MM: 70   **Time: 3 hours**

General Instructions:

Read the following instructions carefully.

   a) There are **35** questions in this question paper with internal choice.
   b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
   c) SECTION B consists of 7 very short answer questions carrying 2 marks each.
   d) SECTION C consists of 5 short answer questions carrying 3 marks each.
   e) SECTION D consists of 2 case- based questions carrying 4 marks each.
   f) SECTION E consists of 3 long answer questions carrying 5 marks each.

   g) **All questions are compulsory.**

   h) **Use of log tables and calculators is not allowed**

Section A

1. The standard reduction potentials at 298 K for the following half-reactions are given **[1]** against each:

   $Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s); E^o = -0.762$ V

   $Cr^{2+}(aq) + 2e \rightleftharpoons Cr(s); E^o = -0.740$ V

   $2H^+(aq) + 2e \rightleftharpoons H_2(g); E^o = -0.000$ V

   $Fe^{3+}(aq) + 2e \rightleftharpoons Fe^{2+}(aq); E^o = -0.770$ V
   which is the strongest reducing agent?

   a) $Fe^{2+}(aq)$ b) $Zn(s)$

   c) $H_2(g)$ d) $Cr(s)$

2. Which of the following acids is a vitamin?   **[1]**

   a) Adipic acid   b) Aspartic acid

   c) Saccharic acid   d) Ascorbic acid

3. Methyl bromide is converted into ethane by heating it in ether medium with   **[1]**
   _____.

   a) Na   b) Al

   c) Cu   d) Zn

4. The correct structure for compound B will be: **[1]**

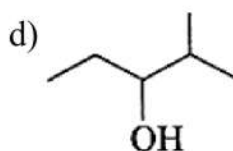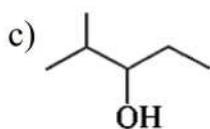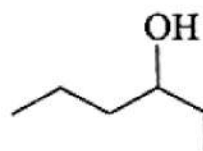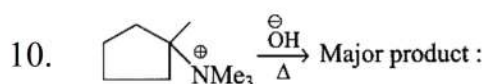   a)   b)

c)

d)

5. One mole of a symmetrical alkane on ozonolysis gives two moles of an aldehyde having a molecular mass of 44u. The alkene is: **[1]**

   a) 1 – butene   b) 2 – butene

   c) Propene   d) Ethene

6. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds? **[1]**

   a) They retain metallic conductivity.   b) They have high melting points in comparison to pure metals.

   c) They are chemically very reactive.   d) They are very hard.

7. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5% solution (by mass) of glucose in water is **[1]**

   a) 271 K   b) 269.07 K

   c) 273.15 K   d) 277.23 K

8. Two solutions have different osmotic pressures. The solution of lower osmotic pressure is called: **[1]**

   a) isotonic solution   b) hypotonic solution

   c) hypertonic solution   d) none of these

9. The cell constant of a conductivity cell _____. **[1]**

   a) changes with temperature of electrolyte   b) changes with change of electrolyte

   c) remains constant for a cell   d) changes with change of concentration of electrolyte

10. $\xrightarrow[\Delta]{\overset{\ominus}{O}H}$ Major product : **[1]**

   Which of following is correct?

a) b)

c) d)

11. How many d–block elements have the ability to evolve hydrogen gas from 2% nitric **[1]** acid?

    a) Many   b) 1

    c) 3   d) 2

12. The minimum number of carbon atoms that should be present in carbohydrate is: **[1]**

    a) 6   b) 2

    c) 4   d) 3

13. When initial concentration of the reactant is doubled, the half-life period of a zero-order reaction: **[1]**

    a) is tripled   b) remains unchanged

    c) is halved   d) is doubled

14. Which of the following complex will show maximum conductance? **[1]**

    a) $Cr(NH_3)_5Cl]Cl_2$ b) $[Cr(NH_3)_4Cl_2]Cl$

    c) $Cr(NH_3)_6]Cl_3$ d) $[Cr(NH_3)_3Cl_3]$

15. **Assertion (A):** S_N2 reaction of an optically active aryl halide with an aqueous **[1]** solution of KOH always gives an alcohol with opposite sign of rotation.
Reason (R): S_N2 reactions always proceed with inversion of configuration.

    a) Both A and R are true and R is   b) Both A and R are true but R is
       the correct explanation of A.   not the correct explanation of A.

    c) A is true but R is false.   d) A is false but R is true.

