pattern by CBSE, we have included MCQ and Assertion- Reason questions , Case based questions in each chapter. To strengthen this, HOTS and Multi-disciplinary questions are also included in it.

I take immense pleasure in bringing out this academic window which can play an instrumental role in developing the skills in chemistry.

Regards,

Ms Anita Thomas
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CLASS XII (2023-24)

THEORY

Time: 3 Hours

70 Marks

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

Unit I: Solutions

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties - relative lowering of vapour pressure, Raoult's law, 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

Redox reactions, 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, 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, fuel cells, corrosion.

Unit III: Chemical Kinetics

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

Unit IV: "d" and "f" Block Elements

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

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

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

Unit V: Coordination Compounds

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

Unit VI: Haloalkanes and Haloarenes.

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

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

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

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

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

Unit VIII: Aldehydes, Ketones and Carboxylic Acids

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

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

Unit IX: Organic compounds containing Nitrogen

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

Cyanides and Isocyanides - will be mentioned at relevant places in text.

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

Unit X: Biomolecules

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

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

Vitamins - Classification and functions.

Nucleic Acids - DNA and RNA.

B. Weightage of questions.

QUESTION WISE BREAK UP

Type of Question	Mark per Question	Total No. of Questions	Total Marks
Objective	1	18	18
SA	2	7	14
LA1	3	5	15
Case based	4	2	8
LA-II	5	3	15
Total		35	70

C. Scheme of Options

1. There will be no overall option.
2. Internal choices (either/or type) in five questions has been given in questions testing higher mental abilities in the following types of questions:-
 - (i) Two in two marks questions.
 - (ii) Two in three marks questions.
 - (iii) All the three in five marks questions.

D. Question Paper Design

S.No.	Typology of Questions	Percentage
1.	Remembering	10
2.	Understanding	30
3.	Application	30
4.	Analysing	20
5.	Evaluation and Creating	10

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

PRACTICALS SYLLABUS

80 Periods

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 enthalpy change during interaction (Hydrogen bond formation) between Acetone and Chloroform.

D. Electrochemistry

Variation of cell potential in $Zn/Zn^{2+} \parallel Cu^{2+}/Cu$ 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

- i) Preparation of double salt of Ferrous Ammonium Sulphate or Potash Alum.
- ii) Preparation of Potassium Ferric Oxalate.

G. Preparation of Organic Compounds

Preparation of any one of the following compounds

- i) Acetanilide
- ii) Di -benzal Acetone
- iii) p-Nitroacetanilide
- iv) Aniline yellow or 2 - Naphthol Aniline dye.

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 food stuffs.

J. Determination of concentration/ molarity of KMnO₄ 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⁺, Co²⁺, Ni²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Mg²⁺, NH₄⁺

Anions - CO₃²⁻, S²⁻, SO₃²⁻, SO₄²⁻, NO₂⁻, Cl⁻, Br⁻, I⁻, PO₄³⁻, C₂O₄²⁻, CH₃COO⁻

(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.

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UNIT: I Solutions

- A Solution is a homogeneous mixture of two or more chemically non reacting substances whose composition can be varied within certain limits.

Units of Concentration of a Solution

(1) Percentage:

$$\text{Percentage by weight} = \frac{W_2}{W_1 + W_2} \times 100$$

$$\text{Parts per million (ppm)} = \frac{W_2}{W_1 + W_2} \times 10^6$$

(2) **Strength:** Strength of a solution is defined as the amount of solute in gms present in one litre of solution.

(3) **Molarity (M):** Molarity of a solution is defined as the no of moles of solute present in one litre of solution.

$$M = \text{no of moles of solute / volume of solution in litres}$$

$$M = \frac{n_2}{V \text{ (in litres)}} \quad n_2 = \frac{W_2}{M_2}$$

$$M = \frac{W_2 \times 1}{M_2 \times V \text{ (in litres)}} \quad \text{Or} \quad M = \frac{W_2 \times 1000}{M_2 \times V \text{ (in ml or cm}^3\text{)}}$$

$$M_1 \times V_1 = M_2 \times V_2$$

(4) **Molality (m):** Molality of a solution is defined as the no of moles of solute present in per kilogram (or 1000 gm) of solvent.

$$m = \text{no of moles of solute / weight of solvent in Kg}$$

$$m = \frac{n_2}{w_1 \text{ (in Kg)}} \quad n_2 = \frac{W_2}{M_2}$$

$$m = \frac{W_2 \times 1}{M_2 \times w_1 \text{ (in Kg)}} \quad \text{Or} \quad m = \frac{W_2 \times 1000}{M_2 \times w_1 \text{ (in gm)}}$$

(5) **Mole fraction (χ):** Mole fraction of a constituent is the fraction obtained by dividing no of moles of that constituent by the total no of moles of all the constituent present in the solution.

$$\text{Mole fraction of solute } (X_B) = \frac{n_B}{n_A + n_B} \quad ; \quad \text{Mole fraction of solvent } (X_A) = \frac{n_A}{n_A + n_B}$$

- Molality is the better method to express the concentration of a solution because it does not change with change in temperature. Molarity changes with change in temperature (Because Molarity depends up on volume of solution which changes with change in temperature).

Solubility of a gas in Liquids:

The solubility of gases increases with increase of pressure. Increase of pressure will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it.

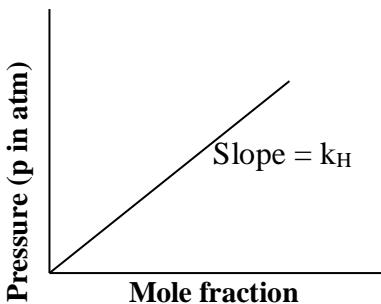
Henry's law: "The solubility of a gas in liquid at a particular temperature is directly proportional to the pressure of the gas above the solution".

$$P \propto X_2$$

$$\boxed{P = K_H X_2}$$

P = Pressure of the gas, X_2 = mole fraction of the gas in solution, K_H = Henry's Constant

- At a particular pressure on increasing temperature, value of K_H increases therefore the solubility of gas in liquid decreases.
- At a particular temperature, A gas having lesser value of k_H will have higher solubility



The solubility of a gas in liquid increases with decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

Applications of Henry's law:

- (i) To increase the solubility of CO_2 in soft drinks the bottles are sealed at high pressure.
- (ii) Deep sea drivers depend up on compressed air for their oxygen supply. Both N_2 and O_2 dissolve considerably in the blood and other fluids. Oxygen is used up for metabolism, but due to high partial pressure and greater solubility, nitrogen remains dissolved and forms bubbles when the driver comes to the atmospheric pressure. These bubbles affect nerve impulse and give rise to a disease called *bends or compression sickness*. Hence nitrogen is replaced by Helium which is much less soluble in biological fluid.
- (iii) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

Boiling point: Temperature at which vapour pressure of liquid becomes equal to atmospheric pressure is called boiling point. Liquid with lesser vapour pressure will have higher boiling point.

On addition of a non-volatile liquid in a solvent reduces its escaping tendency because some of the solute particles occupy the position of the solvent molecules on the liquid surface and thus lowers the vapour pressure of the solvent. Therefore, a solution containing non volatile solute will have lesser vapour pressure and higher boiling point than pure solvent.

Raoult's Law: (For volatile liquids)

"For a solution of volatile liquids the partial vapour pressure of each volatile component in the solution at a given temperature is directly proportional to its mole fraction."

$$P_1 = P^{\circ}_1 X_1 \quad \text{and} \quad P_2 = P^{\circ}_2 X_2$$

According to Dalton's law of partial pressures, the total pressure over the solution phase in the container is

$$P_{\text{total}} = P_1 + P_2 = P^{\circ}_1 X_1 + P^{\circ}_2 X_2$$

$$P_{\text{tot}} = P^{\circ}_1 X_1 + P^{\circ}_2 X_2$$

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the components A and B respectively in the vapour phase then, using Dalton's law of partial pressures:

$$P_1 = y_1 P_{\text{total}} \quad \& \quad P_2 = y_2 P_{\text{total}}$$

Raoult's law for non volatile solute:

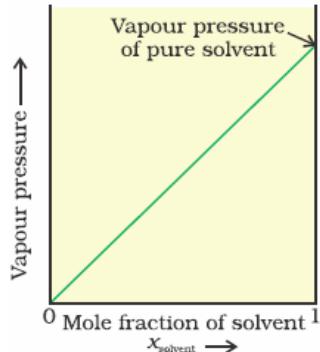
For non volatile soluté $P^o_2 = 0$

$$P_2 = P^o_2 X_2 = 0$$

$$P = P_1 + P_2 = P_1 + 0$$

$$P = P_1 = P^o_1 X_1$$

$$P = P^o_1 X_1$$



Ideal Solutions: A solution which obeys Raoult's law for the entire range of concentration for all conditions of temperature and pressure.

- The intermolecular interactions between the components are of the same magnitude as the intermolecular interaction found in the pure components.

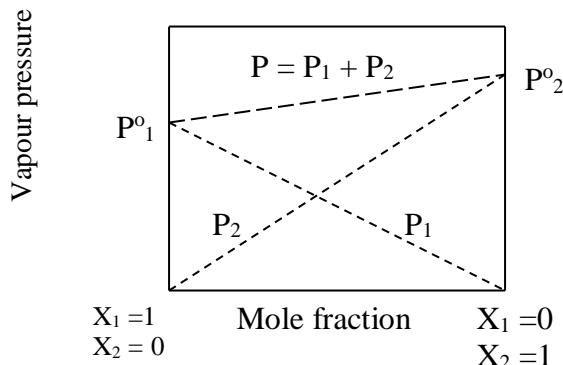
An ideal solution will satisfied the following conditions:

$$(i) \quad P_1 = P^o_1 X_1 \text{ and } P_2 = P^o_2 X_2$$

$$(ii) \Delta H_{\text{mixing}} = 0$$

$$(iii) \Delta V_{\text{mixing}} = 0$$

e.g. Benzene + toluene, n-hexane + n-heptane, ethyl bromide + ethyl iodide, Chlorobenzene + Bromobenzene etc.



Non-ideal Solutions:

A solution which will do not obey Raoult's law over the entire range of concentration for all conditions of temperature and pressure.

$$(i) \quad P_1 \neq P^o_1 X_1 \text{ and } P_2 \neq P^o_2 X_2 \quad (ii) \Delta H_{\text{mixing}} \neq 0 \quad (iii) \Delta V_{\text{mixing}} \neq 0$$

Two types of non ideal solution:

(a) Non-ideal solutions showing positive deviations:

A solution is said to show positive deviation when the individual pressure of the components and the the total pressure is greater than expected by the Raoult's law.

- When the solute-solvent interaction is less than the solute -solute and solvent solvent interaction.

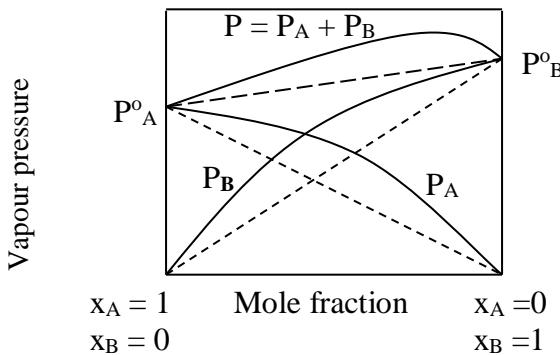
- A non-ideal solution showing positive deviations will satisfy the following conditions:

$$(i) P_1 > P^o_1 X_1 \text{ and } P_2 > P^o_2 X_2 \quad (ii) \Delta H_{\text{mixing}} > 0 \quad (iii) \Delta V_{\text{mixing}} > 0$$

e.g. Ethanol + acetone, Ethanol + cyclohexane, Ethanol + water etc

On adding cyclohexane (or acetone) its molecule gets in between the molecule of ethanol, thus breaking the hydrogen bonds and reducing ethanol-ethanol attraction considerably.

In case of positive deviation a slight increase in volume and absorption of heat takes place on mixing therefore $\Delta H_{\text{mixing}} > 0$ and $\Delta V_{\text{mixing}} > 0$



(b) Non-ideal solutions showing positive deviations:

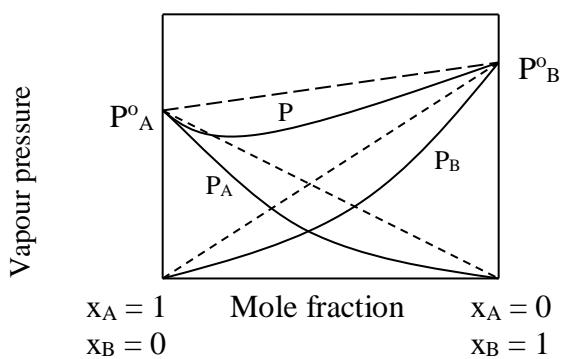
A Non-ideal solution showing positive deviations will satisfy the following conditions:

$P_1 < P^o_1 x_1$ and $P_2 < P^o_2 x_2$ (ii) $\Delta H_{\text{mixing}} < 0$ (iii) $\Delta V_{\text{mixing}} < 0$

e.g. Chloroform and Acetone.

Negative deviation from Raoult's law is exhibited by a mixture of chloroform and acetone. When these are mixed, the hydrogen bonding takes place between the two molecular species due to which the escaping tendency of either of the liquid molecules becomes less.

In case of positive deviation a slight decrease in volume and evolution of heat takes place on mixing therefore $\Delta H_{\text{mixing}} < 0$ and $\Delta V_{\text{mixing}} < 0$



Azeotropes or constant boiling solutions:

Binary mixtures having the same composition in liquid state as well as in gaseous state and boil at a constant temperature. They can be distilled without change in their composition or it is not possible to separate the components by fractional distillation.

- Solution showing positive deviation from Raoult's law form minimum boiling azeotropes. e.g. 95% ethanol and 5% water
- Solution showing negative deviation from Raoult's law form maximum boiling azeotropes. e.g. 68% Nitric acid and 32% water

Colligative properties: Properties of the solution which depend up on number of solute particles in a definite amount of solvent and do not depend up on nature of solute are called Colligative properties.

(i) Relative lowering of vapour pressure:

According to the Raoult's law for non volatile solute

$$P = P^o_1 x_1$$

$$P = P^o_1 (1 - x_2) \quad (\text{as } x_1 + x_2 = 1)$$

$$P = P^o_1 - P^o_1 x_2$$

$$P^o_1 x_2 = P^o_1 - P$$

$$\frac{P^o_1 - P}{P^o_1} = x_2$$

$P^o_1 - P$ = Lowering of vapour pressure

$(P^o_1 - P) / P^o_1$ = Relative Lowering of vapour pressure

$$\frac{P^o - P_s}{P^o} = \frac{n_2}{n_2 + n_1} \quad \text{for dilute solution: } \frac{P^o - P_s}{P^o} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

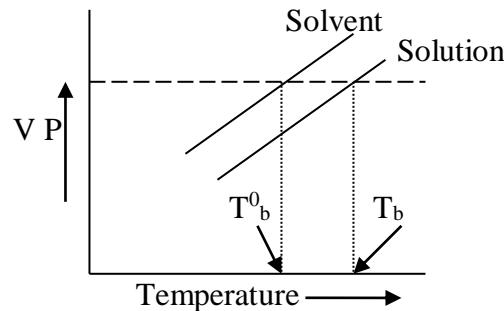
(ii) Elevation in Boiling point:

T_b = Boiling point of solution

T^o_b = Boiling point of solvent

$$\Delta T_b = T_b - T^o_b$$

ΔT_b = elevation in boiling point



$$\Delta T_b = K_b m$$

Where K_b = molal elevation constant or ebullioscopic constant

Calculation of molecular mass of the solute with the help of elevation in boiling point:

$$\Delta T_b = K_b \cdot m = K_b \frac{w_2 \times 1000g}{M_2 \times w_1}$$

(ii) Depression in Freezing point:

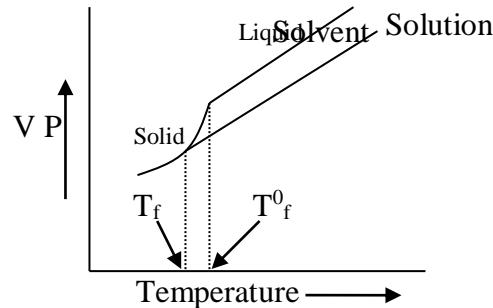
Freezing point of a substance is the temperature at which the solid and the liquid forms of the substance are in equilibrium i.e. the solid and the liquid forms of the substance have same vapour pressure.

T_f = Freezing point of solution

T^o_f = Freezing point of solvent

$$\Delta T_f = T^o_f - T_f$$

ΔT_f = elevation in boiling point



$$\Delta T_f = K_f m$$

Where K_f = molal depression constant or cryoscopic constant

$$\Delta T_f = K_f \cdot m = K_f \frac{w_2 \times 1000g}{M_2 \times w_1}$$

Osmosis

The passage of solvent from pure solvent or from a solution of lower concentration into a solution of higher concentration through a semi-permeable membrane is called **osmosis**.

Osmotic Pressure

The flow of solvent from its side to the solution side can be stopped if some definite extra pressure is applied on the solution. This pressure which just stops the flow of solvent that is to prevent osmosis is called **Osmotic pressure**

Isotonic solutions: Two solutions having same osmotic pressure with respect to each other.

Hypertonic Solution : A solution having higher osmotic pressure with respect to the other solution.

Hypotonic Solution : A solution having lower osmotic pressure with respect to the other solution.

Reverse osmosis And Water Purification

Process of osmosis can be reversed by applying a pressure larger than osmotic pressure on the solution side. Thus pure solvent flows out through SPM from the solution of higher concentration to lower concentration.

Application - Desalination of water

In the above process SPM is made of cellulose acetate which can sustain high pressure.

Osmotic pressure is a colligative property. It depends upon the no. of particles and not their chemical identity

Osmotic pressure \propto Molarity

$$\pi = CRT$$

$$\pi = \frac{n_2 RT}{V}$$

$$\pi = \frac{W_2 R T}{V M_2}$$

Abnormal Molecular Masses:

➤ When the molecular mass of the substance determined by studying any of the colligative properties comes out to be different than the theoretically expected value, the substance is said to be show abnormal molecular mass. Abnormal molecular masses are observed in any one of the following cases

- (i) When the solution is non-ideal (highly concentrated)
- (ii) When the solute undergo association in the solution
- (iii) When the solute undergo dissociation in the solution

To calculate the extent of association and dissociation, van't Hoff in 1886 introduced a factor 'i' called ***van't Hoff factor***.

Experimental value of colligative property

$$i = \frac{\text{Calculated value of colligative property when the solution behaves ideally}}{\text{Normal Molecular mass}}$$

Or

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

Or

$$i = \frac{\text{Number of molecules after dissociation or association}}{\text{Number of molecules before dissociation or association}}$$

	Dissociation $i > 1$	Association $i < 1$
1.		
2.	$\alpha = \frac{i-1}{n-1}$	$\alpha = \frac{i-1}{\frac{1}{n}-1}$
3.	$\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- , \quad n = 2$ $\text{BaCl}_2 \rightarrow \text{Ba}^{2+} + 2\text{Cl}^- \quad n = 3$ $\text{K}_3[\text{Fe}(\text{CN})_6] \rightarrow 3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-} \quad n = 4$ $\text{RCOOH} \rightarrow \text{RCOO}^- + \text{H}^+ \quad n = 2$	$2\text{RCOOH} \rightarrow (\text{RCOOH})_2 \quad n = 2$

Assignment

Question Details

S.No.

I. MCQ QUESTIONS

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

- (a) Chloroform and acetone. (b) Ethanol and acetone. (c) n-hexane and n-heptane. (d) Phenol and aniline

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

- (a) $P_{\text{solute}} = P_{\text{solute}}^0 \cdot X_{\text{solute}}$. (b) $P = K_h \cdot X$. (c) $P_{\text{total}} = P_{\text{solvent}}$. (d) $P_{\text{solute}} = P_{\text{solvent}}^0 \cdot X_{\text{solute}}$

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

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

- (c) shows no deviation from Raoult's law. (d) is saturated.

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

- (a) $< 50 \text{ mL}$. (b) $= 50 \text{ mL}$. (c) $> 50 \text{ mL}$. (d) $= 10 \text{ mL}$

5. Elevation of boiling point is inversely proportional to

- (a) molal elevation constant (K_b). (b) molality (m). (c) molar mass of solute (M). (d) weight of solute (W)

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

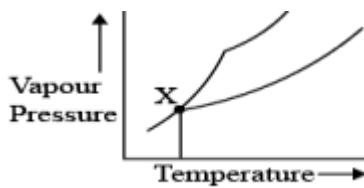
- (a) 0.08. (b) 0.04. (c) 0.02. (d) 0.92

7. The boiling point of a 0.2 m solution of a non-electrolyte in water is (K_b for water = $0.52 \text{ K kg mol}^{-1}$)

- (a) $100 \text{ }^\circ\text{C}$ (b) $100.52 \text{ }^\circ\text{C}$ (c) $100.104 \text{ }^\circ\text{C}$ (d) $100.26 \text{ }^\circ\text{C}$

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

- (a) Boiling point of solution
(b) Freezing point of solvent
(c) Boiling point of solvent
(d) Freezing point of solution



9.

An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because _____.

- (i) it gains water due to osmosis.
(ii) it loses water due to reverse osmosis.
(iii) it gains water due to reverse osmosis.
(iv) it loses water due to osmosis.

10.

On dissolving sugar in water at room temperature solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid?

- (i) Sugar crystals in cold water.
(ii) Sugar crystals in hot water.

(iii) Powdered sugar in cold water.

(iv) Powdered sugar in hot water.

II. ASSERTION & REASON QUESTIONS

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

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

1. **Assertion:** A raw mango placed in a saline solution loses water and shrivel into pickle.

Reason : Through the process of reverse osmosis, raw mango shrivels into pickle

2. **Assertion :** 0.1 M solution of KCl has greater osmotic pressure than 0.1 M solution of glucose at same temperature,

Reason : In solution, KCl dissociates to produce more number of particles.

3. **Assertion :** Elevation in boiling point is a colligative property.

Reason : Elevation in boiling point is directly proportional to molarity.

4. **Assertion :** Molarity of a solution in liquid state changes with temperature.

Reason : The volume of a solution changes with change in temperature.

5. **Assertion :** When methyl alcohol is added to water, boiling point of water increases.

Reason : When a volatile solute is added to a volatile solvent elevation in boiling point is observed.

SA & LA QUESTIONS

- | | | |
|----|-----------------------------------------------------------------------------------------------------------------------------------------------|---|
| 1. | What happens to vapour pressure of water, if a table spoon of sugar is added to it? | 1 |
| 2. | Sodium chloride is used to clear snow from the roads. Explain. | 1 |
| 3. | What is expected from Van't Hoff's factor for $K_3[Fe(CN)_6]$? | 1 |
| 4. | Arrange the following in the increasing order of boiling and freezing point:
1M glucose, 1M $PbCl_2$, 1M $Al_2(SO_4)_3$ | 1 |
| 5. | Which is more concentrated -1M or 1m solution? | 1 |
| 6. | Show that the relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute when solvent alone is volatile. | 2 |
| 7. | A mixture of chloroform and acetone shows negative deviation from Raoult's law. Explain. | 2 |

8. An aqueous solution of sodium chloride freezes below 273K. Explain the lowering in freezing point with the help of suitable diagram. 2
9. What are minimum boiling and maximum boiling azeotropes? 2
10. On dissolving 3.24 g of sulphur in 40g of benzene, boiling point of the solution was higher than that of benzene by 0.81K, K_b value for benzene is $2.53 \text{ K Kg mol}^{-1}$. What is the molecular formula of sulphur? [Ans: $M_2=256$, Formula-S₈] 2
11. a) What happens when R.B.C. are placed in 0.1% NaCl solution? 3
 b) 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein?
 $(R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ and $760 \text{ mm Hg} = 1 \text{ atm.}$) [Ans: $M_2=139.8 \text{ gmol}^{-1}$]
12. a) Which of the two molarity or molality varies with temperature? Why? 3
 b) Calculate the freezing point depression expected for 0.0711m aqueous solution of Na_2SO_4 . If this solution actually freezes at -0.320°C, what would be the value of van't Hoff factor? (K_f for water is $1.86 \text{ K}^{-1} \text{ Kg mol}^{-1}$). [Ans: $i=2.42$]
13. What is osmotic pressure? What advantage the osmotic pressure method has over elevation in boiling point method for determining molecular mass? 3
14. A substance X(molar mass 94) associates as $2X \longrightarrow X_2$ when dissolved in CCl_4 . If 10g of X is dissolved in 2Kg of CCl_4 , the freezing point is lowered by 1.08°C . Calculate the degree of association of X.
 $(K_f \text{ for } \text{CCl}_4 \text{ is } 31.8 \text{ K Kg mol}^{-1})$ [Ans: $\alpha=0.724$] 3
15. a) "The solution of non volatile solute boils at a higher temperature than pure solvent". Show this relation on a graphic diagram.
 b) The freezing point of pure nitro benzene is 278.8K. When 2.5 g of an unknown substance is dissolved in 100 g of nitrobenzene, the freezing point of the solution was found to be 276.8K. What is the molar mass of the unknown substance? (K_f for nitrobenzene is $8.0 \text{ K Kg mol}^{-1}$) [Ans: $M_2=100 \text{ g/mol}$] 3
16. a) Draw a suitable diagram to express the relationship for ideal solutions of A and B between vapour pressures and mole fraction of components at constant temperature.
 b) A solution is made by dissolving 30g of a non-volatile solute in 90g of water. It has a vapour pressure of 2.8kPa at 298K. At 298K, the vapour pressure of pure water is 3.64kPa. Calculate the molar mass of solute. [Ans: $M_2=34.125 \text{ g/mol}$]
 c) What weight of the non-volatile urea needs to be dissolved in 100g of water in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? [Ans: $M_2=83.3 \text{ gmol}^{-1}$] 5
17. a) Under what conditions Van't Hoff factor is (i) equal to 1 (ii) greater than 1 (iii) less than 1? Explain your answer.
 b) Vapour pressure of chloroform and dichloromethane at 298K are 200 mm Hg and 415mm Hg respectively. Calculate:
 (i) the vapour pressure of the solution prepared by mixing 25.5g of chloroform and 40g of dichloromethane at 298K and
 (ii) mole fractions of each component in vapour phase
 [Ans: P total=347.87mm of Hg, $y_1=0.179$, $y_2=0.82$] 5

HIGH ORDER THINKING QUESTIONS

18. a) Why a person suffering from high blood pressure is advised to take minimum quantity of common salt? 2

b) What will happen to freezing point of a potassium iodide aqueous solution when mercuric iodide is added to solution?

19. a) Calculate the molality of sulphuric acid solution in which the mole fraction of water is $0.85[m=65.2m]$ 4

b) An electrolyte AB is 50 % ionized in aq solution. Calculate the freezing point of 1m aq solution.[$T_f=-270.21K$]

20. A solution containing 68g of acetone and 46g of water has a density of 0.926g/cc. Calculate the molarity of water in the solution .[Ans=21.08M]

21 A group of students were allotted a project to determine the molar mass of Benzoic acid in a non-polar solvent (benzene) by Rast Method. But the students observed the value of the molar mass of benzoic acid was double the formula weight., this led them to confusion. 4

a) Why was the molar mass double the theoretical mass?

b) What type of property is useful in determination of molar mass of a non-volatile substance?

c) what will be the value of i as compared to 1.

d) What is the formula to get percentage association of molecules?

CASE BASED QUESTION

Read the passage carefully and answer the questions that follow.

The boiling point of a liquid is the temperature at which the vapour pressure is equal to atmospheric pressure. We know that on the addition of a non-volatile liquid to a pure solvent, the vapour pressure of a solution decrease. Therefore, to make vapour pressure equal to atmospheric pressure we have to increase the temperature of the solution. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed as elevation in boiling point. The freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour of the corresponding solid. According to Raoult's law when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at a lower temperature. The difference between the freezing point of the pure solvent and its solution is called depression in freezing point.

Q1. When a non-volatile liquid is mixed with water, what will happen to its boiling point and freezing point?

Q2. Which of the following aqueous solutions should have the highest boiling point? Solution A 1.0 M NaOH ,

Solution B 1.0 M Na₂SO₄,

Solution C 1.0 M NH₄NO₃

Solution D 1.0 M KNO₃

Q3. How does sprinkling of salt help in clearing the snow-covered roads in hilly areas? Explain the phenomenon involved in the process.

UNIT: II Electrochemistry

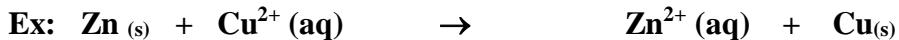
Electrochemistry: The branch of chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reaction.

- Electrolytes are the substances those allow the passage of electrical current either through their molten state or aqueous state and undergo chemical decomposition at the same time.
- Those which conduct electricity without undergoing any decomposition. They are called electronic conductors e.g. metals

Oxidation means	Reduction means
<ul style="list-style-type: none">• addition of oxygen or any electronegative element• removal of Hydrogen or any electropositive element• removal of electron• increase in oxidation number	<ul style="list-style-type: none">• addition of Hydrogen or any electropositive element• removal of oxygen or any electronegative element• addition of electron• Decrease in oxidation number.

GALVANIC CELL OR ELECTROCHEMICAL CELL

The device in which electrical energy is produced from chemical reactions is called Electrochemical or Galvanic or Voltaic Cell.



Function of Salt Bridge:-

- Salt bridge completes the electrical circuit.
- Salt bridge maintains electrical neutrality of two half cell solutions.

Electrode potential: “The electrical potential difference set up between the metal and its ions in the solutions called electrode potential

E.M.F. or Cell Potential of a Cell:-

The difference between the electrode potential of two electrodes constituting an electrochemical cell is known as Electromotive Force or Cell potential.

E.M.F. or E cell = {Reduction potential of Cathode – Reduction potential of anode}

$$= E_{(\text{cathode})} - E_{(\text{anode})} = E_{(\text{Right})} - E_{(\text{left})} = E_R - E_L$$

Electrochemical Series: “The arrangement of various elements in order of increasing value of their standard electrode potential (Reduction potential) is known as **Electrochemical Series**.

NERNST EQUATION: Nernst gave a relationship between electrode potential and the concentration of electrolyte solutions known as Nernst Equation.

For a reaction $a\text{A} + b\text{B} \longrightarrow x\text{X} + y\text{Y}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

If cell reaction is at equilibrium $E_{\text{Cell}} = 0$,
 Equilibrium constant, $K_c = [X]^x [Y]^y / [A]^a [B]^b$

$$\therefore E^{\circ}_{\text{cell}} = \frac{2.303RT}{nF} \log K_c \quad \text{or} \quad E^{\circ}_{\text{cell}} = \frac{0.059}{n} \log K_c$$

Electrochemical Cell and Free Energy:-

$$\Delta G^\circ = -n F E^{\circ}_{\text{cell}}$$

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

$$\Delta G = \text{useful work done by the system} = -nFE^{\circ}_{\text{cell}}$$

Electrical Resistance and Conductance:-

Ohm's Law:- states that the potential difference (v) across the conductor is directly proportional to the current (I) flowing through it.

$$V = I R \quad (V = \text{Potential difference in volts}, I = \text{Current in ampere}, R = \text{Resistance in Ohm's } \Omega)$$

$R = \rho (l/a)$ where l = length of the conductor, a = area of cross section of conductor and ρ (rho) is Resistivity

Conductance (G):- Conductance is reciprocal of the electrical resistance.

$$G = 1/R \quad G = \text{conductance}$$

Conductivity (k):- The reciprocal of resistivity (ρ) is called specific conductance or conductivity.

$$k = \frac{1}{\rho} \quad k \text{ (kappa) is the Conductivity } (S \text{ cm}^{-1} \text{ or } \Omega^{-1} \text{ cm}^{-1})$$

MOLAR CONDUCTIVITY: Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

$$\text{Molar conductivity} = \lambda_m = \kappa \times 1000 / C \quad (S \text{ cm}^2 \text{ mol}^{-1})$$

Variation of Conductivity and Molar Conductivity with Concentration:-

Conductivity always **decreases** with decrease in concentration (increase in dilution) both for weak and strong electrolyte because the number of ions per unit volume that carry the current decreases with decrease in concentration.

Molar conductivity **increases** with decrease in concentration (increase in dilution) both for weak and strong electrolyte this is because both number of ions as well as mobility of ions increases with dilution. When concentration approaches zero the molar conductivity is known as limiting molar conductivity or molar conductance at infinite dilution and is represented by the symbol $\lambda^{\circ}m$ (at 0 concentration) or $\lambda^{\circ}m$ (at infinite dilution).

<p>In strong electrolytes</p> $\lambda^c m = \lambda^0 m - A\sqrt{C}$ <p>Or $\lambda^c m = \lambda^0 m - A\sqrt{C}$ where c = concentration, A = constant</p> <p>If we plot a graph λm against \sqrt{C} we obtain a straight line with intercept equal to $\lambda^0 m$ and slope equal to $-A$. The value of the 'A' for a given solvent and temperature depends on the type of electrolyte, i.e., the charge on the cation and anion produced on dissociation of electrolyte in the solution. All electrolyte of a particular type, i.e., having same number of ions have the same value of A.</p>		
<p>In weak electrolytes (low ionization) the dissociated and un-dissociated molecules are remain in the equilibrium</p> $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ <p>on dilution the un-dissociated molecules undergo ionization and number of ions in total volume of solution that contain 1 mol of electrolyte increases. In such case λm increases steeply on dilution especially near lower concentrations. Therefore, $\lambda^0 m$ cannot be obtained by extrapolation of λ to zero concentration.</p> <p>\therefore the degree of dissociation</p> $(\alpha) = \lambda^c m / \lambda^0 m$ $\text{or } (\alpha) = \lambda^c m / \lambda^\infty m$		

where $\lambda^c m$ = molar conductivity at that dilution $\lambda^\infty m$ = molar conductivity at infinite dilution

At infinite dilution (at zero concentration) electrolyte dissociates completely $\alpha = 1$, but at such a low concentration the conductivity of the solution is so low that it cannot be measured accurately.

Therefore, $\lambda^0 m$ for weak electrolytes is obtained by using Kohlrausch's law of independent migration of ions.

KOHLRAUSCH'S LAW of independent migration of ions: This law states that

"At infinite dilution when the dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated."

$$\lambda^0 m = v_+ \lambda^0_+ + v_- \lambda^0_-$$

Types of Galvanic Cell:-

Primary cells are those galvanic cells where the chemical reactions cannot be reversed due to their irreversible nature called Primary Cell. Primary Cells cannot be recharged e.g. Daniel Cell, Dry Cell etc.

Secondary Cells are the cells which can be recharged and used again and again as a source of electric current. These are also called Accumulators or Storage Cells, e.g. Lead Storage Battery used in automobiles

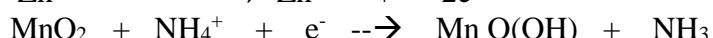
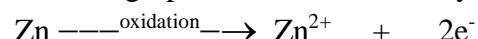
Dry Cell

Anode: zinc container

(Anode)

(Cathode)

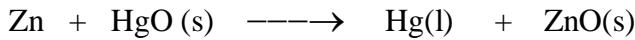
Cathode: graphite rod surrounded by MnO_2 and carbon



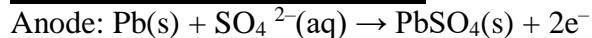
Mercury Cell

Anode : Zn-Hg amalgam

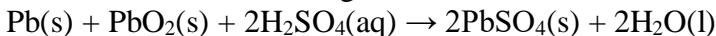
Cathode: HgO and C



LEAD STORAGE BATTERY:



i.e., overall cell reaction consisting of cathode and anode reactions is:



Fuel Cell:-

These are designed to convert the energy from the combustion of fuel such as H_2 , CO , CH_4 etc. directly into electrical energy. Ex: $\text{H}_2 - \text{O}_2$ cell
. The efficiency of this cell is maximum (70 – 75%) and it creates no pollution.

The electrode reactions are

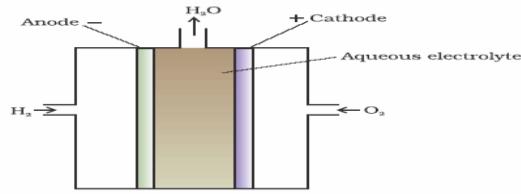
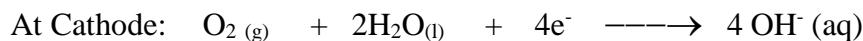
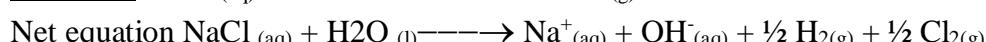
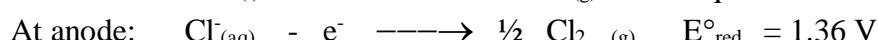
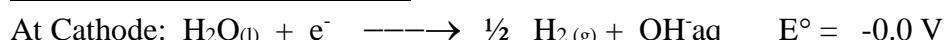


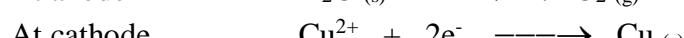
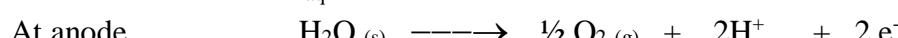
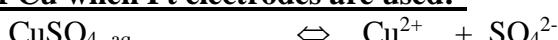
Fig. 3.12: Fuel cell using H_2 and O_2 produces electricity.

Electrolytic Cell:-

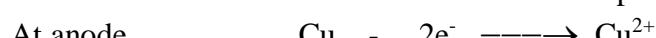
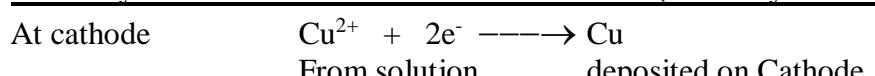
Electrolysis of aqueous NaCl:



Electrolysis of Cu when Pt electrodes are used:-



Electrolysis of Cu when Cu electrodes are used (electrolytic refining):



Faraday's Law of Electrolysis

FIRST LAW: The amount of any substance liberated at the electrode is directly proportional to the quantity of electricity passed through the electrolyte solution $W = Zit$

SECOND LAW: When the same quantity of electricity is passed through different electrolyte solutions connected in series the weight of different substances produced at the electrode are proportional to their equivalent weight.

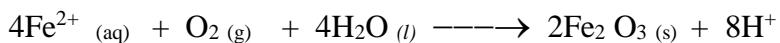
CORROSION is an electrochemical phenomenon in which metal objects decompose or disintegrate when exposed to moist air, rain water.

MECHANISM OF CORROSION

Anodic region: $\text{Fe}_{(s)} \longrightarrow \text{Fe}^{2+}_{(aq)} + 2\text{e}^-$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$

Cathodic region: $\text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}_{(l)}$ $E^\circ_{\text{cell}} = 1.23 \text{ V}$

The overall reaction is the sum of anode reactions and cathode reactions as given below.



Ferric (III) oxide formed is a brown solid which has varying amount of water and is therefore, expressed as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

Assignment

Question Details

I. MULTIPLE CHOICE QUESTIONS

1. An increase in the conductivity of a solid electrolyte with dilution is primarily due to

- a. increased ionic mobility of ions.
- b. 100 percent electrolyte ionisation with natural dilution
- c. increase in both ion numbers and ionic mobility.
- d. A rise in ion counts.

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

- (a) 1 F
- (b) 3 F
- (c) 5 F
- (d) 6 F

3. The cell reaction of the galvanic cell.

$\text{Cu(s)} / \text{Cu}^{2+} \text{ (aq)} // \text{Hg}^{2+} \text{ (aq)} / \text{Hg (l)}$ is

- (a) $\text{Hg} + \text{Cu}^{2+} \longrightarrow \text{Hg}^{2+} + \text{Cu}$
- (b) $\text{Hg} + \text{Cu}^{2+} \longrightarrow \text{Cu}^+ + \text{Hg}^+$
- (c) $\text{Cu} + \text{Hg} \longrightarrow \text{CuHg}$
- (d) $\text{Cu} + \text{Hg}^{2+} \longrightarrow \text{Cu}^{2+} + \text{Hg}$

4. If limiting molar conductivity of Ca^{2+} and Cl^- are 119.0 and 76.3 $\text{S cm}^2 \text{ mol}^{-1}$, then the value of limiting molar conductivity of CaCl_2 will be

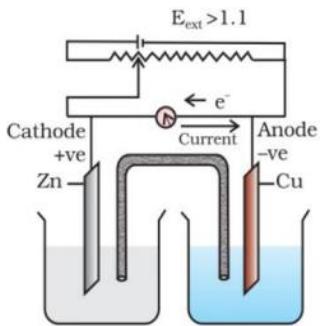
- (a) 195.3 $\text{S cm}^2 \text{ mol}^{-1}$
- (b) 271.6 $\text{S cm}^2 \text{ mol}^{-1}$
- (c) 43.3 $\text{S cm}^2 \text{ mol}^{-1}$
- (d) 314.3 $\text{S cm}^2 \text{ mol}^{-1}$.

5. Cell reaction is spontaneous, when

- (a) E°_{red} is negative
- (b) ΔG° is negative
- (c) E°_{oxid} is Positive
- (d) ΔG° is positive

6. Looking at the setup of an electrochemical cell, what happens when $\text{Ext.} > 1.1 \text{ V}$

- (a) Zn dissolves at anode & copper deposits at cathode
- (b) Current travels from Cu to Zn
- (c) Zinc deposits at anode and copper dissolves at cathode.
- (d) No current is obtained



7. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called _____.

- (i) Cell potential
- (ii) Cell emf
- (iii) Potential difference
- (iv) Cell voltage

8. Which of the following statement is not correct about an inert electrode in a cell?

- (i) It does not participate in the cell reaction.
- (ii) It provides surface either for oxidation or for reduction reaction.
- (iii) It provides surface for conduction of electrons.
- (iv) It provides surface for redox reaction.

9. Which cell will measure standard electrode potential of copper electrode?

- (i) Pt(s) | H₂ (g, 0.1 bar) | H⁺ (aq., 1 M) || Cu²⁺ (aq., 1 M) | Cu
- (ii) Pt(s) | H₂ (g, 1 bar) | H⁺ (aq., 1 M) || Cu²⁺ (aq., 2 M) | Cu
- (iii) Pt(s) | H₂ (g, 1 bar) | H⁺ (aq., 1 M) || Cu²⁺ (aq., 1 M) | Cu
- (iv) Pt(s) | H₂ (g, 1 bar) | H⁺ (aq., 0.1 M) || Cu²⁺ (aq., 1 M) | Cu

10. While charging the lead storage battery _____.

- (i) PbSO₄ anode is reduced to Pb.
- (ii) PbSO₄ cathode is reduced to Pb.
- (iii) PbSO₄ cathode is oxidised to Pb.
- (iv) PbSO₄ anode is oxidised to PbO₂

II ASSERTION & REASON QUESTIONS

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

- (i) Both assertion and reason are correct and the reason is correct explanation of assertion.
- (ii) Both assertion and reason are correct but reason does not explain assertion.
- (iii) Assertion is correct but reason is incorrect.
- (iv) Both assertion and reason are incorrect.
- (v) Assertion is incorrect but reason is correct.

1) **Assertion :** Conductivity of all electrolytes decreases on dilution.

Reason : On dilution number of ions per unit volume decreases.

2) **Assertion :** Am for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

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

3) **Assertion :** Mercury cell does not give steady potential.

Reason : In the cell reaction, ions are not involved in solution.

4) **Assertion :** Electrolysis of NaCl solution gives chlorine at anode instead of O₂.

Reason : Formation of oxygen at anode requires overvoltage.

5) **Assertion :** For measuring resistance of an ionic solution an AC source is used.

Reason : Concentration of ionic solution will change if DC source is used.

SA & LA QUESTIONS

S.No.		Marks
1.	What would happen if the protective tin coating over an iron bucket is broken at some places?	1
2.	Which solution will allow greater conductance of electricity, 1M NaCl at 293K or 1M NaCl at 323K and why?	1

- Ans: ionic mobility increase with increase with temperature so 1MNaCl at 323K carry high conductance.
- 3.** Is rusting of iron faster / slower in saline water? Give reason for your answer. **1**
- 4.** Suggest a way to determine λ_m° value of ethanoic acid. Give reason for your answer. **1**
- 5.** The standard reduction potential values of three metallic cations A, B, C are 0.52, -3.03 and -1.18 V respectively. What will be the order of reducing power of the corresponding metals?
- Ans : arrangement acc. to reduction potential : 0.52, -1.18 V and -3.03.
- Reducing power always opposite to reduction potential : A < C < B
- 6.** What is normal hydrogen electrode? Give the reaction that occurs at this electrode when it acts as a positive electrode in the cell. **2**
- 7.** Explain the meaning of the terms **2**
 (a) Ionic mobility (b) Overvoltage
- 8.** What is the difference between EMF of cell and cell potential? **2**
- 9.** List two points of difference between metallic conductance and electrolytic Conductance. **2**
- 10.** Silver is electrodeposited on a metallic vessel of total surface area 900cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited?
- Ans : Weight of Ag deposited = 2.4156g ;
 Volume of Ag deposited = 0.2307cc
 Thickness of Ag deposited = 2.88×10^{-4} cm.
- 11.** State Faraday's first and second law of electrolysis. Give their mathematical formulae. **3**
- 12.** What type of cell is Lead storage battery? Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery while operating? **3**
- 13.** Formulate the galvanic cell in which the following reaction takes place : **3**
 $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$
 State
 (a) Which one of its electrodes is negatively charged?
 (b) The reaction taking place at each of its electrode.
 (c) The direction of current within this cell.
- 14.** $E^\circ_{\text{Ni+2/Ni}}$ and $E^\circ_{\text{Cu+2/Cu}}$ are respectively – 0.25 V & + 0.34 V at 298K. Formulate the self - operating galvanic cell for this electrode pair. What reaction takes place in its operation? How is ΔG° for this reaction related to the cell? **3**
- 15.** Conductivity of two electrolytic solutions of 0.1 M concentration of the substances A and B are 9.2×10^{-3} and 4.7×10^{-4} S cm^{-1} , which one of these offer less resistance for the flow of current and which one is a stronger electrolyte?
- 16.** Give reasons for : **3**
 (a) For a weak electrolyte, its molar conductivity of dilute solution increases sharply as the concentration of solution is decreased.

(b) Molar conductivity of a strong electrolyte like KCl decrease slightly while increasing concentration?

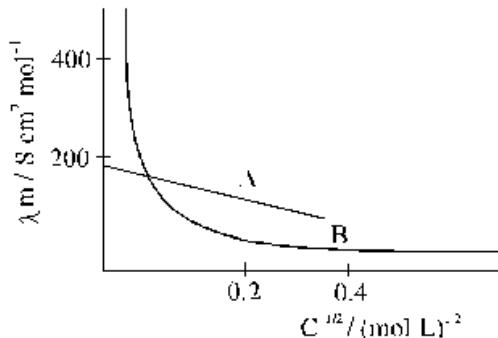
(c) It is not easy to determine λ°_m of a weak electrolyte by extrapolation of \sqrt{c} vs λ_m curves?

17. Explain kohlrausch's law of independent migration of ions. Mention its two applications. 3

18. When a steady current of 2A was passed through two electrolytic cells A and B containing electrolytes ZnSO₄ and CuSO₄ connected in series, 2g of Cu were deposited at the cathode of cell B.

(a) How long did the current flow? (b) What mass of Zn was deposited at cathode of cell A? [Atomic mass: Cu = 63.5 g mol⁻¹, Zn = 65 g mol⁻¹; 1F = 96500 C mol⁻¹]

19. i) A solution of CuSO₄ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?
ii) The following curve is obtained when molar conductivity λ (y-axis) is plotted against the square root of concentration \sqrt{C} (x - axis) for two electrolytes A and B.



(a) What can you say about the nature of the two electrolytes A and B?

(b) How do you account for the increase in molar conductivity λ_m for the electrolytes A and B on dilution?

HIGH ORDER THINKING QUESTIONS

20. What is disproportionation reaction? Calculate the equilibrium constant for the disproportionation of copper (I) ion in aqueous solution. 2

{Given $E^\circ_{Cu^{2+}, Cu} = + 0.34V$; $E^\circ_{Cu^+, Cu} = + 0.52V$ }

Ans : $\Delta G^\circ = 1.2V$; $K_c = 1.268 \times 10^{-2}$

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

- Which cell is used in hearing aids?
- Which cell was used in Apollo Space Programme?
- Which cell is used in automobiles and inverters?
- Which cell does not have long life?

CASE BASED QUESTION

Molar conductivity of a solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional area, so as to contain the electrolyte. In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by Λ_m . The molar conductivity is related to conductivity as: Unity of Λ_m (molar conductivity) shall be ohm $^{-1}$ cm $^{-1}$ mol $^{-1}$ or S cm 2 mol $^{-1}$. Thus, knowing molar concentration (C) and conductivity (k), Λ_m can be calculated. Λ_{om} is called molar conductivity at infinite dilution. The molar conductivity of strong electrolytes is found to vary with concentration according to the equation, This equation is called Debye-Huckel Onsager equation. Here, A is constant depending upon the type of electrolyte taken and nature of solvent and temperature.

In the context of given passage, answer the following questions:

- (i) The molar conductivity of HCl increases with dilution. Can you suggest what may be the reason for this?
- (ii) Here are given the different molarities of NaCl. Which of them will exhibit the highest molar conductivity? 0.005 M NaCl, 0.1 M NaCl, 0.5 M NaCl, 0.01 M NaCl.
- (iii) Molar conductivity of a solution is 1.26×10^2 cm 2 mol $^{-1}$. Its molarity is 0.01. What will be its specific conductivity?

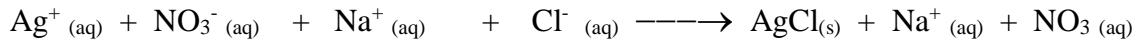
Or

- (i) The conductivity of 0.00241 M acetic acid is 7.896×10^{-5} Scm $^{-1}$. What shall be the molar conductivity of the solution in S cm $^{-1}$ mol $^{-1}$?

UNIT: III Chemical Kinetics

CHEMICAL KINETICS is the Branch of Chemistry which deals with study of rates of chemical reactions.

In a chemical reaction old bonds are broken and new bonds are formed. Ionic reaction involves only the ions and no bonds are broken therefore, they occur very fast and their rates cannot be determined, e.g.



There are certain reactions which occur at an extremely slow speed e.g. rusting of iron and their rates also cannot be determined. Some reactions proceed at moderate speed and their rates can be determined e.g.



RATES OF CHEMICAL REACTIONS:- Rate of reaction can be defined as the “increase in the concentration of product per unit time or decrease in the consent ratio of reactants per time”.

$$\therefore \text{Rate of reaction} = \frac{\text{Change in the amount of a species}}{\text{Time interval}} = \frac{\Delta[\text{Conc.}]}{\Delta t}$$



$$\text{Rate of formation of O}_2 = \frac{\Delta[\text{O}_2]}{\Delta t}$$

$$\text{Rate of decomposition of N}_2\text{O}_5 = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

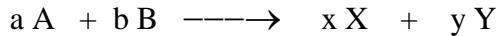
The negative sign indicates that molar concentration of N_2O_5 is decreasing with time.

$$\begin{aligned}\text{Rate of Reaction} &= \frac{\text{Decrease in concentration of reactants}}{\text{Time taken}} \\ &= \frac{\text{Increase in the concentration of Product}}{\text{Time taken}}\end{aligned}$$

\therefore For this reaction

$$\text{Rate of reaction} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Therefore, for the reaction



$$\text{Rate of reaction : } r = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{x} \frac{\Delta[\text{X}]}{\Delta t} = \frac{1}{y} \frac{\Delta[\text{Y}]}{\Delta t}$$

For gaseous substances the change in concentration may also be expressed in terms of change of partial pressure.

Average Rate or Instantaneous Rate:- The rate of reaction measured over a long time interval is called Average Rate of Reaction.

$$\text{Average Rate of Reaction} = \frac{\text{Change in Conc.}}{\text{Time taken}} = \frac{\Delta[\text{X}]}{\Delta t}$$

The rate of reaction measured for an infinitesimally small time interval is called Instantaneous rate of reaction.

Instantaneous rate of reaction = $\frac{dx}{dt}$ here d represents a very small change

Factors which influence the Rate of Reaction:- are as follows:-

i) **Effect of Concentration**

Rate of reaction is directly proportional to the product of molar concentration of reactant at a given temperature where each term raised to the power equal to number of moles of that species in a balanced chemical reaction.