16. **Assertion (A):** The boiling point of 200 mL of 1 M urea solution is less than that of **[1]** 200 mL of 2 M glucose solution.
Reason (R): Elevation of boiling point is directly proportional to the number of species present in the solution.

    a) Both A and R are true and R is   b) Both A and R are true but R is
       the correct explanation of A.   not the correct explanation of A.

    c) A is true but R is false.   d) A is false but R is true.

17. **Assertion (A):** Alcohols have higher boiling points than ethers of comparable **[1]** molecular masses.
Reason (R): Alcohols and ethers are isomeric compounds.

a) Both A and R are true and R is the correct explanation of A.

b) Both A and R are true but R is not the correct explanation of A.

c) A is true but R is false.

d) A is false but R is true.

18. **Assertion (A):** E_{Cell} should have a positive value for the cell to function. [1]

Reason (R): $E_{cathode} < E_{anode}$

a) Both A and R are true and R is the correct explanation of A.

b) Both A and R are true but R is not the correct explanation of A.

c) A is true but R is false.

d) A is false but R is true.

Section B

19. Account for the following: [2]

   i. Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical.

   ii. Sodium bisulphite is used for the purification of aldehyde and ketones.

OR

Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous $AlCl_3$. Name the reaction also.

20. What is meant by hexadentate ligand? Give one example. How is such ligand useful for measuring hardness of water. [2]

21. For a reaction, $A + B \rightarrow$ product, the rate law is given by $r = k[A]^{1/2}[B]^2$. What is the order of the reaction? [2]

22. Square planar complexes with a coordination number 4 exhibits geometrical isomerism whereas tetrahedral complexes do not why? [2]

23. Deduce the shape and magnetic behaviour of the complex ion $[Co(NH_3)_5 NO_2]^{2+}$.[Atomic number of Co = 27] [2]

OR

Using the valence bond theory, predict the shape and magnetic behaviour of $[Cr(NH_3)_5Cl^{2+}$ ion.

24. How is aminomethane obtained from ethanal (acetaldehyde)? [2]

25. What is denaturation and renaturation of proteins? [2]

Section C

26. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 40° C is 1.8×10^{-1} sec^{-1}. Calculate the frequency factor A. [3]

27. Write one chemical reaction each to exemplify the following: [3]

   i. Rosenmund reduction

   ii. Tollen's reagent.

28. Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why? **[3]**

29. In each of the following pairs of compounds, identify the compound which will undergo S_N1 reaction faster. **[3]**

    i. and

    ii. and
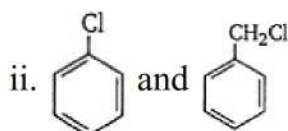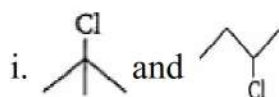
30. Define the following and give one example of each: **[3]**
    a. Isoelectric point
    b. Mutarotation
    c. Enzymes

<center>OR</center>

    Write chemical reactions to show that open structure of D-glucose contains the following:
    i. Straight chain
    ii. Five alcohol groups
    iii. Aldehyde as carbonyl group

<center>**Section D**</center>

31. **Read the text carefully and answer the questions:** **[4]**

    Transition metal oxides are generally formed by the reaction of metals with oxygen at high temperatures. The highest oxidation number in the oxides coincides with the group number. In vanadium, there is a gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give VO^{2+} salts. Potassium dichromate is a very important chemical used in the leather industry and as an oxidant for the preparation of many azo compounds. Dichromates are generally prepared from chromate. Sodium dichromate is more soluble than potassium dichromate. The latter is, therefore, prepared by treating the solution of sodium dichromate with potassium chloride. Sodium and potassium dichromates are strong oxidising agents; sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis.