For the above reaction $r \propto [A]^a [B]^b$

Increase in the concentration of reactants, increases the rate of reaction.

- ii) **Effect of Particle Size:-** (Surface Area) In a heterogeneous system, the rate of reaction will depend upon the area of contact between reactant molecules. In a solid gas and solid liquid system, the fineness of the particle determines the rate of reaction. The smaller the particles, the faster the rate of reaction.
- iii) **Effect of Temperature:-** The increase in temperature increases the rate of reaction.
- iv) **Catalyst:-** A catalyst is a chemical species that increases the rate of reaction and can be recovered unchanged at the end of the reaction.

Dependence of rate of reaction on concentration:- According to the rate law, rate of a chemical reaction is always proportional to initial concentration of reactants.

For a reaction $2\text{NO}_2 \text{ (g)} + \text{F}_2 \text{ (g)} \longrightarrow 2 \text{NO}_2 \text{ F (g)}$

Rate expression according to law of mass action

Rate (r) = $k [\text{NO}_2]^2 [\text{F}_2]$ where k = rate constant

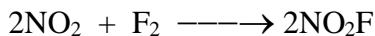
But according to rate law expression

Rate $r = k [\text{NO}_2] [\text{F}_2]$

Experimental observations show that the rate of reaction is proportional to the $[\text{NO}_2] [\text{F}_2]$ and not on the $[\text{NO}_2]^2 [\text{F}_2]$

Note:- $\text{NO}_2 + \text{F}_2 \longrightarrow \text{NO}_2\text{F} + \text{F}$ (Slow)

$\text{NO}_2 + \text{F} \longrightarrow \text{NO}_2\text{F}$ (Fast)



Therefore, rate law or rate equation may be defined as "**The mathematical expression which denotes the experimentally observed rate of a reaction in terms of the concentrations of the reacting species which influence the rate of reaction.**"

Consider a general reaction $a \text{A} + b \text{B} + c \text{C} \longrightarrow \text{Products}$

According to rate law Rate = $k [\text{A}]^p [\text{B}]^q [\text{C}]^r$

The values of p, q and r are determined experimentally and may or may not be equal to a, b and c coefficients.

Here k is the constant of proportionality and is called **rate constant** or **specific reaction rate**.

Rate constant of a reaction at a given temperature may be defined as "Rate of the reaction when the concentration of each of the reactants is unity."

If [Reactants] = 1 \therefore rate of reaction (r) = $k \times 1 = k$

Some of the characteristics of rate constant are:-

- a) Larger the value of k, faster is the reaction or vice versa
- b) Different reactions have different values of k.
- c) At a fixed temperature, the value of k is constant and is characteristic of the reaction. However, it changes with temperature.
- d) For a particular reaction, the rate constant is independent of concentration.

ORDER OF REACTION:- is defined as “The sum of the powers to which the concentration terms are raised in the rate law expression.”

For a chemical reaction $a A + b B + c C \longrightarrow \text{Products}$

Rate = $k [A]^p [B]^q [C]^r$ Where p, q and r are active concentration the reactants.

Order of reaction = $p + q + r$

If the sum is equal to 1 the reaction is **First Order** reaction

If the sum if equal to 2 the reaction is **Second order** reaction.

If the sum if equal to 3 the reaction is **Third order** reaction.

If the rate of reaction is independent on the concentration of reactants, the reaction is called **Zero Order Reaction.** Pt

e.g. $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$

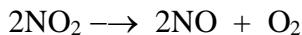
Rate = $-\frac{dx}{dt} = k [\text{NH}_3]^0$ or rate = k (Zero Order Reaction)

Some examples are:-

First Order Reaction: $r = k [\text{Reactant}]$

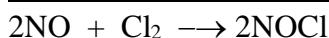


Second Order Reaction



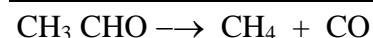
$$r = k [\text{NO}_2]^2$$

Reactions of Third Order



$$r = k [\text{NO}]^2 [\text{Cl}_2]$$

Reaction of Fractional Order



$$r = k [\text{CH}_3\text{CHO}]^{3/2} \text{ Order of reaction} = 1.5$$

Units of Rate Constant:- In general Rate = $k [\text{A}]^n$ for reaction of nth order.

$$\text{Unit of } k = (\text{mol l}^{-1})^{1-n} \text{ sec}^{-1}$$

For First Order Reaction

$$\text{Rate} = \frac{dx}{dt} = k[\text{A}]^1 ; k = \text{Sec}^{-1}$$

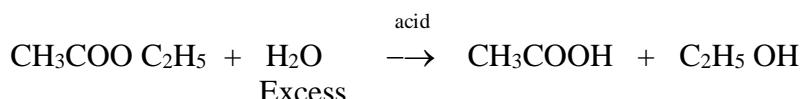
For Second Order Reaction

$$\text{Rate} = \frac{dx}{dt} = k[\text{A}]^2 ; k = \text{L mol}^{-1} \text{ Sec}^{-1}$$

For Third Order Reaction

$$\text{Rate} = \frac{dx}{dt} = k[\text{A}]^3 ; k = \text{L}^2 \text{ mol}^{-2} \text{ Sec}^{-1}$$

PSEUDO FIRST ORDER REACTION:- When one of the reactant is taken in large amount and reaction follows First Order Kinetics then it is called Pseudo Order Reaction



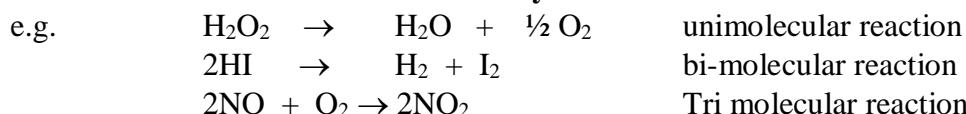
$$r = k [\text{CH}_3\text{COO C}_2\text{H}_5] [\text{H}_2\text{O}]$$

but $[\text{H}_2\text{O}]$ does not change much with time and remain constant

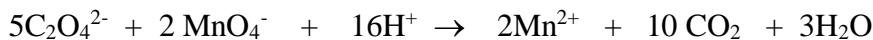
$$\text{therefore } r = k' [\text{CH}_3\text{COO C}_2\text{H}_5]$$

$$\text{Where } k' = k [\text{H}_2\text{O}]$$

Molecularity of the reaction:- The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction



It is supposed that not more than three molecule can collide together at a time. Therefore, a complex reaction (in which large numbers of reacting species are present) will be completed in number of steps e.g.



The steps which contribute to the overall reaction are called elementary processes.

(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer. (ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

Determination of Rate Law, Rate Constant and Order of Reaction:- The following experimental methods used for determination of the rate law, rate constant and order of reaction:-

(i) Initial Rate Method (ii) Integrated Rate Law

(ii) **Initial Rate Method (Ostwald's Isolation Method):-** This method can be used irrespective of the number of reactants involved. In this method a number of experiments are performed to determine the initial rate of reaction.

(iii) **Integrated Rate Law Method:-**

For Zero Order reactions:

Let us illustrate this method by applying it to a Zero Order Reaction.

$$\text{R} \longrightarrow \text{Product} \quad \text{rate} = - \frac{d[\text{R}]}{dt} = k[\text{R}]^0$$

where $[\text{R}] = \text{conc}^n$ of reactant R

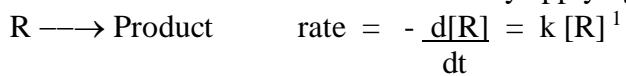
$k = \text{rate constant}$

$$t = \frac{[\text{R}_0] - [\text{R}]}{k}$$

Half Life Period of a reaction: - The time taken for half of the reaction to be completed i.e. the time in which the concentration of the reactant is reduced to half of its original value is called Half Life Period of the Reaction.

$$t_{1/2} = \frac{[\text{R}_0]}{2k} \quad \text{where } t_{1/2} \text{ is half life}$$

First Order reactions: Let us illustrate this method by applying it to a First Order Reaction.



where $[R] = \text{conc}^n$ of reactant R

$k = \text{rate constant}$

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

$$t_{1/2} = \frac{0.693}{k}$$

Let us consider a typical first order gas phase reaction $A(g) \rightarrow B(g) + C(g)$

Let p_i be the initial pressure of A and p_t the total pressure at time 't'. Integrated rate equation for such a reaction can be derived as

Total pressure $p_t = p_A + p_B + p_C$ (pressure units)

p_A , p_B and p_C are the partial pressures of A, B and C, respectively. If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

At $t = 0$	p_i atm	0 atm	+ 0 atm
At time t	$(p_i - x)$ atm	x atm	x atm

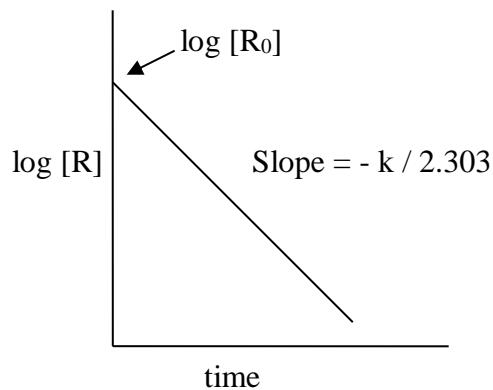
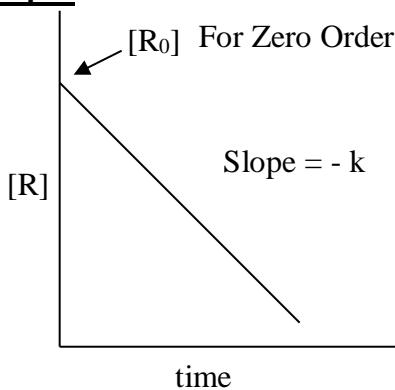
where, p_i is the initial pressure at time $t = 0$.

Total pressure $p_t = (p_i - x) + x + x = p_i + x$ and $x = (p_t - p_i)$

where, $p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$

$$\begin{aligned} k &= \left(\frac{2.303}{t} \right) \left(\log \frac{p_i}{p_A} \right) \\ &= \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)} \end{aligned}$$

Graphs



For First Order

COLLISION THEORY:-

The number of collisions that takes place per second per unit volume of the reaction mixture is known as **Collision Frequency (Z)**.

The collision, which actually produced the products and therefore, result in the chemical reactions are called **Effective Collisions (f)**.

The molecules possessing energy of activation and proper orientation undergo effective collision which results dissociation of bonds of the reactants and formation of new bonds in the products followed by rearrangement of atoms in the molecule. This process results in a chemical reaction and this theory is called **Collision Theory**.

- The minimum amount of energy which the colliding molecules must possess is known as **Threshold Energy**. This means only those collisions are effective in which atom possess energies greater than threshold energy.
- The excess energy (over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called **Activation Energy (E_a)**. E_a is equal to the difference between the threshold energy needed for the reaction and the average kinetic energy of all the reacting molecules

$$\text{Activation Energy} = \text{Threshold Energy} - \text{Average kinetic energy of reacting molecules } E_a = E_{(\text{threshold})} - E_{(\text{reactants})}$$

{Note → lower E_a → Fast reaction or high E_a → slow reaction}

Thus, the main postulates of collision theory are:-

- (i) For a reaction to occur, there must be collision between the reacting species.
- (ii) Only a certain fraction of the total number of collision is effective in forming the products.
- (iii) For effective collision, the molecules should possess sufficient energy (threshold frequency) as well as orientation.

Dependence of Reaction Rates on Temperature:-

It has been experimentally observed that the rate of chemical reaction is generally increased and become twice of its initial rate on every increased of 10°C temperature.

From the figure it is evident that the curve at higher temperature, the molecules has higher energies. Further the curve at higher temperature is flatter than that of lower Temperature which also indicates that the number of molecules with higher energy contents has increased.

The peak of the curve corresponds to the **most probable kinetic energy**, i.e., kinetic energy of maximum fraction of molecules. There is decreasing number of molecules with energies higher or lower than this value.

When the temperature is raised, the maximum of the curve moves to the higher energy value (Fig. 4.9) and the curve broadens out, i.e., spreads to the right such that there are a greater proportion of molecules with much higher energies.

Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a . It is clear from the diagram that in the curve at $(t + 10)$, the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

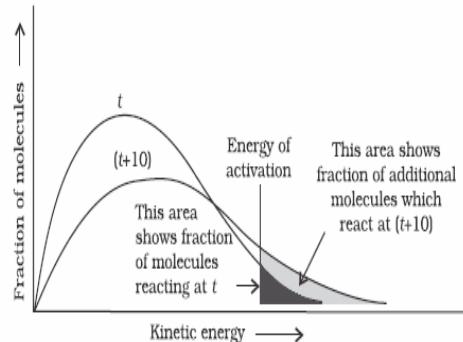


Fig. 4.9: Distribution curve showing temperature dependence of rate of a reaction

Progress of the reaction:- Consider a reaction $A + B \longrightarrow C + D$

The reactants have the average energy E_r and the products have the energy E_p . The reaction cannot occur until the molecules of reactant A colliding with the molecule of reactant B possesses sufficient energy to reach the top of the energy barrier and form activated complex is called the '**activation energy**'. The activated complex formed [A ---- B] has a very short life span and split into its product. Arrhenius equation and calculation of activation energy:-

$$k = A e^{-E_a/RT} \quad \text{where } k = \text{rate constant}$$

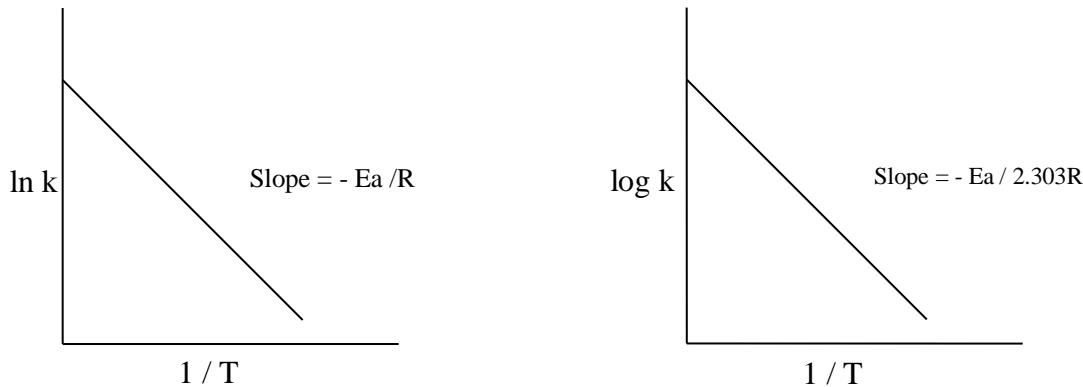
$$\begin{aligned}
 A &= \text{frequency factor} \\
 E_a &= \text{energy of activation} \\
 T &= \text{Temperature} \\
 R &= \text{Gas constant}
 \end{aligned}$$

The equation can also be written as

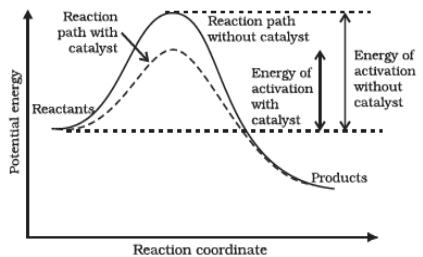
$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{or} \quad \log k = \log A - \frac{E_a}{2.303 RT}$$

If k_1 is the rate constant at Temperature T_1 and k_2 is the rate constant at Temperature T_2
The equations are

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$



Role of catalyst on activation energy:



Assignment

CHEMICAL KINETICS

MCQ QUESTIONS

1) Consider the Arrhenius equation given below and mark the correct option.

$$k = A e^{-E_a / RT}$$

- (i) Rate constant increases exponentially with increasing activation energy and decreasing temperature.
- (ii) Rate constant decreases exponentially with increasing activation energy and decreasing temperature.
- (iii) Rate constant increases exponentially with decreasing activation energy and decreasing temperature.
- (iv) Rate constant increases exponentially with decreasing activation energy and increasing temperature.

1. Which of the following statements is not correct about order of a reaction.

- (i) The order of a reaction can be a fractional number.
- (ii) Order of a reaction is experimentally determined quantity.
- (iii) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
- (iv) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

2. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be Rate = $k [A][B]^2$

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be_____.

- (i) the same
- (ii) doubled
- (iii) quadrupled
- (iv) halved

3. Which of the following statements is incorrect about the collision theory of chemical reaction? (i) It

considers reacting molecules or atoms to be hard spheres and ignores their structural features.

(ii) Number of effective collisions determines the rate of reaction.

(iii) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.

(iv) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

4. In a chemical reaction $X \rightarrow Y$, it is found that the rate of reaction doubles when the concentration of X is increased fourtimes. The order of the reaction with respect to X is

- (a) 1
- (b) 0
- (c) 2
- (d) 1/2

5.

What type of reaction is this?



- (a) Second order
- (b) Unimolecular
- (c) Pseudo-unimolecular
- (d) Third order

- 6.** Which of the following statements about the catalyst is true?
- (a) A catalyst accelerates the rate of reaction by bringing down the activation energy.
 - (b) A catalyst does not participate in reaction mechanism.
 - (c) A catalyst makes the reaction feasible by making ΔG more negative.
 - (d) A catalyst makes equilibrium constant more favourable for forward reaction.
- 7.** The half life of the first order reaction having rate constant $K = 1.7 \times 10^{-5} \text{ s}^{-1}$ is
- (a) 12.1 h
 - (b) 9.7 h
 - (c) 11.3 h
 - (d) 1.8 h
- 8.** For a chemical reaction $A \rightarrow B$, it is found that the rate of reaction doubles when the concentration of A is increased four times. The order of reaction is
- (a) Two
 - (b) One
 - (c) Half
 - (d) Zero
- 9.** In a reaction, $2X \rightarrow Y$, the concentration of X decreases from 0.50 M to 0.38 M in 10 min. What is the rate of reaction in M s^{-1} during this interval ?
- (a) 2×10^{-4}
 - (b) 4×10^{-2}
 - (c) 2×10^{-2}
 - (d) 1×10^{-2}
- 10.** The unit of rate constant for the reaction
$$2\text{H}_2 + 2\text{NO} \rightarrow 2\text{H}_2\text{O} + \text{N}_2$$
which has rate = $K[\text{H}_2][\text{NO}]^2$, is
- (a) $\text{mol L}^{-1} \text{ s}^{-1}$
 - (b) s^{-1}
 - (c) $\text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$
 - (d) mol L^{-1}

II .ASSERTION & REASONS

In the following questions a statement of assertion followed by a statement of reason is given.

1

Choose the correct answer out of the following choices.

- (i) Both assertion and reason are correct and the reason is correct explanation of assertion.
- (ii) Both assertion and reason are correct but reason does not explain assertion.
- (iii) Assertion is correct but reason is incorrect.
- (iv) Both assertion and reason are incorrect.
- (v) Assertion is incorrect but reason is correct.

- 1.** **Assertion :** Order of the reaction can be zero or fractional.

Reason : We cannot determine order from balanced chemical equation.

2. **Assertion :** The enthalpy of reaction remains constant in the presence of a catalyst.

Reason : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

3. **Assertion :** All collision of reactant molecules lead to product formation.

Reason : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

4. **Assertion :** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

Reason : Reactant molecules undergo chemical change irrespective of their orientation during collision

5.

Assertion: The order and molecularity of a reaction are always the same.

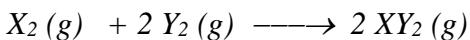
Reason: Order is determined experimentally whereas molecularity by a balanced elementary reaction.

SA & LA QUESTIONS

1. State any one condition under which a biomolecular reaction may be kinetically of the zero order

2. The rate of reaction $2 \text{NO} + \text{Cl}_2 \longrightarrow 2 \text{NOCl}$ is doubled when the concentration of Cl_2 is doubled and it becomes 8 times when concentration of both NO and Cl_2 are doubled. Deduce the order of the reaction.

3. *For the reaction:*



Write rate equation in terms of the rate of disappearance of Y_2

4. Draw the graph showing the variation in the concentration of a reactant [R] with time in a zero-order reaction

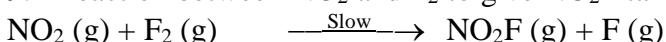
5. When could order and molecularity of a reaction be same and different?

6. Can a reaction have zero activation energy? Explain

7. Find the two-third, $t_{2/3}$ life of a first order reaction in which $k = 5.4 \times 10^{-14} \text{ s}^{-1}$.

8. The reaction between $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is highly feasible yet allowing the gases to stand at room temperature in the same vessel does not lead to the formation of water. Explain.

9. Reaction between NO_2 and F_2 to give NO_2F takes place by the following mechanism.



- a) Write the rate expression for the reaction.

- b) Give the molecularity of both the reactions.

10. For the first order thermal decomposition reaction, following data were obtained:



Time/sec	Total pressure / atm
0	0.30
300	0.50

2

Calculate the rate constant.

(Given: $\log 2 = 0.301$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

$$\text{Ans} = 3.66 \times 10^{-3} \text{ s}^{-1}$$

11. A first order reaction is 15 % complete in 20 mins. How long will it take 60 % of the reaction to be complete? 2
Ans: $k = 0.00813$, $t = 112.71 \text{ min}$
12. a) What is the shape of graph between $\log K$ vs $1/T$? 2
b) What is the relationship between its slope and activation energy E_a ? 2
13. What is the rate of reaction and the order of reaction, if the mechanism is followed by: 2
- $2\text{NO} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}_2$ (slow)
 $\text{H}_2\text{O}_2 + \text{H}_2 \longrightarrow 2\text{H}_2\text{O}$ (fast)
14. The reaction $\text{SO}_2\text{Cl}_2 \longrightarrow \text{SO}_2 + \text{Cl}_2$ is a first order reaction with $k_1 = 2.2 \times 10^{-5} \text{ s}^{-1}$ at 575 K. What percentage of initial amount of SO_2Cl_2 will get decomposed in 90 minutes when the reaction is carried out at 575 K? 3
Ans: 88.8%
15. The rate constant for the first order decomposition of N_2O_5 at 25°C is $3.00 \times 10^{-2} \text{ min}^{-1}$. If the initial concentration of N_2O_5 is $2.00 \times 10^{-3} \text{ mol L}^{-1}$, how long will it take for the concentration to drop to $5.00 \times 10^{-4} \text{ mol L}^{-1}$? 3
Ans: 46.2 min
16. The rate constants of a reaction at 700K and 760K are 0.011 s^{-1} and 0.105 s^{-1} respectively. Calculate the values of Arrhenius parameters. 3
Ans: $E_a = 166.31 \text{ kJ mol}^{-1}$, $A = 2.8 \times 10^{10} \text{ s}^{-1}$
17. The catalytic decomposition of phosphine $4\text{PH}_3(\text{g}) \longrightarrow \text{P}_4 + 6\text{H}_2(\text{g})$ has rate law as $\text{rate} = k[\text{PH}_3]$. The rate constant is $6.0 \times 10^{-4} \text{ s}^{-1}$ at 300 K and E_a is $3.05 \times 10^5 \text{ J mol}^{-1}$. What is the value of rate constant at 310 K? [$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$] 3
Ans: $6.17 \times 10^{-4} \text{ s}^{-1}$
18. The rate constant of a first order reaction becomes 4 times when the temperature is raised from 20°C to 60°C. Calculate the activation energy for the reaction. [Gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$] 3
Ans: $E_a = 52.863 \text{ kJ mol}^{-1}$
19. a) Illustrate graphically the effect of change in temperature on the rate of a reaction. 3
b) For the reaction $\text{A} \longrightarrow \text{B}$, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction? 3
Ans: order = 3
20. The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and it lowers to $50.14 \text{ kJ mol}^{-1}$ with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25°C? 3
Ans: Rate of reaction increases by 2.45×10^4 times.
21. a) Express the relation between the half-life period of a reactant and its initial concentration if the reaction involved is of first order. 3
b) A first-order reaction takes 69.3 minutes for 50% completion. Set up an equation for determining the time needed for 80% completion of this reaction. 3
Ans: 160.9 min
22. a) Catalysts do not have any effect on the equilibrium constant. Why? 3
b) The rate constant of a reaction increases by a factor of 4 if the reaction temperature is changed from 300 K to 320 K. How may we use this data to obtain activation energy of this reaction? What are its units? [$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$] 3

Ans: $55.327 \text{ kJ mol}^{-1}$

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



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

$$\text{Rate} = k [\text{PH}_3]$$

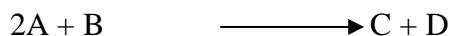
The half-life of PH_3 is 37.9 s at 120°C .

(i) How much time is required for $3/4$ th of PH_3 to decompose?

(ii) What fraction of the original sample of PH_3 remains behind after 1 minute?

Ans: 75.8s, 0.333

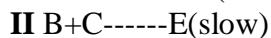
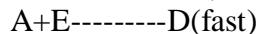
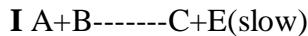
24. For a certain chemical reaction



The experimentally obtained information is tabulated below.

Experiment	$[\text{A}]_0$	$[\text{B}]_0$	Initial rate of reaction
1	0.10	0.10	0.0015
2	0.20	0.20	0.003
3	0.20	0.40	0.006

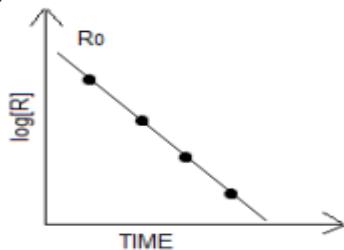
- a) Write the rate law for the reaction.
 b) Calculate the value of the rate constant for the reaction.
 c) Which of the following reaction mechanisms is consistent with the rate law found in (a)?



Ans: Rate = $k[\text{B}]$; $1.5 \times 10^{-2} \text{ min}^{-1}$; II

25. a) After 24 hrs., only 0.125 g out of the initial quantity of 1 g of a radioactive isotope remains behind. What is its half-life period?

- b) Observe the graph in diagram and answer the following questions:



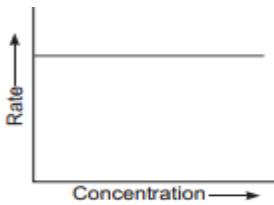
- (i) If slope is equal to -2.0×10^{-6} , what will be the value of rate constant if time is taken in seconds?
 (ii) How does the half-life of zero order reaction relate to its rate constant?

Ans: $t = 8 \text{ hours}$, $k = 4.606 \times 10^{-6} \text{ sec}^{-1}$, $t_{1/2} = [\text{R}_0]/2k$

26. a) Rate constant K for first order reaction has been found to be

$2.54 \times 10^{-3} \text{ s}^{-1}$. Calculate its three-fourth life.

- b) For a chemical reaction variation in rate with concentration is shown below:



- (i) What is the order of the reaction?
(ii) What are the units of rate constant K for the reaction?

Ans: $t_{3/4} = 5.46 \times 10^2$ s, zero order, $\text{mol L}^{-1} \text{s}^{-1}$

27. a) For a certain chemical reaction $A + 2B \longrightarrow 2C + D$

The experimentally obtained information is tabulated below:

Experiment	[A]	[B]	Initial rate of reaction
1	0.3	0.3	0.096
2	0.6	0.3	0.384
3	0.3	0.6	0.192
4	0.6	0.6	0.768

For this reaction:

- (i) Derive the order of reaction w.r.t. both the reactants A and B.
(ii) Write the rate law.
(iii) Calculate the value of rate constant k.
(iv) Write the expression for the rate of reaction in terms of A and C.
b) Illustrate graphically the effect of catalyst on the rate of a reaction.

Ans: $\text{Rate} = k[A]^2[B]$, $k = 3.55 \text{ s}^{-1}$

28. a) Give two differences between order and molecularity.

b) Define activation energy

c) Give an example of pseudo first order reaction.

d) 87.5% of the substance disintegrated in 45 minutes (first order reaction). What is its half-life?

Ans: $t_{1/2} = 15$ minutes.

29. (i) A first order reaction $A_2B_2(g) \rightarrow 2A(g) + 2B(g)$ at the temperature 400°C has the rate constant $K = 2.0 \times 10^{-4} \text{ s}^{-1}$. What % of A_2B_2 is decomposed on heating for 900 secs?

(ii) For a reaction, rate of reaction becomes three times when the conc of reactant is increased by 9 times. What is the order of reaction?

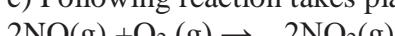
(iii) Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of an example.

Ans: 83.5%, 16.5% of initial concentration has changed into products, order $\frac{1}{2}$,

30. a) For a certain reaction large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow. Why?

b) Why in the redox titration of KMnO_4 vs oxalic acid, we heat oxalic acid solution before starting the titration?

c) Following reaction takes place in one step:



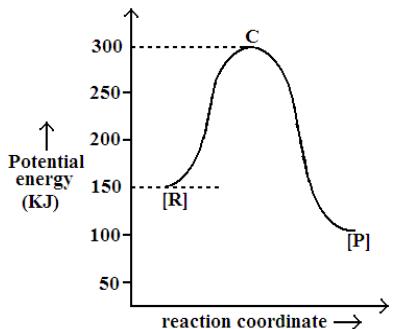
How will the rate of the above reaction change if the volume of the reaction vessel is reduced to one third of its original volume? Will there be any change in the order of the reaction with reduced volume? **Ans:** Rate = 27 times, No effect

HIGH ORDER THINKING QUESTIONS

31. a) A chemical reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction?
b) At 380°C , the half life period for the first order decomposition of H_2O_2 is 360min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C .

Ans: first order, $t=20.36\text{ min}$

32. a) Define Threshold energy and activation energy. How they are related?
b) Answer the following questions on the basis of the given plot of potential energy V/s reaction coordinate



- (i) What is the threshold energy for the reaction?
(ii) What is the activation energy for forward reaction?
(iii) What is the activation energy for backward reaction?
(iv) What is enthalpy change for the forward reaction?

Ans: 300 kJ, 150 kJ, 200 kJ, -50 kJ

CASE BASED QUESTION

The rate law for a chemical reaction relates the reaction rate with the concentrations or partial pressures of the reactants. For a general reaction $a \text{ A} + b \text{ B} \rightarrow c \text{ C}$ with no intermediate steps in its reaction mechanism, meaning that it is an elementary reaction, the rate law is given by $\text{rate} = k[\text{A}]^x [\text{B}]^y$, where $[\text{A}]$ and $[\text{B}]$ express the concentrations of A and B in moles per litre. Exponents x and y vary for each reaction and are determined experimentally. The value of k varies with conditions that affect reaction rate, such as temperature, pressure, surface area, etc. The sum of these exponents is known as overall reaction order. A zero order reaction has a constant rate that is independent of the concentration of the reactants. A first order reaction depends on the concentration of only one reactant. A reaction is said to be second order when the overall order is two. Once we have determined the order of the reaction, we can go back and plug in one set of our initial values and solve for k .

In the context of the given passage, answer the following questions :

- (i) Calculate the overall order of a reaction which has the following rate expression :
Rate = $k[A]^{1/2}[B]^{3/2}$
- (ii) What is the effect of temperature on rate of reaction?
- (iii) A first order reaction takes 77.78 minutes for 50% completion. Calculate the time required for 30% completion of this reaction $\log 10 = 1$, $\log 7 = 0.8450$.
- (iv) A first order reaction has a rate constant 1×10^{-3} per sec. How long will 5g of this reactant take to reduce to 3 g? ($\log 3 = 0.4771$; $\log 5 = 0.6990$)

UNIT IV

The d- and f-Block Elements

d-block elements

<u>Group →</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
<u>↓ Period</u>										
4	21 <u>Sc</u>	22 <u>Ti</u>	23 <u>V</u>	24 <u>Cr</u>	25 <u>Mn</u>	26 <u>Fe</u>	27 <u>Co</u>	28 <u>Ni</u>	29 <u>Cu</u>	30 <u>Zn</u>
5	39 <u>Y</u>	40 <u>Zr</u>	41 <u>Nb</u>	42 <u>Mo</u>	43 <u>Tc</u>	44 <u>Ru</u>	45 <u>Rh</u>	46 <u>Pd</u>	47 <u>Ag</u>	48 <u>Cd</u>
6	57 <u>La</u>	72 <u>Hf</u>	73 <u>Ta</u>	74 <u>W</u>	75 <u>Re</u>	76 <u>Os</u>	77 <u>Ir</u>	78 <u>Pt</u>	79 <u>Au</u>	80 <u>Hg</u>

- The elements which have partially filled d-orbitals either in ground state or one of its oxidation states are called d-block elements or transition elements.
- They are all metals and have electronic configuration $ns^{1-2} (n-1)d^1 \text{ to } 10$
- Their properties are intermediate between s-block elements and p-block elements.
- They form ionic compounds in their lower oxidation state and covalent compounds in higher oxidation states.
- The atomic size of d-block elements decreases from Sc to Zn due to increase in nuclear charge.
- Transition elements show variable state oxidation in their compounds due to very small energy difference in between **(n-1) d** and **ns** orbitals. As a result, electrons of (n-1) d orbitals as well as ns-orbitals take part in bond formation.
- Melting and boiling point of these elements are very high (except Zn). The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)d in addition to the ns electrons in the interatomic metallic bonding.
- They are very hard.
- The metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series; this is an important factor in accounting for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition metals.
- 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 by unity. This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two. 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.
- Sc shows only +3 Oxidation state because after the removal of three electrons it attains a noble gas configuration ,but Mn shows a large number of oxidation states which ranges from +2 to +7 due to 5 unpaired electrons .So both s and d electrons are utilised for the bond formation.
- E° value of copper is positive because the high energy to transform Cu(s) to Cu²⁺_(aq) is not balanced by its hydration enthalpy.

- The general trend towards less negative E° values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.
- It is interesting to note that the value of E° for Mn, Ni and Zn are more negative than expected from the trend. The stability of the half-filled d sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} and for Ni is related to the highest negative hydration enthalpy.
- Many copper (I) compounds are unstable in aqueous solution and undergo disproportionation $2Cu^+ \rightarrow Cu^{2+} + Cu$. The stability of $Cu^{2+}_{(aq)}$ rather than $Cu^+_{(aq)}$ is due to the much more negative hydration enthalpy of $Cu^{2+}_{(aq)}$ than Cu^+ , which more than compensates for the second ionisation enthalpy of Cu.
- Except zinc all the transition metals complex ions are coloured due to presence of unpaired electrons. When an electron from a lower energy d orbital is excited to a high energy d orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed..eg Zn^{2+} salts are white because it has completely filled d-orbitals ($3d^{10}$) while Cu^{2+} salts are blue because it has incompletely filled d-orbitals ($3d^9$).
- Many transition elements are paramagnetic as they are attracted towards a magnetic field. Para magnetism is due to presence of unpaired electron spins in the ions and atoms and magnetic moment is calculated by the spin only formula.
- Transition elements and some of their compounds are commonly used as catalysts in chemical process. The transition elements as catalyst may form unstable intermediate compounds in some cases, and in other cases they provide a suitable surface area where gases are absorbed and their ability to adopt multiple oxidation states and to form complexes.
- They form compounds of indefinite structures and proportions, called interstitial compounds. These compounds are non-stoichiometric. Small atoms such as H, B, C, and N can reside within the holes present in their crystal lattices.
- They form alloys with one another and with other metals. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. For example: brass (Zn-Cu), bronze (Cu-Zn-Sn).
- Transition elements form coordination compounds which are also known as "Complexes". Complex formation of transition elements is due to their small size, highly charged ions and vacant d-orbitals of suitable energy. These vacant d-orbitals accept lone pair of electrons from other atoms or ions or molecules which are called Ligands.

f-block elements

The elements in which last electron enters $(n-2)$ f-orbital are called f-block elements or inner transition elements. Their outer electronic configuration is $ns^2, (n-1)d^{0-1}, (n-2)f^{1-14}$. f-block elements constitute 2 series of elements.

(1) Lanthanoids

(2) Actinoids

LANTHANOID	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SERIES	58	59	60	61	62	63	64	65	66	67	68	69	70	71

- Elements from **Cerium (Ce : Z=58)** to **lutetium (Lu: Z=71)** in the periodic table are known as "**Lanthanoids**".
- It is a series of 14 elements and occurs in the 6th period.
- They are all silvery and fairly reactive metals.

- Most of their compounds contain M^{+3} ions. Some other lanthanides also form M^{+4} complex fluorides.
- They are also known as "**rare earth metals**".
- La, Gd and Lu exhibit only +3 oxidation state leading to empty, a half filled and a completely filled f shell respectively.
- Some elements show +2 and +4 also, when they lead to
 - (a) a noble gas configuration e.g. $Ce^{4+}(f^0)$
 - (b) a half filled f shell e.g. $Eu^{2+}(f^7), Tb^{4+}(f^7)$
 - (c) a completely filled f shell e.g. $Yb^{2+}(f^{14})$
- In lanthanoid series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanoid contraction. This is due to the poor shielding of 4f orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.
- Since the change in ionic radii in lanthanoids is very small their chemical properties are similar. This makes the separation of the elements in pure state very difficult.
- Due to lanthanoid contraction, the difference in size between second (4d) and third (5d) is very small.
- The E° value for Ce^{4+}/ Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.
- As the size of the lanthanoid ions decreases from La^{+3} to Lu^{+3} , the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic.
- The first few members of the series are quite reactive like calcium. However with increasing atomic number, their behaviour becomes similar to that of aluminum.
- A well known alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.

ACTINOID	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
SERIES	90	91	92	93	94	95	96	97	98	99	100	101	102	103

- Elements from **Thorium (Th : Z=90)** to **lawrencium (Lw : Z=103)** in the periodic table are known as "**Actinoids**".
- It is a series of 14 elements occurs in the 7th period.
- All actinoids are radioactive elements which make the study of these elements rather difficult.
- Most of them have very short half life.
- They are fairly reactive metals.
- There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies.
- Most of their compounds contain M^{+3} ions.
- The maximum oxidation state first increases upto the middle of the series and then decreases i.e. it increases from +4 for Th to +5, +6 and +7 for Pa, U and Np but decreases in the succeeding elements.
- The actinoid contraction is greater from element to element in this series resulting from poor shielding by 5f electrons.
- It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, are lower than for the early lanthanoids. The 5f electrons, will be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids.

ASSIGNMENT

Question Details

S.No.

MULTIPLE CHOICE QUESTIONS

1. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$.
Which of the following is correct?
(i) Cu(II) is more stable
(ii) Cu(II) is less stable
(iii) Cu(I) and Cu(II) are equally stable
(iv) Stability of Cu(I) and Cu(II) depends on nature of copper salts

2. Generally, transition elements form coloured salts due to the presence of unpaired electrons.
Which of the following compounds will be coloured in solid state?
(i) Ag_2SO_4 (ii) CuF_2 (iii) ZnF_2 (iv) Cu_2Cl_2

3. On addition of small amount of KMnO_4 to concentrated H_2SO_4 , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.
(i) Mn_2O_7 (ii) MnO_2 (iii) MnSO_4 (iv) Mn_2O_3

4. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.
(i) $3d^7$ (ii) $3d^5$ (iii) $3d^8$ (iv) $3d^2$

5. Which of the following oxidation state is common for transition element and lanthanoids?
(i) +2, +3 (ii) +3, +2 (iii) +4, +2 (iv) +5, +3

6. As an electroplated protective covering, what metal is used?
 - a) Plutonium
 - b) Chromium
 - c) Nickel
 - d) Iron

7. Which of the following statements concerning transuranium elements is incorrect?
 - a) Atomic number > 92
 - b) Example is Thorium
 - c) Decay radioactively as they are unstable
 - d) Elements after Uranium

8. What happens to the atomic size of lanthanides as the atomic number increases?
 - a) The radius remains unchanged
 - b) The radius first increases and then decreases
 - c) The radius increases

d) The radius decreases

9. What is the lanthanide's final element?

a) Ytterbium

b) Erbium

c) Thulium

d) Lutetium

10. Baeyer's reagent is which of the following?

a) Acidified KMnO_4

b) Aqueous KMnO_4

c) Acidified $\text{K}_2\text{Cr}_2\text{O}_7$

d) Alkaline KMnO_4

II ASSERTION & REASONS

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

(i) Both assertion and reason are true, and reason is the correct explanation of the assertion.

(ii) Both assertion and reason are true but reason is not the correct explanation of assertion.

(iii) Assertion is not true but reason is true.

(iv) Both assertion and reason are false.

1. Assertion : Cu^{2+} iodide is not known.

Reason : Cu^{2+} oxidises I^- to iodine.

2. Assertion : Separation of Zr and Hf is difficult.

Reason : Because Zr and Hf lie in the same group of the periodic table.

3. Assertion : Actinoids form relatively less stable complexes as compared to lanthanoids.

Reason : Actinoids can utilise their $5f$ orbitals along with $6d$ orbitals in bonding but lanthanoids do not use their $4f$ orbital for bonding

4. Assertion : Cu cannot liberate hydrogen from acids.

Reason : Because it has positive electrode potential

5. Assertion : The highest oxidation state of osmium is +8.

Reason : Osmium is a 5d-block element

SA & LA QUESTIONS

1. Why are +3 oxidation states of La, Ga and Lu more stable?

2. What is the structure of chromate and dichromate ion?
3. What is misch metal? Give its one use.
4. What happens when KMnO_4 is heated?
5. Predict which of the following will be coloured in aqueous solution: Si^{+3} , Mn^{+2} , Cu^+
6. Explain why:
- Transition elements have higher density than alkaline earth metals.
 - Transition elements exhibit higher enthalpies of atomization.
7. Why do transition elements show different oxidation states?
8. Explain how the colour of an aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ depends on the pH of the solution..
9. A blackish brown coloured solid A when fused with alkali metal hydroxide in presence of air, produces a dark green coloured compound B, which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound C. Identify A, B and C and write the reactions involved.
10. Give reasons:
- Ce^{3+} can be easily oxidized to Ce^{+4} .
 - Cd^{2+} salts are white
11. Account for the following:
- Mn exhibit a large number of oxidation states.
 - Co^{2+} and Ni^{2+} have low magnetic moment.
 - V^{+4} exhibit Para magnetism.
12. Give reasons:
- HCl is not used to acidify potassium permanganate solution in the volumetric estimation of oxalic acid.
 - The lowest oxide of a transition metal (Cr) is basic whereas the highest oxide is usually acidic.
 - There is an irregular variation of ionization enthalpies of transition elements.
13. Give example and suggest reasons for the following features of the transition metal chemistry.
- Cu^+ ions are unstable in aqueous solution.
 - A transition metal exhibits higher oxidation states in oxides and fluorides.
 - The highest oxidation state is exhibited in oxo-anions of a metal.
14. Account for the following:
- Sc^{3+} salts are diamagnetic.
 - First ionization energies of 5d elements are higher than those of 3d and 4d elements.
 - The highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7 .
- Account for the following:
15. a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
- b) Copper (I) is diamagnetic whereas copper (II) is paramagnetic.
- c) Zn, Cd and Hg are not considered as transition elements.
16. Account for the following:
- There is greater range of oxidation states among the actinoids than that in lanthanoids.
 - $\text{La}(\text{OH})_3$ is more basic than $\text{Lu}(\text{OH})_3$
 - $\text{Sm}(\text{II})$ in aqueous solution is a reducing agent
 - $\text{Ce}(\text{IV})$ in aqueous solution is a good oxidizing agent
 - Zr and Hf exhibit similar properties
17. a) Explain the preparation of potassium dichromate from chromite ore.

- b) H_2S is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution. The solution becomes milky. How do you explain it?
- c) Complete the following reaction : $\text{MnO}_4^- + \text{Fe}^{2+} + \text{H}^+$
- 18.** a) With the help of an equation describe what happens when potassium manganate is electrochemically oxidized.
 b) How does acidified KMnO_4 react with oxalic acid.
 c) The outer electronic configuration of a member of the lanthanoid series is
 $4f^75d^06s^2$,
 write its atomic number and predict the oxidation states exhibited by this element.

HIGH ORDER THINKING QUESTIONS

- 19.** “The chromates and dichromates are interconvertible by the change in pH of medium.” Why?
 Give chemical equations in favour of your answer.
- 20.** a) Calculate the magnetic moment (spin only) of manganese in $\text{K}_4[\text{Mn}(\text{NCS})_6]$.
 b) $\text{K}_2[\text{PtCl}_6]$ is a well-known compound, whereas the corresponding Ni compound is not known. State a reason for it.
- 21.** A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating (C) with concentrated sulphuric acid and NaCl chlorine gas is liberated and the compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.
- 22.** Why are Ni^{2+} compounds thermodynamically more stable than Pt^{2+} compounds
 Whilst Pt^{+4} compounds are relatively more stable than Ni^{+4} compounds.
- 23.** When an oxide of manganese (A) is fused with KOH in the presence of an oxidizing agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.

OR

Ram was travelling in a car with his driver. They were stopped by a policeman and the driver was asked to take the breath analyzer test for alcohol. He was asked to blow air into the device which contained a pink solution. The solution faded in colour.

- 24.** What is the pink coloured solution? Why does it fade?
25. Give the laboratory preparation of pink colour solution?
26. What happen when this pink colour solution treated with (i) Iron(ii) ion (ii) H_2S
27. What is the effect of heat on pink colour solution.

CASE BASED QUESTION

Read the passage given below and answer the following questions:

The unique behaviour of Cu, having a positive E° accounts for its inability to liberate H₂ from acids. Only oxidizing acids (nitric and hot concentrated sulphuric acid) react with Cu, the acids being reduced. The stability of the half-filled (d5) subshell in Mn²⁺ and the filled(d10) configuration in Zn²⁺ are related to their E° (M³⁺/M²⁺) values. The low value for Sc reflects the stability of Sc³⁺ which has a noble gas configuration. The comparatively high value for Mn shows that Mn²⁺(d5) is particularly stable, whereas a comparatively low value for Fe shows the extra stability of Fe³⁺(d5). The comparatively low value for V is related to the stability of V²⁺ (half-filled t_{2g} level).

i)

E° M³⁺ / M²⁺ values for the first series of transition elements are given below.

E° (V)	Ti	V	Cr	Mn	Fe	Co
M ³⁺ / M ²⁺	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97

Identify the two strongest oxidizing agents in the aqueous solution from the above data.

ii) Give reasons:

- In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest.
- Cu⁺ ion is not stable in aqueous solutions.
- Mn²⁺compounds more stable than Fe²⁺towards oxidation

UNIT V

Coordination Compounds

Coordination compounds: Complex compounds in which the metal atoms are bound to a number of anions and neutral molecules.

Postulates of Werner's theory:

In coordination compounds metals show two types of linkages.

The primary valances are normally ionisable and are satisfied by negative ions.

The secondary valances are non ionisable which are satisfied by neutral molecules and negative ions and is equal to the coordination number of the compound.

The ions /neutral molecules bound by secondary valances have different spacial arrangements corresponding to different coordination numbers.

Ambidentate Ligand:

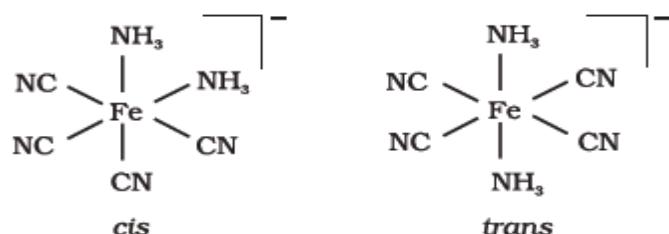
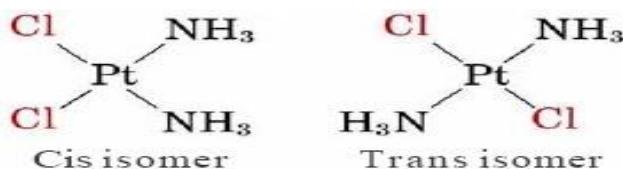
Ligand which can ligate through two different atom. [Eg: NO_2^- and SCN^-]

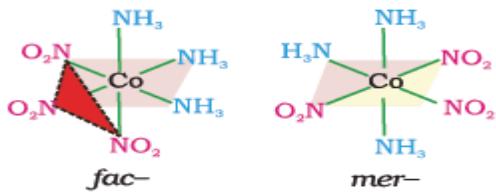
Stereoisomerism:

Stereoisomers have the same molecular formula but different spacial arrangements.

a) **Geometrical isomers**

Complexes which differ by the different possible geometric arrangement of the ligands.





b) Optical isomerism

Optical isomers are mirror images that cannot be superimposed on one another. These are called enantiomers.

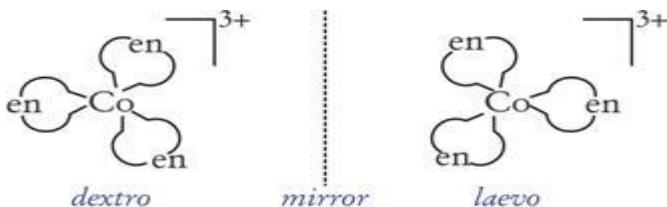


Fig. Optical isomers (*d* and *l*) of $[\text{Co}(\text{en})_3]^{3+}$

Structural isomerism

Structural isomers have the same molecular formula but different bonds.

a) Linkage isomerism

Linkage isomerism arises in compounds having ambidentate ligands
 $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ & $[\text{Co}(\text{NH}_3)_5(\text{O}-\text{N}=\text{O})]\text{Cl}_2$

b) Coordination isomerism

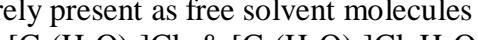
This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.
 $[\text{Co}(\text{NH}_3)_6]\text{[Cr}(\text{CN})_6]$ & $[\text{Cr}(\text{NH}_3)_6]\text{[Co}(\text{CN})_6]$

c) Ionisation isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ & $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$

d) Solvate isomerism

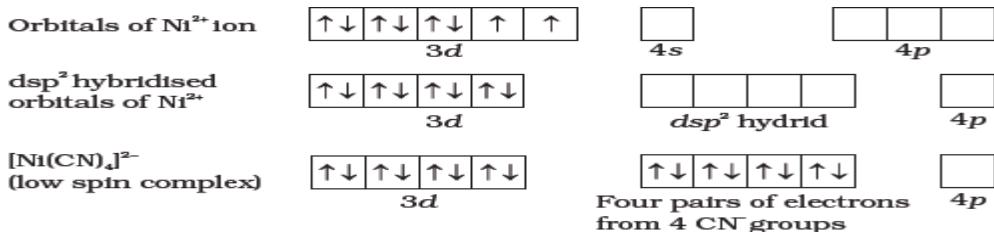
Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal.