    (i) Which of the 3d series of the transition metals exhibits the largest number of oxidation and why?

    (ii) A transition metal exhibits highest oxidation state ih oxides and fluorides. Give reason.

    (iii) How would you account for the increasing oxidising power in the series:

$$VO_2^+ < Cr_2O_7^{2-} < MnO_4^- \ ?$$
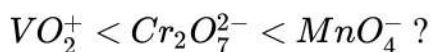
OR

MnO is basic whereas Mn_2O_7 is acidic in nature. Give reason.

32. **Read the text carefully and answer the questions:** [4]

Vapour pressure of a liquid or a solution is the pressure exerted by the vapour in equilibrium with the liquid or solution at a particular temperature. It depends upon the nature of the liquid and temperature. The non-volatile solute in solution reduces the escaping tendency of the solvent molecules in the vapour phase because some of the solute particles occupy the positions of the solvent molecules on the liquid surface. The relative lowering of the vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution. This is also known as Raoult's law. However, for solutions of volatile solutes, the vapour pressure of a component in a solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that pure component. The solutions in which each component obeys Raoult's law is called an ideal solution. For ideal solutions ΔH_{mixing} and ΔV_{mixing} are also zero. Practically no solution is ideal. A non-ideal solution is that solution in which solute and solvent molecules interact with one another with a different force than the forces of interaction between the molecules of the pure components. There are two types of non-ideal solutions, showing positive deviations and negative deviations from ideal behaviour. If for the two components A and B, the forces of interaction between A and B molecules are less than the A-A and B-B interactions, the non-ideal solutions have positive deviations. On the other hand, if the forces of interaction between A and B molecules are more than the A-A and B-B interactions, the non-ideal solutions have negative deviations.

(i) What is the mole fraction of A in solution obeying result's low if the vapour pressure of a pure liquid A is 40 mm of Hg at 300 K. The vapour pressure of this liquid in solution with liquid B is 32 mm of Hg?

(ii) Vapour pressure of a solution of heptane & octane is given by the equation: P(sol.)(mm Hg) = 35 + 65x, where x is the mole fraction of heptane. Calculate the vapour pressure of pure octane.

(iii) What is the value of ΔV_{mixing} and ΔH_{mixing} for non-ideal solution showing negative deviation?

OR

Acetic acid + pyridine, the mixture is an example of which type of solution?

Section E

33. Give one chemical test to distinguish between the following pairs of compounds. [5]
    i. Methylamine and dimethylamine
    ii. Secondary and tertiary amines
    iii. Ethylamine and aniline
    iv. Aniline and benzylamine
    v. Aniline and N-methylaniline.

OR

    a. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

    b. Complete the following reactions:

        i. $C_6H_5NH_2 + CHCl_3 +$ alc. $KOH \rightarrow$

        ii. $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$

34.   Calculate the standard cell potentials of galvanic cells in which the following   **[5]**
reactions take place:

    i. $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$

    ii. $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

    Calculate the $\Delta_r G^{\Theta}$, and equilibrium constant of the reactions.

OR

A strip of nickel metal is placed in a 1-molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1-molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltameter.

Write the balanced equations for the overall reaction occurring in the cell and calculate the cell potential.