Valence Bond Theory

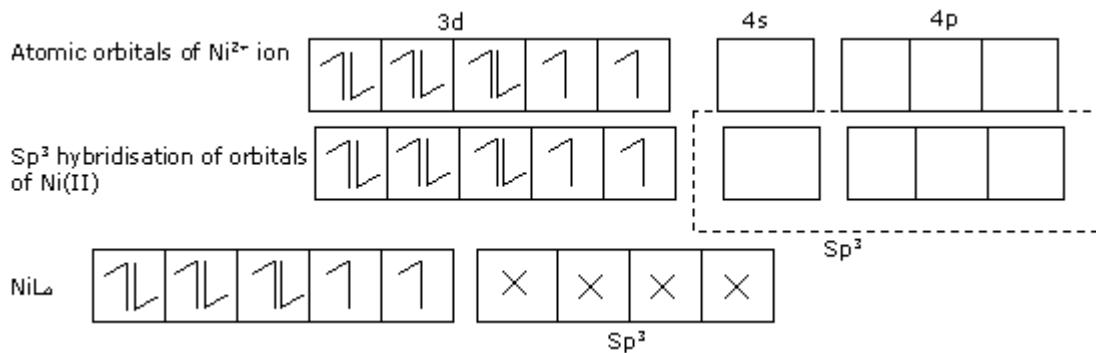
The metal atom or ion under the influence of ligands can use its $(n-1)$ d, ns, np or ns,np,nd orbitals for hybridization to yield a set of equivalent orbitals of definite geometry. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

dsp^2 hybridisation



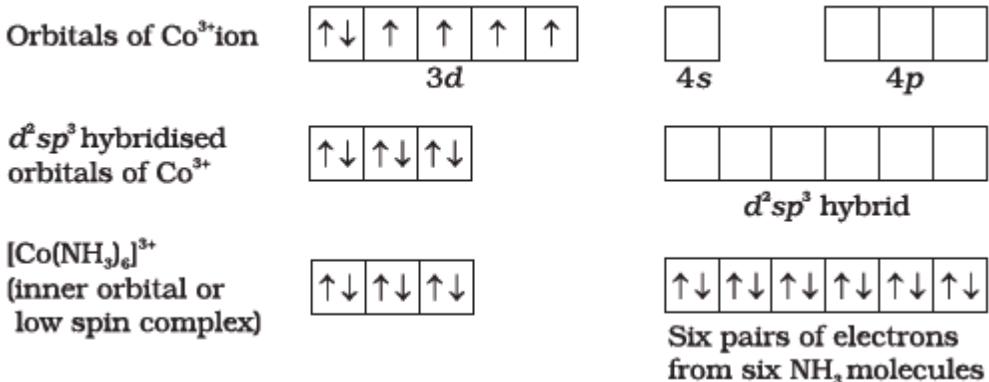
$[\text{Ni}(\text{CN})_4]^{2-}$ has square planar geometry and is diamagnetic.

sp^3 hybridisation



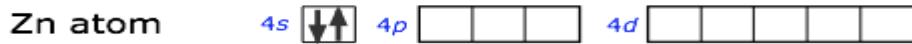
The given complex is tetrahedral and paramagnetic.

d^2sp^3 hybridisation



$[\text{Co}(\text{NH}_3)_6]^{2-}$ has octahedral geometry and is diamagnetic.

sp^3d^2

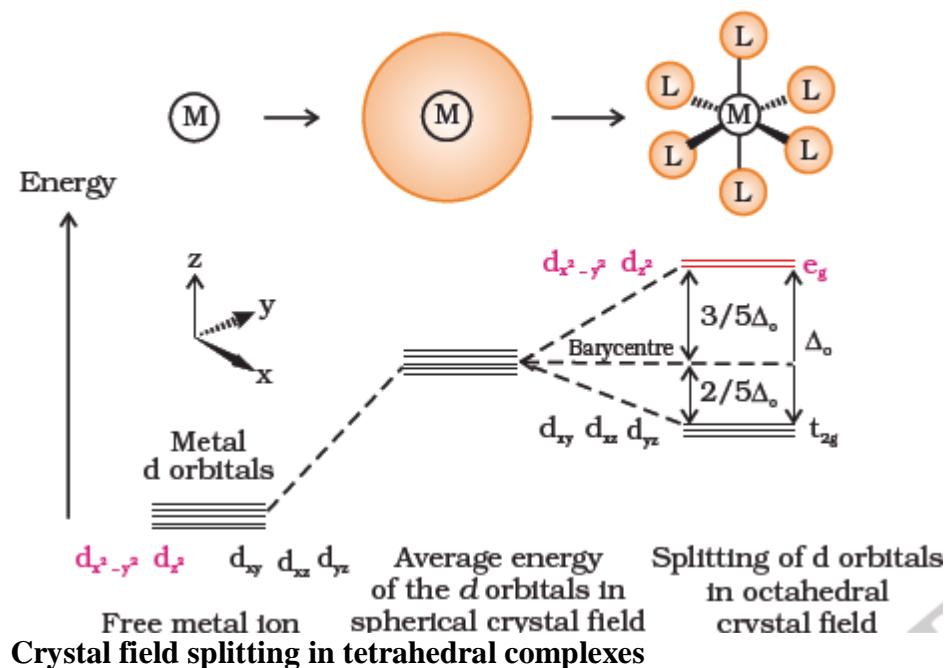


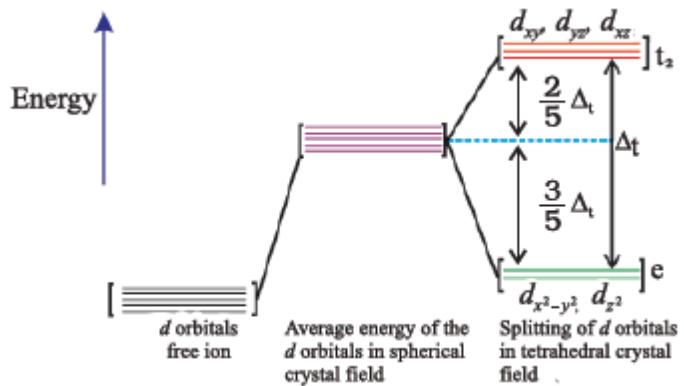
The given complex has an octahedral geometry.

Crystal Field Theory

The splitting of degenerate levels due to the presence of ligands in a definite geometry is termed and the energy separation is denoted by Δ_0 .

Crystal field splitting in octahedral complexes





Spectrochemical series

Ligands are arranged in a series in the order of increasing field strength.

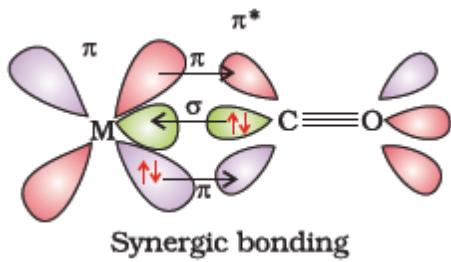
Factors determining the filling of d orbitals in complexes

- If $\Delta_0 < P$ the electrons enter one of the e_g orbitals and form high spin complexes.
- If $\Delta_0 > P$ the electrons enter one of the t_{2g} orbitals and form low spin complexes.

Bonding in metal carbonyls

The metal –carbon bond in metal carbonyls possess both s and p character.

The M-C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M- Π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into vacant antibonding Π^* orbital of CO. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



Stability of coordination compounds

The stability of coordination compounds is measured in terms of the overall stability constant. The instability constant or dissociation constant is defined as the reciprocal of formation constant.

Chelate effect

The stabilization of the coordination compound due to chelation is called the chelate effect.

Assignment

S.No.	Question Details	Marks
I. MULTIPLE CHOICE QUESTIONS		
1.	A coordination complex's core atom/ion is also known as _____ a) Bronsted-Lowry acid b) Lewis base c) Lewis acid d) Bronsted-Lowry base	
2.	Which of the following has a coordination number as a feature? a) Coordination entity b) Ligand c) Central atom d) Coordination compound	
3.	Which of the following determines the position of ligands in a mononuclear coordination entity's formula? a) Atomicity of the ligand b) Charge on the ligand c) The first letter in the name of the ligand d) Denticity of the ligand	

4. Which substance is used to determine the hardness of water using a simple titration?

- a) Mg(EDTA)
- b) Fe(EDTA)
- c) Na₂(EDTA)
- d) Co(EDTA)

5. The core atom of which of the following biologically significant coordination molecules is magnesium?

- a) Vitamin B12
- b) Haemoglobin
- c) Chlorophyll
- d) Carboxypeptidase-A

6. Determine the proper name for K₂[PdCl₄].

- a) Potassium tetrachlorinepalladium(II)
- b) Potassium tetrachloridopalladate(II)Potassium
- c) Potassium tetrachloridopalladium(II)
- d) tetrachlorinepalladate(II)

7. Determine which of the following statements about VBT is inaccurate.

- a) It does not explain the colour of coordination compounds
- b) It can distinguish between strong and weak ligands
- c) It does not explain the kinetic stabilities of coordination compounds
- d) It is unreliable in the prediction of geometries of 4-coordinate complexes

8. More than one sort of hybridization can occur in a complex with geometry.

- a) tetrahedral
- b) octahedral
- c) trigonal bipyramidal
- d) square planar

9. Which of the following statements about coordination compounds' bonding is incorrect?

- a) Crystal Field Theory
- b) VSEPR Theory
- c) Valence Bond Theory
- d) Molecular Orbital Theory

10. Primary and secondary valency of Pt in [Pt(en)₂Cl₂] are

- (a) 4, 4
- (b) 4, 6

- (c) 6, 4
- (d) 2, 6

II ASSERTION & REASON

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are true, reason is correct explanation of assertion.
- (b) Assertion and reason both are true but reason is not the correct explanation of assertion.
- (c) Assertion is true, reason is false.
- (d) Assertion is false, reason is true.

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

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

2. Assertion: Chelates are less stable than ordinary coordination compounds.

Reason: Chelates can be formed by bidentate ligands.

3. Assertion : Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism.

Reason : Geometrical isomerism is not shown by complexes of coordination number 6

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

Reason : Because it has d^2sp^3 type hybridisation

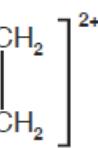
5. Assertion: $[\text{FeF}_6]^{3-}$ is a low spin complex.

Reason : Low spin complexes have lesser number of unpaired electrons.

SA & LA QUESTIONS

- | | | |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| 1. | How many ions are produced from the complex, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ in solution? | 1 |
| 2. | Draw the geometric isomers of $[\text{CoCl}_3(\text{NH}_3)_3]$ | 1 |
| 3. | State for a d^6 ion, how the actual configuration split in d orbital in an octahedral crystal field is decided by the magnitude of Δ° and P. | 1 |
| 4. | Draw one of the geometrical isomers of the complex $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ which is optically active.
[Hint: cis octahedral structure] | 1 |
| 5. | Write the IUPAC name of the linkage isomer of: $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$. | 1 |
| 6. | Draw all the isomers (geometric and optical) of $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+$. | 2 |

7. Name the following compounds according to the IUPAC rule: 2
 K₃[Al(C₂O₄)₃]
 ii) [Pt(NH₃)₄Cl₂][PtCl₄]
8. Explain why K₃[Fe(CN)₆] is more stable than K₄[Fe(CN)₆]? 2
 [Hint: charge of central metal ion]
9. Draw the structure of Ni(CO)₄ and Fe(CO)₅. Give the hybridization of both the complexes. 2
 [Hint: CO is the strongest ligand, the 3d electron pairs up and the 4s electrons are pushed into 3d orbital. One 3d orbital remains empty which along with one 4s and three 4p undergoes dsp^3 hybridisation. Hence it has trigonal bipyramidal geometry and is diamagnetic.]
10. When a co-ordination compound CrCl₃.6H₂O is mixed with AgNO₃, 2 moles of AgCl are precipitated per mole of the compound. Write 2
 (i) Structural formula of the complex.
 (ii) IUPAC name of the complex.
11. Explain the following: 3
 a) Ferro cyanide ion is diamagnetic and ferricyanide ion is paramagnetic.
 b) Solution of potassium ferricyanide does not give test for ferric ions.
 c) [Sc(H₂O)₆]³⁺ is colourless while [Ti(H₂O)₆]³⁺ is coloured.
12. The two complexes of nickel, [Ni(CN)₄]²⁻ and [Ni(CO)₄], have different structures but possess same magnetic behaviour. Explain. 3
 [Hint: [Ni(CN)₄]²⁻ dsp^2 hybridisation, Ni in +2 state all electrons are paired, so diamagnetic.
 [Ni(CO)₄] sp³ hybridisation, Ni in 0 state all electrons are paired so diamagnetic]
13. Write the correct formulae for the following coordination compounds: 3
 (i) CrCl₃.6H₂O (violet with 3 chloride ions precipitated as AgCl)
 (ii) CrCl₃.6H₂O (light green colour, with 2 chloride ions precipitated as AgCl)
 (iii) CrCl₃.6H₂O (dark green colour, with 1 chloride ion precipitated as AgCl).
14. a) What type of structural isomerism is represented by the following pairs : 3
 (i) [Mn(CO)₅SCN] and [Mn(CO)₅NCS]
 (ii) [Co(NH₃)₅NO₃] SO₄ and [Co(NH₃)₅SO₄] NO₃
- b) In the following coordination entity
 (i) Identify the ligand involved and
 (ii) Oxidation state of copper metal.
15. Explain the following by giving one example in each case : 3
 (a) Linkage isomerism
 (b) An outer orbital complex with coordination no. 6.
 (c) A bidentate ligand.
16. i) Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved. 5
 (a) [CoF₆]³⁻
 (b) [Cr(NH₃)₆]³⁺
 (c) [Fe(CN)₆]⁴⁻ [Atomic Number : Co = 27, Cr = 24, Fe = 26]
 ii) Calculate the coordination number of central atom in [Co(C₂O₄)₃]³⁻
 iii) Arrange the following complexes in the increasing order of conductivity of their solution: [Co(NH₃)₃Cl₃], [Co(NH₃)₄Cl₂]Cl, [Co(NH₃)₆]Cl₃, [Cr(NH₃)₅Cl]Cl₂
 [Hint: Co(NH₃)₃Cl₃] < [Cr(NH₃)₅Cl]Cl < [Co(NH₃)₅Cl]Cl₂ < [Co(NH₃)₆]Cl₃]



- 17.** a) Explain using Crystal Field Theory : The $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion contains five unpaired electrons while $[\text{Mn}(\text{CN})_6]^{4-}$ ion contains only one unpaired electron. 5
 b) Which complex compound is used in chemotherapy? Write its formula also.
 c) Draw the structure of
 (i) Cis-dichloridotetracyanochromate (II) ion
 (ii) Mer-triamminetrichloridocobalt (III)
 (iii) Fac-triaquatrinitrito-N-cobalt (III)

HIGH ORDER THINKING SKILLS

- 18.** a) A complex is prepared by mixing CoCl_3 and NH_3 in the molar ratio of 1:4, 0.1 m solution of this complex was found to freeze at -0.372°C . What is the formula of the complex? K_f of water = $1.86^\circ\text{C}/\text{m}$ 5
 b) What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex?
 c) Why are different colours observed in octahedral and tetrahedral complexes for the same metal and same ligands?
 d) Write the IUPAC name of the ionisation isomer of the coordination compound $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$. Give one chemical test to distinguish between the two compounds.
 [Hint: a) Theoretical $\Delta T_f = K_f \times m = 1.86 \times 0.1 = 0.186^\circ\text{C}$ Observed $\Delta T_f = 0.372^\circ\text{C}$
 As observed ΔT_f is double the theoretical value, this shows each molecule of the complex dissociates to form two ions. This can be so only if the formula of the complex is $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 b) When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.
 c) Higher wavelength is absorbed in octahedral complex than tetrahedral complex for same metal and ligands.
 d) Test with BaCl_2]

- 19.** For the complex $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$ identify : 5
 (a) The oxidation no. of iron.
 (b) The hybrid orbitals and the shape of the complex.
 (c) The magnetic behavior of the complex.
 (d) The number of geometrical isomers.
 (e) Whether there is an optical isomer also?
 (f) Name of the complex. [At. No. of Fe = 26]
 [Hint: a) +3, b) sp^3d^2 octahedral c) paramagnetic d) cis and trans e) Yes, only for cis isomer f) Dichloridobis-(ethane-1,2-diamine)iron(III) chloride]

- 20.** a) A chloride of fourth group cation in qualitative analysis gives a green coloured complex [A] in aqueous solution which when treated with ethane -1, 2 - diamine (en) gives pale - yellow solution [B] which on subsequent addition of ethane -1, 2 - diamine turns to blue/purple [C] and finally to violet [D]. Write the structures of complexes [A], [B], [C] and [D].
 b) Why are low spin tetrahedral complexes not formed?
 [Hint:
 A= $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 B= $[\text{Ni}(\text{H}_2\text{O})_4(\text{en})]^{2+}$
 C= $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$
 D= $[\text{Ni}(\text{en})_3]^{2+}$
 a)]

- b) The crystal field stabilisation energy is lower than pairing energy.]

CASE BASED QUESTION

The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. New concepts of chemical bonding and molecular structure have provided insights into the functioning of these compounds as vital components of biological systems. Chlorophyll, haemoglobin and vitamin B12 are coordination compounds of magnesium, iron and cobalt respectively. Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds such as CrCl_3 , CoCl_2 or PdCl_2 have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

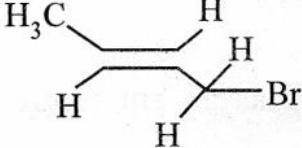
The main postulates are: 1. In coordination compounds metals show two types of linkages (valences)- primary and secondary. 2. The primary valences are normally ionisable and are satisfied by negative ions. 3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.

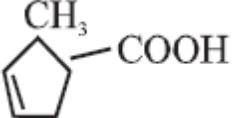
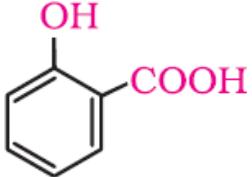
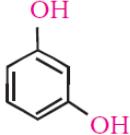
- 1) Write the formulas for the following coordination compounds: and identify primary and secondary valencies.
 - (a) Tetraammineaquachloridocobalt (III) Chloride
 - (b) Potassium tetrahydroxidozincate(II)
- ii) Discuss briefly giving an example in each case the role of coordination compounds in:
 - (i) biological systems
 - (ii) analytical chemistry

Organic Chemistry

Give the IUPAC names of the following organic molecules:

1	(i) $\begin{array}{ccccccc} CH_3 & - & CH & - & CH_2 & - & CH_2 & - CHO \\ & & & & & & & \\ & & CH_3 & & & & & \end{array}$
2	(ii) $\begin{array}{ccccccc} CH_3 & - & CH_2 & - & CH & - & COOCH_3 \\ & & & & & & \\ & & & & CH_3 & & \end{array}$
3	$\begin{array}{ccccc} H_3C & & CH_3 & & \\ & \diagdown & \diagup & & \\ & H & & & \\ & & \diagup & \diagdown & \\ & & CH_3 & & Br \end{array}$
4	$\begin{array}{ccccc} CH_3 & CH_2 & - & N & - CH_3 \\ & & & & \\ & & H & & \end{array}$
5	$\begin{array}{ccccccc} CH_3 & - & CH & - & CH_2 & - & CH = CH_2 \\ & & & & & & \\ & Cl & & & & & \end{array}$

6	$\text{CH}_2 = \text{CHCH}_2\text{Br}$
7	$(\text{CCl}_3)_3 \text{CCl}$
8	$\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2$
9	$\begin{array}{ccccc} \text{CH}_3 & - & \text{C} & = & \text{C} & - & \text{CH}_2\text{OH} \\ & & & & & & \\ & \text{CH}_3 & & \text{Br} & & & \end{array}$
10	$\begin{array}{cccccc} \text{H}_2\text{C} & = & \text{CH} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_3 \\ & & & & & & & & & & & \\ & & & \text{OH} & & & & & & & & \end{array}$
11	$\begin{array}{ccccc} \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 & - & \text{COOH} \\ & & & & & & \\ & \text{OH} & & & & & \end{array}$
12	$\begin{array}{cccccc} \text{H}_3\text{C} & - & \text{CH} = & \text{CH} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_3 \\ & & & & & & & & & \\ & & & & & \text{OH} & & & & \end{array}$
13	$\begin{array}{c} (\text{CH}_3)_3\text{C}-\text{C}-\text{COOH} \\ \parallel \\ \text{O} \end{array}$
14	$\begin{array}{cccccc} \text{H}_3\text{C} & - & \text{CH} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH} & - & \text{CH}_2\text{OH} \\ & & & & & & & & & & \\ & \text{CH}_3 & & & \text{OH} & & \text{CH}_3 & & & & \end{array}$
15	
16	$\begin{array}{c} (\text{CH}_3)_2\text{C} = \text{CH} - \underset{\text{II}}{\text{C}} - \text{CH}_3 \\ \text{O} \end{array}$
17	$\begin{array}{ccccc} \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 & - & \text{CHO} \\ & & & & & & \\ & \text{NH}_2 & & & & & \end{array}$

18	$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \underset{\text{O}}{\overset{ }{\text{C}}} - \text{CH}_3$
19	
20	$\text{C}_6\text{H}_5\text{NH COCH}_3$
21	$\text{OHC} - \text{CH}_2 - \underset{\text{CHO}}{\text{CH}} - \text{CH}_2 - \text{CHO}$
22	
23	$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$
24	$\text{CH}_3 - \underset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{CH} - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$
25	

Write the structures of the following:

1. 3-Methylbutanal
2. 2-Chloro-3-methylbutane
3. 3-Chloro-2,2-dimethylbutane
4. Pentane-2,4 dione
5. 4-Chloropentan-2-one
6. Phenylisopentylether
7. 4-Chloro-2-methyl-3-oxobutanamide
8. 4-Bromo-3-methylpent-2-ene
9. 1-Bromo-4-sec-butyl-2-methylbenzene
10. N-Ethyl-N-methylethanamine
11. 4-Aminobenzenesulphonic acid
12. 3-Oxopentanal
13. N,N-Diethylbenzenesulphonamide
14. 2-Methylcyclohexanone

15.3-Methylcyclohexanecarbaldehyde

16.1,3-Diphenylprop-2-en-1-one

17.2-Phenylethanoic acid

18. Propane-1,2,3-tricarboxylic acid

19. Ethanedioic acid

20.3-Methylbutoxybenzene

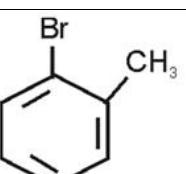
Answer Key

Give the IUPAC names of the following organic molecules:

1	4- Methylpentanal
2	Methyl 2-Methylbutanoate
3	4-Bromo-3-methylpent-2-ene
4	N-Methylethanamine
5	4-Chloropentene
6	3-Bromopropene
7	2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane
8	But-3-en-1-amine
9	2-Bromo-3-methylbut-2-enol
10	Hex-1-en-3-ol
11	3-Hydroxybutanoic acid
12	Hex-4-en-3-ol
13	3,3-Dimethyl-2-oxobutanoic acid
14	2,5-Dimethylhexane-1,3-diol
15	1-Bromobut-2-ene
16	4-Methylpent-3-en-2-one
17	3-Aminobutanal
18	4-Hydroxypentan-2-one
19	2-Methylcyclopent-3-enecarboxylic acid
20	N-Phenylethanamide
21	Propane-1,2,3-tricarbaldehyde
22	2-Hydroxybenzoic acid

23	Ethoxybenzene
24	1-Ethoxy-2-methylbutane
25	Benzene-1,3-diol

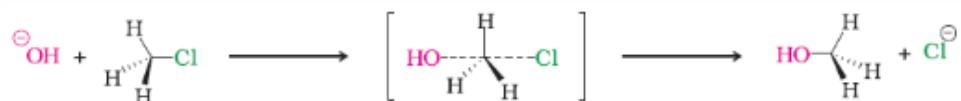
Give the structures of the following:

1	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$
2	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{Cl})\text{CH}_3$
3	$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}(\text{Cl})\text{CH}_3$
4	$\text{CH}_3\text{COCH}_2\text{CO CH}_3$
5	$\text{CH}_3\text{COCH}_2\text{CH}(\text{Cl})\text{CH}_3$
6	$\text{C}_6\text{H}_5 - \text{O} - \text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$
7	$\text{CH}_2(\text{C}\ell)\text{COCH}(\text{CH}_3)\text{CONH}_2$
8	$\text{CH}_3\text{CH} = \underset{\text{CH}_3}{\text{C}} - \underset{\text{Br}}{\text{CH}} - \text{CH}_3$
9	
10	$(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$

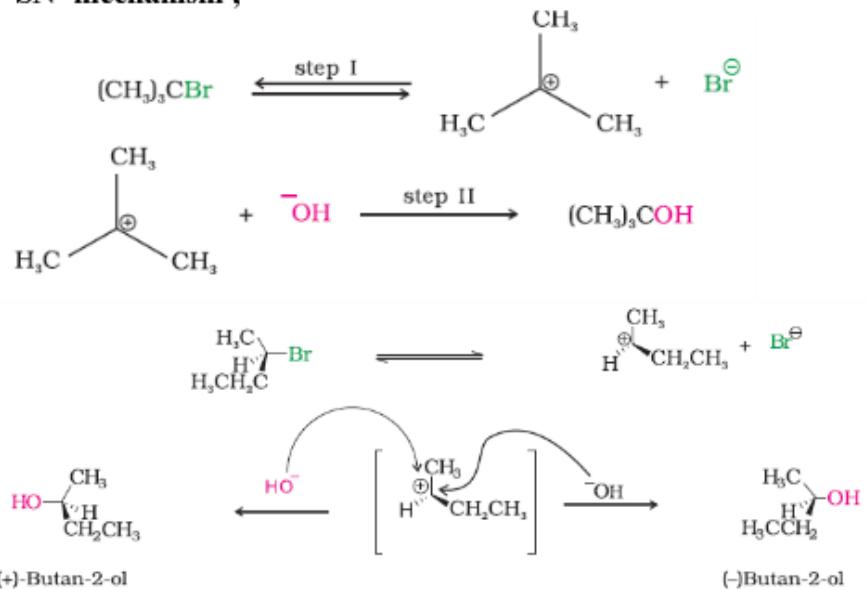
11	
12	
13	
14	
15	
16	
17	
18	HOOC-CH₂-CH(COOH)-CH₂-COOH
19	HOOC-COOH
20	

Mechanism in Organic Chemistry

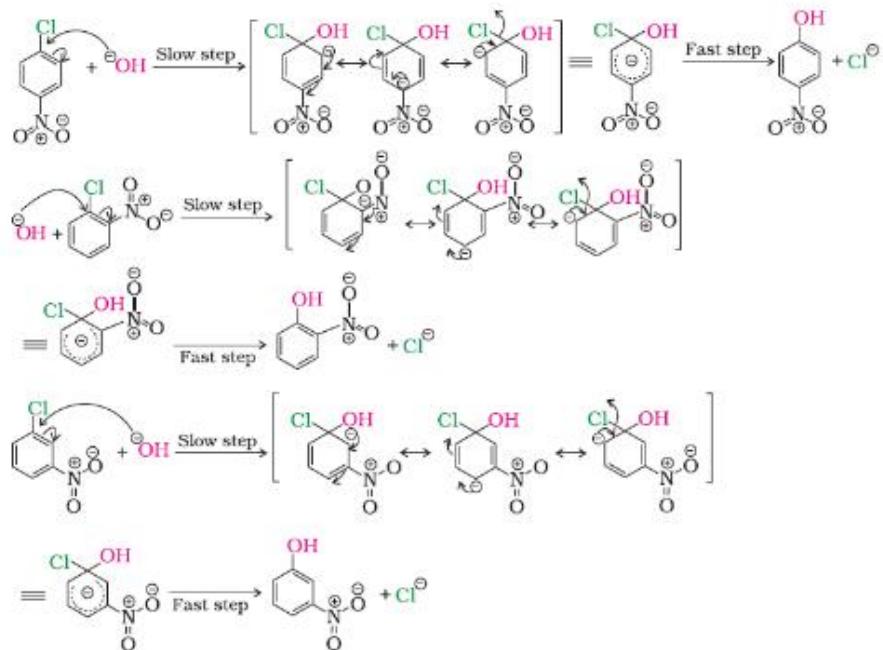
1. SN² Mechanism:



2. SN¹ mechanism :



3. Effect of substituent on nucleophilic substitution in aryl halides

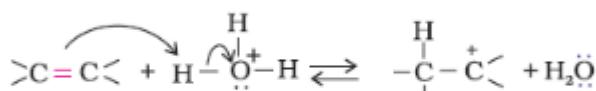


4. Hydration of Alkenes:

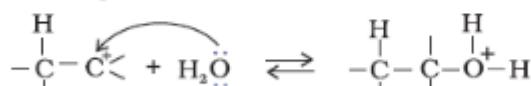
Mechanism

The mechanism of the reaction involves the following three steps:

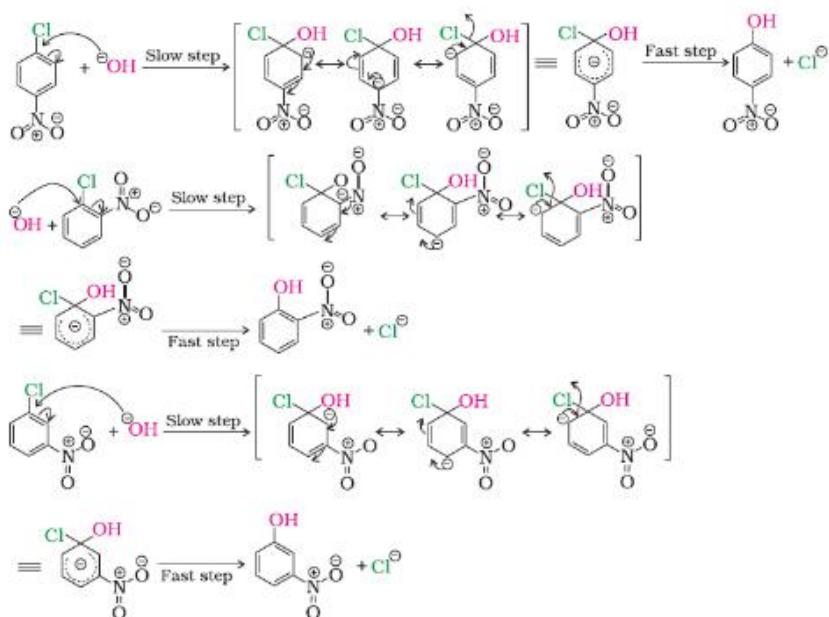
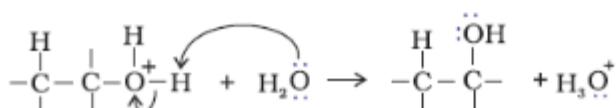
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



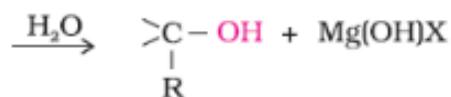
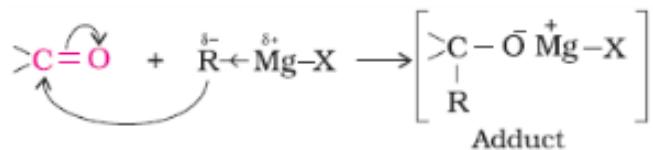
Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.



5. Addition of Grignard reagent to aldehydes and ketones



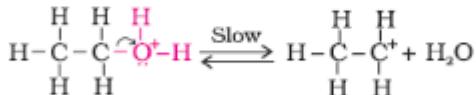
6. Dehydration of alcohols:

Mechanism

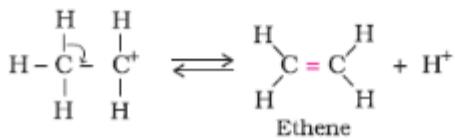
Step 1: Formation of protonated alcohol.



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

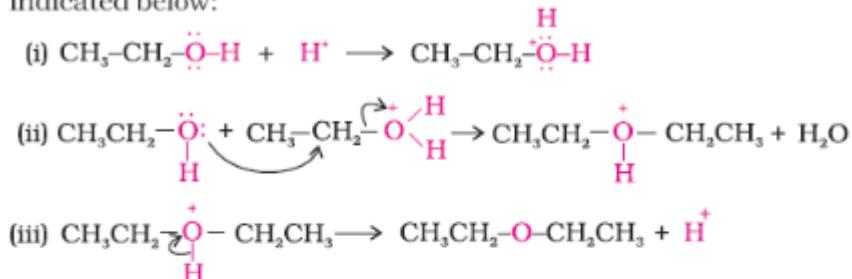


Step 3: Formation of ethene by elimination of a proton.



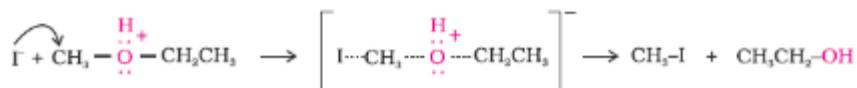
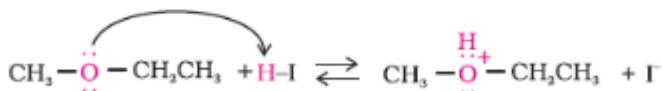
7. Dehydration of alcohols to give Ethers:

indicated below:

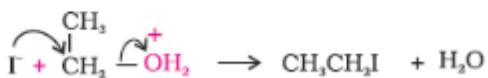
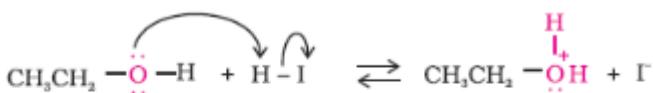


8. Reaction of ether with HI

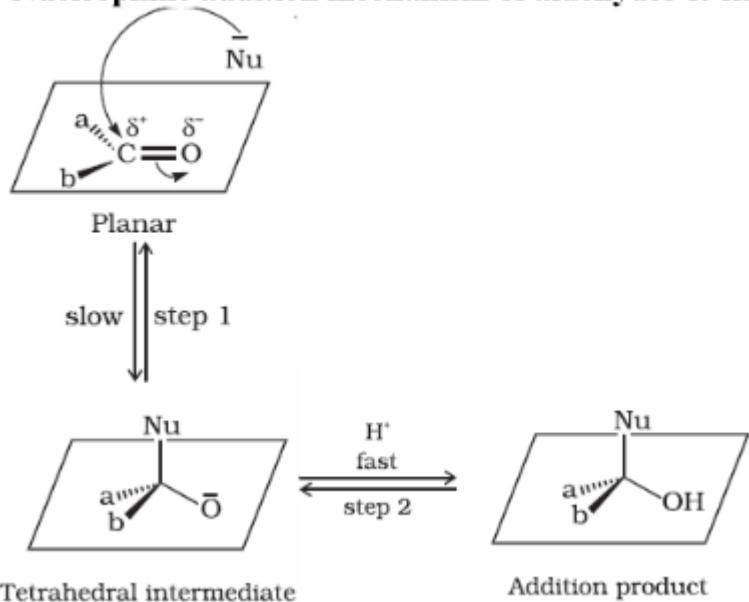
Step 1:



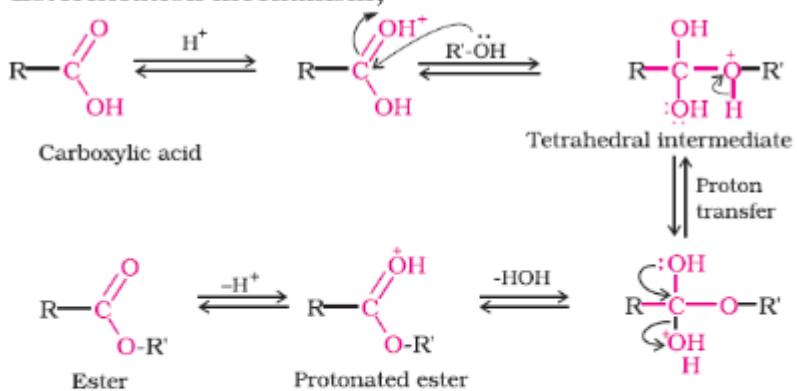
Step 3:



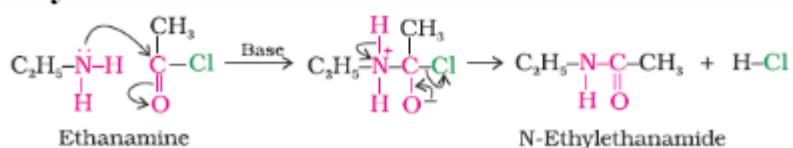
9. Nucleophilic addition mechanism of aldehydes & ketones.



10. Esterification mechanism;



11. Acylation of amines:



Name Reactions (Organic Chemistry)

Finkelstein Reaction

Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.



Wurtz Reaction

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.



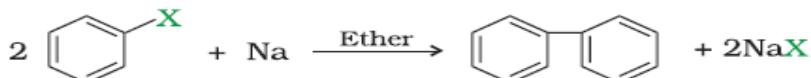
Wurtz-Fittig Reaction

A mixture of an alkyl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.

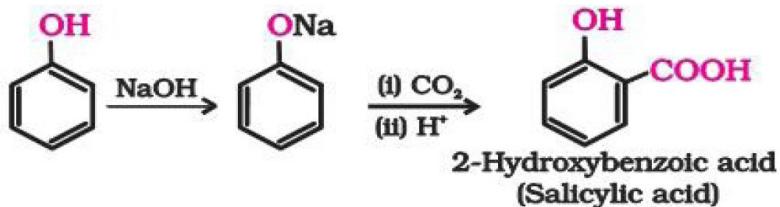


Fittig Reaction

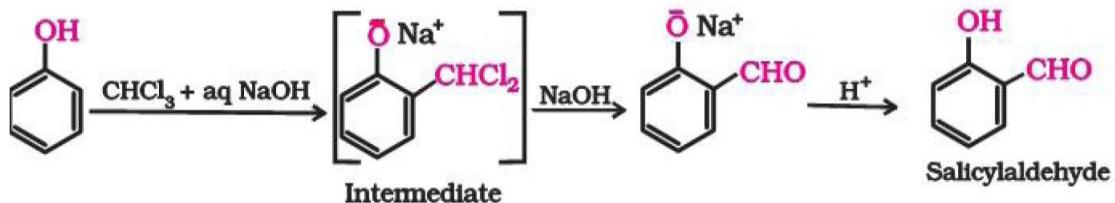
Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction



Kolbe's reaction:



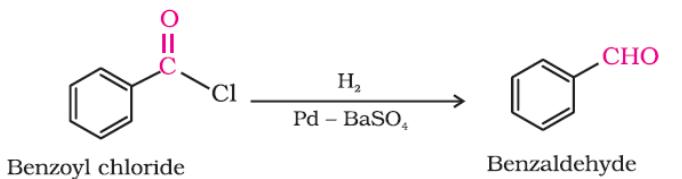
1. Reimer-Tiemann reaction:



Williamson synthesis : $R-X + R'ONa \rightarrow ROR' + NaX$

Name reactions (Aldehyde,Ketones and Carboxylic acid)

Rosenmund reduction: Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund reduction**.

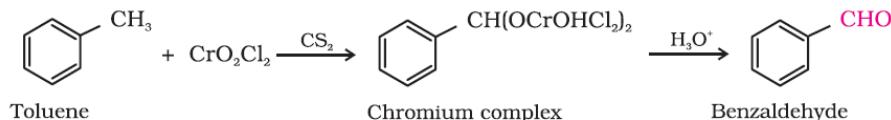


Stephen reaction.

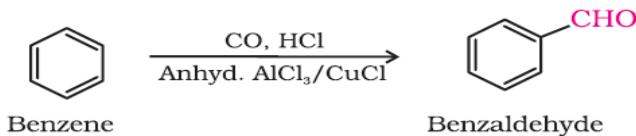
Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde. This reaction is called **Stephen reaction**.



Etard reaction Use of chromyl chloride (CrO_2Cl_2): Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called **Etard reaction**.

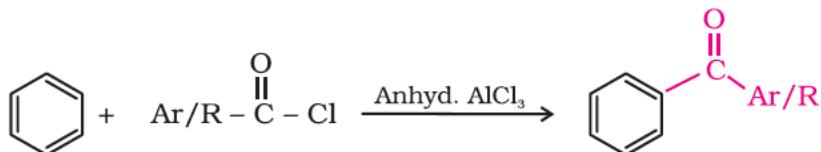


Gatterman-Koch : When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde. This reaction is known as **Gatterman-Koch** reaction.



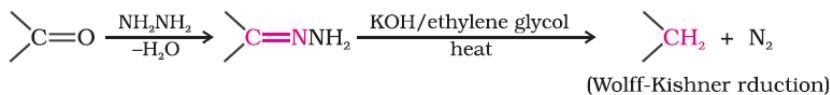
Friedel-Crafts acylation reaction.

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as **Friedel-Crafts acylation reaction**.

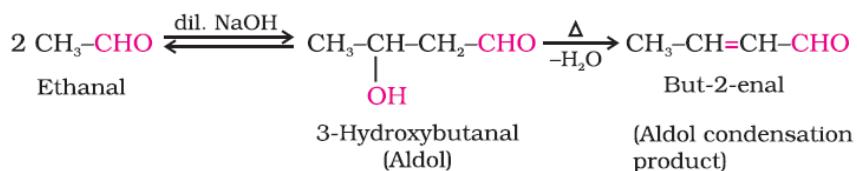


The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid [**Clemmensen reduction**] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as

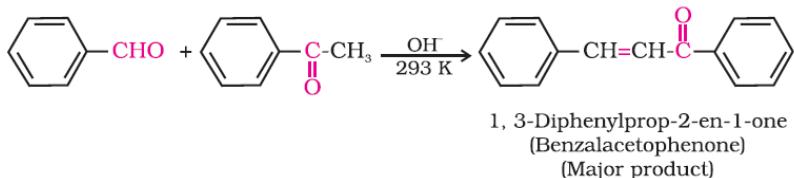
ethylene glycol (**Wolff-Kishner reduction**).



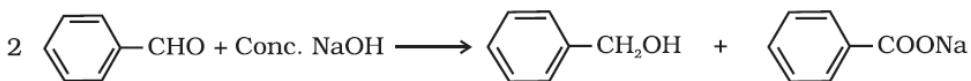
Aldehydes and ketones having at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**



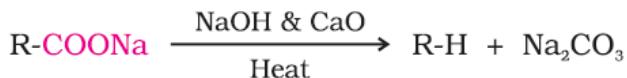
When aldol condensation is carried out between two different aldehydes and / or ketones, it is called **cross aldol condensation**. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



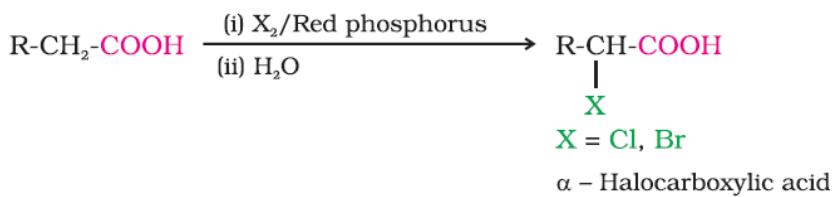
Cannizzaro reaction: Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



Decarboxylation: Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3:1). The reaction is known as decarboxylation.



Halogenation: Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



Tests

- Tollens' test:** On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.



- Fehling's test:** Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



- Iodoform Reaction:** Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform. Iodoform (Yellow Precipitate) reaction with sodium hypoiodite is also used for detection of CH_3CO group or $\text{CH}_3\text{CH}(\text{OH})$ group which produces CH_3CO group on oxidation.

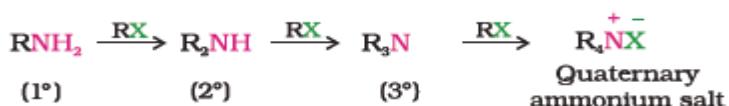
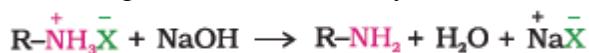


- Carboxylic acid reacts with weaker bases such as carbonates and hydrogen carbonates to evolve carbon dioxide. This reaction is used to detect the presence of carboxyl group in an organic compound.



Name reactions -Amines

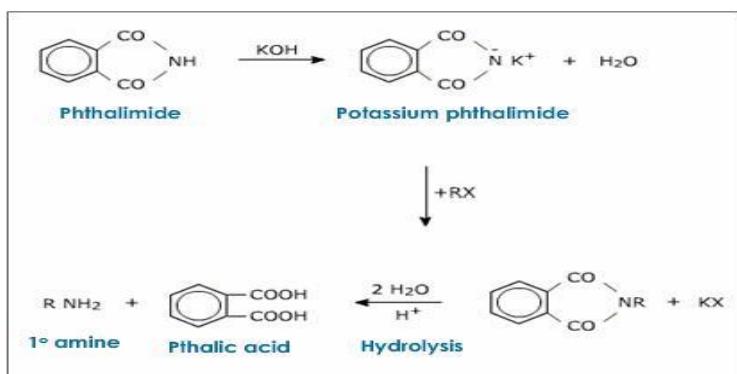
Ammonolysis: An alkyl or benzyl halide on reaction with ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (-NH₂) group. This process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis.



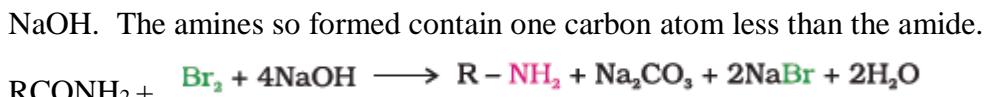
Gabriel phthalimide synthesis:

This method is used for the preparation of primary amines.

Phthalimide on treatment with ethanolic potassium hydroxide form potassium salt of phthalimide which on treatment with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



Primary amines are prepared by treating an amide with bromine in ethanolic solution of NaOH.



Acylation reaction:

Aliphatic and aromatic primary or secondary amines react with acid chloride, anhydrides and esters by nucleophilic substitution reaction .The reaction takes place in the presence of pyridine which removes HCl and shifts the equilibrium to the right hand side.

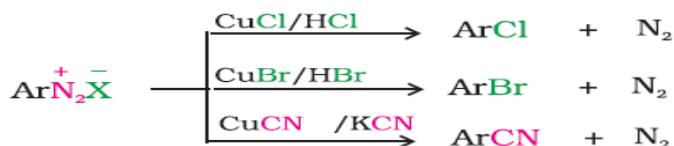
Carbylaminies reaction:

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanide which are foul smelling substances.



Sandmeyer's reaction

The Cl⁻, Br⁻ and CN⁻ nucleophiles can easily be introduced in the benzene ring in the presence of Cu (I) ion.



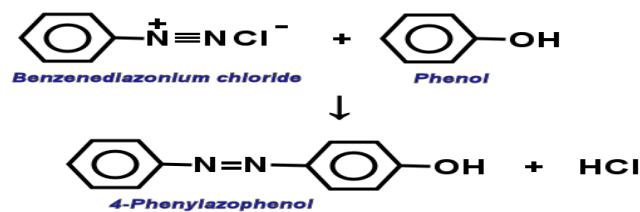
Gatterman reaction

Chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



Coupling reaction

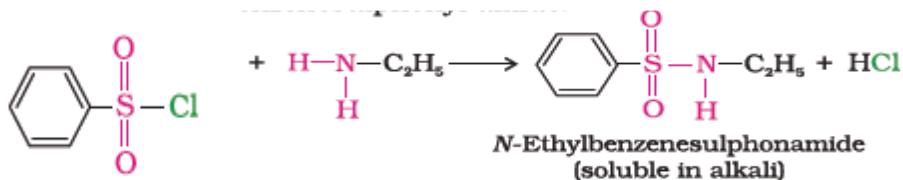
Benzene diazonium chloride reacts with phenol molecule at its para position is coupled with diazonium salt to form p-hydroxy azobenzene.



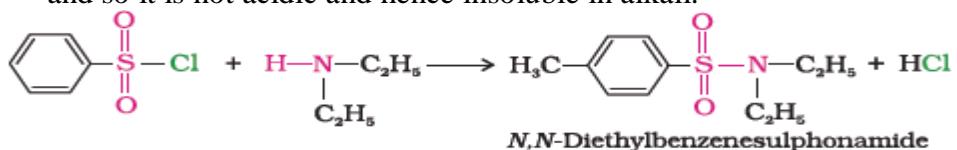
Distinguish the following compounds:

Hinsberg test (To distinguish primary, secondary and tertiary amines)

- a) **Primary amine** - The hydrogen attached to nitrogen in N-ethylbenzenesulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence it is soluble in alkali.

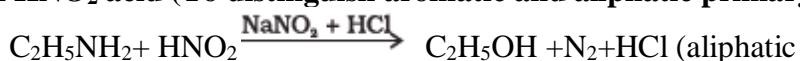


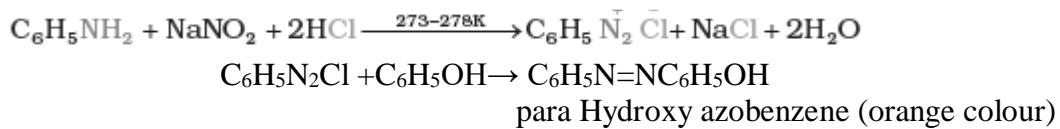
- b) N,N-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom and so it is not acidic and hence insoluble in alkali.



- c) Tertiary amines do not react with benzenesulphonyl chloride.

Reaction with HNO_2 acid (To distinguish aromatic and aliphatic primary amine)





IMPORTANT REASONING QUESTIONS OF ORGANIC CHEMISTRY

UNIT-VI HALOALKANES AND HALOARENES

Q1) Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans) As H_2SO_4 is an oxidizing agent so it converts KI to HI and then oxidizes it to I_2 .

Q2) p-Dichlorobenzene has higher melting point and solubility than those of o- and m- isomers. Discuss.

Ans) p-Dichlorobenzene is symmetrical, therefore having a close packing in its crystal lattice and has higher m.pt. Its higher solubility is due to its symmetrical structure and more force of attraction with the solvent.

Q3) Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution. Explain why?

Ans) Because allyl carbocation is resonance stabilized whereas n-propyl carbocation is stabilized by +I effect only.

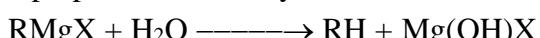
Q4) Haloalkanes react with KCN to give alkyl cyanide as main product while with AgCN they form isocyanide as main product. Give reason.

Ans) KCN is an ionic compound so attack is possible through C as well as through N but as C-C bonds are more stronger than C-N bond so attack will take place through C, therefore with KCN, alkyl cyanide is main product but AgCN is a covalent compound so C is not free but attack can take place through N as it has lone pair of electrons, therefore with AgCN, alkyl isocyanide is main product.

Q5) Assign possible reason for each of the following:

(a) Grignard reagent is prepared under anhydrous conditions.

Ans) Grignard reagents are highly reactive and react with source of proton to give hydrocarbons. Therefore it is prepared under anhydrous conditions as water converts it into hydrocarbon.



(b) Haloalkanes though polar but immiscible with water.

Ans) In order for a haloalkane to dissolve in a water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attraction forces are created between the haloalkane and the water molecules which are not sufficient to overcome the older forces.

(c) Chloroform is stored in dark coloured bottles, completely filled upto the brim.

Ans) Chloroform is slowly oxidised by air in the presence of light to a poisonous gas phosgene. It is therefore stored in dark coloured bottles, completely filled upto the brim so that air is kept out.

(d) Chlorobenzene is less reactive than chloroethane towards nucleophilic substitution reaction.

Ans) Because in Chlorobenzene, C-Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleave between C-Cl is difficult in Chlorobenzene than chloroethane. Therefore Chlorobenzene is less reactive than chloroethane towards nucleophilic substitution reaction.

(e) The dipole moment of Chlorobenzene is lower than that to cyclohexyl chloride.

Ans) Dipole moment is product of the distance between the charges and the magnitude of charge. In Chlorobenzene, C-Cl bond acquires a partial double bond character due to resonance so bond length between C-Cl decreases but there is no resonance in cyclohexyl chloride so having a single bond between C-Cl therefore, dipole moment of cyclohexyl chloride is larger.

Q6) S_N2 mechanism does not take place in tertiary halides. Why?

Ans) In tertiary halides steric hindrance is largest due to the presence of bulky groups which hinder the approaching nucleophiles. Therefore, S_N2 mechanism does not take place in tertiary halides.

Q7) Haloalkanes have higher boiling points than the hydrocarbons of comparable molecular masses. Explain.

Ans) Due to greater polarity as well as high molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction are stronger in haloalkanes than the hydrocarbons of comparable molecular masses. Therefore, haloalkanes have higher boiling points than the hydrocarbons of comparable molecular masses.

Q8) t-Butyl bromide has lower boiling point than n-butyl bromide. Why?

Ans) The boiling point of isomeric haloalkanes decreases with increase in branching as magnitude of Vander Waal force decreases with branching. t-Butyl bromide has less surface area than n-butyl bromide so having less boiling point.

9) Aryl halides cannot be prepared by the action of sodium halide in the presence of H₂SO₄. Why?

A) Due to resonance, the carbon-oxygen bond in phenols has partial double bond & it is stronger than carbon-oxygen single bond.

10) What is the best method to prepare alkyl fluorides?

A) The best method to prepare alkyl fluorides is the halogen exchange method, using AgF.
 $\text{CH}_3\text{Br} + \text{AgF} \rightarrow \text{CH}_3\text{F} + \text{AgBr}$

11) Arrange the following halides in order of increasing S_N2 reactivity:
CH₃CH₂Cl, CH₃Br, CH₃Cl, (CH₃)₂CHCl

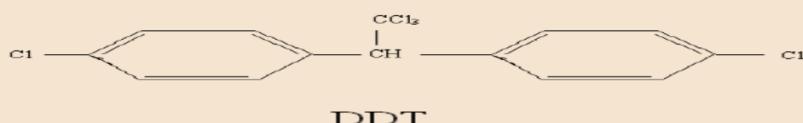
A) (CH₃)₂CHCl < CH₃CH₂Cl < CH₃Cl < CH₃Br

12) What is iodoform test?

A) A compound having structuring unit CH₃-CH(OH) or CH₃-C=O on heating with NaOH & I₂ forms a yellow precipitate of iodoform.

13) Write the Structural formula of DDT?

A)



Q14) The use of DDT is banned in the many countries of the world. Explain.

Ans) Many species of insects developed resistance to DDT, and it was found to have a high toxic effect towards fish. Therefore, the use of DDT is banned in the many countries of the world.

Q 15) Explain why R – Cl is hydrolysed to R – OH slowly but the reaction is rapid if catalytic amounts of KI are added to the reaction mixture?

Ans) KI supplies I^- ions which are strong nucleophiles and hence rapidly react with $R - Cl$ to form $R - I$. I^- is also a better leaving group than Cl^- . Hence RI is hydrolysed easily to ROH.

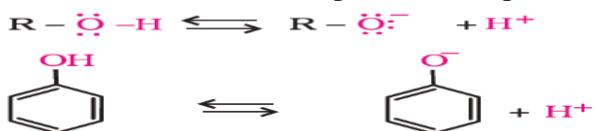
UNIT-VII ALCOHOLS, PHENOLS AND ETHERS

Q1) Alcohols have higher boiling points than ethers of comparable molecular mass. OR Give reason for the higher boiling point of ethanol in comparison to methoxymethane. Why? OR Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Ans) Because the –OH group in alcohols is involved in intermolecular hydrogen bonding while there is no H-bonding in ethers or hydrocarbons.

Q2) Phenols are more acidic than alcohols. Explain.

Ans) The ionisation of an alcohol and a phenol takes place as follows:



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol. Therefore, phenols are more acidic than alcohols.

Q3) Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol?

Ans) Nitro group is an electron withdrawing groups which enhances the acidic strength of phenol due to the effective delocalisation of negative charge in phenoxide ion. On the other hand methoxy group is an electron releasing groups which do not favour the formation of phenoxide ion resulting in decrease in acid strength.

Q4) Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

Ans) Solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules while hydrocarbons are hydrophobic as they can't form H-bonds with water.

Q5) While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Ans) ortho nitrophenol is steam volatile as it has intramolecular hydrogen bonding which is a weaker bond than intermolecular hydrogen bonding which is present in *para* nitrophenol.

Q6) Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution? OR Phenol is more reactive towards electrophilic substitution reaction than benzene. Why?

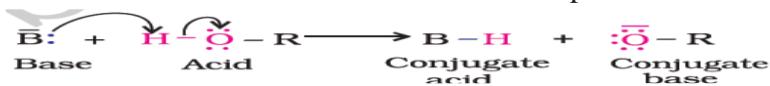
Ans) As –OH group is an activating group so it increases the electron density in the benzene ring specially at ortho and para position due to + R effect. Therefore, the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution.

Q7) Explain why is *ortho* nitrophenol more acidic than phenol?

Ans) Nitro group is an electron withdrawing group which enhances the acidic strength of phenol due to the effective delocalisation of negative charge in phenoxide ion and makes it more stable while in phenol delocalisation of negative charge in phenoxide ion is less than in *ortho* nitrophenol. Therefore *ortho* nitrophenol is more acidic than phenol.

Q8) Alcohols can act as weak base as well as weak acids. Explain.

Ans) Alcohols can act as Brönsted acid as it can donate a proton to a stronger base



Alcohols act as Brönsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

Q9) Which is a stronger acid phenol or cresol? Explain.

Ans) Phenol is a stronger acid than cresol because phenoxide ion is more stable in phenol than in cresol as cresol has an electron releasing group which does not favour the formation of phenoxide ion resulting in decrease in acid strength.

Q11) Phenyl methyl ether reacts with HI to form phenol and iodomethane not iodobenzene and methanol. Explain.

Ans) In case of anisole, methyl phenyl oxonium ion, $C_6H_5O^+ HCH_3$ is formed by protonation of ether. The bond between O–CH₃ is weaker than the bond between O–C₆H₅ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore the attack by I[–] ion breaks O–CH₃ bond to form CH₃I.

Q 12) Explain why phenols do not undergo substitution of – OH group like alcohols?

Ans) The C – OH bond in phenols have partial double bond character due to resonance. As a result, this bond is stronger hence difficult to cleave. In alcohols the C – OH bond is purely single bond and hence can be cleaved relatively easily.

Q13) Why di tert-butyl ether cannot be obtained by Williamson's method?

Ans) In order to prepare the above ether the reagents to be used are tert-butyl bromide and tert- butoxide. Since tertiary bromide preferably undergoes elimination, therefore major products of the reaction will be iso-butylene and not di tert-butyl ether.

UNIT-VII ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Q1) Why do aldehydes and ketones have lower boiling point than alcohols?

Ans) Because the –OH group in alcohols is involved in intermolecular hydrogen bonding while there is no H-bonding in aldehydes and ketones.

Q2) Carboxylic acids have much higher acidity than phenols. Why?

Ans) The higher acidity of carboxylic acids as compared to phenols is due to the following reasons:

- (1) The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a phenoxide ion, has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is less stable than in carboxylate ion.
- (2) The negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

Q3) Why is chloroacetic acid stronger than acetic acid? OR Why is pKa value of chloroacetic acid less than acetic acid.

Ans) –Cl is an electron withdrawing group which increases the acidity of acetic acid by stabilising the conjugate base through delocalisation of the negative charge by negative inductive and/or resonance effects. While in acetic acid CH₃ is an electron donating group which decreases the acidity by destabilising the conjugate base due to + I effect.

Q4) Aldehydes are more reactive than ketones towards nucleophilic addition reactions. Explain.

Ans) Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

- (i) **Sterically**, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.
- (ii) **Electronically**, two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively in ketones than in aldehydes.

Q5) Give plausible explanation for each of the following:

- (i) **Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.**

Ans) In 2,2,6-trimethylcyclohexanone, there is steric hindrance of three methyl groups while in cyclohexanone there is no steric hindrance. Therefore, Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

- (ii) **There are two –NH₂ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.**

Ans) The lone pair of electrons on NH₂ attached to carbonyl group is involved in resonance and hence not available for reaction.

- (iii) **During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.**

Ans) To prevent the hydrolysis of ester formed and to shift the equilibrium toward forward direction so that yield of ester can be increased.

Q6) Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Ans) The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance and hence it is less reactive than propanal.

Q7) Formic acid is stronger than acetic acid. Why?

Ans) In acetic acid CH_3 is an electron donating group which decreases the acidity by destabilising the conjugate base i.e. acetate ion due to +I effect while in formic acid there is no +I effect so conjugate base i.e. formate ion is more stable than acetate ion.

Q8) Explain the following:

(i) Benzaldehyde does not undergo aldol condensation.

Ans) Aldehydes and ketones having at least one α -hydrogen undergo aldol condensation. Benzaldehyde has no α -hydrogen; therefore, it does not undergo aldol condensation.

(ii) Electrophilic substitution in benzoic acid takes place at m-position.

Ans) Benzoic acid undergoes electrophilic substitution reactions because here the carboxyl group acts as a deactivating and meta-directing group.

(iii) Carboxylic acids have higher boiling point than aldehydes, ketones and alcohols of comparable molecular mass.

Ans) This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding as compared to aldehydes, ketones and alcohols of comparable molecular mass.

(iv) Formaldehyde gives Cannizaro's reaction whereas acetaldehyde does not.

Ans) Aldehydes which do not have a α -hydrogen atom, undergo Cannizaro's reaction. As formaldehyde does not have an α -hydrogen, therefore it can undergo Cannizaro's reaction while acetaldehyde has an α -hydrogen so it can't undergo Cannizaro's reaction.

(v) The α -hydrogen atoms are acidic in aldehydes and ketones.

Ans) The acidity of α -hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

UNIT-IX AMINES

Q1) Amino group is o,p-directing for aromatic electrophilic substitution. Why does aniline on nitration give a substantial amount of m-nitroaniline?

Ans) It is because of protonation of aniline to form anilinium ion $C_6H_5NH_3^+$ which is electron withdrawing in nature. Therefore, aniline on nitration gives a substantial amount of m-nitroaniline.

Q2) Account for the following observations:

(i) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

Ans) Methylamine dissolves in water to give OH^- ions which react with $FeCl_3$ to give reddish brown ppt of $Fe(OH)_3$.

(ii) An alkylamine is more basic than ammonia.

Ans) Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom and thus makes the unshared electron pair more available for sharing with the proton of the acid. Hence, alkylamines are stronger bases than ammonia.

(iii) Secondary amines are more basic than primary amines.

Ans) Basic nature of aliphatic amines increases with increase in the number of alkyl groups. As secondary amines have 2 alkyl groups while primary amines have only one alkyl group therefore +I effect is more in secondary amines which increases the electron density on N atom as compared to primary amine.

(iv) Aniline does not undergo Friedel Crafts reaction.

Ans) Aniline does not undergo Friedel-Crafts reaction due to salt formation with aluminium trichloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

(v) Aromatic amines (aniline or aryl amines) are less basic than ammonia and aliphatic amines. OR pK_b of aniline is more than that of methylamine.

Ans) Aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group which causes the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.

(vi) Aromatic primary amines cannot be prepared by Gabriel Phthalimide synthesis.

Ans) Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by Phthalimide.

Q3) Account for the following:

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

Ans) Ethyl amine is soluble in water because it can form hydrogen bonds with water molecules whereas aniline can't form h-bond due to bulky and hydrophobic phenyl ring.

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

Ans) The stability of diazonium salts of aromatic amines are because of resonance stability of diazonium ion.

Q4) Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

Ans) O-H bond of alcohols is more polar than N-H bond of amines as oxygen is more electronegative than nitrogen. Therefore, amines are less acidic than alcohols of comparable molecular masses.

(ii) Why do primary amines have higher boiling point than tertiary amines?

Ans) Primary amines are associated to each other through intermolecular hydrogen bonding.

Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, primary amines have higher boiling point than tertiary amines.

(iii) Aniline readily forms 2,4,6-tribromoaniline on reaction with bromine water.

Ans) Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline because $-NH_2$ group is a powerful activating group. Therefore, aromatic amines have very high reactivity.

Important Reactions used for Organic Chemistry Conversions

In CBSE board exam, word problems (conversions) covering “Properties and Reactions of Functional Groups” usually carry a weightage of 5 marks. So, it is important that you do not miss out on these particular types of questions while preparing for your exams.

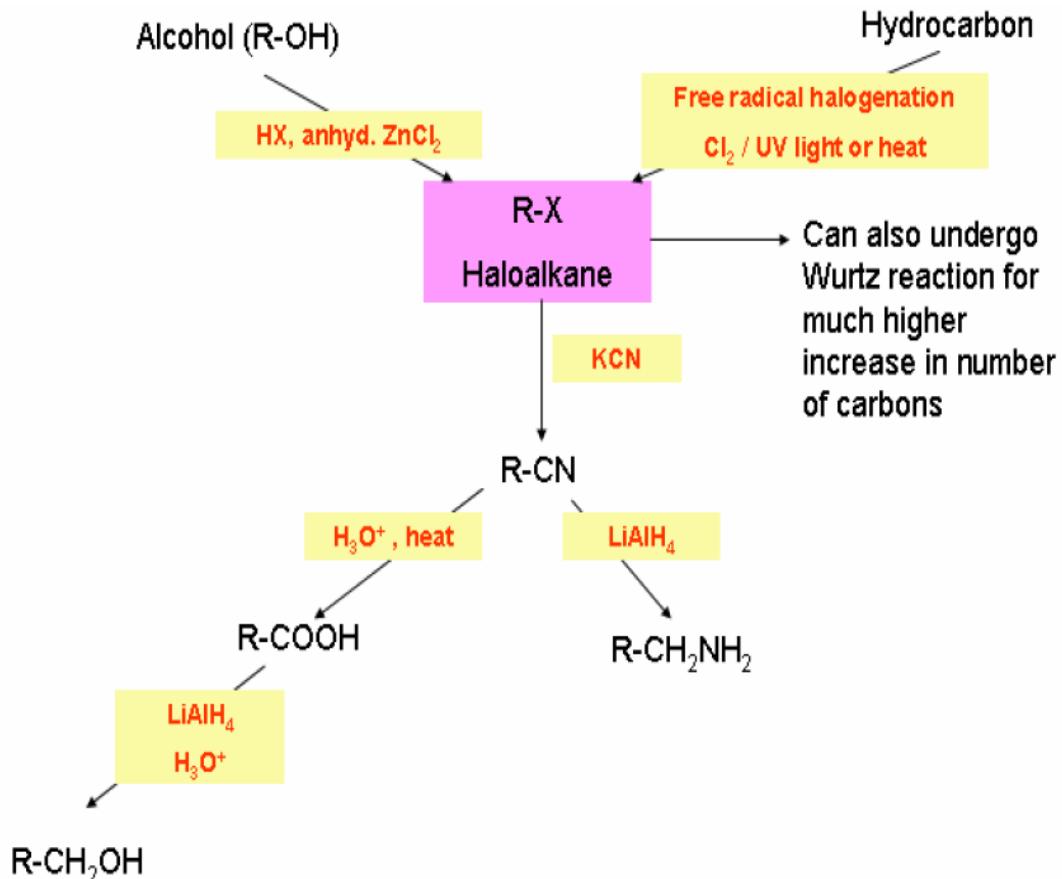
Students tend to get confused while solving questions based on organic conversions. Given below are a few conversions, explained in small logical chunks which are easy to remember.

Broadly you can classify conversions into two types – aliphatic and aromatic.

1. Aliphatic Conversions

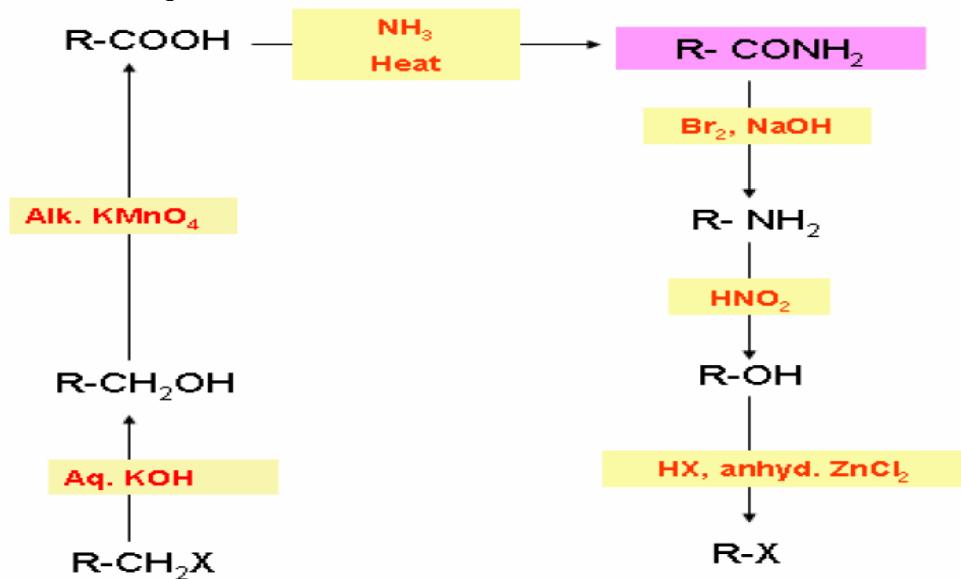
a. For stepping up the series:

Stepping up the series means that the product has one carbon more than that of reactant. For such kind of a conversion, convert the given compound to an alkyl halide and then to a cyanide and then to the required organic compound as asked in the question. This way, the product has one carbon more than the reactant.



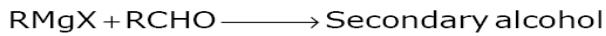
b. For stepping down the series:

Stepping down the series means that the product has one carbon less than that of its reactant. For such kind of a conversion, convert the given compound to an amide and then let it undergo Hoffmann bromamide degradation reaction. Then you convert it to the required product as asked in the question.



c. Reaction with Grignard's reagent:

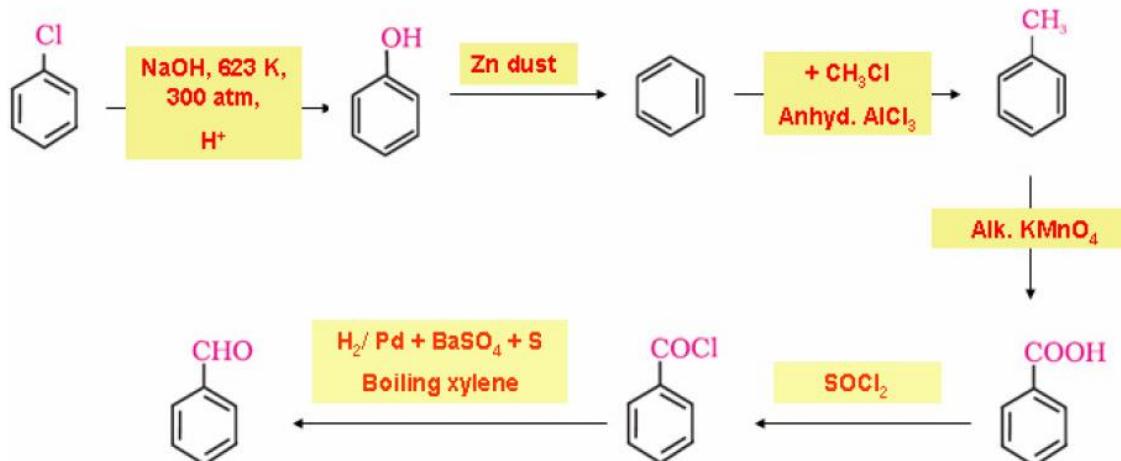
Grignard's reagent is a versatile reagent and can be used for many conversions. Some of its reactions are given below:



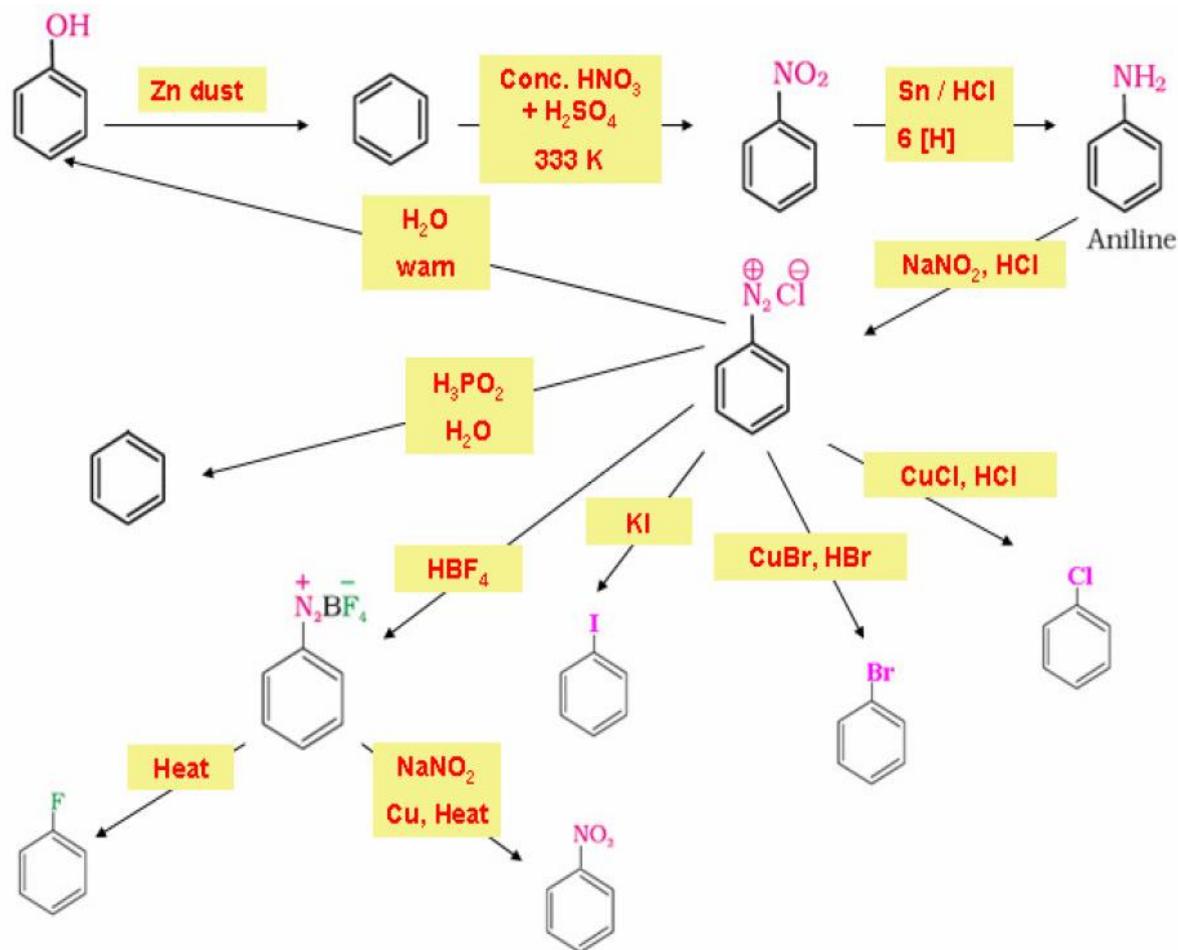
2. Aromatic Conversions

There are two types of conversions possible in this case:

a. When the functional group contains carbon atom:



b. When the functional group does not contain carbon atom:



UNIT-VI HALOALKANES AND HALOARENES

MULTIPLE CHOICE QUESTIONS

1. What is the class of the substitution product of LiAlH_4 and an alkyl halide reaction?
 - a) Haloalkane
 - b) Alkyl nitrite
 - c) Nitroalkane
 - d) Hydrocarbon
2. Which of the following statements about $\text{S}^{\text{N}}\text{2}$ mechanisms is incorrect?
 - a) The transition state is stable
 - b) The complete mechanism takes place in a single step
 - c) The rate of the reaction depends on the concentration of both reactants
 - d) There is an inversion of configuration
3. A mono haloarene is an example of _____
 - a) aliphatic halogen compound
 - b) side-chain substituted aryl halide
 - c) alkyl halide
 - d) aromatic halogen compound
4. What is 3-Bromopropene's common name?
 - a) Allyl bromide
 - b) Vinyl bromide
 - c) Tert-Butyl bromide
 - d) Propylidene bromide
5. Which of the following is the right name for the compound $\text{H}_3\text{C}-\text{CHCl}_2$?
 - a) 1,2-Dichloroethane
 - b) Ethylene dichloride
 - c) Ethyldene chloride
 - d) Vic-dichloride
6. What is the catalyst in the chloroalkane reaction of a primary alcohol with HCl?
 - a) red phosphorous
 - b) concentrated H_2SO_4
 - c) anhydrous ZnCl_2

d) pyridine

7. When ethanol combines with PCl_5 , it produces three products: chloroethane, hydrochloric acid, and _____. What is the third item on the list?

- a) Phosphorus acid
- b) Phosphoryl chloride
- c) Phosphorus trichloride
- d) Phosphoric acid

8. Which of the following substances has the highest melting point?

- a) Chloromethane
- b) Tetrachloromethane
- c) Trichloromethane
- d) Dichloromethane

9. Which sequence should isomeric dichlorobenzenes be boiled in?

- a) para>ortho>meta
- b) meta>ortho>para
- c) ortho>meta>para
- d) para>meta>ortho

10. Which of the following statements about the interaction between C_2H_4 and Cl_2 in CCl_4 is incorrect?

- a) It results in the formation of a vicinal dihalide
- b) It results in the discharge of a reddish-brown colour
- c) It results in the formation of a colourless compound
- d) It results in the breaking of the C-C double bond

ASSERTION & REASON

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

(i) Both assertion and reason are correct and the reason is correct explanation of assertion.

(ii) Both assertion and reason are correct but reason does not explain assertion.

(iii) Assertion is correct but reason is incorrect.

(iv) Both assertion and reason are incorrect.

(v) Assertion is incorrect but reason is correct.

1. Assertion : Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

Reason : Phosphorus chlorides give pure alkyl halides

2. Assertion : The boiling points of alkyl halides decrease in the order : RI > RBr > RCl > RF

Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass

3. Assertion : KCN reacts with methyl chloride to give methyl isocyanide

Reason : CN⁻ is an ambident nucleophile.

4. Assertion: Chloroform is stored in transparent bottles

Reason : Chloroform get oxidised in dark

5. Assertion : Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.

Reason : Oxidising agent oxidises I₂ into HI.

SA & LA QUESTIONS

1. Chloroform contains chlorine but gives no reaction with silver nitrate solution. Why? 1

2. In the following pair of halogen compounds, which compound undergoes faster S_N1 mechanism?



3. State Saytzeff rule. 1

4. Explain why thionyl chloride method is preferred for preparing alkyl chlorides from alcohols? 1

5. Illustrate retention of configuration with an example. 1

6. What is the use of dry acetone in Finkelstein reaction.

7. Give chemical test to distinguish between chlorobenzene and chloroethane.

8. a) Arrange the following halides in order of increasing S_N² reactivity: 2



- b) Arrange each of the following compounds in the order of increasing boiling points:

butane, n-butyl chloride, isobutyl chloride, n-pentylchloride

9. Write the structures of the following compounds and identify them as 1⁰, 2⁰ and 3⁰ halides: 2

- (a) 2-bromo-2-methyl propane (b) 2-bromo-3-methylbutane

10. An alkyl halide (A) on reaction with Mg in dry ether followed by treatment with ethanol gave 2-Methyl butane. Write all structures of (A). 2

11. Explain the following with the help of suitable examples: 2

(i) Finkelstein reaction

(ii) Swarts reaction

12. How will you prepare the following from benzene: 2

(a) m-chloronitrobenzene

(b) p-chloronitrobenzene

13. Convert the following: (i) Phenol to Toluene (ii) Chloroethane to Methane
14. A hydrocarbon of molecular mass 72 gmol⁻¹ gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the structure of the hydrocarbon.
15. An organic compound A with molecular formula C₄H₉Br on treatment with alcoholic KOH gave two isomeric compounds B and C. On ozonolysis, B gave only one product CH₃CHO while C gave two different products. Identify the compounds A, B and C. 3
16. Give reasons: 3
- (a) Ethyl chloride is a gas whereas ethyl iodide is a liquid at room temperature.
 - (b) Haloalkanes react with KNO₂ to form alkyl nitrite as main product while AgNO₂ forms nitroalkanes as chief product.
 - (c) The boiling point of alkyl halide is higher than that of the corresponding alkane.
17. Complete the following and write the formula of main product formed in the following reactions: 3
- | | | | |
|-----|--------------------------------------------------------------------------------------------------------|----------|-------------|
| | ethanol | | |
| (a) | $(\text{CH}_3)_3\text{CBr} + \text{KOH} \rightarrow$ | HBr | NaI |
| (b) | $\text{CH}_3\text{-CH=CH}_2 + \text{-----} \xrightarrow{\text{X}} \text{-----} \xrightarrow{\text{Y}}$ | Peroxide | Dry acetone |
18. Account for the following: 3
- (a) Vinyl chloride is unreactive towards nucleophilic substitution reactions
 - (b) Neopentyl bromide undergoes nucleophilic substitution reaction very slowly.
 - (c) Allylic and benzylic halides show high reactivity towards the S_N¹ reaction.
19. With the help of an example, discuss the stereo chemistry involved in S_N1 and S_N2 Mechanism. 3
20. a) p - nitro chlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structures as well.
b) An optically active compound (d)/(+) having molecular formula C₄H₉Cl with aq.KOH gives (-) alcohol. Write the mechanism of the reaction. 3
21. How will you convert the following? 3
- (a) Benzyl alcohol to phenylethanenitrile
 - (b) Aniline to Iodobenzene
 - (c) Ethyl chloride to Propane
22. How will you distinguish between the following: 3
- (a) Chlorobenzene and benzyl chloride.
 - (b) Chloroethane and bromoethane
 - (c) Chlorobenzene and cyclohexyl chloride.
23. Explain why tert-butyl chloride reacts with aqueous sodium hydroxide by S_N¹ mechanism while n-butyl chloride reacts by S_N² mechanism. 3
24. Give reasons: 3
- (a) Boiling point of bromoethane is higher than that of chloroethane.
 - (b) Haloarenes are insoluble in water but soluble in benzene.

- (c) Anti Markovnikov rule or peroxide effect applies to addition of HBr only and not to the addition of HCl or HI.
25. a) Name the reagent used to convert bromoethane to ethoxyethane. 3
 b) Why are haloarenes much less reactive than haloalkanes towards nucleophilic substitution reactions?
- 26 Compound 'A' with molecular formula C₄H₉Br is treated with aq. KOH solution. 3
 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 aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.
 Write down the structural formula of both compounds 'A' and 'B'.
 Out of these two compounds, which one will be converted to the product with inverted configuration?
 Ans: (A) = tert. Butyl bromide (B) = 2-Bromobutane
27. Find out (A, B, C and D) : (A) $\xrightarrow{\text{Br}_2/\text{hv}}$ (B) $\xrightarrow{\text{alc.KOH}}$ CH₂=CH₂ $\xrightarrow{\text{Br}_2/\text{CCl}_4}$ (C) $\xrightarrow[\text{ii) NaNH}_2]{\text{alc.KOH}}$ (D) 3
28. Explain the following in one or two sentences: 5
 Allyl chloride is hydrolysed more readily than n-propyl chloride
 Vinyl chloride is hydrolysed more slowly than ethyl chloride.
 Complete the following :
- (i) $(\text{CH}_3)_3\text{C-Br} \xrightarrow{\text{Mg}} \dots \xrightarrow{\text{H}_2\text{O}} \dots$
- (ii) $(\text{CH}_3)_3\text{C-CH}_2\text{-Br} \xrightarrow{\text{C}_2\text{H}_5\text{ONa / C}_2\text{H}_5\text{OH}} \dots$
- (iii)  + $(\text{CH}_3)_3\text{C-CH}_2\text{-Br} \xrightarrow{\text{Anhyd AlCl}_3} \dots$
29. Primary alkyl halide (A) C₄H₉Br reacted with alcoholic KOH to give compounds (B). Compound (B) is reacted with HBr to give (C) which is an isomer of (A). 5
 When (A) was reacted with Na metal, it gave a compound C₈H₁₈ that was different than compound when n-butyl bromide was reacted with sodium. Give the structural formula of (A) and write the equation for all the reactions.
 Ans: (A) : 1-Bromo-2-methyl propane (B) : 2-Methyl prop-1-ene (C): 2-Bromo-2-methyl propane (D) : 2,5 Dimethylhexane
30. (a) Compound (A), C₈H₉Br, gives a white precipitate when warmed with alcoholic AgNO₃. Oxidation of A gives an acid (B), C₈H₆O₄. (B) easily forms anhydride on heating. Identify the compound (A). Give equations for all reactions.
 (b) Haloalkanes react with KCN to give alkyl cyanide as main product while with AgCN they form isocyanide as main product. Give reason.

HIGH ORDER THINKING QUESTIONS

31. a) Organic halogen compounds used in industry as solvents are chlorides rather than bromides and iodides. Give reason.
 b) Iodoform has antiseptic properties Give one reason to support your answer.
 c) How do the polar solvents help in the first step in S_N1 mechanism? 3

32. Optically active 2-Iodoctane with NaI in dry acetone gives a product which does not show optical activity. 2

CASE BASED QUESTIONS

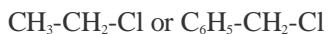
Read the passage given below and answer the following questions:

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (S_N2) and substitution nucleophilic unimolecular (S_N1) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards S_N1 and S_N2 reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. S_N2 reaction mechanism is favoured mostly by primary alkyl halide or transition state and polarity of solvent, S_N2 reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of S_N1 reactions.

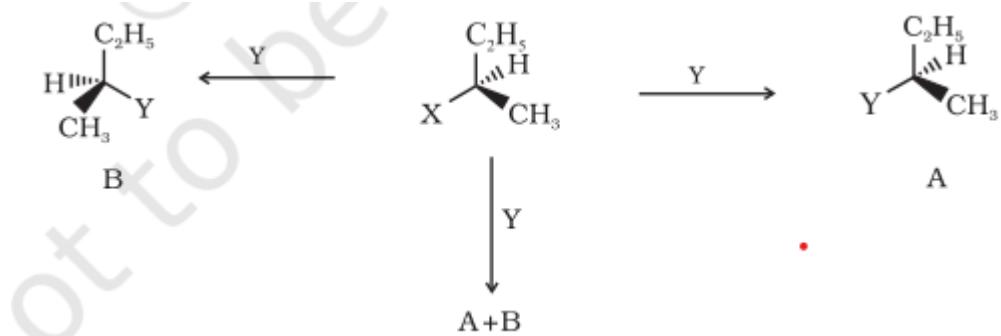
- i) **Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism**
Why?

ii)

Which of the compounds will react faster in S_N1 reaction with the “OH” ion?



ii) Identify the configuration A, B, and A+B



Assignment
Alcohols, Phenols and Ethers

S.No	Question Details
MCQ QUESTIONS	
1.	Phenol reacts with bromine in CS₂ at low temperature to give
	2. m-bromophenol 3. o-and p-bromophenol 4. p-bromophenol 5. 2,4,6-tribromophenol
2.	When phenol is treated with excess bromine water it gives
	6. m-bromophenol 7. o- and p-bromophenol 8. 2,4-dibromophenol 9. 2,4,6-tribromophenol
3.	Phenol on reduction with H₂in the presence of Ni catalyst gives
	10. benzene 11. toluene 12. cyclohexane 13. Cyclohexanol
4.	Dehydration of alcohol is an example of
	14. addition reaction 15. elimination reaction 16. substitution reaction 17. redox reaction
5.	The compound obtained by the reaction of ethene with diborane followed by hydrolysis with alkaline H₂O₂ is
	18. ethanol 19. propanol 20. ethanol 21. triethyl bromide
6.	The alcohol which does not react with Lucas reagent is
	22. isobutyl alcohol 23. n-butanol 24. tert-butyl alcohol 25. sec-butyl alcohol

7. Phenol is less acidic than

- 26. p-ehoxy phenol
- 27. p-methoxyphenol
- 28. p-nitrophenol
- 29. Ethanol

8. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives

- 30. diphenyl ether
- 31. p-hydroxyazobenzene
- 32. chlorobenzene
- 33. Benzene

9. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields

- (a) o - cresol
- (b) m - cresol
- (c) 2, 4 - dihydroxytoluene
- (d) benzyl alcohol

10. $\text{CH}_3\text{CH}_2\text{OH}$ can be converted into CH_3CHO by _____.

- (i) catalytic hydrogenation
- (ii) treatment with LiAlH_4
- (iii) treatment with pyridinium chlorochromate
- (iv) treatment with KMnO_4

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

- (i) Assertion and reason both are correct and reason is correct explanation of assertion.
- (ii) Assertion and reason both are wrong statements.
- (iii) Assertion is correct statement but reason is wrong statement.
- (iv) Assertion is wrong statement but reason is correct statement.

1. Assertion : Ethyl phenyl ether on reaction with HBr form phenol and ethyl bromide.

Reason : Cleavage of C—O bond takes place on ethyl oxygen bond due to the more stable phenyl-oxygen bond.

2. Assertion (A) Boiling points of alcohols and ethers are high.

Reason (R) They can form intermolecular hydrogen-bonding.

3. 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.

4. Assertion : Bond angle in ethers is slightly less than the tetrahedral angle.

Reason : There is a repulsion between the two bulky ($-\text{R}$) groups.

5. Assertion : Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason : Lewis acid polarises the bromine molecule

SA & LA QUESTIONS

1. Why doesn't Phenol undergo protonation readily? 1
2. Mention two important uses of methanol. 1
3. Sodium ethoxide is stronger base than sodium hydroxide. Why? 1
4. Explain why phenols do not undergo substitution of the --OH group like alcohols? 1
5. How will you know whether a given -OH group is alcoholic or phenolic in nature? 1
6. What happens when : 2
 - (i) aluminium reacts with *t*-butylalcohol
 - (ii) phenol is oxidised with chromic acid
7. (a) Starting from phenol, how will you get salicylic acid? 2
 (b) Convert ethylbromide to diethyl ether.
8. Account for the following: 2
 - (a) Alcohols act as weak bases.
 - (b) Phenols exhibit an acidic character.
9. Explain why cleavage of phenyl alkyl ethers with HBr always produces phenol & alkyl bromides and not bromobenzene & alkanols. Also write the equation involved. 2
10. Show with the help of chemical equations what happens when : 2
 - (a) ethanol is treated with phosphorus tribromide
 - (b) Cumene Hydroperoxide is treated with dil. H_2SO_4
11. Give chemical test to distinguish the following pairs of compounds: 3
 - (a) Methanol & Ethanol
 - (b) Isopropyl alcohol & n-propyl alcohol
 - (c) ethanol & phenol
12. Identify X, Y and Z in the following sequence of reactions : 3
 - (i) Phenol $\xrightarrow{Zn \text{ dust}}$ X $\xrightarrow[\text{Anhyd. } AlCl_3]{CH_3Cl}$ Y $\xrightarrow[\text{OH}^-]{KMnO_4}$ Z
 - (ii) Ethanol $\xrightarrow{PBr_3}$ X $\xrightarrow{\text{alc. KOH}}$ Y $\xrightarrow{\text{dil. } H_2SO_4}$ Z
13. How are the following conversions carried out? 3
 - 1 Propane to propan-2-ol
 - 2 Ethyl magnesium chloride to propan-1-ol
 - 3 Methyl magnesium bromide to 2-methylpropan-2-ol
14. Explain with reasons: 3
 - 1 Alcohols are comparatively more soluble in water than the corresponding hydrocarbons.
 - (b) Bond angle of methanol is lesser than the methoxy methane.
 - (c) C-O bond length in methanol is more than phenol.
15. Account for the following: 3

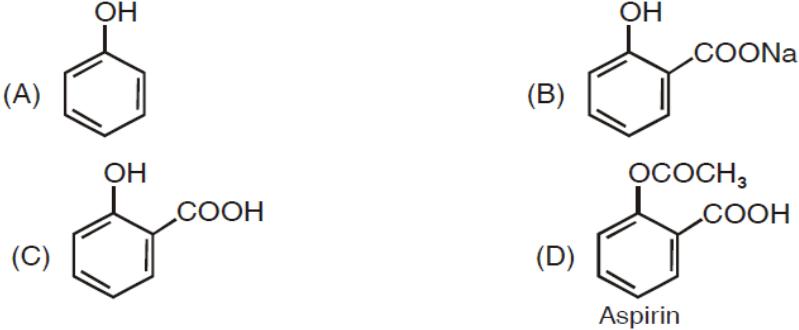
- (a) phenol has smaller dipole moment than methanol
 (b) For iodination of alcohols, H_3PO_4 is used and not H_2SO_4 with KI.
 (c) Boiling points of ether are much lower than corresponding alcohols.

- 16.** An alcohol A ($C_4H_{10}O$) on oxidation with acidified potassium dichromate gives carboxylic acid B ($C_4H_8O_2$). Compound A when dehydrated with conc. H_2SO_4 at 443 K gives compound C. Treatment of C with aqueous H_2SO_4 gives compound D. ($C_4H_{10}O$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D and write their structures. 5

[Ans. : [A] : $(CH_3)_2CHCH_2OH$ [B] : $CH_3CH(CH_3)COOH$
 [C] : $(CH_3)_2C = CH_2$ [D] : $(CH_3)_3C - OH$

- 17.** An organic compound A having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$. When A is treated with NaOH and CO_2 at 400 K under pressure compound B is obtained. Compound B on acidification gives, compound C which reacts with acetyl chloride to form D, which is a popular pain killer. Deduce the structure of A, B, C and D. What is the common name of Drug D? 5

[Ans. :



HIGH ORDER THINKING QUESTIONS

- 18.** (a) Why is preparation of ethers by acid catalysed dehydration of 2° and 3°alcohols not a suitable method ? 3
 (b) Why is Sulphuric acid not used during reaction of alcohol with KI?
 (c) How will you account for the following Ethers possess a net dipole moment even if they are symmetrical in structure?
- 19.** (a) R—Cl is hydrolysed to R—OH slowly but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture. 3
 (b) What is formed if cyclopentanone is reduced with H_2 / Pt . Give equation for the reaction.
- 20.** (a) Explain why ethers can be cleaved with acids not with bases?
 (b) Arrange the following in increasing order of basicity: H_2O , OH^- , CH_3OH , CH_3O^- . Give reasons for your answer. 3

Miss Usha was asked to synthesize alcohol by acidic hydration of 1-butene. She was unaware of the fact that the vessel she used had some coating of a metal , and in addition to alcohol ,compound X was isolated .X forms bisulphate compound Y as well as 2,4-dinitrophenylhydrazone. Separation of alcohol could be made by physical as well as by chemical methods. Answer the following Qs.

- 21.** How are alcohol acid X formed?
22. Can alcohol acid X give iodoform test?

23. Write down all reactions involve?
24. What is the name of Y compound?

CASE BASED QUESTION

Read the passage given below and answer the following questions:

Although chlorobenzene is inert to nucleophilic substitution, however it gives quantitative yield of phenol when heated with aq. NaOH at high temperature and under high pressure. As far as electrophilic substitution in phenol is concerned the - OH group is an activating group, hence, its presence enhances the electrophilic substitution at o- and p-positions.

- i Phenol undergoes electrophilic substitution more readily than benzene. Why?
- ii) Write the reaction
a) Phenol on treatment with excess of conc. HNO_3
b) Phenol on treatment with dilute HNO_3 .
- iii) Compare the acidity of alcohols and phenols. Give proof for your answer.

Unit VIII - Aldehydes, Ketones and Carboxylic acids

S.No.	Question Details
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MULTIPLE CHOICE QUESTIONS

1. Which of the reactions below can result in ketones?

- a) Oxidation of primary alcohols
- b) Oxidation of secondary alcohols
- c) Dehydrogenation of tertiary alcohols
- d) Dehydrogenation of primary alcohols

2. The Rosenmund reaction can produce which of the following carbonyl compounds?

- a) Methanal
- b) Benzaldehyde
- c) Butanone
- d) Acetone

3. Acetone combines with ethylene glycol in dry HCl gas to generate _____

- a) hemiacetals
- b) cyclic ketals
- c) cyclic acetals
- d) acetals

4. Which of the following compounds is formed when benzyl alcohol is oxidised with KMnO_4 ?

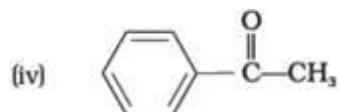
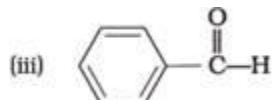
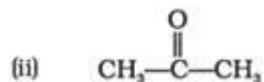
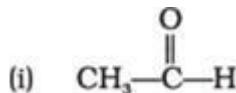
- a) CO_2 and H_2O
- b) Benzoic acid
- c) Benzaldehyde
- d) Benzophenone

5. Which of the following substances is the least water-soluble?

- a) Methanal
- b) Pentanal
- c) Propanone
- d) Ethanal

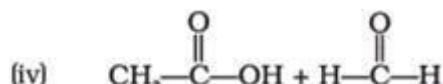
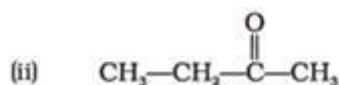
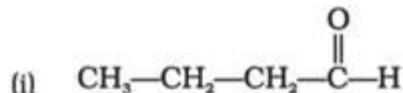
6.

Which of the following compounds is most reactive towards nucleophilic addition reactions?



7.

Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following products will be formed on addition of water to but-1-yne under these conditions.



8.

The correct order of increasing acidic strength is _____.

(i) Phenol < Ethanol < Chloroacetic acid < Acetic acid

(ii) Ethanol < Phenol < Chloroacetic acid < Acetic acid

(iii) Ethanol < Phenol < Acetic acid < Chloroacetic acid

(iv) Chloroacetic acid < Acetic acid < Phenol < Ethanol

9.

. Cannizzaro's reaction is not given by _____.



(iii) H CHO

(iv) CH₃CHO

10.

The reagent which does not react with both, acetone and benzaldehyde.

(i) Sodium hydrogensulphite

(ii) Phenyl hydrazine

(iii) Fehling's solution

(iv) Grignard reagent

ASSERTION and REASONS

1. Assertion (A): Carboxylic acids contain a carbonyl group but do not give characteristic reactions of the carbonyl group.

Reason (R): Due to resonance, the electrophilic nature of the carboxyl carbon is greatly reduced as compared to the carbonyl carbon in aldehydes and ketones.

2. 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.

3. **Assertion :** Compounds containing –CHO group are easily oxidised to corresponding carboxylic acids.

Reason : Carboxylic acids can be reduced to alcohols by treatment with LiAlH_4 .

4. **Assertion :** Formaldehyde is a planar molecule.

Reason : It contains sp^2 hybridised carbon atom.

5. Assertion (A):, Aldehydes and ketones both react with Tollen's reagent to form a silver mirror.

Reason (R):, Both aldehydes and ketones contain a carbonyl group

SA & LA QUESTIONS

- | | | |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|
| 1. | Write the structure of the 2-formyl pentanoic acid | 1 |
| 2. | Arrange the following compounds in increasing order of their property as indicated:
Acetaldehyde, acetone, Di tert butyl ketone, Methyl tert butyl ketone (reactivity towards HCN) | 1 |
| 3. | Arrange the following compounds in decreasing order of their boiling points:
CH_3CHO , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{CH}_3$ | 1 |
| 4. | Write the IUPAC name of the following compound:
$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_2\text{CHO}$ | 1 |
| 5. | Carboxylic acids do not give characteristics reactions of carbonyl groups why? | 1 |
| 6. | Give chemical tests to distinguish between the following pairs of compounds:
(a) Acetophenone and benzophenone (b) propanal and propanone | 2 |
| 7. | An aliphatic compound A with a molecular formula of $\text{C}_3\text{H}_6\text{O}$ reacts with phenyl hydrazine to give compound B. reaction of A with I_2 in alkaline medium on warming, gives a yellow precipitate C. Identify the compounds A, B and C. | 2 |
| 8. | Two moles of an organic compound A on treatment with a strong base gives two compounds B and C. Compound B on dehydrogenation with Cu gives A while acidification of C yields carboxylic acid D having molecular formula of CH_2O_2 . Identify the compounds A, B, C and D. | 2 |
| 9. | How are the following conversations carried out?
(a) Acetic acid to methylamine (b) Acetaldehyde to methane | 2 |
| 10. | Give reasons:
Butanol & butanal have the same solubility in water but they have large difference in boiling points.
(b) Aldehydes & ketones have high dipole moments. | 2 |
| 11. | A compound (X), $\text{C}_2\text{H}_4\text{O}$ on oxidation gives (Y), $\text{C}_2\text{H}_4\text{O}_2$. (X) undergoes haloform reaction. On treatment with HCN, (X) forms a product (Z) which on hydrolysis gives 2-Hydroxy propanoic acid.
(a) Write down structures of X and Y.
(b) Name the product when X reacts with dil. NaOH.
(c) Write down the equations for the reactions involved. | 3 |
| 12. | Give reasons: | 3 |

- (a) Aliphatic carboxylic acids are stronger than phenol.
 A carboxylic acid does not form a hydrazone although it contains $>\text{C}=\text{O}$ group.
 Acetic acid can be halogenated in the presence of red P & Br_2 but formic acid cannot be halogenated in the same way.
- 13.** Give reasons: 3
 (a) Sodium bisulphite is used for the purification of aldehydes & ketones.
 Oxidation of Toluene with CrO_3 to benzaldehyde is carried out in the presence of acetic anhydride.
 (c) Hydrazones of aldehydes are not prepared in highly acidic medium.
- 14.** An organic compound A (molecular formula $\text{C}_3\text{H}_6\text{O}$) is resistant to oxidation but forms a compound B ($\text{C}_3\text{H}_8\text{O}$) on reduction. B reacts with HBr to form a bromide C which on treatment with alcoholic KOH forms an alkene D (C_3H_6). Deduce the structures of A, B, C and D. 3
- 15.** Give reasons: 3
 (a) Benzaldehyde does not undergo aldol condensation.
 (b) Aldehydes are more volatile than corresponding alcohols.
 (c) Reaction of ethanal and ethanol takes place in the presence of dry HCl.
- 16.** Give reasons: 3
 (a) The melting & boiling point of aromatic acids are usually higher than aliphatic acids of comparable molecular masses.
 (b) Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid.
 (c) During the preparation of ammonia derivatives from aldehydes & ketones, pH of the solution is fully controlled.
- 17.** Write the equations and conditions to show how the following conversions are carried out: 3
 (a) propanol to butan-2-one.
 (b) Isopropyl chloride to 2-methylpropanaldehyde
 (c) benzoic acid to benzyl chloride
- 18.** How would you obtain the following from the named sources: 3
 (a) Tertiary butyl alcohol from acetone
 (b) Benzene from toluene
 (c) Acetone from acetic acid
- 19.** Compound A of molecular formula $\text{C}_5\text{H}_{11}\text{Br}$ yields a compound B of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ when treated with aqueous NaOH. On oxidation, the compound B yields a ketone C. Vigorous oxidation of the ketone yields a mixture of ethanoic & propanoic acid. Deduce the structure of A, B & C. 3
- 20.** State one chemical method each to distinguish between the following pairs of organic compounds: 3
 (a) Acetaldehyde and acetone
 (b) Phenol and benzoic acid
 (c) Propanone and ethanol.
- 21.** (a) What happens when:
 (i) Acetaldehyde reacts with HCN.
 (ii) Propanoic acid is treated with chlorine in the presence of a small amount of red phosphorus. 5

Although phenoxide ion has more resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Give reason.

(c) Give the probable mechanism of esterification.

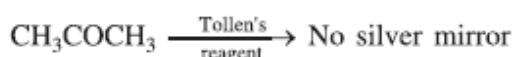
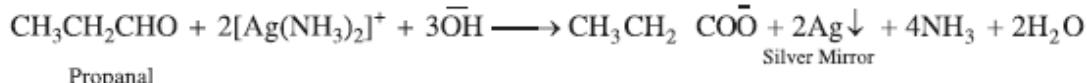
HIGH ORDER THINKING QUESTIONS

22. (a) Give simple chemical tests to distinguish between the following: 3
- (i) Propanal and propanone
 - (ii) Benzaldehyde and acetophenone
 - (b) How would you obtain
 - (i) But-2-enal from ethanal?
 - (ii) Butanoic acid from butanol?
 - (iii) Benzoic acid from ethylbenzene?
23. (b) Arrange the following compounds in an increasing order of their indicated property: 2
- Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acids strength)
 $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$,
 $(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (acid strength)
- (b) How would you bring about the following conversions:
- (i) Propanone to Propene
 - (ii) Benzoic acid to Benzaldehyde
 - (iii) Bromobenzene to 1-phenylethanol

Q No 24

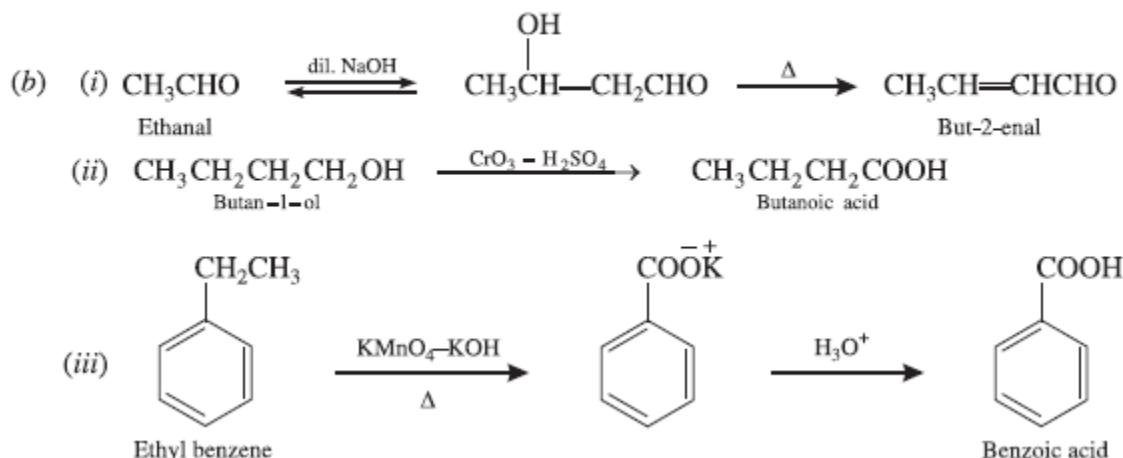
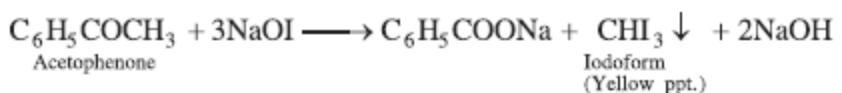
- (a) (i) Propanal and propanone

Tollen's reagent test: Propanal being an aldehyde reduces Tollen's reagent to silver mirror but propanone being a ketone does not.