$(E^{\theta}_{Ni^2/Ni} = -0.25V; E^{\theta}_{Ag^+/Ag} = 0.80V)$

35.   Answer the following questions: **[5]**

(i)   For the homogeneous decomposition of N_2O_5 into NO_2 and O_2;
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
Rate = k $[N_2O_5]$
Find out the order of reaction with respect to N_2O_5.
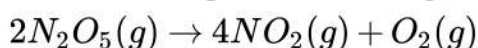
(ii)   Give IUPAC name of :
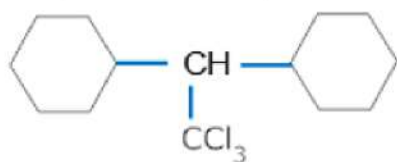
(iii)   Write IUPAC name of :-

$$CH_3 - \overset{\overset{\displaystyle Cl}{|}}{CH} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle SH}{|}}{CH} - CH_3$$
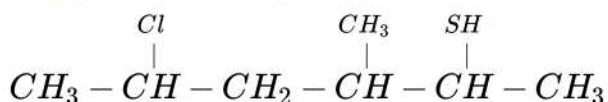
(iv)   What is the role of HNO_3 in the nitrating mixture used for nitration of benzene?

(v)   Why is the E^{θ} value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}? Explain.

SOLUTION

1. **(a)** Fe^{2+}(aq)

   Explanation: E_{OP}° for Fe^{2+}/Fe^{3+} = +0.77 V (maximum in given values). More positive is E_{OP}°, more is the tendency to get it self oxidised or strong reducing agent.

2. **(d)** Ascorbic acid

   Explanation: Ascorbic acid is vitamin C. Aspartic acid is an amino acid. Adipic acid and saccharic acid are dicarboxylic acids.
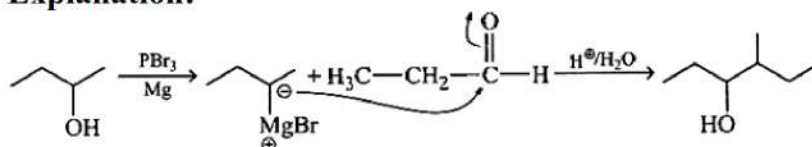
3. **(a)** Na

   Explanation: $2CH_3Br + 2Na \rightarrow CH_3CH_3 + 2NaBr$

4. **(d)**
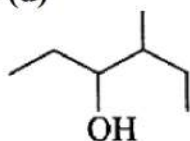
   Explanation:

5. **(b)** 2 – butene

   Explanation: 2-butene on reductive ozonolysis with O_3/Zn will give CH_3CHO which has a molecular mass of 44u.

   $CH_3CH=CHCH_3 + O_3/Zn \rightarrow 2CH_3CHO$

   Molecular mass of $CH_3CHO = 12 + 3 + 12 + 1 + 16 = 44u$

6. **(c)** They are chemically very reactive.

   Explanation: Interstitial compounds are chemically inert not reactive.

7. **(b)** 269.07 K

   Explanation: For cane sugar ? T_f=273.15 -271.0 =2.15 K

   Thus K_f= (? T_f x M_B X W_A)/(W_B X1000)

   =2.15 X 342 X100/(5 X1000)

   =14.71 K Kg mol-1

   For glucose solution

   ? T_f =K_fxW_B X1000/(M_B XW_A)

   = 14.71 X1000 X 5 /(100 X180)

   =4.085

   Therefore freezing point of v 5% glucose solution is =273.15 -4.085=269.07K

8. **(b)** hypotonic solution

   Explanation: In a pair of two solutions the one having higher osmotic pressure is called hypertonic and the other having lower osmotic pressure is called hypotonic.

9. **(c)** remains constant for a cell

   Explanation: The cell constant of a conductivity (k) cell remains constant for a battery cell.

10. **(a)**

    Explanation:

Quaternary ammonium salt produce less substituted alkene as major product.
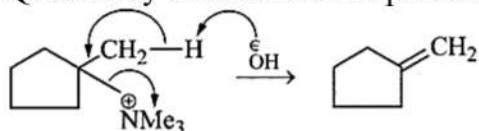
11. **(d)** 2

    Explanation: Both Zn and Fe can displace Hydrogen from HNO_3.