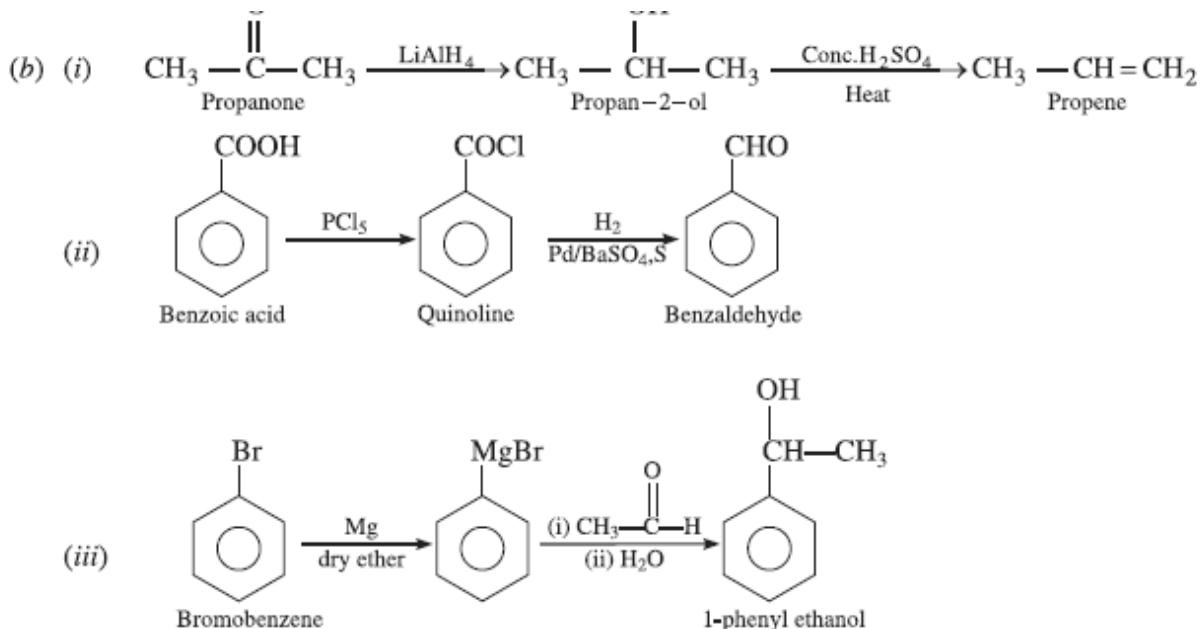
- (ii) Benzaldehyde and acetophenone

Iodoform test: Acetophenone being a methyl ketone on treatment with I_2/NaOH undergoes Iodoform reaction to give yellow ppt. of iodoform but benzaldehyde does not.



Q No 25

- (a) (i) Acid strength: 4-Methoxy benzoic acid < Benzoic acid < 4-Nitrobenzoic acid
< 3, 4-Dinitrobenzoic acid.
- (ii) Acid strength: $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} < \text{CH}_3\text{CH(Br)CH}_2\text{COOH}$
< $\text{CH}_3\text{CH}_2\text{CH(Br)COOH}$

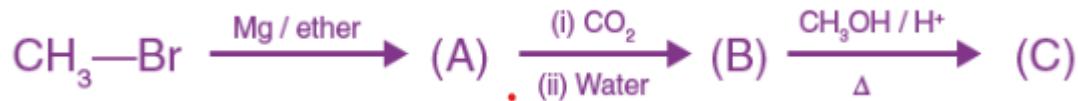


CASE BASED QUESTIONS

Aldehydes, Ketones, and Carboxylic Acids are carbonyl compounds which contain a carbon-oxygen double bond. These organic compounds are very important in the field of organic chemistry and also have many industrial applications.

Alkenes undergo electrophilic addition, whereas aldehydes and ketones undergo nucleophilic addition because, in alkenes, the double bond joins two carbon atoms, and there is no resultant polarity. While in carbonyl compounds, the double bond joins atoms having different polarities. The polarity in the carbonyl bond makes it vulnerable to a nucleophile addition reaction. Aldehydes, Ketones, and Carboxylic Acids are carbonyl compounds which contain a carbon-oxygen double bond. These organic compounds are very important in the field of organic chemistry and also have many industrial applications.

- i) Carboxylic acids contain the carbonyl group but do not show the nucleophilic addition reaction like aldehydes or ketones. Why?
- ii) Why are carboxylic acids more acidic than alcohols or phenols, although they all have hydrogen atoms attached to an oxygen atom (-O-H)?
- iii) Identify the compounds A, B, C



Organic Compounds containing Nitrogen

S.No.	Question Details	Marks
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MULTIPLE CHOICE QUESTIONS

1.

Acetamide can be converted to methenamine by which of the following reactions?

1. Stephen's reaction
2. Hoffmann bromamide reaction
3. Carbylamine reaction
4. Gabriel phthalimide synthesis

2. An aldehyde on reaction with primary amine forms

- a) ketone
- b) Schiff's base
- c) aromatic acid
- d) carboxylic acid

3. Benzene-diazonium chloride on reaction with phenol in weakly basic medium gives

- a) Diphenyl ether
- b) p-hydroxyazobenzene
- c) Chlorobenzene
- d) Benzene

4. Which one of the following does not contain the -COOH group?

- a) Picric acid
- b) Aspirin
- c) Benzoic acid
- d) Ethanoic acid

5. C_3H_9N can have how many structural isomers?

- a) 2
- b) 3
- c) 4
- d) 5

6. The bad-smelling substance formed by the action of alcoholic caustic potash on chloroform and aniline is

- a) Phenyl isocynide
- b) Chloroprin
- c) Acetanilide
- d) cyanide

7. Which of the following compound will form secondary amine on reaction with $LiAlH_4$?

- a) Methyl cyanide
- b) Methyl isocyanide
- c) Acetamide
- d) Nitroethane

8. Find the compound which is more basic than aniline

- a) Benylamine
- b) Diphenylamine
- c) Triphenylamine
- d) P-nitro aniline

9. Treatment of NH_3 with excess of ethyl chloride gives:

- (a) diethylamine (b) ethane (c) tetraethylammonium chloride (d) methylamine

10. Which among the following amines will give carbylamine reaction?

- (a) $CH_3-CH_2-NH_2$ (b) $CH_3-NH-CH_3$ (c) $(C_6H_5)_3N$ (d) $CH_3-CH_2-NH-OH$

ASSERTION and REASON

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

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

(v) Assertion is wrong statement but reason is correct statement

1. Assertion : Amines are basic in nature
 - . Reason : Amines have lone pair of electrons on nitrogen atom. . The lone pair can be easily donated.
 2. Assertion (A):, Amines have a higher boiling point than the corresponding alcohols.
Reason (R):, **Alcohols possess intramolecular H-bonding.**
 3. **Assertion:** Aromatic 1° amines can be prepared by Gabriel Phthalimide Synthesis.
Reason: Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.
 4. Assertion: Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.
Reason: Acyl group sterically hinders the approach of further acyl groups.
 5. **Assertion :** Hoffmann's bromamide reaction is given by primary amines.
Reason : Primary amines are more basic than secondary amines.

SA & LA QUESTIONS

essential constituent of Tincture iodine. (B) on reaction with chloroform and alkali gave an offensive smelling substance (D). Identify A, B, C and D.

15. Give possible explanations for the following: 3

- The presence of a base is needed in the ammonolysis of alkyl halides.
- Although trimethyl amine and n-propyl amine have the same molecular weight, the former boils at a lower temperature than the latter.
- Paramethoxy aniline is a stronger base than aniline but paranitroaniline is a weaker base than aniline.

16. Account for the following observation: 3

Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

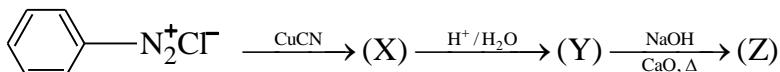
17. (1) How will you convert benzene to aniline? 3

- Why aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis?

18. (1) Write the structure of the foul smelling compound obtained when aniline is treated with chloroform in the presence of KOH. 3

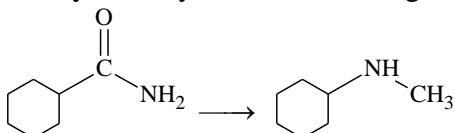
- While preparing monobromoaniline why is aniline acetylated before reacting it with bromine?
Explain.

19. Identify X,Y,Z 3



20. (1) Nitrobenzene does not undergo Friedel crafts alkylation. Give Reason. 3

- How will you carry out the following conversions?



21. (1) Consider the following reaction, 3



Identify A,B,C

- (2) Which of the following reaction gives are RCH_2NH_2

- $\text{R-CN} \xrightarrow{\text{LiAlH}_4}$
- $\text{RCONH}_2 \xrightarrow{\text{KOH} + \text{Br}_2}$
- $\text{R-CH = N - OH} \xrightarrow{\text{LiAlH}_4}$
- $\text{RCH}_2\text{NC} \xrightarrow{\text{H}_3\text{O}^+}$

Solution: (a, c, d)

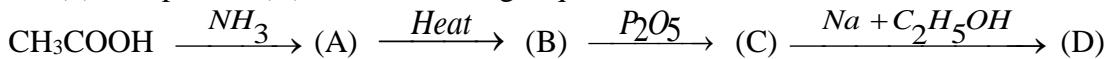
22. (1) Why is it difficult to prepare pure amines by ammonolysis of alkyl halide? 5

- Aniline dissolves in aqueous HCl. Why?

- Why are aryldiazonium ion more stable than alkyl diazonium ion?

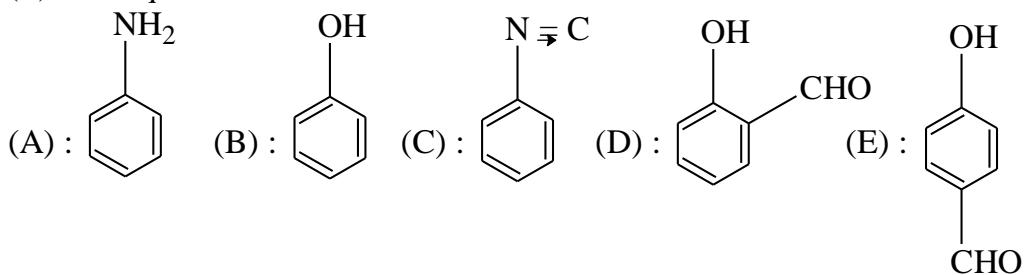
- Write chemical reaction of aniline with benzoyl chloride and write name of the product obtained.

- The product(D) in the following sequence of reactions is,



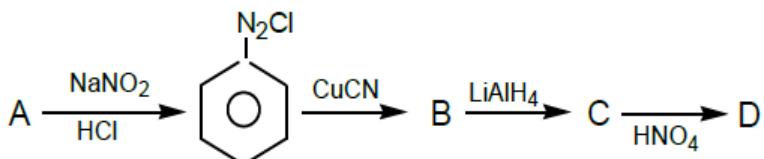
23. A mixture of two aromatic compounds (A) and (B) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound (A), when heated with alcoholic solution of KOH produced a compound (C) ($\text{C}_7\text{H}_5\text{N}$) associated with an unpleasant odour. The

alkaline aqueous layer on the other hand, when heated with chloroform and then acidified, gives a mixture of two isomeric compounds (D) and (E) of molecular formula $C_7H_6O_2$. Identify the compounds (A), (B), (C), (D) and (E). Give equations.

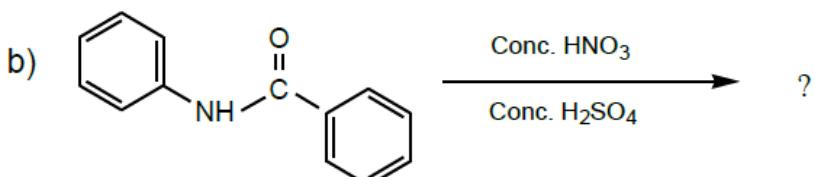
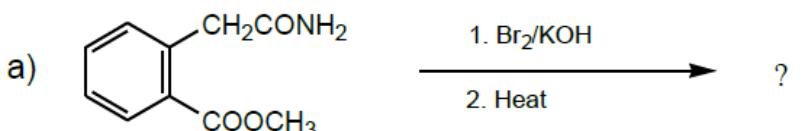


HIGH ORDER THINKING QUESTIONS

24. Identify A, B, C & D



25. Complete the following:-



26. Three isomeric amines A, B and C have the molecular formula C_3H_9N . Compound A on reaction with benzene sulphonyl chloride forms a product which is soluble in NaOH. Compound B on reaction with benzene sulphonyl chloride forms a product which is insoluble in NaOH and compound C does not react with benzene sulphonyl chloride. Identify A, B and C. [Ans. : (A) $CH_3CH_2CH_2NH_2$ (B) $CH_3CH_2NHCH_3$ (C) $(CH_3)_3N$]

CASE BASED QUESTION

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 C_7H_5N (C) associated with unpleasant odour.

- i) What is A?
- ii) The reaction of (A) with alcoholic solution of KOH to produce (C) of unpleasant odour is called?
- iii) 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 ?
- iv) In the chemical reaction,
 $CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow (A) + (B) + 3H_2O$,
the compounds (A) and (B) ?

UNIT: X Biomolecules

Carbohydrates

The carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.

Reducing sugars

Carbohydrates which reduce Fehling's solution and Tollen's reagent. Eg: monosaccharides.

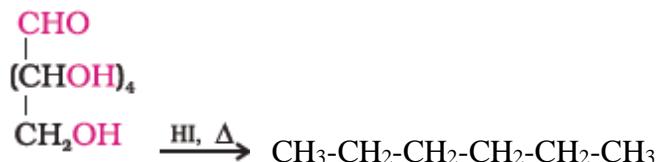
Non-reducing sugars

If the reducing group of monosaccharides is bonded the carbohydrates are non-reducing sugars. Eg: Sucrose.

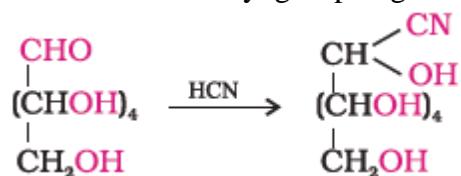
Glucose

Reactions which explains the structure of glucose

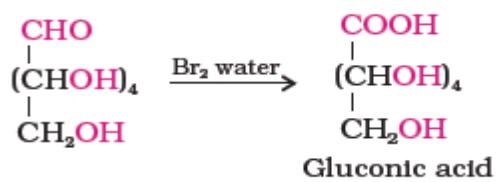
1) This reaction shows that all the six carbon atoms are linked in a straight chain.



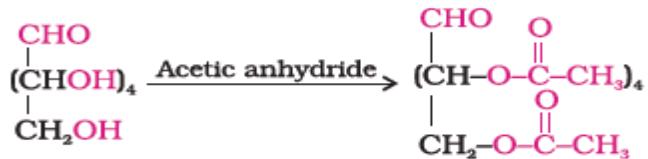
2) This reaction confirms the presence of a carbonyl group in glucose.



3) This indicates that carbonyl group is present as an aldehydic group.



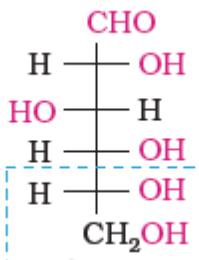
- 4) This indicates the presence of five –OH groups and since it exists as a stable compound the five –OH groups are attached to different carbon atoms.



- 5) This indicates the presence of primary alcoholic group in glucose.



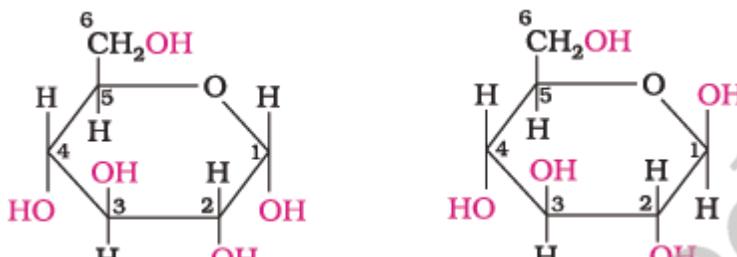
Fischer Projection formula of D-(+)-Glucose



Anomers

The two cyclic hemiacetal forms of glucose which differ in the configuration of the hydroxyl group at C1 called anomers. α -glucose and β -glucose are the two anomers.

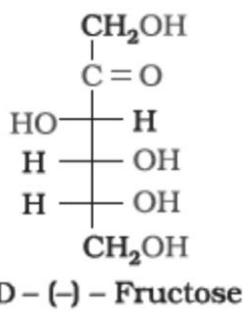
Pyranose /Haworth Structure of D-(+)-glucose



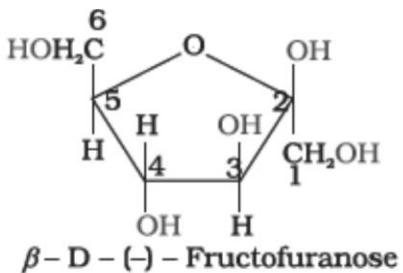
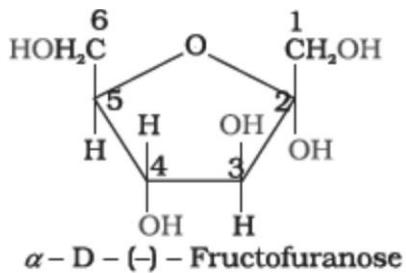
α -D-(+)-glucose

β -D-(+)-glucose

Open chain structure of D-(-)-Fructose



Furanose structure of D-(-)-Fructose

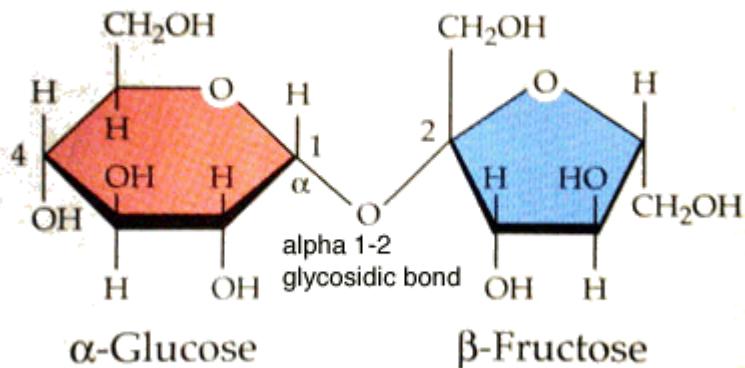


Glycosidic linkages

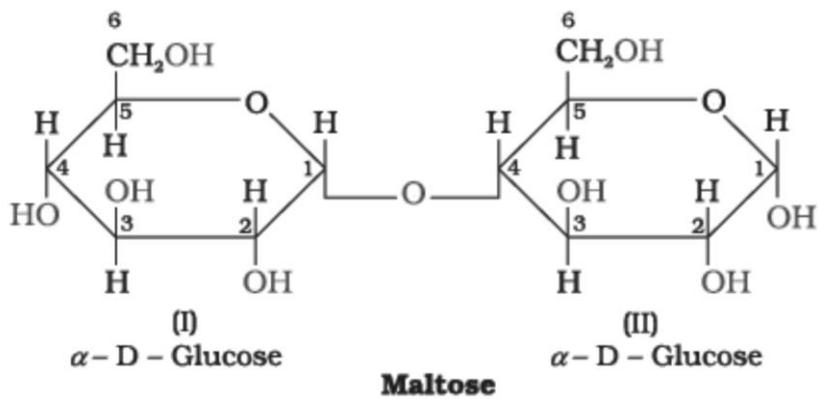
The two monosaccharides joined together by an oxide linkage formed by the loss of water molecule.

Structure of Sucrose

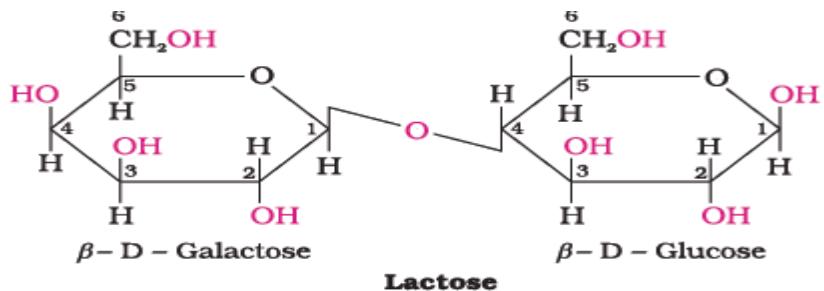
Sucrose has the molecular formula C₁₂H₂₂O₁₁



Structure of Maltose



Structure of Lactose



Differences between Amylose and Amylopectin

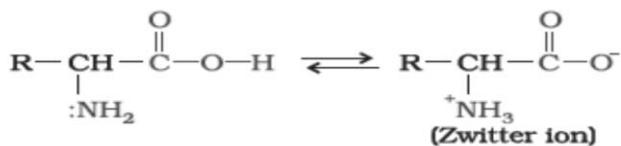
Amylose	Amylopectin
1.Water soluble component	1.Insoluble in water
2.Constitutes about 15-20% starch	2.Constitutes about 80-85% starch
3.A long unbranched chain with α D-(+)-Glucose units held by C1 –C4 glycosidic linkage	3.It is a branched chain polymer of α D-(+)-Glucose units in which the chain is formed by C1 –C4 glycosidic linkage whereas branching occurs by C1 –C6 glycosidic linkage

Differences between Starch and Cellulose

Starch	Cellulose
1.Main storage polysaccharide in plants	1.It is a predominant constituent of cell wall of plants.
2.It contains two components Amylose: A long unbranched chain with α D-(+)-Glucose units held by C1 –C4 glycosidic linkage. Amylopectin: It is a branched chain polymer of α D-(+)-Glucose units in which the chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.	2.It is a long chain polymer of β D-(+)-Glucose units in which the chain is formed by C1 –C4 glycosidic linkage.

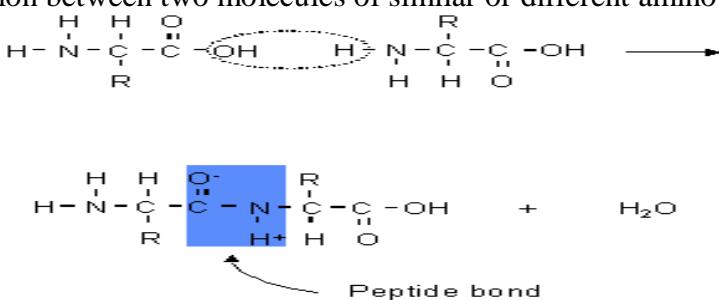
Amino acids

- Amino acids are colourless, crystalline solids, water-soluble, high melting solids and behave like salts due to the presence of both basic (amino) and acidic (carboxyl group).
- In aqueous solution amino acids form Zwitter ion which shows amphoteric behaviour as they act with both acids and bases.



Peptide bond /Peptide linkage

It is an amide or peptide bond (-CO-NH-) formed between -COOH and -NH₂ group during the reaction between two molecules of similar or different amino acids.



Primary structure of proteins

The sequence of the amino acids is said to be the primary structure of the proteins.

Secondary structure of the proteins

It refers to the shape in which a long polypeptide chain can exist. These structures arise due to the regular folding of the backbone of the polypeptide chain due to hydrogen bonding between $>\text{C}=\text{O}$ and $-\text{NH}$ groups of the peptide bond.

■ α -Helix structure

A polypeptide chain forms hydrogen bonds by twisting into a right handed screw (helix) with $-\text{NH}$ group of each amino acid residue hydrogen bonded to the $>\text{C}=\text{O}$ of an adjacent turn of the helix.

■ β -pleated sheet structure

All the polypeptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds.

Tertiary structure of the proteins

It represents overall folding of the secondary structure.

■ Fibrous protein

When the polypeptide chains run parallel and are held together by hydrogen bonds and disulphide bonds, then fibre like structure is formed. It is insoluble in water. Eg: Keratin and myosin.

■ Globular protein

When the chains of the polypeptides coil around to give a spherical shape. It is soluble in water. Eg: Insulin and albumin.

Quaternary structure of proteins

The spatial arrangement of the subunits (two or more polypeptide chains in a protein) with respect to each other.

- The main forces which stabilize the secondary and tertiary structure of the proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces.

Native protein

Protein found in the biological system with a unique three dimensional structure and biological activity.

Denaturation of protein

When a protein in its native form is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed .Due to this the globules unfold and helix gets uncoiled and protein loses its biological activity.

Eg.: Coagulation of egg white on boiling and curdling of milk.

- During denaturation the 2⁰ and 3⁰ structures are destroyed but 1⁰ structure remains intact.

Nucleic acids

Long chain polymers of nucleotides joined together by phosphodiester linkage between 5' and 3' carbon atoms of pentose sugar.

Differences between DNA (deoxyribonucleic acid) and RNA(ribonucleic acid)

DNA (deoxyribonucleic acid)	RNA(ribonucleic acid)
1.The sugar moiety is β-D-2-deoxyribose	1. The sugar moiety is β-D-ribose
2.The four bases are adenine(A), guanine(G), cytosine(C) and thymine(T)	2.The four bases are adenine(A), guanine(G), cytosine(C) and uracil(U)

Differences between nucleoside and nucleotide

Nucleoside	Nucleotide
1. A unit formed by the attachment of a base to 1' position of sugar moiety.	1. When nucleoside is linked to phosphoric acid at 5' position of sugar moiety.

Structure of DNA

DNA has a double strand helix structure .The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine (A=T) whereas cytosine forms hydrogen bonds with guanine (C≡G).

Structure of RNA

RNA has a single strand helix structure .Sometimes they fold back on themselves to form a double s helix structure. The three types of RNA are **messenger RNA(m-RNA)**, **ribosomal RNA(r-RNA)** and **transfer RNA(t-RNA)**.

Biological functions of nucleic acid

- DNA is chemical basis of heredity and the reserve of genetic information.
- Proteins are synthesized by the various RNA molecules but the message for the synthesis of a particular protein is present in DNA.

**Assignment
BIOMOLECULES**

MULTIPLE CHOICE QUESTIONS

1.

A disaccharide is formed when two monosaccharides are bonded together by a bond.

- a) glycosidic
- b) peptide
- c) ionic
- d) phosphodiester

2. Sucrose is a _____ chemical, and the hydrolysis product combination is _____ in nature.

- a) dextrorotatory; dextrorotatory
- b) laevorotatory; laevorotatory
- c) laevorotatory; dextrorotatory
- d) dextrorotatory; laevorotatory

3. Which of the following statements about maltose is incorrect?

- a) It consists of two glucopyranose units
- b) It is a disaccharide
- c) Glycosidic bond between C1 of one unit and C4 of the other unit
- d) It is a non-reducing sugar

4. Which of the following statements about starch is incorrect?

- a) It gives blue colour with iodine
- b) It is a polymer of α -D-glucose
- c) It is a reducing carbohydrate
- d) It consists of branched chains

5. RNA lacks the nitrogen base of _____

- a) Thymine
- b) Cytosine
- c) Uracil
- d) Adenine

6. Which of the following chemical classes does not belong to the vast group of carbohydrates?

- a) Polyhydroxy ketones
- b) Polyhalo aldehydes
- c) Polyamino aldehydes
- d) Polyhydroxy carboxylic acids

7. When converting a disaccharide to monosaccharides, which bond is hydrolyzed?

- a) Disulfide bond
- b) Glycosidic bond
- c) Phosphodiester bond
- d) Hydrogen bond

8. The number of tripeptide formed by 3 different amino acids.

- (a) Three
- (b) Four
- (c) Five
- (d) Six.

9. The number of tripeptide formed by 3 different amino acids

- (a) Three
- (b) Four

- (c) Five
- (d) Six.

ASSERTION and REASON

These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

Q.1. Assertion : D(+)- Glucose is dextrorotatory in nature.

Reason : ‘D’ represents its dextrorotatory nature.

2. Assertion : Sucrose is called an invert sugar.

Reason : On hydrolysis, sucrose bring the change in the sign of rotation from dextro (+) to laevo(-).

3. Assertion : At isoelectric point, the amino group does not migrate under the influence of electric field.

Reason : At isoelectric point, amino acid exists as a zwitterion.

4. Assertion : Vitamin D cannot be stored in our body

Reason : Vitamin D is fat soluble vitamin and is excreted from the body in urine

5. 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.

SA & LA QUESTIONS

1.	What happens when protein is denatured?	1
2.	Which types of bonds are responsible for the secondary and tertiary structure of proteins?	1
3.	What are the products obtained by the complete hydrolysis of DNA?	1
4.	If a fragment of one strand in DNA molecule has the base sequence CCATGCATG, what is the base sequence of the complementary strand?	1
5.	What type of bonding helps in the α helix structure of proteins?	1
6.	Draw the Haworth structure of α -D-(+)-Glucopyranose. What is the significance of D and + here?	2
7.	What are reducing and non-reducing sugars? Give examples.	2
8.	What are essential and non-essential amino acids? Give examples.	2
9.	What is glycogen? How it is different from starch?	2
10.	Differentiate between Purine and Pyrimidine bases.	2
11.	a) Draw the open chain structural formula of aldohexose. b) What is a peptide bond? Illustrate its formation with an example.	3
12.	a) What is glycosidic linkage? b) Enumerate the reactions of D-glucose which cannot be explained by its open chain structure.	3
13.	a) Write the three types of RNA. b) Give the examples of water soluble vitamins, its sources and the deficiency disease caused by them.	3
14.	What are the polysaccharides that make up starch and what is the difference between them?	3
15.	Write chemical equations for the reactions of glucose with: (i) acetic anhydride (ii) HI (iii) Conc. Nitric acid	3
16.	Differentiate between: (i) Starch and cellulose (ii) RNA and DNA (iii) α -helix and β -sheet structure (iv) nucleotide and nucleoside (v) globular protein and fibrous protein	5
17.	(i) Account for the following: a) Despite having an aldehydic group glucose does not give 2, 4 DNP test. b) Amino acids have relatively higher melting points as compared to corresponding halo acids. (c) Amino acids have amphoteric behavior. (ii) What are nucleic acids? Give its functions.	5

HIGH ORDER THINKING QUESTIONS

21.	A compound (A) $C_6H_{12}O_6$ is oxidized by bromine water into monobasic acid. It also reduces tollen's reagent and reacts with HCN to give a compound (B) which on hydrolysis give compound (C). On treating (C) with HI/red P, n-heptatonic acid is obtained. Compound (A) on treatment with excess of phenyl hydrazine gave D-glucosazone (D). Give the structures of A,B,C and D and draw the cyclic form of A.	3
22.	An optically active amino acid (A) can exist in three forms depending on the pH of the medium. The molecular formula of (A) is $C_3H_7NO_2$. (i) Write the structure of compound (A) in aqueous medium. What are such ions called? (ii) In which medium the cationic form of compound (A) exist? (iii) In alkaline medium towards which electrode will the compound (A) migrate in electric field?	3
23.	(i) Amino acids show amphoteric behavior. Why? (ii) Starch forms an emulsion rather than solution with water. Why?	3

(iii) When DNA is hydrolysed, there is a definite relation among the quantities of different bases obtained. But for hydrolysis of RNA, it is not so. What does this suggest about the structure of DNA and RNA?

.

CASE BASED QUESTION

Read the passage given below and answer the following questions:

Proteins are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc. They occur in every part of the body and form the fundamental basis of structure and functions of life. 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. 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, curding of milk, formation of cheese when an acid is added to milk.

- i) α -helix and β -pleated structures of proteins are classified as?
- ii) Name the monomer present in proteins.
- iii) What do you meant by Zwitter ion? Give example.
- iv) Where does the water present in the egg go after boiling the egg?



مدرسۃ دلھی الخاصۃ ذ.م.م.
DELHI PRIVATE SCHOOL L.L.C.

Affiliated to C.B.S.E., DELHI

(Approved & Recognized By Ministry of Education - United Arab Emirates)

PERIODIC TEST 1 (2022-23)

Subject: CHEMISTRY

Max. Marks:35

Grade: XII

Time:1Hr15mts

Name:

Section:

Roll No:

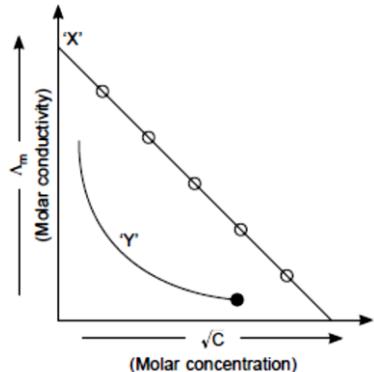
General Instructions:

- GENERAL INSTRUCTIONS: Read the following instructions carefully.
 - There are 16 questions in this question paper.
 - SECTION A - Q. No. 1 to 5 are multiple choice questions carrying 1marks each.
 - SECTION B - Q. No. 6 to 10 are short answer questions carrying 2 marks each.
 - SECTION C- Q. No. 11 to 15 are short answer questions carrying 3 marks each.
 - SECTION C- Q. No. 16 is a long answer question carrying 5 mark.
 - All questions are compulsory.
 - Use of calculators is not allowed

SECTION A

1. The azeotropic mixture of water and ethanol boils at 78.15°C. When this mixture is distilled, it is 1
possible to obtain:
(a) pure H₂O
(b) pure C₂H₅OH
(c) pure H₂O as well as pure C₂H₅OH
(d) neither H₂O nor C₂H₅OH in their pure state
- 2 Determine the value of E°cell for the following reaction, 1
 $Cu^{2+} + Sn^{+2} \rightarrow Cu + Sn^{+4}$, if the equilibrium constant is 10⁶.
(a) 0.1773
(b) 0.01773
(c) 0.2153
(d) 1.773
- 3 The unit of ebullioscopic constant is _____. 1
(a) K kg mol⁻¹ or K (molality)⁻¹
(b) mol kg K⁻¹ or K⁻¹(molality)
(c) kg mol⁻¹ K⁻¹ or K⁻¹(molality)⁻¹
(d) K mol kg⁻¹ or K (molality)
- 4 The value of $\Lambda^{\circ} m$ for NH₄Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 Ohm⁻¹ cm² mol⁻¹ 1
respectively. Calculate $\Lambda^{\circ} m$ for NH₄OH solution.
(a) 215.5
(b) 251.5
(c) 244.7
(d) 351.5
- 5 Which of the following solutions are isotonic with respect to one another? 1
(1) 0.15 M urea (2) 0.05 M CaCl₂ (3) 0.1 M MgSO₄ (4) 0.15 M glucose
Select the correct answer using the codes given below:
(a) 1 and 4
(b) 1, 2 and 4
(c) 2 and 3
(d) 2, 3 and 4
- SECTION B**
- 6 What happens when R.B.C. are placed in : 2
a) 0.1% NaCl solution?
b) 1 % NaCl solution?
- 7 Consider the electrochemical cell : Zn (s) / Zn²⁺ (aq) // Cu²⁺ (aq) / Cu. It has an electrical 2
potential of 1.1 V when concentration of Zn²⁺ and Cu²⁺ ions is unity. State the direction of flow
of electrons and also specify if Zinc and Copper are deposited or dissolved at their respective
electrodes. When :
a) an external opposite potential of 0.8 V is applied.
b) an external opposite potential of 1.4 V is applied.
- 8 2 g of benzoic acid (C₆H₅COOH) dissolved in 25 g of benzene shows a depression in freezing 2
point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol⁻¹. What is the
percentage association of acid if it forms dimer in solution?

- 9 Calculate the degree of dissociation (α) of acetic acid, if its molar conductivity (λ_m) is 39.05 S cm² mol⁻¹. 2
 Given : $\lambda^\circ (H^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ (CH_3COO^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$
- 10 Observe the graph shown in figure between λ_m (molar conductivity) Vs C (Molar concentration) and answer the questions based on graph. 2



- a) The curve 'Y' is for KCl or CH₃COOH?
- b) What is the intercept on λ_m axis for 'X' equal to?
- c) Give mathematical equation representing straight line.

SECTION C

- 11 (a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution: 3
- $$Ag^+ (aq) + e^- \rightarrow Ag (s) \quad E^\circ = +0.80 \text{ V}$$
- $$H^+ (aq) + e^- \rightarrow \frac{1}{2}H_2 (g) \quad E^\circ = 0.00 \text{ V}$$
- On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?
- (b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration?
- 12 The electrical resistance of a column of 0.05M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. 3
- 13 Given reason for the following :— 3
- (a) Aquatic species are more comfortable in cold waters than in warm waters.
 - (b) To avoid bends scuba divers use air diluted with helium.
 - (c) Cold drinks bottles are sealed under high pressure of CO₂.
- 14 $E^\circ (Cu^{2+}/Cu)$ and $E^\circ (Ag^+/Ag)$ is + 0.337 V and + 0.799 V respectively. Make a cell whose EMF is positive. If the concentration of Cu²⁺ is 0.01M and E_{cell} at 25°C is zero, calculate the concentration of Ag⁺. 3
- 15 a) Draw the total vapour pressure vs. mol fraction diagram for a binary solution exhibiting non-ideal behaviour with negative deviation. 3

b) When 1 mole of NaCl is added to 1 litre water, the boiling point increases but when 1 mole of CH₃OH is added to 1 litre water, the boiling point decreases. Suggest reasons.

SECTION D

- 16 a) Why do gases always tend to be less soluble in liquids as the temperature is raised? 5
b) What is osmotic pressure? What advantage the osmotic pressure method has over elevation in boiling point method for determining molecular mass?
c) What are azeotropic mixtures? Give the types of azeotropic mixtures mentioning one example for each.



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PT 1 – SUBJECTIVE PAPER (2022-2023)

Subject: Chemistry	Max. Marks: 35
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Grade: XII	Time:
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Name:	Section:	Roll No:
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- | | | |
|----|---------------------------------------------------------------------------------------|---|
| 1. | (d) neither H ₂ O nor C ₂ H ₅ OH in their pure state | 1 |
| 2 | (a) 0.1773 | 1 |
| 3 | (a) K kg mol ⁻¹ or K (molality) ⁻¹ | 1 |
| 4 | (b) 251.5 | 1 |
| 5 | (b) 1, 2 and 4 | 1 |

6 a) 0.1% NaCl solution is hypotonic solution in which RBC will swell up due to difference in osmotic pressure and burst 2

b) 1 % NaCl solution is hypertonic solution in which RBC cell shrinks.

7 c) Electrons will flow from Zn to Cu ; Zn dissolves and Cu gets deposited 2
d) Electrons will flow from Cu to Zn ; Zn gets deposited and Cu dissolves

8 $\Delta T_f = i K_f w_2 \times 1000 / M_2 \times w_1$ 2

$$i = 0.504$$

$$\alpha = i-1 / 1/n - 1 = 0.992$$

$$\% \alpha = 99.2 \%$$

$$\begin{aligned} 9 \quad \Lambda^{\circ}_{\text{CH}_3\text{COOH}} &= \lambda^{\circ}_{\text{CH}_3\text{COO}^-} + \lambda^{\circ}_{\text{H}^+} \\ &= 40.9 + 349.6 = 390.5 \text{ S cm}^2/\text{mol} \\ &= 39.05/390.5 \\ &= 0.1 \end{aligned} \quad 2$$

10 d) CH₃COOH 2
e) λ^0_m
f) $\lambda_m = \lambda^0_m - A\sqrt{c}$

11 a) Ag⁺ + e⁻ → Ag 3
The one with higher E⁰ value will undergo reduction at cathode

b) When the concentration of the electrolyte approaches zero, the molar conductivity is known as **limiting molar conductivity**.

Conductivity is due to number of ions per unit volume, which decreases on dilution.

12 Diameter = 1 cm, radius = 0.5 cm 3

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

$$\rho = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \times 0.785}{50}$$

$$= 87.135 \text{ ohm cm}$$

$$\text{Conductivity (k)} = \frac{1}{\rho} = \frac{1}{87.135} = 0.01148 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$= 0.01148 \text{ ohm cm}$$

$$\text{Molar conductivity } \Lambda_m^c = \frac{K \times 1000}{M} = \frac{0.01148 \times 1000}{0.05}$$

$$= 229.6 \text{ Scm}^2 \text{ mol}^{-1}$$

13 Given reason for the following :— 3

- (a) Solubility of oxygen in water increases with decrease in temperature as solubility of a gas in given liquid decreases with increase in temperature.
(b) Since Helium has a very high Kh value, it decreases the solubility of air in blood.

(c) At high pressure the K_h value decreases thereby increasing the solubility of CO_2 in water.

14

3

Cu is more reactive than silver, so that the cell is as Cu/Cu^{2+} (0.01M) $\parallel \text{Ag}^+(\text{C})/\text{Ag}$ or cell reaction

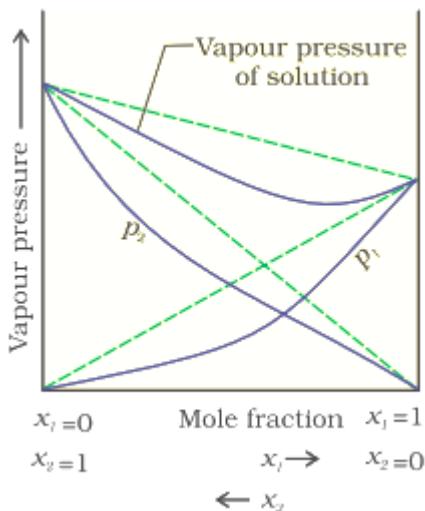


$$\begin{aligned}E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}][\text{Ag}]}{[\text{Cu}][\text{Ag}^+]^2} \\&= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{(0.01) \times 1^2}{1 \times [\text{Ag}^+]^2}\end{aligned}$$

Or $[\text{Ag}^+] = 1.47 \times 10^{-9} \text{ M}$

15

3



b) Methyl alcohol is more volatile than water. But NaCl is non-volatile solute. On addition of NaCl in water , vapour pressure is lowered and as a result boiling point of water increased. But on addition of methyl alcohol ,vapour pressure is more than that of water. Hence boiling point decreases.

5



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PERIODIC TEST 2 (2022-23)

Subject: CHEMISTRY

Max. Marks:35

Grade: XII

Time:1Hr15mts

Name:

Section:

Roll No:

General Instructions:

- GENERAL INSTRUCTIONS: Read the following instructions carefully.
 1. There are 16 questions in this question paper.
 2. SECTION A - Q. No. 1 to 5 are questions carrying 1mark each.
 3. SECTION B - Q. No. 6 to 10 are short answer questions carrying 2 marks each.
 4. SECTION C- Q. No. 11 to 15 are short answer questions carrying 3 marks each.
 5. SECTION C- Q. No. 16 is a long answer question carrying 5 marks.
 6. All questions are compulsory.
 7. Use of calculators is not allowed

SECTION A

1. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because
- it has variable ionisation enthalpy
 - it has a tendency to attain noble gas configuration
 - it has a tendency to attain f^7 configuration
 - it resembles Pb^{4+}

- 2 In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not because 1
 a) Cr (VI) is more stable than Mo(VI) and W(VI).
 b) Mo (VI) and W (VI) are more stable than Cr(VI).
 c) Higher oxidation states of heavier members of group-6 of transition series are less stable.
 d) Lower oxidation states of heavier members of group-6 of transition series are more stable.
- 3 Which cell will measure standard electrode potential of copper electrode? 1
 (a) $\text{Pt}(\text{s}) | \text{H}_2(\text{g}, 0.1 \text{ bar}) | \text{H}^+(\text{aq., 1 M}) || \text{Cu}^{2+}(\text{aq., 1 M}) | \text{Cu}$
 (b) $\text{Pt}(\text{s}) | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(\text{aq., 1 M}) || \text{Cu}^{2+}(\text{aq., 2 M}) | \text{Cu}$
 (c) $\text{Pt}(\text{s}) | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(\text{aq., 1 M}) || \text{Cu}^{2+}(\text{aq., 1 M}) | \text{Cu}$
 (d) $\text{Pt}(\text{s}) | \text{H}_2(\text{g}, 0.1 \text{ bar}) | \text{H}^+(\text{aq., 0.1 M}) || \text{Cu}^{2+}(\text{aq., 1 M}) | \text{Cu}$
- 4 The reaction which is taking place in nickel - cadmium battery can be represented by which of the following equation? 1
 (a) $\text{Cd} + \text{NiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Cd}(\text{OH})_2 + \text{Ni}(\text{OH})_2$
 (b) $\text{Cd} + \text{NiO}_2 + 2\text{OH}^- \rightarrow \text{Ni} + \text{Cd}(\text{OH})_2$
 (c) $\text{Ni} + \text{Cd}(\text{OH})_2 \rightarrow \text{Cd} + \text{Ni}(\text{OH})_2$
 (d) $\text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2 \rightarrow \text{Ni} + \text{Cd} + 2\text{H}_2\text{O}$
- 5 How much electricity in terms of Faraday is required to produce 100g of Ca from molten CaCl_2 1
 a) 2F
 b) 3F
 c) 4F
 d) 5F
- SECTION B**
- 6 Explain why does colour of KMnO_4 disappears when oxalic acid is added to its solution in acidic medium? 2
- 7 Calculate the emf of the following cell at 298 K: 2
 $\text{Al}(\text{s})/\text{Al}^{3+}(0.15\text{M})//\text{Cu}^{2+}(0.025\text{M})/\text{Cu}(\text{s})$
 (Given $E^\circ(\text{Al}^{3+}/\text{Al}) = -1.66 \text{ V}$, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$, $\log 0.15 = -0.8239$, $\log 0.025 = -1.6020$)
- 8 Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why? 2
- 9 Define fuel cell with an example and write the cathode and anode reaction for it. 2
- 10 Mention the type of compounds formed when small atoms like H, C and N get trapped inside the crystal lattice of transition metals. Also, give physical and chemical characteristics of these compounds. (Any two) 2
- SECTION C**
- 11 Observed and calculated values for the standard electrode potentials of elements from Ti to Zn in the first reactivity series are depicted in figure (1): 3

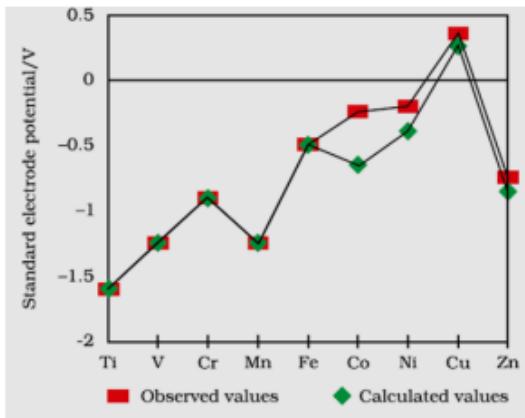


FIGURE 1

Explain the following observations:

- i. The general trend towards less negative E° values across the series
- ii. The unique behaviour of Copper
- iii. More negative E° values of Mn and Zn

- 12 a) Write the products of electrolysis of aqueous solution of NaCl with platinum electrodes 3
- b) 0.1 M KCl solution offered a resistance of 100 ohms in a conductivity cell at 298 K. If the cell constant of the cell is 1.29 cm^{-1} , calculate the molar conductivity of KCl solution
- 13 When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and explain the reactions. 3
- 14 What is disproportionation reaction? Calculate the equilibrium constant for the disproportionation of copper (I) ion in aqueous solution. {Given $E^\circ \text{Cu}^{2+}, \text{Cu} = +0.34 \text{ V}$; $E^\circ \text{Cu}^+, \text{Cu} = +0.52 \text{ V}$ } 3
- 15 Explain the following: 3
- a) Out of Sc^{3+} , Co^{2+} and Cr^{3+} ions, only Sc^{3+} is colourless in aqueous solutions.
 - b) $\text{La}(\text{OH})_3$ is more basic than $\text{Lu}(\text{OH})_3$.
 - c) Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?

SECTION D

- 16 a) i) What type of cell is Lead storage battery? 5
- ii) Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery while operating?
- iii) How does the density of the electrolyte change when the battery is discharged?
- b) How many moles of mercury will be produced by electrolysing 1.0 M $\text{Hg}(\text{NO}_3)_2$ solution with a current of 2.00 A for three hours?

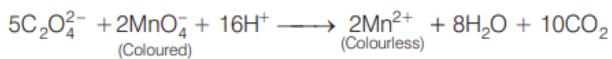


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PT 2 ANSWER KEY (2022-2023)

Subject: Chemistry	Max. Marks: 35	
Grade: XII	Time:	
Name:	Section:	Roll No:

1. b 1
2. b 1
3. c 1
4. a 1
5. d 1
6. When oxalic acid is added to acidic solution of KMnO₄, its colour disappear due to reduction of MnO₄⁻ ion to Mn²⁺. Chemical reaction occurring during this neutralisation reaction is as follows



7. (ii) E°cell = E°cathode - E°anode = 0.34 - (-1.66) = 2.00 V 2
 $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$

Here n = 6

$$\begin{aligned}E_{\text{cell}} &= 2 - \frac{0.059}{6} \log \frac{[0.15]^2}{[0.025]^3} \\&= 2 - 0.059/6 (2\log 0.15 - 3\log 0.025) \\&= 2 - 0.059/6 (-1.6478 + 4.8062) = 2 - 0.0311 = 1.9689\text{V}\end{aligned}$$

- 8 For Th, Pa and U, 5f electrons start filling and they have lower penetration than 4f electrons for Ce, Pr and Nd. **Removal of weakly bound 5f electrons is easier than removing 4f electrons**, so ionization enthalpy for Th, Pa and U is lower than Ce, Pr and Nd. 2
- 9 Galvanic cell that are designed to convert the energy of combustion of fuel like hydrogen, methane, methanol directly into electrical energy are called fuel cell. 2
 Cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ Anode reaction: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$ Overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- 10 Interstitial compounds are formed when small atoms like H, C or N are trapped inside the crystal lattices of metal. They are usually non-stoichiometric and are neither typically ionic nor covalent. 2
 The principal physical and chemical characteristics of these compounds are as follows:
 (i) They have high melting points, higher than those of pure metals.
 (ii) They are very hard, some borides approach diamond in hardness.
 (iii) They retain metallic conductivity.
 (iv) They are chemically inert.
- 11 (i) The general trend towards less negative E_V values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. 3
 (ii) The high energy to transform Cu(s) to Cu²⁺(aq) is not balanced by its hydration enthalpy.
 (iii) The stability of the half-filled d sub-shell in Mn²⁺ and the completely filled d 10 configuration in Zn²⁺ are related to their more negative E_{oV} values
- 12 a) Anode: Cl₂ ↑ Cathode: H₂ ↑ 3
Explanation: in the electrolysis of aqueous NaCl, the ions produced will be -Na⁺, Cl⁻, H⁺ and OH⁻ released by the dissociation of NaCl and H₂O respectively.
- At the Cathode:
 $Na^+(aq) + e^- \rightarrow Na(s)$, E_(red)⁰ = - 2.71 V
 $H^+(aq) + e^- \rightarrow 1/2 H_2(s)$, E_(red)⁰ = 0.00 V
 As the reaction with high E_{cell} is preferred, H is released at cathode
- At the anode:
 $Cl^-(aq) \rightarrow 1/2 Cl_2(g)$, E_(cell)⁰ = - 2.71 V
 Chlorine gets oxidized at anode to give chlorine at the anode.
- b)
- $$\begin{aligned} G' &= \kappa R \\ \kappa &= \frac{1.29}{100} = 0.0129 \text{ S cm}^{-1} \\ \Lambda_m &= \frac{1000 \kappa}{C} \\ \Lambda_m &= \frac{1000 \times 0.0129}{0.1} \\ \Lambda_m &= 129 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$
- 13 K₂Cr₂O₇ is an orange compound. It is formed when Na₂Cr₂O₇ reacts with KCl. In acidic medium, yellow coloured CrO₄²⁻ (chromate ion) changes into dichromate. The given process is the preparation method of potassium dichromate from chromite ore. 3
 $A = FeCr_2O_4$; $B = Na_2CrO_4$; $C = Na_2Cr_2O_7$; $D = K_2Cr_2O_7$.
- (i) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{[A]}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2 \xrightarrow{\text{[B]}}$
- (ii) $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$
- (iii) $Na_2Cr_2O_7 + 2KCl \xrightarrow{\text{[C]}} K_2Cr_2O_7 + 2NaCl \xrightarrow{\text{[D]}}$

14

3

$$\begin{aligned}2 Cu^+ &\rightarrow Cu + Cu^{2+} \\At \text{ Anode} : Cu^+ &\rightarrow Cu^{2+} + e^- \\At \text{ cathode} Cu^+ + e^- &\rightarrow Cu \\E^0 &= E^0_{ox} + E^0_{Red} \\&= E^0_{Cu^+/Cu^{2+}} + E^0_{Cu^{2+}/Cu} \\&= -0.34 + 0.52 \\&= 0.18 \text{ V}\end{aligned}$$

The relationship between ΔG and equilibrium constant is

$$\Delta G = -2.303 RT \log K$$

$$\Delta G = -nFE^0$$

So

$$-nFE^0 = -2.303 RT \log K$$

$$nfE^0 = 2.303 RT \log K$$

$$\log K = \frac{nfE^0}{2.303 RT} = \frac{1 \times 96500 \times 0.18}{2.303 \times 8.314 \times 298} \quad (\text{at the std condition } T = 298 \text{ K})$$

$$\log K = 3.044$$

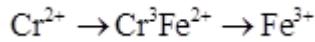
$$K = A \log (3.044) = 1.11 \times 10^3$$

15

3

- a) Co^{2+} : [Ar]3d7 Sc^{3+} : [Ar]3d0 Cr^{3+} : [Ar]3d3 Co^{2+} and Cr^{3+} have unpaired electrons. Thus, they are coloured in aqueous solution. Sc^{3+} has no unpaired electron. Thus it is colourless.
- b) Due to lanthanoid contraction the size of lanthanoid ion decreases regularly with increase in atomic size. Thus covalent character between lanthanoid ion and OH^- increases from La^{3+} to Lu^{3+} . Thus the basic character of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$

- c) The following reactions are involved when Cr^{2+} and Fe^{2+} act as reducing agents.



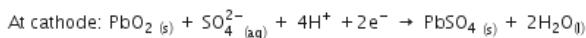
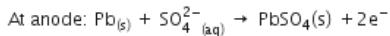
The $E^0_{Cr^{3+}/Cr^{2+}}$ value is -0.41 V and $E^0_{Fe^{3+}/Fe^{2+}}$ is +0.77 V. This means that Cr^{2+} can be easily oxidized to Cr^{3+} , but Fe^{2+} does not get oxidized to Fe^{3+} easily. Therefore, Cr^{2+} is a better reducing agent than Fe^{3+} .

16

5

- (a) A lead storage battery is a secondary battery.

The following chemical equations take place in a lead storage battery.



The overall cell reaction is given by,



- e) Density of electrolyte depends upon number of constituent ions present in per unit volume of electrolyte solution. In this case density of electrolyte decreases as water is formed and sulphuric acid is consumed as the product during discharge of the battery

f)

Ans. Current = 2A

Time = 3h = 3(60)(60)s

w = ZIt

Z for Hg in compound = 200.6/2F

$$w = 200.6 \times 2 \times (3)(60)(60) / 2(96500)$$

$$w = 22.45 \text{ g}$$

$$\text{number of moles} = 22.45 / 200.6 = 0.112 \text{ mol}$$



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HALF YEARLY EXAM (2022-23)

Subject: CHEMISTRY

Max. Marks:70

Grade: XII

Time: 3Hrs

Name:

Section:

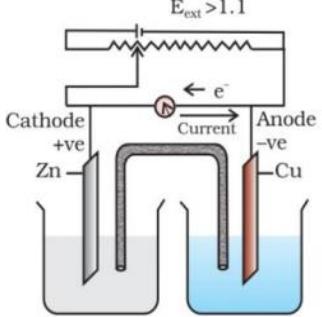
Roll No:

General Instructions:

- GENERAL INSTRUCTIONS: Read the following instructions carefully.
 1. There are 37 questions in this question paper.
 2. SECTION A - Q. No. 1 to 10 are multiple choice questions carrying 1mark each.
 3. SECTION B - Q. No. 11 to 20 are very short answer questions carrying 1 mark each.
 4. SECTION C- Q. No. 21 to 27 are short answer questions carrying 2 marks each.
 5. SECTION D- Q. No. 28 to 34 are short answer questions carrying 3 marks each.
 5. SECTION E- Q. No. 35 to 37 are long answer question carrying 5 marks.
 6. All questions are compulsory.
 7. Use of calculators is not allowed

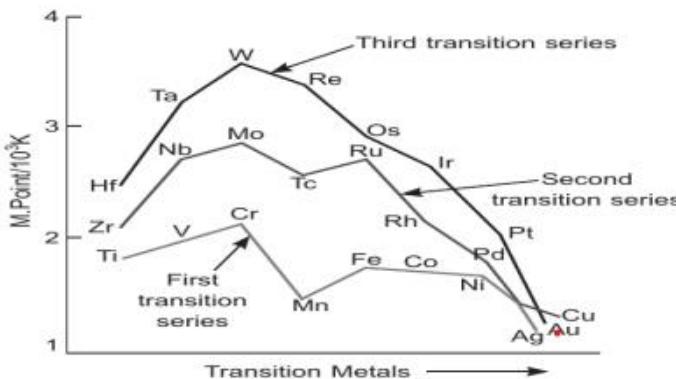
SECTION A

1	When mercuric iodide is added to the aqueous solution of potassium iodide, the: (a) Freezing point is raised (b) Freezing point does not change (c) Freezing point is lowered (d) Boiling point does not change	1
2	The molal elevation constant depends upon (a) nature of solute.	1

	(b) nature of the solvent. (c) vapour pressure of the solution. (d) enthalpy change.	
3	Limiting molar conductivity of NH_4OH is equal to :- (a) $\Lambda^\circ \text{mNH}_4\text{Cl} + \Lambda^\circ \text{mNaCl} + \Lambda^\circ \text{mNaOH}$ (b) $\Lambda^\circ \text{mNaOH} + \Lambda^\circ \text{mNaCl} - \Lambda^\circ \text{mNH}_4\text{Cl}$ (c) $\Lambda^\circ \text{mNaOH} - \Lambda^\circ \text{mNH}_4\text{Cl} - \Lambda^\circ \text{mHCl}$ (d) $\Lambda^\circ \text{mNH}_4\text{Cl} + \Lambda^\circ \text{mNaOH} - \Lambda^\circ \text{mNaCl}$	1
4	The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is (a) 2.87 B.M. (b) 3.87 B.M. (c) 3.47 B.M (d) 3.57 B.M	1
5	 <p>Looking at the setup of an electrochemical cell, what happens when $E_{\text{ext}} > 1.1 \text{ V}$</p> <p>(a) Zn dissolves at anode & copper deposits at cathode (b) Current travels from Cu to Zn (c) Zinc deposits at anode and copper dissolves at cathode. (d) No current is obtained</p>	1
6	Molar conductivity of ionic solution depends on _____. (a) pressure (b) distance between electrodes (c) concentration of electrolytes in solution (d) surface area of electrodes	1
7	Solutions of two electrolytes 'A' and 'B' are diluted. The λ_m of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte? (a) electrolyte A (b) electrolyte B (c) electrolyte A & B (d) None of these	1
8	When 0.1 mol $\text{COCl}_3(\text{NH}_3)_5$ is treated with excess AgNO_3 ; 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to- (a) 1: 3 electrolyte	1

	(b) 1: 2 electrolyte (c) 1: 1 electrolyte (d) 3: 1 electrolyte											
9	Metallic radii of some transition elements are given below. Which of these elements will have highest density? <table style="margin-left: auto; margin-right: auto;"><tr><td>Element</td><td>Fe</td><td>Co</td><td>Ni</td><td>Cu</td></tr><tr><td>Metallic radii/pm</td><td>126</td><td>125</td><td>125</td><td>128</td></tr></table> (a) Fe (b) Ni (c) Co (d) Cu	Element	Fe	Co	Ni	Cu	Metallic radii/pm	126	125	125	128	1
Element	Fe	Co	Ni	Cu								
Metallic radii/pm	126	125	125	128								
10	In an octahedral crystal field, the t _{2g} orbital are (a) raised in energy by 0.4 Δ _o (b) lowered in energy by 0.4 Δ _o (c) raised in energy by 0.6 Δ _o (d) lowered in energy by 0.6 Δ _o	1										
	SECTION B											
11	Why a person suffering from high blood pressure is advised to take minimum quantity of common salt?	1										
12	What happens to vapour pressure of water, if a tablespoon of sugar is added to it? Give reason to your answer.	1										
13	The conductivity of metals decreases while that of electrolytes increases with increase in temperature. Why?	1										
14	Give reason: It is not easy to determine λ°m of a weak electrolyte by extrapolation of √c vs λm curves?	1										
15	What is the use of the platinum foil in hydrogen electrode?	1										
16	Write the IUPAC name of the linkage isomer of: [Co(NH ₃) ₅ NO ₂]Cl ₂	1										
17	What happens when KMnO ₄ is heated? Write the equation.	1										
18	Why is Cu ²⁺ ion coloured while Zn ²⁺ ion is colourless?	1										
19	Why is mercury a liquid?	1										
20	Why is Cr ³⁺ more stable than Cr ²⁺ ?	1										
	SECTION C											
21	Henry's law constant for the solubility of methane in benzene at 298 K is 4.27×10^5 mm Hg. What is the solubility of methane in benzene at 298 K under 760 mm Hg?	2										
22	How many electrons flow when a current of 5 amps is passed through a solution for 193 sec?	2										
23	"The chromates and dichromates are interconvertible by the change in pH of medium." Why? Give chemical equations in favour of your answer.	2										
24	a) How is the variability in oxidation states of transition metals different from that of the non-transition metals? b) The enthalpies of atomisation of the transition metals are high. Why?	2										

25	Explain that the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic on the basis of valence bond theory.	2
26	Explain the following: a) The coordination-complexes are known for transition elements only. b) Nickel (II) does not form low spin octahedral complexes.	2
27	a) When does electrochemical cell behaves like an electrolytic cell? b) What will happen if salt bridge is removed?	2
SECTION D		
28	Some ethylene glycol is added to your car's cooling system along with 5 kg of water. If the freezing point of water glycol solution is -15°C , what is the boiling point of the solution? ($K_b = 0.52 \text{ Kkg/mol}$, $K_f = 1.86 \text{ Kkg/mol}$ for water) OR On dissolving 19.5 g of CH_2FCOOH in 500 g of water a depression of 1°C in freezing point of water is observed. Calculate the Vant Hoff factor. Given $K_f = 1.86 \text{ K Kg mol}^{-1}$.	3
29	a) From the given molar conductivities at infinite dilution, calculate Λ_m^0 for NH_4OH Λ_m^0 for $\text{Ba}(\text{OH})_2 = 457.6 \text{ Scm}^2/\text{mol}$ Λ_m^0 for $\text{BaCl}_2 = 240.6 \text{ Scm}^2/\text{mol}$ Λ_m^0 for $\text{NH}_4\text{Cl} = 129.8 \text{ Scm}^2/\text{mol}$ b) The conductivity of 0.20M solution of KCl at 298K is 0.025 S/cm. Calculate its molar conductivity.	3
30	a) What is the role of ZnCl_2 in a dry cell? b) Calculate emf of the following cell $\text{Cd}/\text{Cd}^{2+} (.10 \text{ M})//\text{H}^+ (.20 \text{ M})/\text{H}_2 (0.5 \text{ atm})/\text{Pt}$ [Given E° for $\text{Cd}^{2+}/\text{Cd} = -0.403 \text{ V}$]	3
31	Answer the following questions: a) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (aq) is green in colour whereas $[\text{Ni}(\text{H}_2\text{O})_4(\text{en})]^{2+}$ (aq) is blue in colour , give reason in support of your answer . b) Write the formula and hybridization of the following compound: tris(ethane-1,2-diamine) cobalt (III) sulphate	3
32	Observe the graph of transition metal and answer the questions.	3



- a) Why does W (tungsten) has highest melting point in aqueous solution?
 b) Which element in 3d series has lowest enthalpy of atomization and why?
 c) How does density vary from left to right in 3d series and why?

33 a) Draw figure to show the splitting of d orbitals in an octahedral crystal field
 b) What is spectrochemical series ?

34 Explain Lanthanoid contraction, its cause & any two consequences? 3

. SECTION E

35 a) With the help of suitable diagram illustrate the two types of non-ideal solutions.
 b) At 25°C the saturated vapour pressure of water is 3.165kPa . Find the saturated vapour pressure of a 5% aqueous solution of urea at the same temperature.
 (molar mass of urea = 60 g/mol)

OR

- a) State Raoult's law for the solution containing volatile components. Write one difference between an ideal solution and a non-ideal solution
 b) Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25°C , assuming that it is completely dissociated.
 (Atomic mass of K = 39u , O = 16u , S = 32u)

36 For the complex $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$, identify :

- (a) The oxidation no. of iron.
- (b) The hybrid orbitals and the shape of the complex.
- (c) The magnetic behavior of the complex.
- (d) Draw the isomers of the complex.
- (e) Name of the complex. [At. No. of Fe = 26]

OR

- a) A metal ion Mn^{+} having d^4 valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta_o > P$:
- i) Write the electronic configuration of the valence electrons of the metal Mn^{+} in t_{2g} and e_g .
- ii) What type of hybridization will Mn^{+} have?
- iii) Name the type of isomerism exhibited by this complex.
- b) Give evidence that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ are ionisation isomers.

	c) Draw the isomers of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	
37	<p>a) Describe the preparation of potassium permanganate.</p> <p>d) How does the acidified permanganate solution react with iron (II) ions?</p> <p>e) Compare the chemistry of the actinoids with that of lanthanoids with reference to: (i) electronic configuration (ii) oxidation states</p> <p style="text-align: center;">OR</p> <p>a) Indicate the steps in the preparation of potassium dichromate from chromite ore.</p> <p>b) Write the ionic equations for its reaction with iron (II) solution.</p> <p>c) What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.</p>	



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DELHI PRIVATE SCHOOL L.L.C.

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(Approved & Recognized By Ministry of Education - United Arab Emirates)

HALF YEARLY EXAM (2022-23)

Subject: CHEMISTRY

Max. Marks:70

Grade: XII

Time: 3Hrs

Name:

Section:

Roll No:

SECTION A

1	(c) $\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$	1
2	(a) free energy change	1
3	(b)26	1
4	a)Unidentate	1
5	(a) A	1
6	$\odot 8,000 \text{ cm}^{-1}$	1
7	(b) $\Lambda = \lambda_0$ as $C \rightarrow 0$	1
8	c)Conductivity does not depend upon solvation of ions present in solution.	1
9	(b) lowered in energy by $0.4 \Delta\text{o}$	1
10	(d)It provides surface for redox reaction.	1

SECTION B

11	KI forms a complex with HgI ₂ . 2KI+HgI ₂ →K ₂ HgI ₄ Therefore, the number of particles in solution decreases resulting in the decrease in relative lowering of vapour pressure. Hence, vapour pressure increases.	1
12	All Cu(II) halides are known except the iodine because Cu ²⁺ oxidizes iodine to iodine 2Cu ²⁺ +4I ⁻ →2CuI(S)+I ₂ .	1
13	Chelating ligand is a ligand which is mostly attached to a central metal ion by bonds that are from two or more donor atoms. Example – en, EDTA	1
14	a. increase in concentration of Mn ⁺ ions in solution b. by increasing the temperature.	1
15	If the zinc coating is broken, the galvanized object remains protected against rusting because zinc is more reactive than iron and hence can be easily oxidized. Thus when zinc layer breaks down, the zinc continues to react and get oxidized. Hence iron object is protected.	1
16	$\Delta m(CH_3COOH)^\infty = \Delta HCl^\infty + \Delta CH_3COONa^\infty - \Delta NaCl^\infty$ $= \Delta CH_3COO^- + \Delta H^+$ $\Delta m^\infty CH_3COOH = 426 + 91 - 126$ $= 391 \text{ Scm}^2 \text{mol}^{-1}$	1
17	The process of movement of solvent through a semipermeable membrane from the solution to the pure solvent by applying excess pressure on the solution side is called reverse osmosis . It is used in desalination of water.	1
18	Because interionic forces of attractions are large.	1
19	Zr and Hf have almost identical atomic radii due to lanthanoid contraction. Hf is post lanthanoid element. As a result of lanthanoid contraction, the atomic size of Hf is similar to Zr	1
20	Cis-trans and optical isomerism	1
SECTION C		
21	According to electrochemical theory of rusting the impure iron surface behaves like small electrochemical cell in the presence of water containing dissolved oxygen or carbon dioxide. In this cell pure iron acts as anode and impure iron surface acts as cathode. Moisture having dissolved CO ₂ or O ₂ acts as an electrolyte.	2

	<p>At anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$; $E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$</p> <p>At cathode: $2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$; $E_{\text{H}^+/\text{O}_2/\text{H}_2\text{O}}^\circ = 1.23 \text{ V}$</p> <p>Overall reaction: $\text{Fe} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \longrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$; $E_{\text{cell}}^\circ = 1.67 \text{ V}$</p> <p>The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} ions, which come out in the form of hydrated ferric oxide (rust).</p> $2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + 4\text{H}^+$ $\text{Fe}_2\text{O}_3 + x\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} \text{ (Rust)}$	
22	<p>a) The large negative hydration enthalpy of Cu(II) ion compensates for the high second ionization enthalpy.</p> <p>b) Oxygen can form multiple bonds with metals, while fluorine can't form multiple bond with metals. Hence, oxygen has more ability to stabilize higher oxidation state rather than fluorine.</p>	2
23	<p>a) Dichlorido-bis(triphenylphosphine)nickel(II)</p> <p>b) Tetraammminechloridonitrito-Ncobalt(III) chloride</p>	2
24	$2\text{NaCl}(l) \rightarrow 2\text{Na}^+(l) + 2\text{Cl}^-(l)$ $2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2\text{e}^- \quad (2 \text{ mol})$ <p>The charge Q on n mol of electrons is given by, $Q=nF$ Thus,</p> $Q = 2\text{mol} \times 96500 \text{ C mol}^{-1} = 193000\text{C} = 1.93 \times 10^5\text{C}$ <p>Quantity of electricity used = Current in amperes \times Time in seconds $= (1.0\text{A}) \times (15 \times 60)\text{s}$ $1.0 \times 15 \times 60\text{A.s} = 900\text{C} \quad (\therefore \text{A.s} = \text{C})$ Molar mass of chlorine (Cl_2) = $2 \times 35.5 \text{ g mol}^{-1} = 71 \text{ g mol}^{-1}$ $1.93 \times 10^5\text{C}$ of charge produce chlorine = $1 \text{ mol} = 71 \text{ g}$ Therefore, 900 C of charge produce chlorine $= \frac{(71\text{g})}{(1.93 \times 10^5\text{C})} \times (900\text{C}) = 0.331\text{g.}$</p>	2
25	<p>What type of structural isomerism is represented by the following complexes:</p> <p>(a) Linkage</p> <p>(b) Ionisation</p>	2
26	<p>Account for the following :</p> <p>a) Due to lanthanide contraction, the size of Lu^{3+} is decreased and therefore Lu(OH)_3 shows more covalent character (Small cation, more is covalent character - Fajan's rule). Thus La(OH)_3 is more ionic and thus more basic.</p> <p>b) Their tendency to form complexes is due to two reasons.</p> <ol style="list-style-type: none"> Small size and high nuclear charge of these metals. 	2

	2. Availability of vacant d-orbitals of suitable energy to accommodate lone pairs of electrons donated by the ligands.	
27		2
	SECTION D	
28	<p>The cell may be represented as</p> $Pt H_2(1\text{ atm}) _{10^{-4}\text{M}} H^+ \parallel H^+ H_2(1\text{ atm}) Pt$ <p>underset (-ve) Anode underset (+ve) Cathode</p> $H_2 \rightarrow 2H^+ + 2e^- \quad 2H^+ + 2e^- \rightarrow H_2$ $E_{\text{cell}} = \frac{0.0591}{2} \log \frac{[H^-]_{\text{Cathode}}^2}{[10^{-6}]^2}$ $0.118 = (0.0591) \log \frac{[H^-]_{\text{Cathode}}}{10^{-6}}$ $\log \frac{[H^+]_{\text{Cathode}}}{10^{-6}} = \frac{0.118}{0.0591} = 2$ $\frac{[H^+]_{\text{Cathode}}}{10^{-6}} = 10^2$ $[H^+]_{\text{Cathode}} = 10^{-6} \times 10^2 = 10^{-4}\text{M.}$	3
29	<p>$Ni^{2+} \rightarrow [Ar] 3d$ and CN^- is a strong field ligand, so it causes pairing</p> <p>$[Ni(CN)_4]^- \longrightarrow$ </p> <p style="text-align: center;">dsp^2 Hybridisation Geometry square planar</p> <p>In $[Ni(CO)_4]$, Ni exist in Ni(o) state and electrons of 4s gets paired up in 3d orbital due to strong field ligand-CO.</p> <p>$[Ni(CO)_4] \longrightarrow$ </p> <p style="text-align: center;">sp^3 Hybridisation Geometry tetrahedral</p> <p>As discussed above, geometry is different in both the cases but none of these have impaired electrons, hence both are diamagnetic.</p>	3

30	<p>Let the vapour pressure of X be p_1 and Y be p_2 and x_1 and x_2 be their mole fraction. Then according to Raoult's law, total pressure P is</p> $P = p_1x_1 + p_2x_2$ <p>In the first solution,</p> $x_1 = \frac{3}{3+1} = 0.75 ; x_2 = \frac{1}{3+1} = 0.25$ $p_1 \times 0.75 + p_2 \times 0.25 = 550 \text{ mm} \quad \dots(1)$ <p>In the second solution,</p> $p_1 \times 0.80 + 0.20 = 560 \text{ mm} \quad \dots(2)$ $x_1 = \frac{4}{4+1} = 0.80 ; x_2 = \frac{1}{4+1} = 0.20$ <p>(1) $\times 4$ and (2) $\times 5$ gives</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%;">3 $p_1 + p_2 =$</td> <td style="width: 40%; text-align: center;">2200 mm</td> </tr> <tr> <td>4 $p_1 + p_2 =$</td> <td style="text-align: center;">2800 mm</td> </tr> <tr> <td colspan="2"><hr style="border-top: 1px dashed black;"/></td> </tr> <tr> <td>-$p_1 =$</td> <td style="text-align: center;">-600mm</td> </tr> </table> $p_1 = 600 \text{ mm of Hg.}$ $p_1 = 600 \text{ mm of Hg.}$ <p>Substituting in eq (1) we get</p> $p_2 = 400 \text{ mm of Hg.}$ <p>Vapour pressure of pure component X = 600 mm of Hg</p> <p>Vapour pressure of pure Component Y = 400 mm of Hg.</p>	3 $p_1 + p_2 =$	2200 mm	4 $p_1 + p_2 =$	2800 mm	<hr style="border-top: 1px dashed black;"/>		- $p_1 =$	-600mm	
3 $p_1 + p_2 =$	2200 mm									
4 $p_1 + p_2 =$	2800 mm									
<hr style="border-top: 1px dashed black;"/>										
- $p_1 =$	-600mm									
31	<p>a) Arrange the following in the increasing order of boiling and freezing point: 1M glucose > 1M PbCl_2 > 1M $\text{Al}_2(\text{SO}_4)_3$</p> <p>b) Metallic conductance involves the movement of electrons throughout a metal. Electrolytic conduction involves the movement of ions throughout a pure liquid or solution. The major difference between them is that one involves the movement of electrons and the other involves the movement of ions.</p>	3								
32	<p>L A = MnO_2, B = K_2MnO_4, C = KMnO_4</p> <p>Pyrolusite ore Potassium manganate Potassium permanganate</p> <p>Reactions involved:</p> $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$ $\text{MnO}_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} 2\text{MnO}_4^- + e^-$ <p>Manganese (Green) Permanganate (Purple)</p>	3								
33	<p>Write the correct formulae for the following coordination compounds:</p> <p>(a) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (b) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (c) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$</p>									

34	<p>Chromates are stable in basic medium while dichromates are stable in acidic medium.</p> $2 \text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + \text{H}_2\text{O}$ <p>Chromate ion Dichromate ion</p>	
. SECTION E		
35	<p>According to Henry's law, $p\text{O}_2 = K_H \cdot x\text{O}_2$</p> $x\text{O}_2 = \frac{p\text{O}_2}{K_H} = \frac{0.987 \text{ bar}}{34.86 \times 10^3 \text{ bar}} = 2.83 \times 10^{-5}$ <p>Mass of 1 litre water = 1000 g</p> <p>Number of moles of water in 1 litre = $\frac{1000}{18} = 55.5$</p> <p>If n represents number of moles of O_2 in solution,</p> $x\text{O}_2 = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} \approx \frac{n}{55.5} = 2.83 \times 10^{-5}$ $n = 2.83 \times 10^{-5} \times 55.5 \text{ mol} = 1.57 \times 10^{-3} \text{ mol}$ $= 1.57 \times 10^{-3} \text{ mol} \times \frac{1000 \text{ m mol}}{1 \text{ mol}} = 1.57 \text{ m mol}$ <p>a)</p> <p>b) Given reason for the following :-</p> <ul style="list-style-type: none"> i) NaCl is an electrolyte and it dissociates completely whereas glucose being a non-electrolyte does not dissociate. Hence, the number of particles in 0.1 M NaCl solution is nearly double for NaCl solution than that for glucose solution of same molarity. ii) When the RBCs are placed in the 0.1% NaCl solution the water will flow inside the cells as it moves from less concentrated to more concentrated solution. At a point the cell will be so swollen, enough to burst. <p>iii) On taking large amounts of common salt, Na^+ and Cl^- ions enter into the body fluid thereby raising the concentration of the solutes. As a result, osmotic pressure increases which may rupture the blood cells.</p>	5

OR

a) Definitions and examples.

b) Weight of Solute = 10 gram

Weight of Solvent = 2000 gram

Theoretical Molecular mass = 94

Depression in Freezing point = 1.08

Cryoscopic constant = 31.8 C

	$\Delta T_f = K_f \times \text{weight of solute} \times \text{Observed molecular mass of Solvent CCl}_4$ $\text{weight of solvent} \times \text{Observed molecular mass of solute} \times$ $\Delta T_f = 31.8 \times 10 \times 1000$ 2000×1.08 <p>degree of association = Theoretical mol mass/Observed Molecular Mass</p> <p>$94/147.22$</p> <p>0.639</p>	
36	<p>When ionization isomers are dissolved in water, they ionize to give different ions. These ions then react differently with different reagents to give different products.</p> $[\text{CO}(\text{NH}_3)_5\text{Cl}]^{\text{SO}_4} + \text{Ba}^{2+} \longrightarrow \text{BaSO}_4 \downarrow$ <p style="text-align: center;">White precipitate</p> $[\text{CO}(\text{NH}_3)_5\text{Cl}]^{\text{SO}_4} + \text{Ag}^+ \longrightarrow \text{No reaction}$ $[\text{CO}(\text{NH}_3)_5\text{SO}_4]^{\text{Cl}} + \text{Ba}^{2+} \longrightarrow \text{No reaction}$ $[\text{CO}(\text{NH}_3)_5\text{SO}_4]^{\text{Cl}} + \text{Ag}^+ \longrightarrow \text{AgCl} \downarrow$ <p style="text-align: center;">White precipitate</p> <p>a) Out of the following two coordination entities which is chiral (optically active)? (i) cis-[CrCl₂(ox)₂]³⁻</p> <p>b) For d₆ configuration, if P < Δ₀, electrons will pair up in t_{2g} orbitals, giving the configuration t_{2g}6 eg₀ and if Δ₀ < P, two electrons will enter into e_g orbitals and one will pair up in t_{2g} giving the configuration t_{2g}4eg₂.</p> <p style="text-align: center;">OR</p> <p>a)</p>	

	<p>(i) Biological systems Thus, chlorophyll is a coordination compound containing Mg(II) ions. It is green pigment present in plants and is used in photosynthesis.</p> <p>(ii) Medicinal chemistry To remove metal poisoning, complexing agents are used, cis platin $[\text{PtCl}_2(\text{NH}_3)_2]$ is used in cancer chemotherapy.</p> <p>i) Explain the following:</p> <p>Ferrocyanide ion</p> <p>In ferrocyanide ion, the oxidation state of Fe is +2 however in ferricyanide ion, the oxidation number of Fe is +3. Generally, the higher the oxidation state of the metal, the greater the crystal field splitting. It means crystal field splitting in ferrocyanide ion is lower than that of ferricyanide ion.</p> <p>ii) Fe^{+3} is present inside the coordination sphere and hence does not ionize. iii) $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ has d0 configuration i.e no d-d transition is possible while $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has d1 configuration which undergoes d-d transition.</p>
37	<p>a) Misch metal is an alloy of lanthanum metal and iron and traces of S, Ca, C or Al. It is used in making bullets and lighter flint. KMnO_4 when heated to 473 K, readily decomposes giving oxygen.</p> <p>b) $2\text{KMnO}_4 \xrightarrow{\text{heat}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$</p> <p>c) Give reasons: i) KMnO_4 is strong oxidizing agent and it oxidizes HCl. ii) Permanganate will react with hydrochloric acid to liberate chlorine. The lowest oxide of transition metal is basic because some valence electron are involved in bonding thus act as a base due to the availability of free electrons. The oxide of transition metal electrons of metal is involved in the bonding. Therefore, electrons are not available for donation. Hence, they are acidic in nature. iii) The irregular variations of ionization enthalpies can be attributed to the extra stability of configurations such as d0, d5, d10. Since these states are exceptionally stable, their ionization enthalpies are very high.</p> <p style="text-align: center;">OR</p>

	<p>A=KMnO₄(violet)</p> <p>B=K₂MnO₄</p> <p>C=MnO₂</p> <p>D=MnCl₂</p> <p>KMnO₄ → K₂MnO₄+MnO₂+O₂ (Green) ↓KOH/KNO₃ K₂MnO₄</p> <p>MnO₂ conc.H₂SO₄,NaClΔ → MnCl₂+Cl₂</p>	
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PERIODIC TEST 3 (2022-23)

Subject: CHEMISTRY

Max. Marks:35

Grade: XII

Time:1Hr 15mts

Name:

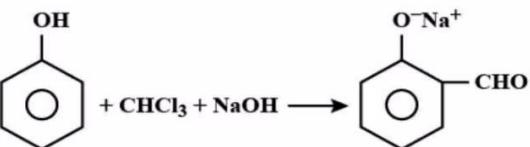
Section:

Roll No:

General Instructions:

- GENERAL INSTRUCTIONS: Read the following instructions carefully.
 - There are 16 questions in this question paper.
 - SECTION A - Q. No. 1 to 5 are multiple choice questions carrying 1marks each.
 - SECTION B - Q. No. 6 to 10 are short answer questions carrying 2 marks each.

4. SECTION C- Q. No. 11 to 15 are short answer questions carrying 3 marks each.
 5. SECTION D- Q. No. 16 is a long answer question carrying 5 marks.
 6. All questions are compulsory.
 7. Use of calculators is not allowed

SECTION A		
1.	The electrophile involved in the given reaction is:  a) ${}^+ \text{CHCl}_2$ b) $: \text{CCl}_2$ c) ${}^- \text{CCl}_3$ d) ${}^+ \text{CHO}$	1
2.	Which of the following methods cannot produce aldehydes? a) Oxidation of primary alcohols b) Dehydrogenation of secondary alcohols c) Ozonolysis of alkenes d) Hydration of ethyne with acid	1
3.	Give the IUPAC name of the following compound $(\text{CH}_3)_2\text{C}=\text{CHCOOH}$ a) 2-Methylbut-2-enoic acid b) 3-Methylbut-2-enoic acid c) 2-Methylpentenoic acid d) 3-Methylbutenoic acid	1
4.	Which would undergo S_{N}^2 reaction faster in the following pair and why? $\text{CH}_3-\text{CH}_2-\text{Br}$ and $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{Br}}{\text{C}}}-\text{CH}_3$	1
5.	The question is given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer. (a) Both assertion and reason are CORRECT, and the reason is the CORRECT explanation of the assertion. (b) Both assertion and reason are CORRECT, but the reason is NOT the CORRECT explanation of the assertion. (c) The assertion is CORRECT, but the reason is INCORRECT. (d) The assertion is INCORRECT, but the reason is CORRECT. Assertion: The boiling point of alcohols is higher than those of hydrocarbons of comparable molecular mass. Reason: Alcohols show intramolecular hydrogen banding.	1
SECTION B		
6.	Complete the reactions- a)	2

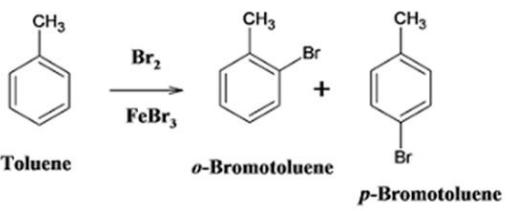
	<p>Toluene</p> <p>b)</p> <p>Toluene</p>	
7.	<p>Two sets of reactants for the preparation of 1-methoxy-4-nitrobenzene are given below. Identify the appropriate set and justify your choice.</p> <p>i) + CH₃ONa ii) + CH₃Br</p>	2
8.	<p>a) Why ditert-butyl ether cannot be obtained by Williamson's method? b) Name the reagents required to prepare ditert-butyl ethyl ether.</p>	2
9.	<p>Effect the following conversions-</p> <p>a) Phenol to picric acid b) Phenol to p-hydroxy acetophenone</p>	2
10.	<p>(CH₃)₃C—O—CH₃ on reaction with HI gives (CH₃)₃C—I and, CH₃—OH as the main products and not (CH₃)₃C—OH and CH₃—I. Why?</p>	2
	SECTION C	
11.	<p>Consider the three types of replacement of group X by group Y as shown below</p> <p>This can result in the formation of compound (A) or (B) or both. What is the process called if</p> <ol style="list-style-type: none"> (A) is the only compound obtained? (B) is the only compound obtained? (A) and (B) are formed in equal proportions? 	3
12.	<p>Write the chemical equations involved in-</p> <ol style="list-style-type: none"> Friedel-Craft alkylation of Anisole Reimer-Tiemann reaction Williamson synthesis of Anisole 	3
13.	<p>Give reasons:</p>	3

	a) Chloroform is stored in dark-colored bottles, filled up to the brim. b) Allyl chloride is more reactive than n-propyl chloride towards nucleophilic substitution. c) S_N^1 reactions are accompanied by racemization in optically active alkyl halides.	
14.	Give one test to distinguish between- a) Propan-2-ol and 2-Methylpropan-2-ol b) Phenol and Ethanol c) Dimethyl ether and Ethanol	3
15.	Write the chemical equations to illustrate the following name reactions: a) Rosenmund reduction b) Gatterman-Koch reaction c) Etard reaction	3
SECTION D		
16.	Give reasons: a) (\pm) Butan-2-ol optically inactive b) Reaction of alcohol with acid chloride is carried out in presence of a base pyridine. c) An alkoxide is a stronger base than a hydroxide ion. d) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride. e) Electrophilic reactions in haloarenes occur slowly.	5



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Periodic test-3-ANSWER KEY (2022-2023)

Subject: Chemistry	Max. Marks: 35	
Grade: XII	Time: hr	
Name:	Section:	Roll No:
1. b) : CCl_2	1	
2. b) Dehydrogenation of secondary alcohols	1	
3. b) 3-Methyl but-2-en-1-oic acid	1	
4. CH_3CH_2Br will react faster due to less steric hindrance.	1	
5. (c) The assertion is CORRECT, but the reason is INCORRECT.	1	
6. 	2	

	<p>Toluene + $\xrightarrow[\text{h}\nu]{\text{Br}_2}$ Benzyl bromide + HBr</p>	
7.	Set (ii) is an appropriate set of reactants. In set (i), sodium methoxide is a strong nucleophile as well as a strong base. Hence, an elimination reaction predominates over a substitution reaction.	2
8.	a) tert-butyl bromide being 3° -alkyl halide prefers to undergo elimination rather than substitution, therefore the product obtained is isobutylene rather than ditert- butyl ether. b) tert-butyl bromide and sodium tertiary butoxide.	2
9.	Account for the following: c) In Chlorobenzene C-Cl bond is sp^2 hybridized whereas in cyclohexyl chloride the C-Cl bond is sp^3 hybridized. As sp^2 has more s character and is more electronegative than sp^3 chlorobenzene is less polar than cyclohexyl chloride. d) —I effect of halogens, deactivates the benzene ring towards electrophilic substitution reactions	2
10.	The reaction between $(\text{CH}_3)_3\text{C-O-CH}_3$, and HI follows the $\text{S}_{\text{N}}1$ mechanism. For an $\text{S}_{\text{N}}1$ reaction, the formation of the product is decided by the stability of the carbocation formed in the slowest step. As tert-butyl carbocation formed after the cleavage of the C-O bond in the slowest step is more stable than methyl carbocation, therefore $(\text{CH}_3)_3\text{C-I}$ and CH_3OH are formed as main products.	2
11.	i) Retention of configuration, ii) Inversion of configuration (Walden Inversion), iii) Racemization takes place	3
12.	a) RCl/AlCl_3 , where 'R' is a alkyl group. <p>Anisole + $\text{RCl} \xrightarrow{\text{AlCl}_3}$ 2-Alkyl anisole + 4-Alkyl anisole + HCl</p> (b) Reimer-Tiemann reaction: <p>Phenol + $\text{CHCl}_3 + 3\text{KOH} \xrightarrow{60^\circ\text{C}}$ Formaldehyde (CHO) + $3\text{KCl} + 3\text{H}_2\text{O}$</p> c) $\text{C}_6\text{H}_5\text{ONa} + \text{CH}_3\text{Br} \longrightarrow \text{C}_6\text{H}_5\text{OCH}_3 + \text{NaBr}$ Methoxybenzene (Anisole)	3
13.	d) In the presence of air and sunlight, chloroform gets oxidized to phosgene (Carbonyl chloride - COCl_2) a poisonous compound e) Allyl carbocation is a more stable intermediate as it has conjugation and is stabilized by resonance. f) Carbocations, the intermediates in $\text{S}_{\text{N}}1$ reactions are sp^2 hybridized and planar species. Therefore, an attack of the nucleophile on it can occur from both front and rear with almost equal ease, giving a racemic mixture.	3
14.	Lucas test- Propan-2-ol gives turbidity after a few minutes, while 2-Methylpropan-2-ol answers the test in a few seconds.	3

	Ferric chloride Test- Phenol forms a violet complex while ethanol does not/ Ethanol gives a positive iodoform test while phenol does not Iodoform test-Ethanol gives a yellow precipitate of iodoform while ether does not.	
15.	<p style="text-align: center;"> a) Acyl chloride Aldehyde </p> <p style="text-align: center;"> $\text{C}_6\text{H}_5 \xrightarrow[\text{Benzene}]{\text{Anhy. AlCl}_3/\text{CuCl}} \text{C}_6\text{H}_5-\text{CHO}$ Benzaldehyde </p> <p style="text-align: center;"> $\text{C}_6\text{H}_5-\text{CH}_3 + \text{CrO}_2\text{Cl}_2 \xrightarrow{\text{CS}_2} \text{C}_6\text{H}_5-\text{CH}(\text{OCrOHCl}_2)_2 \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5-\text{CHO}$ Benzaldehyde </p>	3
16.	<p>a. i) (\pm)-Butan-2-ol is a racemic mixture of (+)-butan-2-ol and (-)-2-butanol which rotate the plane polarized light in different directions but to an equal extent. ii) To neutralize the HCl formed during the reaction iii) The presence of an electron-donating alkyl group results in high electron density</p> <p>b)i)</p> <p style="text-align: center;"> ii) </p> <p style="text-align: center;"> Friedel Craft's acylation </p>	5



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PRE-BOARD-I (2022-23)		
Subject: CHEMISTRY		Max. Marks:70
Grade: XII		Time: 3Hrs
Name:	Section:	Roll No:

General Instructions:

- GENERAL INSTRUCTIONS: Read the following instructions carefully.
 1. There are 35 questions in this question paper.
 2. SECTION A consist of 18 multiple choice questions carrying 1marks each.
 3. SECTION B consist of 7 very short answer questions carrying 2 marks each.
 4. SECTION C consist of 5 short answer questions carrying 3 marks each.
 5. SECTION D consist of 2 case-based questions carrying 4 marks each.
 6. SECTION E consist of 3 long answer question carrying 5 marks.
 7. All questions are compulsory.
 7. Use of calculators is not allowed

SECTION A		
1	<p>Which one of the following compounds is more reactive towards SN1 reaction?</p> <ol style="list-style-type: none"> a. $\text{CH}_2=\text{CHCH}_2\text{Br}$ b. $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ c. $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ d. $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ 	1
2	<p>Following reactions are taking place in a Galvanic cell, $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \rightarrow \text{Ag}^+ + e^- \rightarrow \text{Ag}$</p> <p>Which of the given representations is the correct method of depicting the cell?</p> <ol style="list-style-type: none"> (a) $\text{Zn(s)} \text{Zn}^{2+}(\text{aq}) \text{Ag}^+(\text{aq}) \text{Ag(s)}$ (b) $\text{Zn}^{2+} \text{Zn} \text{Ag} \text{Ag}^+$ (c) $\text{Zn(aq)} \text{Zn}^{2+}(\text{s}) \text{Ag}^+(\text{s}) \text{Ag(aq)}$ (d) $\text{Zn(s)} \text{Ag}^+(\text{aq}) \text{Zn}^{2+}(\text{aq}) \text{Ag(s)}$ 	1
3	The molar conductivity of CH_3COOH at infinite dilution is 390 Scm^2/mol . Using the graph and given information, the molar conductivity of CH_3COOK will be:	1

	<table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>$(c/M)^{1/2}$</th> <th>Λ (HCl) $S\text{ cm}^2/\text{mol}$</th> <th>Λ (KCl) $S\text{ cm}^2/\text{mol}$</th> </tr> </thead> <tbody> <tr><td>0.00</td><td>425</td><td>140</td></tr> <tr><td>0.05</td><td>415</td><td>135</td></tr> <tr><td>0.10</td><td>405</td><td>130</td></tr> <tr><td>0.15</td><td>400</td><td>128</td></tr> <tr><td>0.20</td><td>395</td><td>125</td></tr> <tr><td>0.25</td><td>390</td><td>123</td></tr> <tr><td>0.30</td><td>385</td><td>121</td></tr> </tbody> </table> <p>a. 100 Scm^2/mol b. 115 Scm^2/mol c. 150 Scm^2/mol d. 125 Scm^2/mol</p>	$(c/M)^{1/2}$	Λ (HCl) $S\text{ cm}^2/\text{mol}$	Λ (KCl) $S\text{ cm}^2/\text{mol}$	0.00	425	140	0.05	415	135	0.10	405	130	0.15	400	128	0.20	395	125	0.25	390	123	0.30	385	121	
$(c/M)^{1/2}$	Λ (HCl) $S\text{ cm}^2/\text{mol}$	Λ (KCl) $S\text{ cm}^2/\text{mol}$																								
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0.20	395	125																								
0.25	390	123																								
0.30	385	121																								
4	<p>What would be the major product of the following reaction?</p> $\text{C}_6\text{H}_5-\text{CH}_2-\text{OC}_6\text{H}_5 + \text{HBr} \rightarrow \text{A} + \text{B}$ <p>a. A= $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, B= C_6H_6 b. A= $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, B= $\text{C}_6\text{H}_5\text{Br}$ c. A= $\text{C}_6\text{H}_5\text{CH}_3$, B= $\text{C}_6\text{H}_5\text{Br}$ d. A= $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, B= $\text{C}_6\text{H}_5\text{OH}$</p>	1																								
5	<p>$R-\text{CH}=\text{CH}-\text{CHO} + \text{NH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NNHNH}_2 \xrightarrow{\text{H}^+} X$</p> <p>(X) in the above reaction is</p> <p>(a) $R-\text{CH}=\text{CH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{NH}_2\text{CONHNH}_2$</p> <p>(b) $R-\text{CH}=\text{CH}-\text{CH}=\text{N}-\text{NH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$</p> <p>(c) $R-\text{CH}=\text{NH}_2\text{CONH}_2$</p> <p>(d) $R-\text{CH}=\text{CH}-\overset{\text{OH}}{\underset{ }{\text{CH}}}-\text{NH}_2\text{COCH}=\text{NNHNH}_2$</p>	1																								
6	<p>Which of the following aqueous solutions should have the highest boiling point?</p> <p>(a) 1.0 M NaOH (b) 1.0 M Na_2SO_4 (c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3</p>	1																								
7	<p>Identify the configuration of transition element, which shows highest magnetic moment.</p> <p>(a) 3d^7 (b) 3d^5 (c) 3d^8 (d) 3d^2</p>	1																								
8	<p>KMnO₄ is coloured due to:</p> <p>a) d-d transitions b) Charge transfer from ligand to metal c) Unpaired electrons in d orbital of Mn</p>	1																								

	d) Charge transfer from metal to ligand	
9	Which of the following species is not expected to be a ligand? (a) NO (b) CO (c) $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (d) NH_4^+	1
10	The correct IUPAC name of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is (a) Diamminedichloridoplatinum (II) (b) Diamminedichloridoplatinum (IV) (c) Diamminedichloridoplatinum (0) (d) Dichloridodiammineplatinum (IV)	1
11	Electronic configuration of $[\text{Cu}(\text{NH}_3)_6]^{2+}$ on the basis of crystal field splitting theory is (a) $t_{2g}\ 4\ e_g\ 5$ (b) $t_{2g}\ 6\ e_g\ 3$ (c) $t_{2g}\ 9\ e_g\ 0$ (d) $t_{2g}\ 5\ e_g\ 4$.	1
12	Which of the following primary and secondary valencies are not correctly marked against the compound? (a) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ $p = 3, s = 6$ (b) $\text{K}_2[\text{PtCl}_4]$ $p = 2, s = 4$ (c) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ $p = 2, s = 4$ (d) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ $p = 4, s = 4$	1
13	Which of the following can exist as zwitter ion? (a) p-Aminoacetophenone (b) Sulphanilic acid (c) p-Nitroaminobenzene (d) p-Methoxyphenol	1
14	The major product of acid catalysed dehydration of 1-methylcyclohexanol is: (a). 1-methylcyclohexane (b). 1-methylcyclohexene (c.) 1-cyclohexylmethanol (d). 1-methylenecyclohexane	1
15	Choose the correct answer out of the following choices. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion. (b) Assertion and reason both are correct statements, but reason is not correct explanation for assertion. (c) Assertion is correct statement, but reason is wrong statement. (d) Assertion is wrong statement, but reason is correct statement Assertion: α -Hydrogen atoms in aldehydes and ketones are acidic. Reason: The anion left after the removal of α -hydrogen is stabilized by inductive effect.	1

16	Assertion : Actinoids form relatively less stable complexes as compared to lanthanoids. Reason : Actinoids can utilize their 5f orbitals along with 6d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.	1															
17	Assertion : An ether is more volatile than an alcohol of comparable molecular mass. Reason : Ethers are polar in nature	1															
18	Assertion : Tertiary amines are more basic than corresponding secondary and primary amines in gaseous state. Reason : Tertiary amines have three alkyl groups which cause +I effect.	1															
	SECTION B																
19	a. Name the suitable alcohol and reagent, from which 2-Chloro-2-methyl propane can be prepared b. Out of the Chloromethane and Fluoromethane , which one is has higher dipole moment and why?	2															
20	Assign reasons for the following: a) Depression in freezing point be same if 0.1 mole of sugar or 0.1 mole of glucose is dissolved in one liter of water? b) Chilled cold drink is tastier than a hot cold drink.	2															
21	Use the data to answer the following and also justify giving reasons : <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th></th><th>Cr</th><th>Mn</th><th>Fe</th><th>Co</th></tr> </thead> <tbody> <tr> <td>$E_{M^{2+}/M}$</td><td>-0.91</td><td>-1.18</td><td>-0.44</td><td>-0.28</td></tr> <tr> <td>$E_{M^{3+}/M^{2+}}$</td><td>-0.41</td><td>+1.57</td><td>+0.77</td><td>+1.97</td></tr> </tbody> </table> (a) Which is a stronger reducing agent in aqueous medium, Cr ²⁺ or Fe ²⁺ and why? (b) Which is the most stable ion in +2 oxidation state and why?		Cr	Mn	Fe	Co	$E_{M^{2+}/M}$	-0.91	-1.18	-0.44	-0.28	$E_{M^{3+}/M^{2+}}$	-0.41	+1.57	+0.77	+1.97	2
	Cr	Mn	Fe	Co													
$E_{M^{2+}/M}$	-0.91	-1.18	-0.44	-0.28													
$E_{M^{3+}/M^{2+}}$	-0.41	+1.57	+0.77	+1.97													
22	a) What do you understand by ‘denticity of a ligand’? b) What is the difference between a complex and a double salt? OR a) [Mn(CN) ₆] ³⁻ has two unpaired electrons whereas [MnCl ₆] ³⁻ has four unpaired electrons. Why? b) Anhydrous CuSO ₄ is white while hydrated CuSO ₄ is blue in colour. Why?	2															
23	Write the equations for the following reaction: a) Salicylic acid is treated with acetic anhydride in the presence of conc. H ₂ SO ₄ b) Phenol is treated with chloroform in the presence of NaOH	2															
24	a) Arrange the following in the increasing order of their boiling points. CH ₃ CHO, CH ₃ COOH, CH ₃ CH ₂ OH b) Write chemical equation for the following reaction: Benzoyl chloride is hydrogenated in presence of Pd/BaSO ₄	2															
25	a) Give one chemical test to distinguish between the following pair of compounds Aniline and ethylamine. b) Write short note on Coupling reaction	2															

SECTION C		
26	<p>Give reasons for the following observations:</p> <ol style="list-style-type: none"> Aniline is acetylated before nitration reaction. Primary amine on treatment with benzenesulphonyl chloride forms a product which is soluble in NaOH however secondary amine gives product which is insoluble in NaOH. Aniline does not react with methyl chloride in the presence of anhydrous AlCl₃ catalyst. 	3
27	<ol style="list-style-type: none"> Identify the major product formed when 2-cyclohexylchloroethane undergoes a dehydrohalogenation reaction. Name the reagent which is used to carry out the reaction. Write the reactions involved. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why? 	3
28	<p>i) Write the structures of compounds A, B and C in each of the following reactions :</p> <p>(a) $\text{C}_6\text{H}_5\text{Br} \xrightarrow{\text{Mg/dry ether}} A \xrightarrow[\text{(b) H}_3\text{O}^+]{\text{(a) CO}_2(g)} B \downarrow \text{PCl}_5 C$</p> <p>(b) $\text{CH}_3\text{CN} \xrightarrow[\text{(b) H}_3\text{O}^+]{\text{(a) SnCl}_2/\text{HCl}} A \xrightarrow{\text{dil NaOH}} B \downarrow \Delta C$</p> <p>ii) Do the following conversion in not more than two steps : Benzoic acid to benzaldehyde</p> <p style="text-align: center;">OR</p> <p>Two moles of organic compound 'A' on treatment with a strong base gives two compounds 'B' and 'C'. Compound 'B' on dehydrogenation with Cu gives 'A' while acidification of 'C' yields carboxylic acid 'D' with molecular formula of CH₂O₂. Identify the compounds A, B, C and D and write all chemical reactions involved.</p>	3
29	<p>a) The following is not an appropriate reaction for the preparation of tert.-butyl ethyl ether:</p> $\text{C}_2\text{H}_5\text{ONa} + (\text{CH}_3)_3\text{C}-\text{Cl} \rightarrow (\text{CH}_3)_3\text{C}-\text{OC}_2\text{H}_5$ <p>(i) What would be the major product of the given reaction? (ii) Write a suitable reaction for the preparation of tert.-butyl ethyl ether, specifying the names of reagents used. Justify your answer in both cases.</p>	3
30	<p>E° cell for the given redox reaction is 2.71 V.</p> $\text{Mg}_{(s)} + \text{Cu}^{2+} (0.01 \text{ M}) \longrightarrow \text{Mg}^{2+} (0.001 \text{ M}) + \text{Cu}_{(s)}$ <p>a) Calculate E_{cell} for the reaction. b) Write the direction of flow of current when the external opposite potential applied is: (i) Less than 2.71 V and (ii) Greater than 2.71 V</p>	3
SECTION D		

31

Read the passage given below and answer the following questions:

The unique behaviour of Cu, having a positive E° accounts for its inability to liberate H₂ from acids. Only oxidizing acids (nitric and hot concentrated sulphuric acid) react with Cu, the acids being reduced. The stability of the half-filled (d5) subshell in Mn²⁺ and the filled (d10) configuration in Zn²⁺ are related to their E° (M^{3+}/M^{2+}) values. The low value for Sc reflects the stability of Sc³⁺ which has a noble gas configuration. The comparatively high value for Mn shows that Mn²⁺(d5) is particularly stable, whereas a comparatively low value for Fe shows the extra stability of Fe³⁺(d5). The comparatively low value for V is related to the stability of V²⁺ (half-filled t_{2g} level).

i)

$E^\circ M^{3+} / M^{2+}$ values for the first series of transition elements are given below.