12. **(d)** 3

    Explanation: A monosaccharide is a single polyhydroxy aldehyde (aldose) or ketone (ketose) unit. Glucose is a single polyhydroxy aldehyde, while fructose is a single polyhydroxy ketone. A monosaccharide contains a skeleton, of carbon atoms. The minimum number of carbon atoms is three and it can go up to seven.

13. **(d)** is doubled

    Explanation: Half-life of zero order

    $t_{1/2} = \frac{[A_0]}{2K}$

    $\therefore (t_{1/2})_1 = \frac{[A_0]}{2K}$

    $\therefore (t_{1/2})_1 = \frac{2[A_0]}{2K}$

    $t_{1/2}$ will be doubled on doubling the initial concentration.

14. **(c)** $Cr(NH_3)_6]Cl_3$

    Explanation: Coordination number of Cr is six and thus $[Cr(NH_3)_6]Cl_3$ furnishes four ions to give maximum conductance.

    $[Cr(NH_3)_6]Cl_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 3Cl^-$
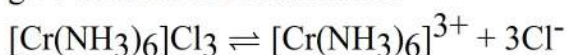
15. **(d)** A is false but R is true.

    Explanation: Assertion is false, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon– chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles. However Reason is true.

16. **(a)** Both A and R are true and R is the correct explanation of A.

    Explanation: Both A and R are true and R is the correct explanation of A.

17. **(b)** Both A and R are true but R is not the correct explanation of A.

    Explanation: Both A and R are true but R is not the correct explanation of A.

18. **(c)** A is true but R is false.

    Explanation: $E_{cell} = E_{cathode} - E_{anode}$. To have a positive value of E_{cell} then, $E_{cathode} > E_{anode}$.

Section B

19. i. Ethers are bent molecules where the oxygen-alkyl bond dipoles do not get cancelled. Therefore, ethers show a net dipole moment.

    ii. Aldehydes and ketones react with $NaHSO_3$ whereas the impurities do not react. The bisulphite salt thus obtained can be hydrolysed to get pure aldehydes and ketones back.

    OR

    Benzene, on reaction with benzoyl chloride, undergoes the formation of benzophenone in the presence of anhydrous aluminium chloride through intermediate benzoylinium cation.
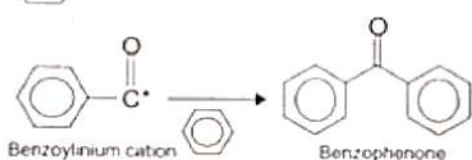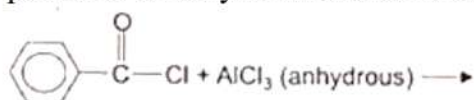
    This is an example of a Friedel-Craft acylation reaction.

20. Hexadentate ligand is a ligand which has 6 donor atoms, e.g. EDTA.

EDTA forms complex with Ca^{2+} and Mg^{2+} therefore it is used for estimating hardness of water.

21. Order of reaction $= \frac{1}{2} + 2$

$= 2\frac{1}{2}$ or 2.5

22. The tetrahedral complexes do not show geometrical isomerism because the relative positions of the atoms with respect to each other will be the same. The square planar complexes on the other hand show geometrical isomerism because if same kind of ligands occupy positions adjacent to each other it is called cis-form and if these are opposite to each other it is called trans-form.

23. Co: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

Co^{3+} ion has outer electronic configuration: $4s^0 3d^6$. NH_3 causes pairing of electrons in d-orbital as shown below:

It has octahedral shape. It is diamagnetic because it does not have unpaired electrons.