$E^\circ (V)$	Ti	V	Cr	Mn	Fe	Co
M^{3+} / M^{2+}	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97

Identify the two strongest oxidizing agents in the aqueous solution from the above data.

ii) Give reasons:

- (a) In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomisation of zinc is the lowest.
- (b) Cu⁺ ion is not stable in aqueous solutions.
- (c) Mn²⁺-compounds more stable than Fe²⁺-towards oxidation

32

Suleiman, 14, used to spend 4 hours each day, traveling by donkey to collect water from a river. By the time he reached school, he would feel very tired and have difficulties concentrating. He would also often complain of stomach pains from drinking the river water. With the RO system now in his community, this is no longer the case. "Today, I slept more in the morning and just walked 20 minutes to collect the water from the tap. I had enough time to do my school homework and play with my friends. In school, our Chemistry teacher always said that clean water is tasteless and without color and smell. Today for first time I was able to taste real clean water." Reverse osmosis differs from filtration in that the mechanism of fluid flow is by osmosis across a membrane. The predominant removal mechanism in membrane filtration is straining, or size exclusion, where the pores are 0.01 micrometers or larger, so the process can theoretically achieve perfect efficiency regardless of parameters such as the solution's pressure and concentration. Reverse osmosis instead involves solvent diffusion across a membrane that is either nonporous or uses nanofiltration with pores 0.001 micrometers in size.

Answer the following questions:

Given below the sketch of a plant for carrying out a process.

4

4

	<p>a) Name the process occurring in the given plant. b) To which container does the net flow of water take place? c) Name one SPM which can be used in this plant. d) At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?</p>	
	SECTION E	
33	<p>(a) What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d₄ in terms of t_{2g} and e_g in an octahedral field when (i) Δo > P (ii) Δo < P</p> <p>(b) Write two limitations of crystal field theory.</p> <p>(C) Give reason: [CoF₆]³⁻ is outer orbital but [Co(NH₃)₆]³⁺ is inner orbital complex.</p> <p style="text-align: center;">OR</p> <p>a)</p> <p>What type of structural isomerism is represented by the following pairs :</p> <p>(i) [Mn(CO)₅SCN] and [Mn(CO)₅NCS] (ii) [Co(NH₃)₅NO₃] SO₄ and [Co(NH₃)₅SO₄] NO₃</p> <p>b)</p> <p>Draw all the isomers (geometric and optical) of following complex:</p> <p style="text-align: center;">[Co(NH₃)Cl(en)₂]²⁺</p> <p>c)</p> <p>The two complexes of nickel, [Ni(CN)₄]²⁻ and [Ni(CO)₄], have different structures but possess same magnetic behaviour. Explain.</p>	5
34	<p>a) For the cell reaction,</p> $\text{Ni}_{(s)} \text{Ni}^{2+}_{(aq)} \text{Ag}^+_{(aq)} \text{Ag}_{(s)}$ <p>Calculate the equilibrium constant at 25°C.</p> $E^\circ_{(\text{Ni}^{2+}/\text{Ni})} = -0.25 \text{ V} \text{ and } E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$ <p>b) What is the use of platinum foil in the hydrogen electrode</p> <p>c) Out of HCl and NaCl, which do you expect will have greater value for molar conductivity and why?</p> <p style="text-align: center;">OR</p>	5

	<p>a) The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm² /mol.</p> <p>b) Give reason :</p> <ul style="list-style-type: none"> (i) On the basis of E° values, O₂ gas should be liberated at anode but it is Cl₂ gas which is liberated in the electrolysis of aqueous NaCl. (ii) Molar conductivity of CH₃COOH increases on dilution. 	
35	<p>A hydrocarbon (A) with molecular formula C₅H₁₀ on ozonolysis gives two products (B) and (C). Both (B) and (C) give a yellow precipitate when heated with iodine in presence of NaOH while only (B) give a silver mirror on reaction with Tollen's reagent.</p> <p>a. Identify (A), (B) and (C).</p> <p>b. Write the reaction of B with Tollen's reagent</p> <p>c. Write the equation for iodoform test for C</p> <p>d. Write down the equation for aldol condensation reaction of B and C.</p> <p style="text-align: center;">OR</p> <p>An organic compound (A) with molecular formula C₂Cl₃O₂H is obtained when (B) reacts with Red P and Cl₂. The organic compound (B) can be obtained on the reaction of methyl magnesium chloride with dry ice followed by acid hydrolysis.</p> <p>a. Identify A and B</p> <p>b. Write down the reaction for the formation of A from B. What is this reaction called?</p> <p>c. Give any one method by which organic compound B can be prepared from its corresponding acid chloride.</p> <p>d. Which will be the more acidic compound (A) or (B)? Why?</p> <p>e. Write down the reaction to prepare methane from the compound (B).</p>	



مَدْرَسَةُ دَلْهِي الْخَاصَّةُ ذ.م.م.

DELHI PRIVATE SCHOOL L.L.C.

Affiliated to C.B.S.E., DELHI

(Approved & Recognized By Ministry of Education - United Arab Emirates)

DPS
SHARJAH

ANSWER KEY

PRE-BOARD-I (2022-23)

Subject: CHEMISTRY

Max. Marks:70

Grade: XII

Time: 3Hrs

Name:

Section:

Roll No:

General Instructions:

- GENERAL INSTRUCTIONS: Read the following instructions carefully.
 - There are 35 questions in this question paper.
 - SECTION A consist of 18 multiple choice questions carrying 1marks each.
 - SECTION B consist of 7 very short answer questions carrying 2 marks each.
 - SECTION C consist of 5 short answer questions carrying 3 marks each.
 - SECTION D consist of 2 case based questions carrying 4 marks each.
 - SECTION E consist of 3 long answer question carrying 5 mark.
 - All questions are compulsory.
 - Use of calculators is not allowed

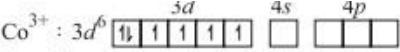
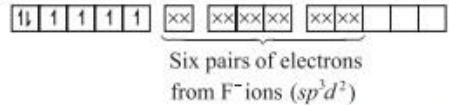
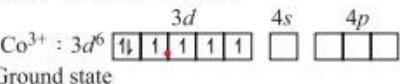
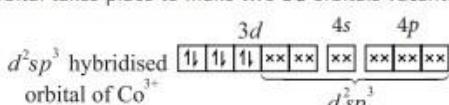
SECTION A

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

SECTION B		
19	<p>a. Tert butyl alcohol or 2-methyl propan-2-ol using Lucas reagent , mixture of concHCl and ZnCl₂the reaction will follow the SN 1 pathway.</p> <p>b.Chloromethane is having higher dipole moment . Due to smaller size of fluorine the dipole moment of fluromethane is comparatively lesser.</p>	2
20	<p>a) Both the compounds are non-electrolytes, non-volatile with same molality. So, it is same as $\Delta T_a m$.</p> <p>b) At higher temperature, solubility of oxygen decreases or amount of CO₂ dissolved is greater at lower temperature rather than the hot cold drink.</p>	2
21	<p>a) Cr²⁺ is a stronger reducing agent than Fe²⁺. E°Cr³⁺/Cr²⁺ is negative (-0.41 V) whereas E°Fe³⁺/Fe²⁺ is positive (+ 0.77 V). Thus Cr²⁺ is easily oxidized to Cr³⁺ but Fe²⁺ cannot be easily oxidized to Fe³⁺. Hence, Cr²⁺ is stronger reducing agent than Fe²⁺.</p> <p>(b) More positive is the value of E°, reaction will be more feasible. As E°Co³⁺/Co²⁺ is maximum, thus Co²⁺ ion is most stable</p>	2
22	<p>a) Denticity : The number of coordinating groups present in a ligand is called the denticity of ligand. For example, bidentate ligand ethane-1, 2-diamine has two donor nitrogen atoms which can link to central metal atom.</p> <p>b) Double salts dissociate into ions completely when dissolved in water. On the other hand, in complexes, the complex ion does not dissociate.</p> <p style="text-align: center;">OR</p> <p>a) In [Mn(CN)₆]³⁻, Mn is in +3 state so, it has configuration of 3d 4 . Since CN⁻ is a strong field ligand hence pairing of electrons in 3d-orbital takes place. So, [Mn(CN)₆]³⁻ has two unpaired electrons. But in [MnCl₆]³⁻, Cl⁻ is a weak field ligand, so no pairing takes place and it has 4 unpaired electrons</p> <p>b) Anhydrous CuSO₄ has no ligand. So, crystal field splitting does not occur so, it does not show any colour but in hydrated form it is linked with H₂O ligand so, it shows colour due to d-d transition</p>	2
23	<p>a)</p> <p>b) o-hydroxybenzaldehyde will be formed (Equation required)</p>	2
24	<p>1. Increasing order of boiling point :</p> $\text{CH}_3\text{-CHO} < \text{C}_2\text{H}_5\text{OH} < \text{CH}_3\text{-COOH}$ <p>2. $\text{C}_6\text{H}_5\text{COCl} \xrightarrow[\text{Pd-BaSO}_4]{\text{H}_2} \text{C}_6\text{H}_5\text{CHO}$ Benzaldehyde</p>	2
25	<p>a) Nitrous acid test</p> <p>b) Coupling reaction (equation)</p>	2
SECTION C		
26	<p>a. Aniline is acetylated, before nitration reaction in order to avoid formation of tarry oxidation products and protecting the amino group, so that p -nitro derivative can be obtained as major product.</p>	3

	b. Due to the presence of acidic hydrogen in the N-alkylbenzenesulphonamide formed by the treatment of primary amines. c. Aniline does not react with methylchloride in the presence of AlCl ₃ catalyst, because aniline is a base and AlCl ₃ is Lewis acid which lead to formation of salt.	
27	a. The major product formed when 2-cyclohexylchloroethane undergoes dehydrohalogenation reaction is 1-cyclohexylethene. (Equation) The reagent which is used to carry out the reaction is ethanolic KOH. b. Allyl chloride shows high reactivity as the carbocation formed in the first step is stabilised by resonance while no such stabilization of carbocation exists in the case of n-propyl chloride.	3
28	<p>Reaction scheme for question 28:</p> <ul style="list-style-type: none"> (i) Bromobenzene reacts with Mg/dry ether to form phenylmagnesium bromide (A). Then, reaction with (a) CO_{2(g)} and (b) H₃O⁺ yields benzaldehyde (C). (ii) Phenylcarboxylic acid (B) reacts with PCl₅ to form benzoyl chloride (C). (iii) Benzaldehyde (C) reacts with (a) SnCl₂/HCl and (b) H₃O⁺ to form formaldehyde (A). (iv) Formaldehyde (A) reacts with dilute NaOH to form sodium formate (B). (v) Benzaldehyde (C) reacts with heat to form benzaldehyde (C) via a Cannizzaro reaction. (vi) Benzaldehyde (C) reacts with SOCl₂ to form benzoyl chloride (C). (vii) Benzoyl chloride (C) reacts with H₂/Pd-S, BaSO₄ via Rosenmund's reduction to form benzaldehyde (C). (viii) Benzaldehyde (C) reacts with NaOH to form methanol (B) and sodium formate (C). (ix) Methanol (B) reacts with Cu (dehydrogenation) to form formaldehyde (A). (x) Sodium formate (C) reacts with acidification to form formic acid (D). (xi) Formaldehyde (A) and formic acid (D) combine to form HCHO (formaldehyde) and HCOOH (formic acid). <p>Reaction scheme for OR:</p> <p>2HCHO $\xrightarrow{\text{NaOH}}$ CH₃OH + HCOONa</p> <p>A B C</p> <p>Formaldehyde Methanol Sodium formate</p> <p>\downarrow Cu (dehydrogenation) Acidification</p> <p>HCHO * HCOOH</p> <p>A D</p> <p>formaldehyde formic acid</p>	

29	<p>a)(i) Since the alkyl halide is a 3° halide and C₂H₅ONa is a strong base, therefore elimination occurs preferably. The product obtained is 2-Methylprop-1-ene. CH₃-C(CH₃)=CH₂</p> <p>(ii) To prepare t-Butyl ethyl ether, the alkyl halide should be 1° i.e. chloroethane and the nucleophile should be sodium t-butoxide because the 3° nucleophile is able to attack 1° alkyl halide.</p> $(CH_3)_3C-O^-Na^+ + CH_3CH_2-Cl \rightarrow (CH_3)_3C-OCH_2CH_3$	3
29	$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$ $= 2.71 - \frac{0.0591}{2} \log \frac{0.001}{0.01} = 2.73955 \text{ V}$ <p>(i) If external opposing potential is less than 2.71 V then current will flow from Cu to Mg.</p> <p>(ii) If external opposing potential is greater than 2.71 V then current will flow in opposite direction i.e. from Mg to Cu.</p>	3
SECTION D		
30	<p>i) Mn³⁺ and Co³⁺ are the strongest oxidizing agents from the data given</p> <p>ii)</p> <p>(a) In 3d series from Sc to Zn, all elements have one or more unpaired e⁻¹s except Zn which has no unpaired electron as its outer EC is 3d¹⁰4s². Hence, the intermetallic bonding is weakest in zinc. Therefore, enthalpy of atomisation is lowest.</p> <p>(b) Cu⁺ (aq) is not stable, while Cu²⁺ (aq) is stable. This is because $\Delta_{\text{hyd}}H$ of Cu²⁺(aq) is much higher than that of Cu⁺(aq) and hence it compensates for the 2nd IE of Cu. Thus, many Cu(I) compounds are unstable in aqueous solution and undergo disproportionation as follows :</p> $2 \text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$ <p>(c) Electronic configuration of Mn²⁺ is 3d⁵. This is a half-filled configuration and hence stable. Therefore, third ionization enthalpy is very high, i.e., third electron cannot be lost easily. Electronic configuration of Fe²⁺ is 3d⁶. It can lose one electron easily to achieve a stable configuration 3d⁵.</p>	4
31	<p>a) Reverse osmosis</p> <p>b) Fresh water container</p> <p>c) Cellulose acetate</p> <p>d)</p>	4

	$4.98 = \frac{36}{180} RT \dots\dots(i)$ $1.52 = C_2 RT \dots\dots(ii)$ <p>Divide equation (ii) with equation (i),</p> $\frac{C_2}{36} \times 180 = \frac{1.52}{4.98}$ $C_2 = 0.061 \text{ M}$	
33	<p style="text-align: center;">SECTION E</p> <p>(a) (a) The difference of energy between two splitted levels of d-orbitals is called crystal field splitting energy</p> <p>(i) When $\Delta_o > P$, $t_{2g}^4 e_g^0$ (ii) When $\Delta_o < P$, $t_{2g}^3 e_g^1$</p> <p>(b) (i) It assumes ligand to be point charges. (ii) It does not take into account the covalent character of bonding between the ligand and the central atom.</p> <p>(c) n [CoF₆] 3-, Co is in +3 state and has 3d 6 configuration</p> <p>Co³⁺ : 3d⁶  Ground state</p> <p>Since F⁻ is a weak field ligand. So, outer d-orbitals will be used.</p> <p></p> <p>Since, outer d-orbital is used for hybridisation. So, it is outer orbital complex.</p> <p>In [Co(NH₃)₆]³⁺, Co is in +3 state.</p> <p>Co³⁺ : 3d⁶ </p> <p>Since NH₃ is a strong field ligand pairing of electrons in 3d-orbital takes place to make two 3d orbitals vacant.</p> <p></p> <p>Since it uses inner d-orbital for its hybridisation so, it is inner orbital complex.</p> <p style="text-align: center;">OR</p> <p>a) (i) Linkage isomerism (ii) Ionization isomerism</p> <p>b)</p>	5

	<p>c)</p> <p>$[\text{Ni}(\text{CN})_4]^{2-}$ - dsp₂ hybridisation, Ni in +2 state all electrons are paired, so diamagnetic.</p> <p>$[\text{Ni}(\text{CO})_4]$ - sp₃ hybridisation, Ni in 0 state all electrons are paired so diamagnetic.</p>	
34	<p>a)</p> <p>Cell reaction : $\text{Ni} + 2\text{Ag}^+ \longrightarrow \text{Ni}^{2+} + 2\text{Ag}$</p> $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$ $= E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Ni}^{2+}/\text{Ni}}^\circ = 0.80 \text{ V} - (-0.25) \text{ V}$ $E_{\text{cell}}^\circ = 1.05 \text{ V}$ $E_{\text{cell}}^\circ = \frac{0.0591}{n} \log K_c$ $\log K_c = \frac{E_{\text{cell}}^\circ \times n}{0.0591} = \frac{1.05 \times 2}{0.0591}$ $\log K_c = 35.53$ $K_c = \text{antilog } 35.53 = 3.38 \times 10^{35}$ <p>b) It is used for the inflow and outflow of electrons. c) HCl will have greater value of molar conductivity because H⁺ ions are smaller than Na⁺ ions and hence H⁺ ions have greater ionic mobility than Na⁺ ions.</p> <p style="text-align: center;">OR</p> <p>a)</p> $\Lambda_m^c = \frac{\kappa \times 1000}{C}$ <p>Substituting the values,</p> $\Lambda_m^c = \frac{4 \times 10^{-5} \times 1000}{0.001} = 40 \text{ S cm}^2/\text{mol}$	5

	$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{40}{390} = 0.10256 \approx 0.103$ $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ <table style="margin-left: 100px;"> <tr><td>c</td><td>0</td><td>0</td></tr> <tr><td>c(1 - α)</td><td>•α</td><td>α</td></tr> </table> $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{\alpha \cdot \alpha}{c(1 - \alpha)} = \frac{\alpha^2}{1 - \alpha}$ $K_a = \frac{0.001(0.103)^2}{(1 - 0.103)} = \frac{1.061 \times 10^{-5}}{0.897} = 1.18 \times 10^{-5}$ <p>b) The reaction at anode with lower value of E° is preferred i.e., O₂ gas should be liberated but on account of over potential of oxygen reaction at anode, preferred reaction is</p> $\text{Cl}_{(\text{aq})}^- \rightarrow \frac{1}{2} \text{Cl}_{(\text{g})} + e^-$ <p>i.e., Cl₂ gas is liberated at anode in the electrolysis of aq. NaCl.</p> <p>c) Molar conductivity increases with decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in K on dilution of a solution is more than compensated by increase in its volume.</p>	c	0	0	c(1 - α)	•α	α
c	0	0					
c(1 - α)	•α	α					
35	<p>A is an alkene B is an aldehyde with -CH₃ group C is a methyl ketone</p> <p>A : CH(CH₃)=C(CH₃)₂ B: CH₃CHO C: O=C(CH₃)₂</p> $\text{CH}_3\text{CHO} + [\text{Ag}(\text{NH}_3)_2]^+ + \text{OH}^- \longrightarrow \text{CH}_3\text{COO}^- + \text{Ag} + \text{NH}_3 + \text{H}_2\text{O}$ $\text{CH}_3\text{COCH}_3 + \text{NaOH} + \text{I}_2 \longrightarrow \text{CHI}_3 + \text{CH}_3\text{COONa}$ $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{CHO}$ $\downarrow \text{Ba}(\text{OH})_2$ $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} + (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CHO}$ $+ \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COCH}_3$ $\downarrow \text{heat}$ $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3 + \text{CH}_3\text{CH}=\text{CHCHO} + (\text{CH}_3)_2\text{C}=\text{CHCHO} + \text{CH}_3\text{CH}=\text{CHCOCH}_3$ <p style="text-align: center;">OR</p> <p>a. (A): CCl₃COOH (B): CH₃COOH (1)</p> <hr/> <p>b. CH₃COOH (i) Red P / Cl₂ CCl₃COOH, Hell Volhard Zelinsky reaction (1/2 + 1/2) (ii) H₂O</p> <p>c. CH₃COCl $\xrightarrow{\text{H}_2\text{O}}$ CH₃COOH (1)</p> <p>d. A will be more acidic due to presence of 3 Cl groups (electron withdrawing groups) which increase acidity of carboxylic acid. (1)</p> <p>e. CH₃COOH (i) NaOH, CaO (ii) heat CH₄ + Na₂CO₃ (1)</p>						



PRE-BOARD (EEE CONSORTIUM) EXAMINATION, 2022 – 23

SET- 2

CHEMISTRY THEORY

CLASS: XII

MAX. MARKS: 70

TIME : 3 HOURS

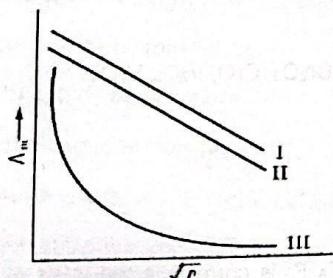
General Instructions. Read the following instructions carefully.
There are 35 questions in this question paper with internal choice.

- SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
 - SECTION B consists of 7 very short answer questions carrying 2 marks each.
 - SECTION C consists of 5 short answer questions carrying 3 marks each.
 - SECTION D consists of 2 case- based questions carrying 4 marks each.
 - SECTION E consists of 3 long answer questions carrying 5 marks each.
- Use of loa tables and calculators is not allowed

SECTION A

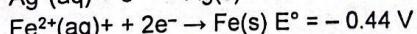
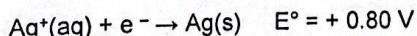
The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section

1. A graph was plotted between the molar conductivity of various electrolytes (NaCl , HCl and NH_4OH) and c (in mol L^{-1}). Which of the following is the correct set? 1



- I (NH_4OH), II (HCl), III (NaCl)
- I (NaCl), II (HCl), (III) (NH_4OH)
- I (HCl), II (NaCl), III (NH_4OH)
- I (NH_4OH), II (NaCl), III (HCl)

2. Given that:



What is the emf of $\text{Fe}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$

- 1.16 V
- 1.24 V
- 2.04 V
- 1.16 V

3 For the reaction, $2X + Y \rightarrow X_2Y$ 1

What will be the expression for instantaneous rate of the reaction?

(a) $+\frac{1}{2} \frac{d(Y)}{dt}$

(b) $-\frac{1}{2} \frac{d(X_2Y)}{dt}$

(c) $-\frac{d(X)}{2dt}$

(d) None of these

4 Consider the reaction, $2A + B \rightarrow$ products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is 1

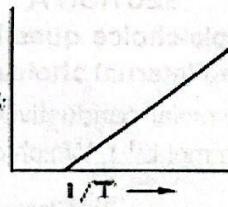
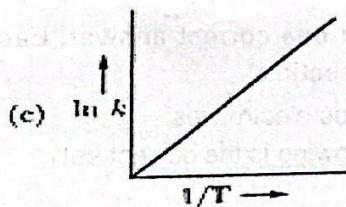
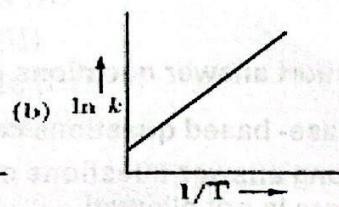
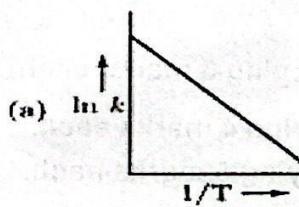
(a) s^{-1}

(b) $L \text{ mol}^{-1} s^{-1}$

(c) no unit

(d) $\text{mol L}^{-1} s^{-1}$

5 According to Arrhenius equation, rate constant $k = A e^{-E_a/RT}$. Which of the following options represent the graph of $\ln k$ vs $1/T$? 1



6 Which of the following is amphoteric oxide? Mn_2O_7 , CrO_3 , Cr_2O_3 , CrO , V_2O_5 , V_2O_4 1

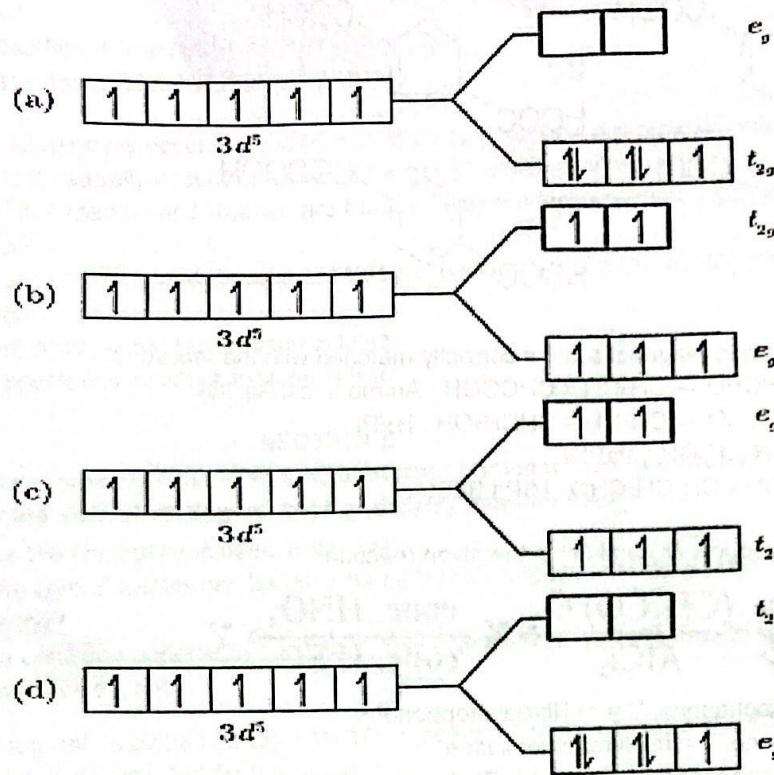
(a) V_2O_5 , Cr_2O_3

(b) Mn_2O_7 , CrO_3

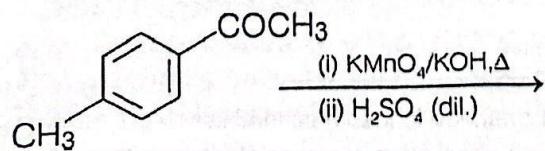
(c) CrO , V_2O_5

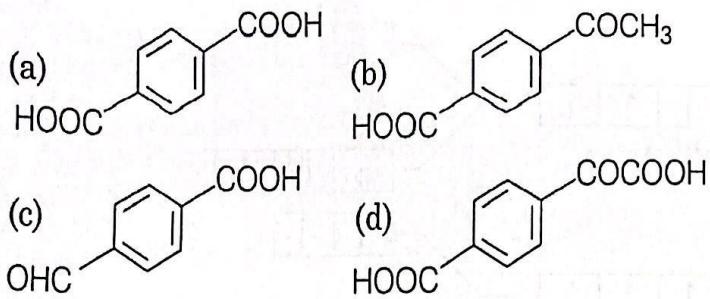
(d) V_2O_5 , V_2O_4

7 Which of the following energy level diagram for $[FeF_6]^{3-}$ is correct on the basis of the crystal field theory? 1



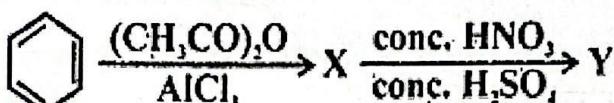
- 8 The IUPAC name of the coordination compound $K_3[Fe(CN)_6]$ is 1
 (a) tripotassium hexacyanoiron (II)
 (b) potassium hexacyanoiron (II)
 (c) potassium hexacyanoferrate (III)
 (d) potassium hexacyanoferrate (II)
- 9 Which of the following isomer has the highest melting point? 1
 (a) 1, 4-dichlorobenzene
 (b) 1, 2-dichlorobenzene
 (c) 1, 3-dichlorobenzene
 (d) All isomers have same melting points
- 10 Which of the following will not give aldol condensation? 1
 (a) Phenylacetaldehyde
 (b) 2-Methylpentanal
 (c) Benzaldehyde
 (d) 1-Phenylpropanone
- 11 The major product of the following reaction is 1





- 12 Which of the following reagents are not correctly matched with the reaction? 1
 (a) $\text{CH}_3\text{CH} = \text{CHCHO} \rightarrow \text{CH}_3\text{CH} = \text{CHCOOH}$: Ammoniacal AgNO_3
 (b) $\text{CH}_3\text{CH} = \text{CHCHO} \rightarrow \text{CH}_3\text{CH} = \text{CHCH}_2\text{OH}$: H_2/Pt
 (c) $\text{R-COOH} \rightarrow \text{R-CH}_2\text{OH}$: NaBH_4
 (d) $\text{CH}_3\text{CH}_2\text{COCl} \rightarrow \text{CH}_3\text{CH}_2\text{CHO}$: $\text{H}_2\text{Pd}/\text{BaSO}_4$

- 13 Identify the products (X) and (Y) in the given reaction 1



- (a) X = Acetophenone, Y = m-Nitroacetophenone
 (b) X = Toluene, Y = m-Nitroacetotoluene
 (c) X = Acetophenone, Y = o- and p-Dinitroacetophenone
 (d) X = Benzaldehyde, Y = m-Nitrobenzaldehyde

- 14 The reaction between $\text{RNH}_2 + \text{CHCl}_3 + \text{KOH}$ (alc.) is known as: 1
 (a) Coupling reaction
 (b) Carbylamine reaction
 (c) Hoffmann bromamide reaction
 (d) Schmidt reaction

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

- 15 Assertion : Transition metals show variable valency. 1
 Reason : Transition metals have a large energy difference between the ns^2 and $(n - 1)\text{d}$ electrons.
 (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion .
 (b) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.
 (c) Assertion is true but Reason is false.
 (d) Assertion is false but Reason is true.

- 16 Assertion : With HI at 373 K, ter-butyl methyl ether gives ter-butyl iodide and methanol. 1
 Reason : The reaction occurs by $\text{S}^{\text{N}}2$ mechanism.
 (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion
 (b) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.
 (c) Assertion is true but Reason is false.
 (d) Assertion is false but Reason is true.

- 17 Assertion : N, N-Diethylbenzene sulphonamide is insoluble in alkali. 1
 Reason: Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.
 (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion

(b) Both Assertion and Reason are true but Reason is not a correct explanation of Assertion.

(c) Assertion is true but Reason is false.

(d) Assertion is false but Reason is true.

- 18 Assertion : All naturally occurring α -amino acids except glycine are optically inactive.

1

Reason : Most naturally occurring amino acids have L-configuration.

(a) Both Assertion and Reason are true and Reason is the correct explanation of assertion

(b) Both Assertion and Reason are true but Reason is not a correct explanation of assertion.

(c) Assertion is true but Reason is false.

(d) Assertion is false but Reason is true.

SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

- 19 i) Name the electrolyte used in dry cell?

2

(ii) What type of metals can be used for cathodic protection of iron against rusting?

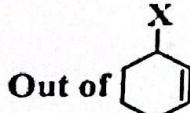
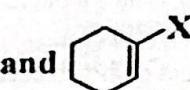
- 20 State a condition under which a bimolecular reaction is kinetically first order reaction. Give example.

- 21 When a graph is plotted for $\log k$ Vs $1/T$, a straight line with a slope of -4250 K is obtained. Calculate ' E_a ' for the reaction.

2

- 22 For the complex $[\text{Fe}(\text{CO})_5]$, write the hybridization state and magnetic character of the complex. (At. number: Fe = 26)

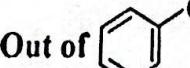
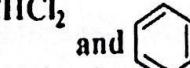
2

- 23 Out of  and 

(i) which is an example of allylic halide ??

(ii) which will react faster in S_N^1 reaction with OH and why ?

OR

Out of  and 

(i) which is an example of a benzylic halide?

(ii) which will react faster in S_N^1 reaction with OH and why ?

- 24 Write chemical equations to illustrate the following name reactions:

2

(1) Williamson's synthesis. (2) Esterification reaction

- 25 What are the hydrolysis products of (i) sucrose (ii) lactose?

2

OR

What are essential and non-essential amino acids? Give two examples of each type

SECTION C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

- 26 The elevation in boiling point when 0.30 g of acetic acid is dissolved in 100 g of benzene is $0.0633\text{ }^\circ\text{C}$. Calculate the molecular weight of acetic acid from this data. What conclusion can you draw about the molecular state of the solute in the solution? (Given K_b for benzene = $2.53\text{ K kg mol}^{-1}$, at. wt. of C = 12, H = 1, O = 16)

- 27 Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of
 (i) strong field ligand, and (ii) weak field ligand. (Atomic no. of Fe = 26)
 (ii) If the CFSE for octahedral $[CoCl_6]^{4-}$ is $18,000 \text{ cm}^{-1}$, then find the value for CFSE for tetrahedral $[CoCl_4]^{2-}$? 3
- 28 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal, it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) to (d) and write the equations for all the reactions. 3

[OR]

A compound 'A' having molecular formula C_4H_9Br on reaction with alcoholic KOH gives a compound 'B'. Bromination of 'B' gives compound 'C'. Compound 'C' on treatment with soda amide gives a gaseous compound 'D'. The gas 'D' when passed through ammonical silver nitrate solution forms white precipitate. Identify compounds A, B, C and D and write down the reactions involved.

- 29 How are the following conversions carried out? 3
- Anisole to phenol
 - Methyl magnesium bromide to 2-Methylpropan-2-ol
 - Phenol to picric acid

[OR]

Explain the mechanism of the dehydration of Ethanol at 443K.

- 30 Give a chemical test to distinguish between the following pair of compounds: 3
- $(CH_3)_2NH$ and $(CH_3)_3N$
 - Aniline and N-methylaniline
 - Ethylamine and diethylamine

SECTION -D

This section consists of 2 case-based questions carrying 4 marks each.

Read the passage carefully and answer the questions that follow.

- 31 Colligative properties are not dependent on the chemical nature of the solution's components. Thus, colligative properties can be linked to several quantities that express the concentration of a solution, such as molarity, normality, and molality. The four colligative properties that can be exhibited by a solution are: Boiling point elevation, Freezing point depression, Relative lowering of vapour pressure and Osmotic pressure. These properties are mostly seen in dilute solutions. Colligative properties are said to be inversely proportional to the solute molar mass.

On the addition of a non-volatile liquid to a pure solvent, the vapour pressure of a solution decrease. Therefore, to make vapour pressure equal to atmospheric pressure we have to increase the temperature of the solution. This is termed as elevation in boiling point.

The phenomenon of the spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution is called osmosis. The flow of solvent molecules can be stopped if some extra pressure is applied from the solution side. This pressure that just stops the flow of solvent is called osmotic pressure of the solution.

- a) Arrange the following in the increasing order of boiling and freezing point:
 1M glucose, 1M $PbCl_2$, 1M $Al_2(SO_4)_3$.

b) A mixture of chloroform and acetone shows negative deviation from Raoult's law. Explain.

- c) When 1.5 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point of benzene was raised from 353.23 K to 353.93 K. Calculate the molar mass of the solute.
 (K_b for benzene = $2.52 \text{ K kg mol}^{-1}$) 4

32 Carbohydrates, proteins, nucleic acids, etc. form the basis of life and are responsible for the growth and maintenance of living systems. Therefore, they are referred to as biomolecules. Carbohydrates are widely distributed in nature. Carbohydrates are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Glucose, fructose, sucrose, starch, cellulose, etc. are some naturally occurring carbohydrates. They act as the major source of energy for animals and human beings. Monosaccharides are the simple carbohydrates that cannot be broken further into smaller units on hydrolysis, e.g., glucose and fructose, ribose, etc. Oligosaccharides are the carbohydrates which on hydrolysis give two to ten units of monosaccharides, e.g., sucrose, maltose, raffinose, stachyose, etc. Polysaccharides are the carbohydrates which produce a large number of monosaccharide units on hydrolysis, e.g., starch, cellulose, etc.

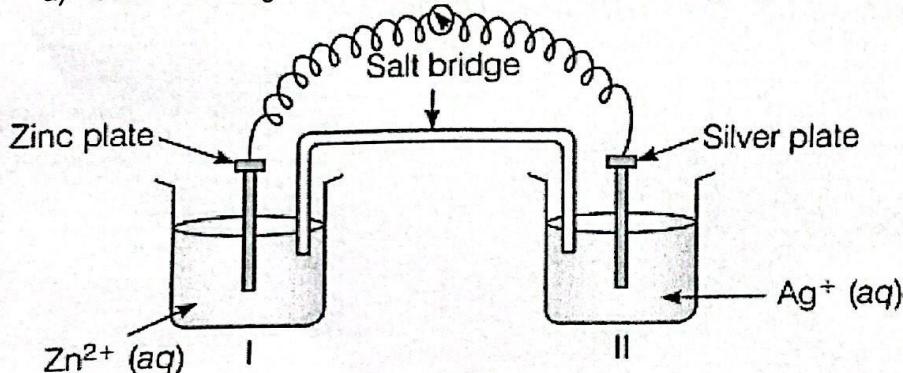
- Name the products of hydrolysis of lactose?
- Which disaccharide is found only in animals and not in plants? Which carbohydrate is the main constituent of plant cell wall?
- Represent the glycosidic linkage in sucrose.

4

SECTION E

The following questions (33 to 35) are long answer type and carry 5 marks each. Two questions have an internal choice.

- 33 a) Consider the figure below and answer the questions (i) to (iii) given below.



5

- What will happen if salt bridge is removed?
- How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions?
- Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100Ω . If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520Ω , calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution.
The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S/m .

OR

- Give equations showing the chemistry of the lead storage battery when it is in use.
- The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

5

- 34 a) Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?
 b) Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?
 c) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised. Explain.
 d) Transition elements form alloys easily.
 e) Give reason. The lowest oxide of transition metal is basic the highest is amphoteric/acidic.

OR

Explain giving reasons:

- a) Transition metals and many of their compounds are paramagnetic.
- b) The enthalpies of atomisation of the transition metals are high.
- c) The transition metals generally form coloured compounds.
- d) Transition metals and their many compounds act as good catalysts.
- e) Of the d⁴ species, Cr²⁺ is strongly reducing while manganese (III) is strongly oxidizing.

35 a) Write the equations involved in the following reactions:

5

- (i) Wolff-Kishner reduction (ii) Etard reaction

(b) An organic compound (A) has characteristic odour of bitter almonds. On treatment with NaOH, it forms compounds (B) and (C). Compound (B) has molecular formula C₇H₈O which on oxidation gives back (A). The compound (C) is a sodium salt of an acid. When (C) is treated with soda-lime, it yields an aromatic compound (D). Deduce the structures of (A), (B), (C) and (D). Write the sequence of reactions involved.

OR

(a) Give reason for following :

- ((i) The alpha hydrogen of aldehydes and ketones are acidic in nature.
- (ii) Propanone is less reactive than ethanal towards addition of HCN.
- (iii) Benzoic acid does not give Friedel-Crafts reaction.

(b) Arrange the following in order of property indicated for each set.

- (i) CH₃CHO, CH₃CH₂OH, CH₃OCH₃, CH₃CH₂CH₃ (increasing order of boiling points)
- (ii) (CH₃)₂CHCOOH, CH₃CH₂CH(Br)COOH, CH₃CH(Br)CH₂COOH (increasing order of their acid strengths)

5

Practicals

EXPERIMENT 1 TITRATION 1 – MOHR'S SALT

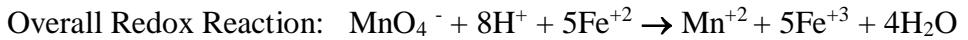
AIM: To prepare 100 ml of M/10 Mohr's salt solution and with its help determine the molarity and strength of the given solution of KMnO_4 .

APPARATUS: Chemical balance, 100ml measuring flask, wash bottle, glass rod, burette, glass funnel, pipette, burette stand, watch glass and weighing bottle.

CHEMICALS REQUIRED: High purity Mohr's salt, concentrated sulphuric acid and distilled water.

THEORY:

The strength of KMnO_4 solution (oxidizing agent) is determined by titrating it against a standard solution of Mohr's salt (reducing agent) in acidic medium. The redox reaction that takes place can be represented as:



The titration is carried out in cold at room temperature as the reaction takes place immediately.

END POINT: colorless to pink.

INDICATOR: Potassium permanganate solution (self-Indicator).

PROCEDURE:

(A) PREPARATION OF STANDARD SOLUTION OF M/10 MOHR'S SALT:

Mohr's salt being a primary standard; its solution can be prepared by direct weighing. Further, molecular formula of Mohr's salt is $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. Take a square piece of paper, weigh it accurately and tare its weight. Now put crystalline Mohr's salt in the paper and weigh till the weight of the Mohr's salt is about 3.92gm. Record this reading in the note book.

Add 2-3ml of concentrated sulphuric acid to 100 ml volumetric flask through a glass funnel kept over it. Sulphuric acid is added to prevent the hydrolysis of Mohr's salt. , Transfer the weighed Mohr's salt from the paper to a glass funnel placed above 100ml measuring flask. Give fine spray of water from wash bottle to the funnel so that everything comes down to the volumetric flask. Dissolve the Mohr's salt by shaking the measuring flask when the salt dissolves

completely add distilled water up to just a little below the mark on the flask. Now add the last few drops of water carefully until the lower meniscus just touches the graduated mark. Close the measuring flask and shake will to get a uniformly concentrated solution.

(B) TITRATION:

Take a clean burette and rinse it with KMnO₄ solution. Fill the burette with KMnO₄ solution. Note down the upper meniscus of KMnO₄ solution and record it is the initial reading. Pipette out 10ml of Mohr's salt solution in a clean conical flask. Add one test tube full of dilute sulphuric acid (5N) to it. Titrate it against KMnO₄ solution till a permanent pink colour is obtained. This is the end point. Note down the reading and record it. Repeat the titration till concordant values are obtained.

RESULT: 1) The molarity of given KMnO₄ solution = M
 2) The strength of given KMnO₄ solution = g/L

PRECAUTIONS:

- 1) For preparing standard solution, apparatus should be clean.
- 2) Standard solution should be prepared in distilled water.
- 3) Weighing should be done accurately.
- 4) Last drops in the measuring flask must be added accurately.

OBSERVATIONS & CALCULATIONS: (NOTE: to be written on blank page)

Determination of the weight of Mohr's salt:

$$M = \frac{W_A \times 1000}{M_A \times 100}$$

$$W_A = 392/10 \times 100/1000 = 3.92\text{g}$$

Molarity of Mohr's salt = 0.1M

S.No .	VOLUME OF MOHR'S SALT SOLUTION(ml)	INITIAL BURETTE READINGS(ml)	FINAL BURETTE READINGS(ml)	VOL. OF KMnO ₄ USED(ml)	CONCORDEN T READING(ml)

Molarity of KMnO₄ solution:

$$\frac{M_{Fe^{+2}} \times V_{Fe^{+2}}}{M_{KMnO_4} \times V_{KMnO_4}} = \frac{\text{No. of moles of Mohr's salt}}{\text{No. of moles of KMnO}_4} = \frac{5}{1}$$

$$M_{KMnO_4} = \frac{M_{Fe^{+2}} \times V_{Fe^{+2}} \times 1}{V_{KMnO_4} \times 5} = \dots\dots\dots M$$

Strength of KMnO_4 = Molarity of $\text{KMnO}_4 \times$ Molecular Mass
=Molarity of $\text{KMnO}_4 \times 158 = \dots\dots\dots\text{g/L}$

EXPERIMENT 2 **TITRATION 2 - OXALIC ACID**

AIM: To prepare 100 ml of M/20 oxalic acid solution and with its help determine the molarity and strength of the given KMnO_4 solution.

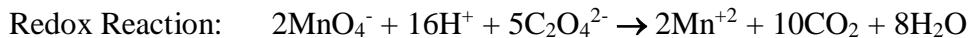
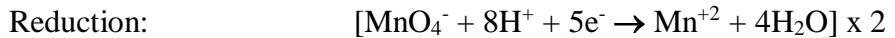
APPARATUS: Chemical balance, 100 ml measuring flask, wash bottle, glass funnel, glass rod, burette, pipette, burette stand, tripod stand, wire gauge, Bunsen burner and weighing bottle.

CHEMICALS REQUIRED: High purity oxalic acid, KMnO_4 , sulphuric acid and distilled water.

THEORY:

(A) Being a primary standard oxalic acid can be prepared by directly weighing crystalline oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, its molecular Wt. is 126).

(B) Potassium permanganate solution oxidizes oxalic acid in CO_2 in acidic medium at a temp. of around 60°C and itself gets reduced to colorless manganous ions. The reaction that occurs is represented as:



In the above reaction CO_2 gas is evolved. Since this gas is soluble in cold solution, it prevents the above reaction to proceed to completion. Therefore the reaction is to be carried out at $60-70^{\circ}\text{C}$ to expel CO_2 from the solution.

END POINT: Colorless to pink.

INDICATOR: KMnO_4 solution (self indicator).

PROCEDURE:

(A) PREPARATION OF STANDARD SOLUTION:

Being a primary standard oxalic acid can be prepared by directly weighing crystalline oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, its molecular Wt. is 126),

Take a filter paper and weigh it. Tare its weight. Now put oxalic acid crystals to the filter paper and weigh it till the weight of oxalic acid is about 0.63g. Record this value. Transfer the weighed oxalic acid to a glass funnel placed above a 100 ml-measuring flask. Give a fine spray of distilled

water from the wash bottle to the funnel so that everything comes down to the measuring flask. Shake the solution well to get a concentrated solution.

(B) TITRATION:

Rinse the burette with KMnO₄ solution and fill it with the same solution. Remove all the air bubbles from burette. Rinse the pipette with oxalic acid solution. Pipette out 10 ml of M/20 oxalic acid solution to a clean conceal flask. Take one test tube full with dil. H₂SO₄ and add to the oxalic acid solution. Shake that mixture. Warm the mixture to 60-70°C and titrate it against KMnO₄ solution in the burette and allow the KMnO₄ solution to run into the flask with constant shaking till a permanent pink color is reached. Read the upper meniscus of the burette and record it as final reading. Read the titration till concordant values are obtained.

RESULT: 1) The molarity of given KMnO₄ solution = M
 2) The strength of given KMnO₄ solution = g/L

PRECAUTIONS:

- 1) For preparing the standard solution apparatus should be clean.
- 2) Standard solution should be prepared in distilled water.
- 3) Weighing should be done accurately.
- 4) Since the lower meniscus of KMnO₄ is not visible, read the upper meniscus.
- 5) Rinse burette and pipette before use.
- 6) Do not use rubber pinch cork burette as rubber is an organic matter and gets attached by KMnO₄.

OBSERVATIONS & CALCULATIONS: (NOTE: to be written on blank page)

Determination of the weight of oxalic acid:

$$M = \frac{W_A \times 1000}{M_A \times 100}$$

$$W_A = 126/20 \times 100/1000 = 0.63\text{g}$$

$$\text{Molarity of oxalic acid} = 0.05\text{M}$$

S.N o	VOLUME OF OXALIC ACID(ml)	INITIAL BURETTE READING(ml)	FINAL BURETTE READING(ml)	VOL. OF KMnO ₄ USED(ml)	CONCORDENT READING(ml)

$$\text{Volume of KMnO}_4 \text{ used} = \dots \text{ml}$$

Molarity of KMnO₄ solution:

$$\frac{M_{\text{oxalic acid}} \times V_{\text{oxalic acid}}}{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}} = \frac{5}{2}$$

$$M_{\text{KMnO}_4} = M_{\text{oxalic acid}} \times V_{\text{oxalic acid}} \times 2 = \dots \text{M}$$

$$V_{\text{KMnO}_4} \times 5$$

Strength of KMnO_4 = Molarity of KMnO_4 x Molecular Mass.
= Molarity of KMnO_4 x 158 =g/L

EXPERIMENT 3 **CHROMATOGRAPHY**

AIM: To separate the mixture of red and blue inks by paper chromatography.

APPARATUS: Beaker, chromatographic paper, a mixture of red and blue inks and gas jar.

CHEMICALS REQUIRED: A mixture of red and blue inks

THEORY:

Paper chromatography is mainly a type of partition chromatography in which a special adsorbent paper is used instead of a column. The mixture adsorbed by this acts as a stationary phase the solvent as the moving phase. The mixture to be separated is put on one end of a paper strip as a small spot. This paper is placed in a suitable container with a suitable solvent vertically in such a way that the lower end dips in the solvent and the remains slightly above the solvent level. The solvent rises up the paper due to capillary action and the component of the mixture rise up at different rates thus gets separated from one another. This type of paper chromatography is called ascending paper chromatography.

PROCEDURE:

- 1) Take a chromatographic paper and draw a line with a pencil above 4cm from one end. Draw another line lengthwise from the centre of the paper.
- 2) Put a drop of the mixture of red and blue inks at the point P.
- 3) Let it dry in air. Suspend chromatographic paper vertically in a glass jar in such a way that the pencil line and the spot remain about 2cm above the solvent level. Keep the jar undisturbed. Notice the rising solvent along with the mixture of red and blue ink.
- 4) After solvent has risen 15cm you will notice two different spots of red and blue colours on chromatographic paper.
- 5) Take out the chromatographic paper from the jar and mark the distance that the solvent has risen on the paper with a pencil. This is called SOLVENT FRONT.
- 6) Dry the paper Put pencil marks on the centre of red and blue spots. Measure the distance of two points from the original line and the solvent from the original line.

Rf values

It may be defined as the ratio of the distance moved up or travelled by the components from the origin or point of application to the distance moved up by the solvent from the same point.

$$R_f = \frac{\text{Distance travelled by the solute from the original line}}{\text{Distance travelled by solvent from the original line}}$$

PRECAUTIONS:

- 1) Keep the jar undisturbed and cover during the experiment.
- 2) The spot should be small and rich in mixture.

- 3) Allow the spot to dry before putting the strip in the jar.
- 4) Keep the strip erect do not let it get curled.
- 5) Do not allow the spot to dip in the solvent.

RESULT: 1) Rf_r =
2) Rf_b =

EXPERIMENT 4 **PREPARATION OF LYOPHILIC SOL**

AIM: To prepare colloidal solution of starch.

APPARATUS: Glass rod, Beaker (250 ml), Tripod stand and Burner.

CHEMICALS REQUIRED: 1) Soluble starch 1g
2) Distilled Water

THEORY:

Starch forms hydrophilic solution and water is used as dispersion medium. Formation of sol is accelerated by heating starch and water at about 100°C . It is quite stable and is not affected by the presence of any electrolytic impurity.

PROCEDURE:

- 1) Take one gram of starch in 10 ml of distilled water.
- 2) Take about 125 ml of distilled water in 250 ml beaker and heat the beaker so that water starts boiling.
- 3) Pour the starch solution slowly with stirring into boiling water in the beaker. Continue boiling for 2-3 minutes and allow the beaker to cool.
- 4) Label the filtrate as starch sol.

PRECAUTIONS:

- 1) The starch sol is prepared in hot solution.
- 2) The apparatus should be thoroughly clean.
- 3) Constant stirring of the contents is necessary, during the preparation of colloidal sol.

EXPERIMENT 5 **PREPARATION OF LYOPHOBIC SOL**

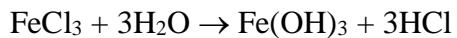
AIM: To prepare ferric hydroxide sol.

APPARATUS: Test tube, Glass rod, Beaker (250 ml), Tripod stand and Burner.

CHEMICALS REQUIRED: 2% Solution of FeCl_3 .

THEORY:

When FeCl_3 salt is hydrolyzed with water under suitable conditions, it gives wine red Fe(OH)_3 this reaction can be represented as:



Fe(OH)_3 sol is hydrophobic in nature and is contaminated with HCl produced by hydrolysis of FeCl_3 .

PROCEDURE:

- 1) Take 125ml of distilled water and heat it to boil by placing it on burner.
- 2) Add ferric chloride solution slowly to the boiling water.
- 3) Continue heating until deep red or brown solution is obtained.
- 4) Keep the contents of the beaker undisturbed at room temperature and label the sol as ferric hydroxide sol.

PRECAUTIONS:

- 1) Since ferric hydroxide sol is affected by impurities, the apparatus required for the preparation of sol should be thoroughly cleaned by steaming out process.
- 2) Add ferric chloride solution drop wise.
- 3) Heating is continued till the desired sol is obtained.

EXPERIMENT 6 **SYSTEMATIC QUALITATIVE ANALYSIS**

TEST FOR ANIONS:

Preliminary Test:

1. **Action of dilute H₂SO₄:** Anions that can be identified by the action of dil. H₂SO₄ are CO₃⁻², S⁻², SO₃⁻² and NO₂⁻¹

EXPERIMENT	OBSERVATION	INFERENCE
Take a small amount of the substance in a test tube and add 2-3 ml of dil. H ₂ SO ₄ to it.	a) Brisk effervescence of colourless gas which turns limewater milky.	May be CO ₃ ⁻²

2. **Action of conc. H₂SO₄:** Anions that can be identified by the action of conc. H₂SO₄ are Cl⁻¹, Br⁻¹, I⁻¹, CH₃COO⁻¹ and NO₃⁻¹

EXPERIMENT	OBSERVATION	INFERENCE
Heat little of the given substance with 2-3 drops of Conc. H ₂ SO ₄ .	a) Colourless gas pungent smell and gives dense white fumes with a glass rod dipped in NH ₄ OH. b) Colourless gas with smell of vinegar. c) brown fumes Heat and add Cu turnings to the above solution - Dense brown fumes and the solution turn blue.	May be Cl ⁻ May be CH ₃ COO ⁻ May be NO ₃ ⁻

3. If the test with dil. and conc. H₂SO₄ is negative then test for SO₄²⁻ directly.

Confirmatory Test of Anions:

Preparation of the test solution:

Take a small amount of the salt in a test tube and add water. The substance dissolves completely, this solution is referred to as the test solution or water extract.

EXPERIMENT	OBSERVATION	INFERENCE
CO₃²⁻ 1. To water extract add BaCl ₂ . 2. To the water extract add MgSO ₄ solution.	White ppt. soluble in dil. HCl and dil. HNO ₃ White precipitate.	CO ₃ ²⁻ confirmed CO ₃ ²⁻ confirmed
Cl⁻ 1. Silver Nitrate Test: To the water extract add AgNO ₃ soln. 2. Chromyl Chloride test: Heat the mixture or salt with K ₂ Cr ₂ O ₇ (solid) and conc. H ₂ SO ₄ . Pass the red vapours through NaOH solution. Add lead acetate to the yellow solution.	Curdy white ppt which is soluble in NH ₄ OH. Red vapours Yellow solution Yellow ppt.	Cl ⁻ confirmed Cl ⁻ confirmed
NO₃⁻ Ring test: To the water extract add equal volume of freshly prepared FeSO ₄ and add few drops of conc. H ₂ SO ₄ by the sides of the test tube.	Brown ring at the junction of the two liquids.	NO ₃ ⁻ confirmed
CH₃COO⁻ 1. To 1ml of the water extract add few drops of FeCl ₃ solution. Dilute red colour solution with little water and boil the solution. 2. Rub a pinch of the salt with oxalic acid and water between the fingers and smell.	Red colour appears Reddish brown ppt. Smell of Vinegar	CH ₃ COO ⁻ confirmed CH ₃ COO ⁻ confirmed

SO₄²⁻		
1. To the water extract add BaCl ₂ solution.	White ppt. which is insoluble in conc. HNO ₃ and conc. HCl.	SO ₄ ²⁻ confirmed
2. To the water extract add lead acetate solution.	White ppt. which is insoluble in dil. HCl but soluble in ammonium acetate solution.	SO ₄ ²⁻ confirmed

TEST FOR CATIONS:

Preliminary Tests:

EXPERIMENT	OBSERVATION	INFERENCE
1. Colour of the substance	Blue	Cu ⁺² suspected
	Brown or yellowish brown	Fe ⁺³ suspected
	Green	Fe ⁺² salts
	Pink or Flesh colour	Mn ⁺² suspected
2. Flame test: Make a paste of the salt or mixture with conc. HCl in a watch glass. Dip the platinum wire/glass rod in the paste and introduce into the non-luminous flame.	Apple green	Presence of Ba ⁺²
	Brick red	Presence of Ca ⁺²
3. Ash test: To a little of the salt in a watch glass, add cobalt nitrate and concentrated nitric acid, dip a filter paper in this solution and burn it, note the colour of the ash.	Green ash	Presence of Zn ⁺²
	Blue Ash	Presence of Al ⁺³
	Light Pink coloured ash	Presence of Mg ⁺²

Confirmatory Test of Cations:

EXPERIMENT	OBSERVATION	INFERENCE
Zero group Heat a pinch of the salt with NaOH solution.	Smell of NH ₃ gas which gives dense white fumes with a glass rod dipped in conc. HCl.	NH ₄ ⁺ present

1. Bring moist red litmus paper near the mouth of test tube.	Red litmus turns to blue.	NH_4^+ confirmed.
2. To the water extract add Nesseler's reagent followed by the addition of excess of NaOH.	Reddish brown ppt.	NH_4^+ confirmed.

Preparation of Original Solution:

Take a small amount of the salt in a test tube and add water. The substance dissolves completely, this solution is referred to as Original Solution.

❖ INTERGROUP SEPARATION

EXPERIMENT	OBSERVATION	INFERENCE
1. Add dil. HCl to the Original solution.	White precipitate.	1 st group (Pb^{2+})
2. Add dil. HCl and H_2S to the Original solution.	Black precipitate.	2 nd group (Cu^{2+})
3. To the Original solution, add solid NH_4Cl and add NH_4OH in excess.	White gelatinous precipitate.	3 rd group (Al^{3+})
4. To the Original solution, add solid NH_4Cl add NH_4OH and H_2S .	Dirty white precipitate. Buff or flesh precipitate.	Zn^{2+} (4 th group) Mn^{2+} (4 th group)
5. To the Original solution. add solid NH_4Cl add NH_4OH and ammonium carbonate solution	White precipitate.	5 th group ($\text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$)
6. To the Original solution. add NH_4Cl boil, add NH_4OH and then add Na_2HPO_4 (sodium hydrogen phosphate) solution	White precipitate.	6 th group. (Mg^{2+})

Confirmatory tests from Group I to Group VI:

EXPERIMENT	OBSERVATION	INFERENCE
Group I If white precipitate Dissolve the white precipitate. in hot water and divide the hot solution in 2 parts. 1. To 1 st part, add K_2CrO_4 .	Yellow precipitate.	Pb^{2+} confirmed

2. To 2 nd part, add KI solution.	Yellow precipitate.	Pb ²⁺ confirmed
Group II If black precipitate. Dissolve the black precipitate in 50% HNO ₃ 1. To 1st part add NH ₄ OH drop by drop and then in excess. 2. To 2nd add acetic acid and [K ₄ Fe(CN) ₆] potassium ferrocyanide.	Light blue precipitate which dissolves in excess of NH ₄ OH and gives deep blue colour. Chocolate brown precipitate.	Cu ²⁺ confirmed. Cu ²⁺ confirmed.
Group III Brown ppt. Dissolve brown ppt in dil. HCl and divide the solution in 2 parts. 1. To 1st part add potassium ferrocyanide K ₄ Fe(CN) ₆ . 2. To 2nd part add ammonium thio-cyanate. (NH ₄ CNS) White ppt.[for Al ³⁺] 1. Dissolve the white precipitate in dil. HCl and add two drops of litmus solution .To this add NH ₄ OH dropwise till blue colour develops. 2. Ash test - To a little of the precipitate in a watch glass, add cobalt nitrate and concentrated nitric acid, dip a filter paper in this solution and burn it, note the colour of the ash.	Prussian blue colour or precipitate. Blood red colour Blue precipitate floating in the colourless solution. Blue ash	Fe ³⁺ confirmed Fe ³⁺ confirmed Al ³⁺ confirmed Al ³⁺ confirmed

<p>Group IV</p> <p>White precipitate.[for Zinc] Dissolve white precipitate in dil HCl and divide the solution in 2 parts.</p> <ol style="list-style-type: none"> 1. 1st part, add NaOH. 2. To 2nd part add potassium ferrocyanide $K_4Fe(CN)_6$ solution. <p>Buff ppt.[for Mn²⁺]</p> <ol style="list-style-type: none"> 1.Dissolve buff precipitate in dil. HCl and add NaOH. 2. Boil the 4th group precipitate with conc. HNO_3 and PbO_2. 	<p>White precipitate which is soluble in excess of NaOH. White precipitate</p> <p>White precipitate turns brown Purple colour</p>	<p>Zn²⁺ confirmed Zn²⁺ confirmed.</p> <p>Mn²⁺ confirmed Mn²⁺ confirmed</p>
<p>Group V</p> <p>Dissolve white precipitate in dilute acetic acid .</p> <p>For Ba²⁺</p> <ol style="list-style-type: none"> 1.To the above solution add K_2CrO_4. [potassium chromate] 2.Flame test - Make a paste of the precipitate with conc. HCl in a watch glass. Dip the platinum wire/glass rod in the paste and introduce into the non-luminous flame 	<p>Yellow precipitate Apple green colour</p>	<p>Ba²⁺ confirmed Ba²⁺ confirmed</p>
<p>For Ca²⁺</p> <ol style="list-style-type: none"> 1. Add ammonium oxalate to the groupV precipitate dissolved in acetic acid. 2.Flame test- Make a paste of the precipitate with conc. HCl in a watch glass. Dip the platinum wire/glass rod in the paste and introduce into the non-luminous flame 	<p>White precipitate Brick red colour</p>	<p>Ca²⁺ confirmed. Ca²⁺ confirmed</p>
<p>Group VI</p> <p>White precipitate To the white precipitate, add cobalt nitrate solution.</p>	<p>Violet or purple precipitate Pink ash</p>	<p>Mg²⁺ confirmed Mg²⁺ confirmed</p>

Ash test- To a little of the precipitate in a watch glass, add cobalt nitrate and concentrated nitric acid, dip a filter paper in this solution and burn it, note the colour of the ash.

SPECIMEN RECORD OF ANALYSIS OF A SALT

AIM

To analyze the anion and cation present in the given salt.

EXPERIMENT	OBSERVATION	INFERENCE
1. Take a small amount of the substance in a test tube and add 2-3 ml of dil. H_2SO_4 to it.	Brisk effervescence of colourless gas which turns limewater milky.	May be CO_3^{2-}
2. To water extract add BaCl_2 solution. 3. To water extract add MgSO_4 solution.	White ppt. soluble in dil. HCl and dil. HNO_3 White precipitate.	CO_3^{2-} confirmed CO_3^{2-} confirmed
4. Colour of the substance	Colour less	$\text{Cu}^{2+}, \text{Fe}^{+3}, \text{Mn}^{2+}$ absent
5. Flame test: Make a paste of the salt or mixture with conc. HCl in a watch glass. Dip the platinum wire/ glass rod in the paste and introduce into the non-luminous flame	No Characteristic colour of the flame	$\text{Ba}^{2+}, \text{Ca}^{+2}$ absent.
6. Ash test: To a little of the salt in a watch glass, add cobalt nitrate and concentrated nitric acid, dip a filter paper in this solution and burn it, note the colour of the ash.	No Characteristic coloured ash.	$\text{Al}^{3+}, \text{Zn}^{2+}, \text{Mg}^{2+}$ absent .
7. Heat a pinch of the salt with NaOH solution. 8. Bring moist red litmus paper near the mouth of test tube. 9. To the water extract add Nessler's reagent followed by the addition of excess of NaOH .	Smell of NH_3 gas which gives dense white fumes with a glass rod dipped in conc. HCl. Red litmus turns to blue. Reddish brown ppt.	NH_4^+ present NH_4^+ confirmed. NH_4^+ confirmed.

RESULT

The given salt contains NH_4^+ as cation and CO_3^{2-} as anion.

SALT NO:2

AIM

To analyse the anion and cation present in the given salt.

EXPERIMENT	OBSERVATION	INFERENCE
1.Take a small amount of the substance in a test tube and add 2-3 ml of dil. H_2SO_4 to it.	No Brisk effervescence .	CO_3^{2-} absent
2.Heat little of the given substance with 2-3 drops of Conc. H_2SO_4 .	Brown fumes Heat and add Cu turnings to the above solution Dense brown fumes and the solution turn blue.	May be NO_3^-
3.Ring test: Acidify the water extract with dil. H_2SO_4 and add equal volume of freshly prepared FeSO_4 and add few drops of conc. H_2SO_4 by the sides of the test tube.	Brown ring at the junction of the two liquids.	NO_3^- confirmed
4.Colour of the substance	Colourless	$\text{Cu}^{2+}, \text{Fe}^{+3}, \text{Mn}^{2+}$ absent.
5.Flame test: Make a paste of the salt or mixture with conc. HCl in a watch glass. Dip the platinum wire/ glass rod in the paste and introduce into the non-luminous flame.	Apple Green Color	Ba^{2+} present.
6.Ash test: To a little of the salt in a watch glass, add cobalt nitrate and concentrated nitric acid, dip a filter paper in this solution and burn it, note the colour of the ash.	No Characteristic coloured ash.	$\text{Al}^{3+}, \text{Zn}^{2+}$ and Mg^{2+} are absent .
Inter group separation: 7.Heat a pinch of the salt with NaOH solution.	No smell of ammonia	NH_4^+ absent

8.Add dil. HCl to the original solution.	No characteristic precipitate.	1 st group (Pb^{2+}) absent .
9. Add dil. HCl and H_2S to the original solution.	No characteristic precipitate.	2 nd group(Cu^{2+}) absent.
10.To the original solution, add solid NH_4Cl and add NH_4OH in excess.	No characteristic precipitate.	3 rd group(Al^{3+}) absent.
11. To the original solution, add solid NH_4Cl add NH_4OH and H_2S .	No characteristic precipitate.	Zn^{2+} , Mn^{2+} (4 th group) absent.
12.To the original solution. add solid NH_4Cl add NH_4OH and ammonium carbonate solution	White precipitate .	5 th group (Ba^{2+}) present.

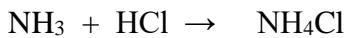
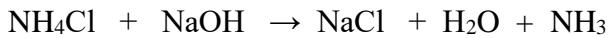
Confirmatory Test For Ba^{2+} Dissolve white precipitate in dilute acetic acid . 13.To the above solution, add K_2CrO_4 . [potassium chromate] 14.Flame test: Make a paste of the precipitate with conc. HCl in a watch glass. Dip the platinum wire/glass rod in the paste and introduce into the non-luminous flame.	Yellow precipitate Apple green colour	Ba^{2+} confirmed
-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	----------------------------------------------	---------------------

RESULT

The given salt contains Ba^{2+} as cation and NO_3^- as anion. The salt is $Ba(NO_3)_2$

CHEMICAL REACTIONS INVOLVED IN THE DETECTION OF BASIC RADICALS (CATIONS):

Zero Group (NH_4^+)



White fumes

Nessler's Reagent Test

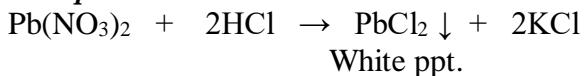


Nessler's Reagent

Brown ppt.

Group I (Pb^{2+})

Group Test:

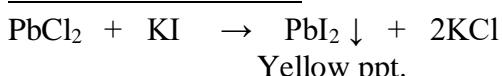


White ppt.

Confirmatory tests:

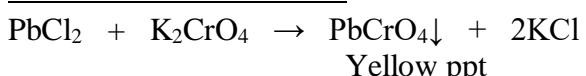
1. On cooling, precipitates settle down as PbCl_2 is less soluble in cold water.

2. **Potassium Iodide Test:**



Yellow ppt.

3. **Potassium Chromate Test:**



Yellow ppt

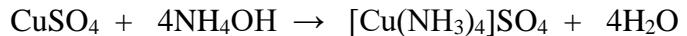
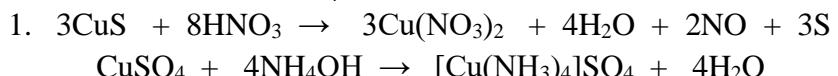
Group II (Cu^{2+})

Group Test:

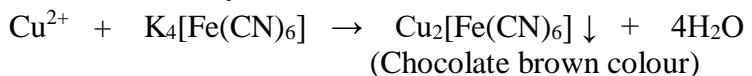


Confirmatory tests:

Black ppt. of CuS dissolves in 50% nitric acid and a blue solution is obtained on addition of excess of NH_4OH



2. **Potassium ferrocyanide test:**



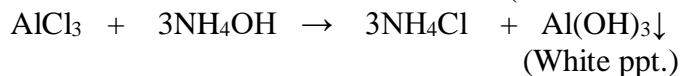
(Chocolate brown colour)

Group III ($\text{Fe}^{3+}/\text{Al}^{3+}$)

Group Test



(Reddish brown ppt.)

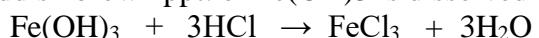


(White ppt.)

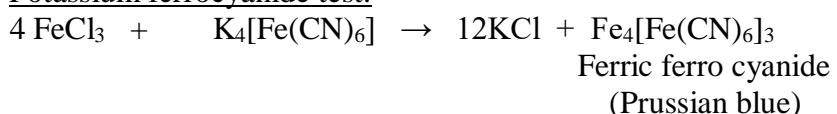
Confirmatory tests:

Fe³⁺

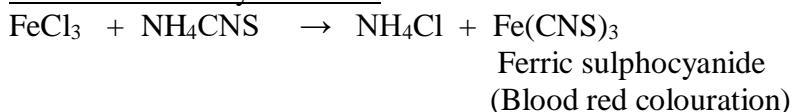
The reddish brown ppt. of Fe(OH)₃ is dissolved in HCl.



1. Potassium ferrocyanide test:

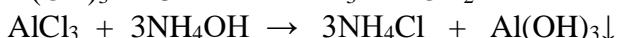
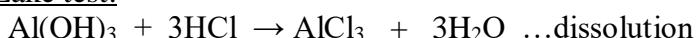


2. Ammonium thiocyanate test:



Al³⁺

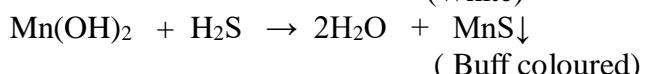
Lake test:



Blue colour absorbs on this ppt.

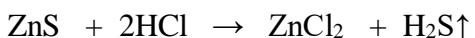
Group III (Zn²⁺/Mn²⁺)

Group Test:

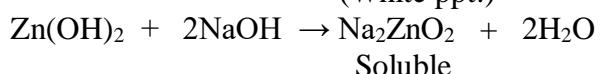
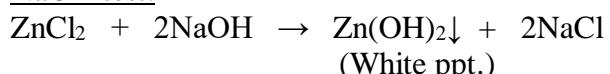


Confirmatory tests:

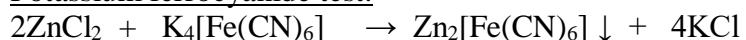
Zn²⁺



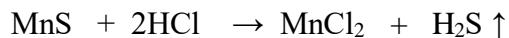
1. NaOH test:



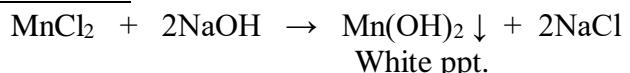
2. Potassium ferrocyanide test:



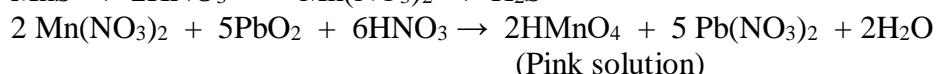
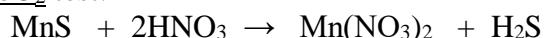
Mn²⁺



1. NaOH test:

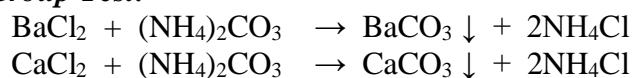


2. PbO₂ test:



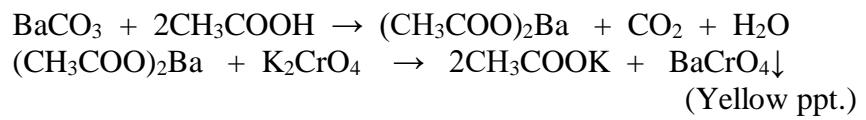
Group V (Ba²⁺/Ca²⁺)

Group Test:

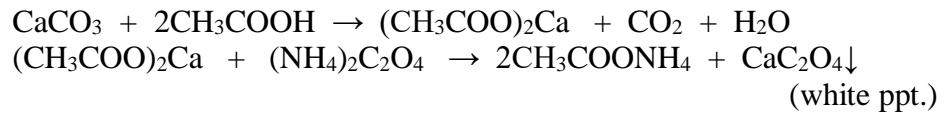


Confirmatory tests:

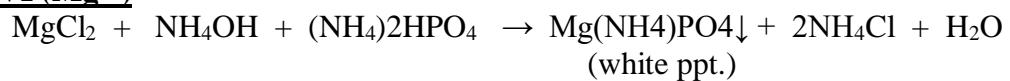
Ba²⁺



Ca²⁺



Group VI (Mg²⁺)



EXPERIMENT 7 A
SYSTEMATIC ORGANIC ANALYSIS

Aim: To distinguish the given organic samples A and B as phenol and carboxylic acid.

EXPERIMENT	OBSERVATION	INFERENCE
Sample A : <p>1. Sodium bicarbonate test Take 1ml of the given liquid in a clean test tube add a pinch of NaHCO_3.</p> <p>2. Litmus test Place a drop of the given liquid on a moist blue litmus paper and note the change in colour.</p>	<p>A brisk effervescence due to the evolution of CO_2 gas.</p> <p>Colour changes to red</p>	Presence of carboxylic group Presence of carboxylic group
Sample B : <p>1. Ferric Chloride test Take 1 ml of the given organic sample in a test tube and add a drop of neutral Ferric Chloride solution.</p> <p>2. Liebermann's test Place 2-3 crystals of NaNO_2 in a clean dry test tube and add about 1 ml of phenol. Heat gently for about half a minute and allow it to cool. Then add about 1ml of conc.H_2SO_4 and shake the tube to mix the contents.</p>	<p>Violet colouration</p> <p>A deep blue or green colour appears and turns red on dilution with water</p>	Presence of phenolic group Presence of phenolic group

RESULT: Sample A is carboxylic acid and sample B is phenol.

REACTIONS (To be written on the blank side)

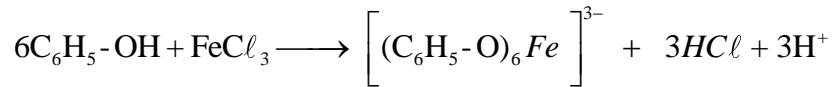
Sodium Hydrogen Carbonate Test-Carboxylic Acids



**Carboxylic
acid**

**Brisk
effervescence**

Ferric chloride test –for Phenols



Phenol

Violet colour

EXPERIMENT 7 B

Aim: To distinguish the given organic samples A and B as aldehyde and ketone.

EXPERIMENT	OBSERVATION	INFERENCE
<u>Sample A :</u> 1. Tollen's test Tollen's test: Add two three drops of the given organic compound to the Tollen's reagent and warm the test tube on a water-bath for about 5 min. [Preparation of Tollen's reagent: Place 1ml of AgNO_3 solution in a clean test tube and add 2-3 ml of NaOH solution. A brown precipitate forms. Now add dilute ammonia solution drop wise till the brown colour dissolves.]	Appearance of silver mirror on the walls of the test tube.	Presence of aldehydic group
3. Fehling's test Take 1ml each of the Fehling's solution A and B in a test tube. Add 1ml of the given organic compound and warm the test tube in a warm water bath for 4-5 min.	Appearance of a red precipitate	Presence of aldehydic group
<u>Sample B :</u> 1. Sodium nitroprusside test Dissolve a crystal of sodium nitroprusside in 1ml of distilled water in a clean test tube and add 1ml of the given compound .Shake and add NaOH solution dropwise.	A red colouration	Presence of ketonic group
2. Tollen's test: Add two drops of the given liquid to the Tollen's reagent and warm the test tube on a water-bath for about 5 min.	No silver mirror on the walls of the test tube.	Presence of ketonic group

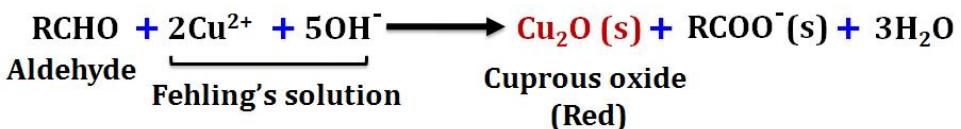
RESULT: Sample A is aldehyde and sample B is a ketone.

REACTIONS (To be written on the blank side)

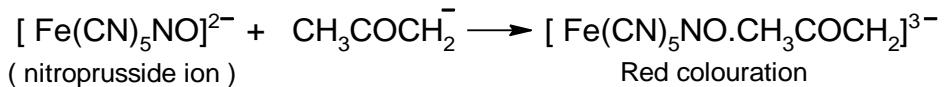
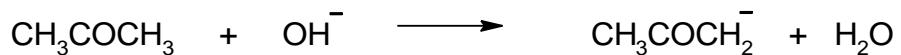
Tollen's Test-for Aldehydes



Fehling's Test-Aldehydes



Sodium nitroprusside Test –for ketones



EXPERIMENT 7 C

AIM: To distinguish the given Organic samples A & B as Alcohol and Amine.

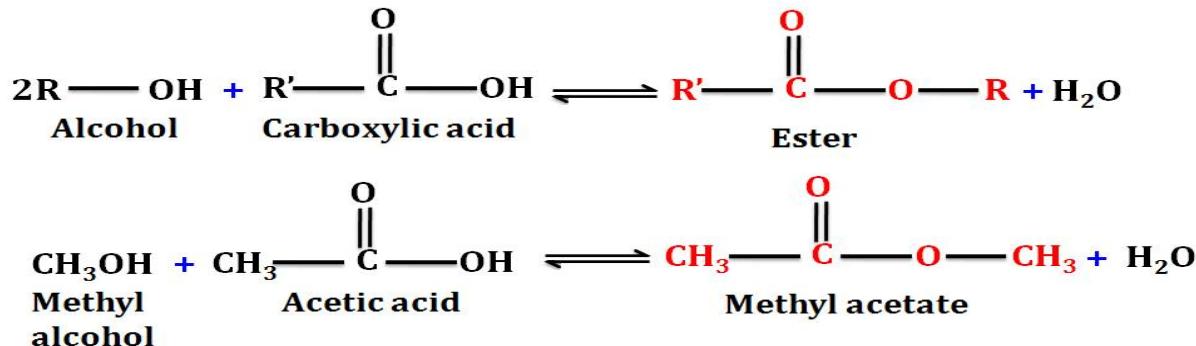
EXPERIMENT	OBSERVATION	INFERENCE
Sample A : <p>1. Ester test Take 1ml of the given liquid in a clean dry test tube and add 1ml of glacial acetic acid and 2-3 drops of conc. H_2SO_4. Warm the mixture on the waterbath for about 10min. Pour it into about 20 ml of cold water taken in a beaker and smell.</p> <p>2. Sodium metal test Take 1ml of the given liquid in a clean dry test tube and add and add about 1gm of anhydrous $CaSO_4$ and shake well to remove the water. Decant the liquid to another clean dry test tube and add a small piece of Na metal.</p>	A fruity smell A brisk effervescence due to the evolution of H_2 gas.	Presence of alcoholic group Presence of alcoholic group

EXPERIMENT	OBSERVATION	INFERENCE
Sample B : <p>1. Litmus test Place a drop of the given liquid on the moist red litmus paper and note the colour.</p> <p>2. Azo-Dye test Dissolve 1ml of organic compound in 2 ml conc. HCl and cool in ice. Add 0.5g of $NaNO_2$ dissolved in 5ml ice-cold water slowly with shaking. Then add a cold solution of β-naphthol in NaOH solution to it.</p>	Colour changes to blue Formation of orange precipitate	Presence of amino group Presence of amino group

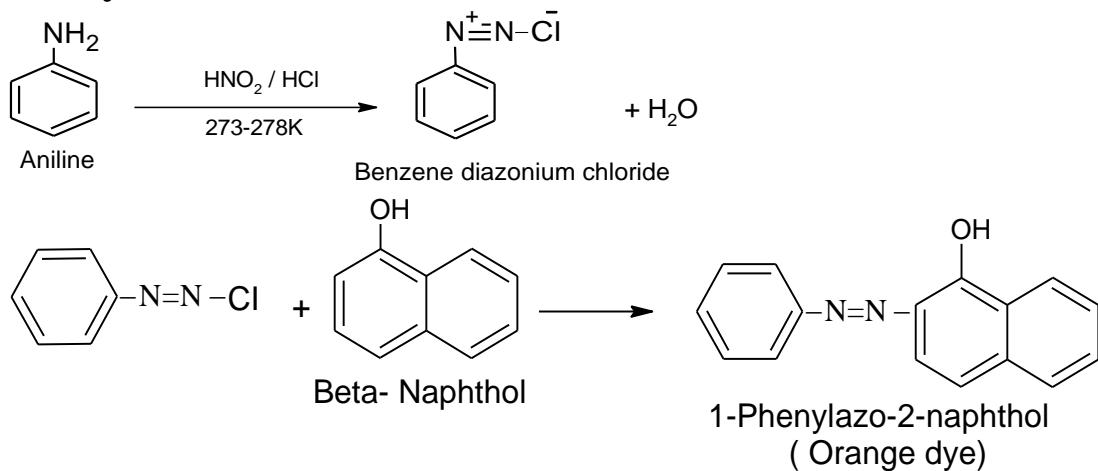
Result: Sample A is alcohol and sample B is an amine. .

REACTIONS (To be written on the blank side)

Ester test- Alcohols



Azo dye Test – Amines



VIVA QUESTIONS SALT ANALYSIS

1. What is qualitative analysis?

It is type of analysis that deals with the methods which are used to determine the constituents of a compound.

2. What is the chemistry of flame test?

In flame test, the valence electron of the atom gets excited and jumps to the higher level. When the electron jumps back to the ground state, the radiation is emitted whose frequency falls in the visible region.

3. Why do we use conc. HCl in preparing a paste of the salt for flame test?

In order to convert metal salts into metal chlorides which are more volatile than other salts.

4. Why can't we use glass rod instead of platinum wire for performing flame test?

This is because glass contains sodium silicate which imparts its own golden yellow color to the flame.

5. Why is platinum metal preferred to other metals for flame test?

Because it does not react with acids and does not itself impart any characteristic colour to the flame.

6. Why do barium salts not impart color to the flame immediately?

Because barium chloride is less volatile, it imparts color to the flame after some time.

7. Why dil. H_2SO_4 is preferred while testing acid radicals over dil. HCl?

When the salt is treated with HCl, during reaction HCl gas is also given out along with the gas evolved by the salt. So the actual gas cannot be identified whereas with dil. H_2SO_4 , no such problem arises.

8. Why the hot reaction mixture in case of conc. H_2SO_4 test is not thrown into the sink?

In order to avoid spouting, due to which H_2SO_4 may fly and spoil clothes and may result into serious injuries.

9. Why a dark brown ring is formed at the junction of two layers in ring test for nitrate ion?

H_2SO_4 being heavier forms the lower layer and reacts only with a small amount of nitrate and $FeSO_4$ at its surface, therefore, a brown ring appears only at the junction of the two layers.

10. Name the group reagents for different groups.

Group I- Dil. HCl

Group II- H_2S in the presence of dil. HCl

Group III – NH_4OH in the presence of NH_4Cl

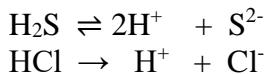
Group IV- H_2S in the presence of NH_4Cl and NH_4OH

Group V- $(NH_4)_2CO_3$ in presence of NH_4Cl and NH_4OH

Group VI- No specific group reagent

11. Why is it essential to add dil. HCl before proceeding to the test for the basic radicals of group II?

In the precipitation of group II radicals as their sulphides, H_2S is used in the presence of HCl. H_2S itself is a weak acid and dissociates as follows:



HCl being a strong acid is largely ionized to H^+ . Thus, hydrogen ion concentration is increased and consequently the concentration of sulphide ions produced by the ionization of H_2S is sufficiently decreased due to common ion effect as a result of which the sulphide ion concentration is sufficient only to exceed the solubility product of the sulphides of group II cations.

Since the solubility products (K_{sp}) for the sulphides of group III and IV cations are very high, those cations are not precipitated out under the above conditions.

12. Why is NH_4Cl added along with NH_4OH in III group?

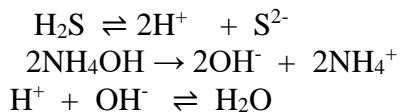
It is done in order to decrease the concentration of OH^- ions by suppressing the ionization of NH_4OH by common ion effect. If NH_4OH alone is used in that case, the concentration of OH^- is enough to precipitate the hydroxides of IV, V and VI groups.

13. What is blue lake?

It is blue particles, blue litmus adsorbed on white ppt. of $\text{Al}(\text{OH})_3$, floating in colourless solution.

14. H_2S is passed in presence of NH_4OH in group IV. Explain, why?

When H_2S is passed in alkaline medium or NH_4OH , the H^+ ions from the dissociation of H_2S gas combine with the hydroxyl ions (OH^-) from the dissociation of NH_4OH to form nearly unionized water and thereby they are not precipitated in V group.



15. Presence of NH_4Cl is quite essential before the addition of $(\text{NH}_4)_2\text{CO}_3$ in group V. Explain why?

Ammonium chloride suppresses the ionization of NH_4OH and due to common ion effect which results in the decrease in the concentration of OH^- and CO_3^{2-} ions. So the ionic product does not exceed the solubility product of $\text{Mg}(\text{OH})_2$ or MgCO_3 .

16. What is salt? What are its two parts?

Salt is the neutralized product of acid and base. The two essential parts are acidic radical (Anion) and Basic radical (cation).

17. What is meant by “ion”?

Ion is an atom with positive or negative charge or charges.

18. What is meant by radical?

Charged atom or group of atoms. Which exists as a single unit in crystal or in solution form is known as a radical.

19. What is Acid radical?

The radical which is contributed by an acid during salt formation and having a negative charge is called acid radical (Anion).

20. What is Basic radical?

The radical which is contributed by a base during salt formation and having a positive charge is called basic radical (cation).

21. Why positive radical is called cation?

On passing the current through a solution it moves towards cathode.

22. Why negative radical is called Anion?

Negative ions moves towards anode during electrolysis hence they are called Anion.

23. What is meant by group reagent?

It is the reagent or chemical, used to find out a particular group of cations or Anions.

24. How many groups are there for Anion?

There are three main group for Anion.

25. How many groups are there for cation?

There are six groups for cation.

26. What are the group reagents for I, II & III group of cation?

The group reagent for I group is HCl, HCl + H₂S for II group and NH₄Cl + NH₄OH are the group reagent for III group.

27. What are the group reagents for I, II and III of Anion?

For I group H₂SO₄ or HCl (dilute) is a group reagent for II groups H₂SO₄ while III group gives precipitation by BaCl₂ or Ammonium molybdate (NH₄)₂ MoO₄.

28. How the cations of group VI are precipitated?

There is no any specific reagent to precipitate all the cations of the group at once, hence they are analysed individually e.g. BaCl₂ for SO₄²⁻.

29. What is the group reagent for cation in group II?

Hydrogen Sulphate (H₂S) in presence of Hydrochloric acid (HCl)

30. What is Nessler's reagent and what for its used?

It is alkaline solution of potassium mercuric iodide K₂HgI₄. It gives brown precipitation with ammonium salts.

31. What is chromyl chloride test?

When solid chloride is heated with potassium dichromate and Conc. Sulphate acid it gives red vapours of chromyl chloride CrO₂Cl₂.

32. Why water and HCl are preferred for the preparation of the original solution (O.S) in the detection of basic radical?

Because no interference is caused by H₂O and HCl while other acids like HNO₃ and H₂SO₄ interfere e.g. Cation like Pb²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ form insoluble sulphates with H₂SO₄ and HNO₃ being oxidizing agent interferes in the second groups by oxidizing H₂S to S.

33. What do you mean by qualitative analysis?

It is the process by which the components of a substance or a mixture can be detected.

34. What fruity smell indicates?

The fruity smell is generally due to the formation of an ester which indicates the presence of CH_3COO ion due to the formation of ethyl acetate $\text{CH}_3\text{COOC}_2\text{H}_5$ or mixed ester fruity smell obtained.

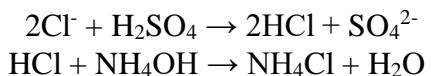
35. What is functional group?

It is a group of atoms responsible for their specific properties to the compound possessing it e.g.

- i) Carbonyl group $> \text{C}=\text{O}$
- ii) Carboxylic acid group $-\text{COOH}$
- iii) Hydroxyl group $-\text{OH}$
- iv) Amino group $-\text{NH}_2$ etc.

36. Why is testing Cl^- radical, when a rod dipped in NH_4OH is held over the mouth of test tube, a dense white fumes are produced?

Because chloride with conc. H_2SO_4 produces HCl gas which forms white fumes of NH_4Cl with NH_4OH .

**37. During testing of 2nd group of acidic radicals a brown gas may evolve, which may be due to Br^- radical or due to NO_3^- radical, how will you distinguish them?**

If evolved gas becomes denser on adding MnO_2 then it is Br_2 gas if it increased by adding copper turnings then it is NO_2 gas.

38. Why it is necessary to prepare the original solution (O.S) of the salt for the detection of basic radicals except NH_4^+ radical?

All the basic radicals are metallic ions except NH_4^+ therefore they cannot form a volatile substance which can be detected by evolution of a gas by a particular smell. Hence they are detected only by precipitation method from their solution.

39. Why NH_4^+ radical can be detected, directly from its salt?

On testing with an alkali, like NaOH it evolves NH_3 gas the smell of which confirms the NH_4 radical.

**40. Why the basic radicals are divided into six groups?**

Actually they are divided on the basis of solubility product of their corresponding compounds.

41. If original solution is prepared in HCl , Why it is concluded that 1st group of basic radicals is absent?

The first group radicals from in soluble chlorides with HCl , Hence if the solution is clear in HCl it means that 1st group radicals are absent.

42. What is brisk effervescence?

Brisk effervescence is due to the evolution of CO_2 gas.

43. Why the ppt. of AgCl is soluble in NH₄OH?

Because AgCl is insoluble in water but in the presence of NH₄OH, it forms a complex diamine compound which can be dissolved easily in water.

44. How does lime water turn milky on passing CO₂ gas through it?

Lime water turns milky due to the formation of insoluble CaCO₃.

45. What is lime water?

It is a solution of Ca(OH)₂.

46. What is red gas?

Chromyl chloride is called red gas CrO₂Cl₂.

47. Mention some cations with their characteristics flames?

Cations Colour of the flame:

Ca²⁺ Brick red Sr²⁺ Deep red Ba²⁺ Grass green Cu²⁺ Bluish green

48. If the salt is coloured what cations may be present?

If the salt is coloured the following cations may be present e.g. Cu²⁺, CO²⁺, Fe²⁺, Ni²⁺, Mn²⁺ and Fe³⁺ etc.

49. Give the name of a non-metallic basic radical?

The non-metallic basic radical is Ammonium NH₄⁺ radical.

50. In the preparation of original solution for cation, why H₂SO₄ is never used?

Because it is oxidizing agent and precipitate various cations in different groups e.g. Ba²⁺, Sr²⁺ and Pb²⁺ are precipitated as sulphate in group II. In this way the whole scheme of cation will disturb.

51. Lead may be precipitated in group I as well in group II of cation why?

In first group PbCl₂ is sparingly soluble and hence not all the lead ions Pb²⁺ are precipitated. Thus the remaining Pb²⁺ ions are separated out in group II as PbS.

52. What is Fehling's solution?

It is a mixture of two solutions i.e. A & B the solution "A" contains copper sulphate solution while solution "B" contain a solution of sodium potassium tartrate (alkaline medium) along with NaOH.

53. What is Tollen's reagent?

Ammonical silver nitrate solution is known as Tollen's reagent.

54. What is Roschell's salt?

Sodium potassium tartrate is also known as Roschell's salt which is used in the preparation of Fehling's solution.

VIVA QUESTIONS

VOLUMETRIC ANALYSIS

1. What is volumetric analysis?

In volumetric analysis, the concentration of a solution is determined by allowing a known volume of this to react quantitatively with another solution of known concentration.

2. What is titration?

The process of adding one solution from the burette to another in the titration flask in order to complete the chemical reaction involved, is known as titration.

3. What is titrand?

The solution whose strength or concentration is to be determined is called titrand.

4. What is titrant?

The solution of known strength is called titrant.

5. What is indicator?

Indicator is a chemical substance which changes colour at the end point.

6. What is end point?

The stage during titration at which the reaction is just complete is known as the end point of the titration.

7. What is molarity?

Molarity is defined as number of moles of solute dissolved per litre of solution.

8. Why a titration flask should not be rinsed?

This is because during rinsing, some liquid will remain sticking to the titration flask therefore the pipetted volume taken in the titration flask will increase.

9. What are primary and secondary standard substances?

A substance is known as primary standard if it is available in high degree of purity, if it is stable and unaffected by air, if it does not lose or gain moisture in air, if it is readily soluble and its solution in water remains as such for long time.

On the other hand, a substance which does not possess the above characteristics is called a secondary standard substance. Primary standards are crystalline oxalic acid, anhydrous Na_2CO_3 , Mohr's salt etc.

10. Burette and pipette must be rinsed with the solution with which they are filled, why?

They are rinsed in order to remove any substances sticking to their sides, which otherwise would decrease the volume of the liquids to be taken in them.

11. It is customary to read the lower meniscus in case of colourless and transparent solutions and upper meniscus in case of highly coloured solutions, why?

Because it is easy to read the lower meniscus in case of colourless solutions, while the upper meniscus in case of coloured solutions.

12. Why the last drop of pipette must not be blown out of a pipette?

Since the drop left in the jet end is extra of the volume measured by the pipette.

13. Why pipette should not be held from its bulb?

The heat of our body may expand the glass bulb and introduce an error in the measurement of the volume.

14. Why is temperature mentioned on pipette?

Volume of pipette is most accurate at that temperature.

15. What is meant by concordant reading?

Volume of acid used remaining same, i.e difference in final and initial reading should be same.

16. What is strength of a solution?

Strength of a solution is defined as amount of solute dissolved per litre of solution.

$$\text{Strength} = \text{Molarity} \times \text{Molecular weight}$$

17. What is basicity of an acid?

It is the number of replaceable hydrogen atoms in a molecule of the acid.

18. What is the relation between equivalent mass of acid and molecular mass?

$$\text{Equivalent mass of acid} = \frac{\text{Molecular mass}}{\text{Basicity}}$$

19. What is standard solution?

The solution whose concentration i.e. is known is called standard solution.

Attempt it yourself:

1. What is the principle of chromatography?
2. Define R_f value.
3. Which type of filter paper is generally used in paper chromatography?
4. What are the advantages of chromatography over other techniques?
5. What is solvent front?
6. What is the stationary phase in paper chromatography?
7. What is the principle of crystallization?
8. What is mother liquor?
9. What is a double salt?
10. Why is dilute Sulphuric acid added to the solution during the dissolution of ferrous sulphate?
11. Why is water used for the preparation of Mohr's salt solution boiled for 5 minutes?
12. What is the shape of Mohr's salt crystal?
13. Which is more acidic: an alcohol or a phenol?
14. Which of the two is more acidic: phenol or carboxylic acid?
15. What happens when sodium bicarbonate is added to carboxylic acid?
16. Which carboxylic acid contains both carboxylic and hydroxyl group at ortho position in benzene?
17. Name two tests to distinguish aldehydes and ketones?
18. Name a reagent used to detect carbonyl group in a compound?
19. Carbylamine reaction is used to test which functional group?
20. What is carbylamine test?
21. Why titration flask should not be rinsed?
22. Why is the upper meniscus of the burette read in case of coloured solutions?
23. What is primary standard?
24. What do you understand by a secondary standard?
25. What should be done before filling a pipette or burette with the solution?
26. What do you understand by self- indicator?
27. What is an oxidizing agent?
28. What is an reducing agent?
29. What happens if dilute sulphuric acid is not added in KMnO₄ titrations?
30. Which indicator is used in KMnO₄ titrations?
31. Is KMnO₄ a primary standard?
32. Why it is necessary to heat the solution of oxalates of oxalic acid to 60°-70°C while titrating against kmno4 solution?
33. What is the end point in KMnO₄ titrations?

34. What is meant by acid and basic radicals?
35. Name the basic radicals which are absent, if the given mixture is not coloured?
36. Why blue crystals of copper sulphate are rendered colourless on heating?
37. NO_2 and Br_2 both are brown in colour. How will you distinguish between them?
38. Can we use a glass rod in place of platinum wire for performing flame test?
39. Name the radicals which are detected by dilute acid test?
40. Name the radicals which are detected by concentrated sulphuric acid test?
41. Which gas is evolved by the action of dilute acids on carbonates?
42. What happens when CO_2 is passed through lime water?
43. Why H_2S lead acetate paper black?
44. Why is lime water stored in a stoppered bottle?
45. Why do barium salts impart colour to flame after heating for some time?
46. Why do we add copper chips or paper pellets, in conc. H_2SO_4 acid test for nitrates?
47. What is the cause of formation of brown ring in the test for nitrates?
48. Can we use dilute HNO_3 in place of dilute HCl or H_2SO_4 and dilute acid test?
49. Why Br_2 and I_2 are evolved instead of HBr and HI in conc. H_2SO_4 test?
50. What is chromyl chloride?
51. Why do bromides and iodides do not give the chromyl chloride test?
52. Why is silver nitrate solution stored in coloured bottles?
53. What is the function of HCl in second group?
54. What is the function of NH_4Cl in III group?
55. What is the function of NH_4OH in IV group?
56. Can we use NaOH instead of NH_4OH in group III?
57. Name a cation which is not obtained from a metal.
58. What is the formula of chocolate brown precipitate formed by copper ions on adding potassium ferrocyanide solution?
59. Why only acetic acid is used for dissolving group V precipitates?
60. Why is freshly prepared FeSO_4 solution used for the ring test for nitrates?
61. What is blue lake?
62. What is the compound formed when a phosphate is treated with conc. HNO_3 and ammonium molybdate?
63. Why is original solution prepared for the detection of basic radicals?

Representative elements

PERIOD NUMBER	GROUP NUMBER	1	2
	IA	IIA	
2	Li	Be $2s^2$	
3	Na	Mg $3s^2$	
4	K	Ca $4s^2$	
5	Rb	Sc $3d^1 4s^2$	
6	Cs	Ba $5s^2$	
7	Fr	Ra $7s^2$	

d-Transition elements

PERIOD NUMBER	GROUP NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IVA	VIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	VIIA	Noble gases	
2	Ti $3d^2 4s^2$	V $3d^3 4s^1$	Cr $3d^4 4s^1$	Mn $3d^5 4s^1$	Fe $3d^6 4s^1$	Co $3d^7 4s^1$	Ni $3d^8 4s^1$	Cu $3d^9 4s^1$	Zn $3d^{10} 4s^1$	Ga $3d^{11} 4s^1$	Al $3s^2 3p^1$	Li $2s^2 2p^1$	Be $2s^2$	H $1s^1$					
3	Nb $4d^1 5s^2$	Ta $4d^2 5s^2$	W $4d^3 5s^2$	Re $4d^4 5s^2$	Os $4d^5 5s^2$	Pt $4d^6 5s^2$	Au $4d^7 5s^2$	Hg $4d^8 5s^2$	Tl $4d^9 5s^2$	In $4d^{10} 5s^2$	Sn $5s^2 5p^1$	Sb $5s^2 5p^3$	Te $5s^2 5p^5$	Br $4s^2 4p^5$	Cl $3s^2 3p^5$	F $2s^2 2p^5$	Ne $1s^2$		
4	Cr $4s^1$	Mn $4s^2$	Tc $4d^1 5s^2$	Ru $4d^2 5s^2$	Rh $4d^3 5s^2$	Pd $4d^4 5s^2$	Pt $4d^5 5s^2$	Ir $4d^6 5s^2$	Pt $4d^7 5s^2$	Pd $4d^8 5s^2$	Pd $4d^9 5s^2$	Pd $4d^{10} 5s^2$	Pd $4d^{11} 5s^2$	Pd $4d^{12} 5s^2$	Pd $4d^{13} 5s^2$	Pd $4d^{14} 5s^2$	Pd $4d^{15} 5s^2$		
5	Zr $4s^2$	Nb $4d^1 5s^2$	Ta $4d^2 5s^2$	W $4d^3 5s^2$	Re $4d^4 5s^2$	Os $4d^5 5s^2$	Pt $4d^6 5s^2$	Ir $4d^7 5s^2$	Pt $4d^8 5s^2$	Ir $4d^9 5s^2$	Pt $4d^{10} 5s^2$	Pt $4d^{11} 5s^2$	Pt $4d^{12} 5s^2$	Pt $4d^{13} 5s^2$	Pt $4d^{14} 5s^2$	Pt $4d^{15} 5s^2$	Pt $4d^{16} 5s^2$		
6	La* $5s^2$	La* $5d^2 6s^2$	La* $4f^1 5d^6 6s^2$	Ta $5d^3 6s^2$	W $5d^4 6s^2$	Re $5d^5 6s^2$	Os $5d^6 6s^2$	Pt $5d^7 6s^2$	Ir $5d^8 6s^2$	Pt $5d^9 6s^2$	Pt $5d^{10} 6s^2$	Pt $5d^{11} 6s^2$	Pt $5d^{12} 6s^2$	Pt $5d^{13} 6s^2$	Pt $5d^{14} 6s^2$	Pt $5d^{15} 6s^2$	Pt $5d^{16} 6s^2$		
7	Ra $7s^2$	Ra $6d^1 7s^2$	Ra $5f^1 6d^1 7s^2$	Ra $5f^2 6d^1 7s^2$	Ra $5f^3 6d^1 7s^2$	Ra $5f^4 6d^1 7s^2$	Ra $5f^5 6d^1 7s^2$	Ra $5f^6 6d^1 7s^2$	Ra $5f^7 6d^1 7s^2$	Ra $5f^8 6d^1 7s^2$	Ra $5f^9 6d^1 7s^2$	Ra $5f^{10} 6d^1 7s^2$	Ra $5f^{11} 6d^1 7s^2$	Ra $5f^{12} 6d^1 7s^2$	Ra $5f^{13} 6d^1 7s^2$	Ra $5f^{14} 6d^1 7s^2$	Ra $5f^{15} 6d^1 7s^2$		

Representative elements

PERIOD NUMBER	GROUP NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	III A	IV A	V A	VI A	VII A	Noble gases											
2	Li	Be $2s^2$																	
3	Na	Mg $3s^2$																	
4	K	Ca $4s^2$																	
5	Rb	Sc $3d^1 4s^2$																	
6	Cs	Ba $5s^2$																	
7	Fr	Ra $7s^2$																	

f - Inner transition elements

Lanthanoids $4f^3 5d^1 6s^2$	Pr $4f^2 5d^1 6s^2$	Nd $4f^3 5d^1 6s^2$	Pm $4f^4 5d^1 6s^2$	Sm $4f^5 5d^1 6s^2$	Eu $4f^6 5d^1 6s^2$	Gd $4f^7 5d^1 6s^2$	Tb $4f^8 5d^1 6s^2$	Dy $4f^9 5d^1 6s^2$	Ho $4f^{10} 5d^1 6s^2$	Er $4f^{11} 5d^1 6s^2$	Tm $4f^{12} 5d^1 6s^2$	Yb $4f^{13} 5d^1 6s^2$	Lu $4f^{14} 5d^1 6s^2$
Actinoids $5f^2 6d^1 7s^2$	Pa $5f^2 6d^1 7s^2$	U $5f^3 6d^1 7s^2$	Am $5f^4 6d^1 7s^2$	Pu $5f^5 6d^1 7s^2$	Cm $5f^6 6d^1 7s^2$	Bk $5f^7 6d^1 7s^2$	Cf $5f^8 6d^1 7s^2$	Es $5f^9 6d^1 7s^2$	Fm $5f^{10} 6d^1 7s^2$	Md $5f^{11} 6d^1 7s^2$	No $5f^{12} 6d^1 7s^2$	Lr $5f^{13} 6d^1 7s^2$	

LOGARITHMS

TABLE I

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6471	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

TABLE 1 (Continued)

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7768	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9997	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

TABLE II

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	3	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	3	4	5	6	6

ANTILOGARITHMS

TABLE II (Continued)

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20