OR

Electronic configuration of Cr: $[Ar] 4s^4 3d^5$

Electronic configuration of Cr^{3+} : $[Ar] 4s^0 3d^3$
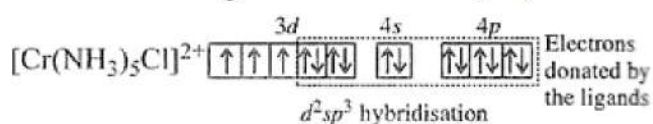
It has octahedral shape. It is paramagnetic in nature due to the presence of unpaired electrons.

24.
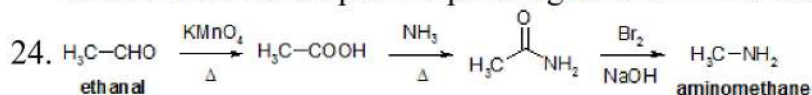
25. The process of disruption of 2° and 3° structure without changing its primary structure is called denaturation. If the disruptive agent is removed and protein recovers its original structure it is called renaturation.

Section C

26. Given, $E_a = 94.14 \times 10^3$ J mol^{-1}, T = 40 + 273 = 313 K, K = 1.8×10^{-1} sec^{-1}
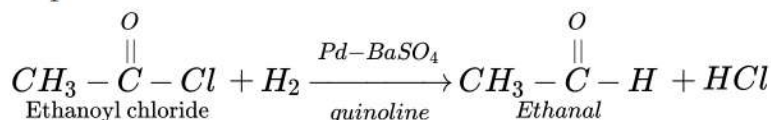
By using, $\log K = \log A - \frac{E_a}{2.303 RT}$

Or $\log K = \log A - \frac{E_a}{2.303 RT}$

Or $\log (1.8 \times 10^{-1}) + \frac{94.19 \times 10^3}{2.303 \times 8.314 \times 313} = \log A$

Or A = antilog (10.9635) = 9.194×10^{10} sec^{-1}

27. 1. **Rosenmund reduction:** Acyl chloride is hydrogenated over a catalyst, palladium on barium sulphate. This reaction is called Rosenmund Reaction.

$$CH_3 - \overset{\overset{O}{\|}}{C} - Cl + H_2 \xrightarrow[quinoline]{Pd-BaSO_4} CH_3 - \overset{\overset{O}{\|}}{C} - H + HCl$$

Ethanoyl chloride → Ethanal

2. **Tollen's reagent:** On warming an aldehyde with freshly prepared ammonical silver nitrate solution (Tollen's 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.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3\,\overline{O}H \rightarrow RCO\overline{O} + 2Ag + 2H_2O + 4NH_3$$
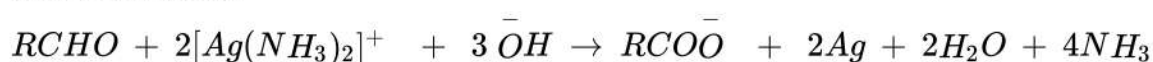
28. Phenol is more easily nitrated than benzene because the oxygen of the -OH group in phenol contains lone pairs and then showed + M effect, which increases the electron density at 0 and p-positions in the benzene ring as a result electrophiles attacks at more faster than benzene

Nitration which is an electrophilic substitution reaction takes place more readily where the electron density is more.

29. i. Since 3° carbocations are more stable than 2° carbon cations therefore will react faster.

   ii. Benzyl chloride readily forms benzyl cation which is stabilized by resonance. Thus, benzyl chloride undergoes S_N1 reaction faster than chlorobenzene.

30. a. **Isoelectric point.** It is the pH at which +ve and -ve charges on zwitter ion are equal, e.g. amino acid exists as zwitterions at pH = 5.5 to 6.3

   b. **Mutarotation.** It is a spontaneous change in optical rotation when an optically active substance is dissolved in water, e.g. α-glucose, when dissolved in water, its optical rotation changes from 111° to 52.5°.

   c. **Enzymes.** Enzymes are biocatalysts which speed up the reactions in biosystems. They are very specific and selective in their action. Chemically all enzymes are proteins.

OR

   i. Chemical reaction to show that open structure of D-glucose contains straight chain:
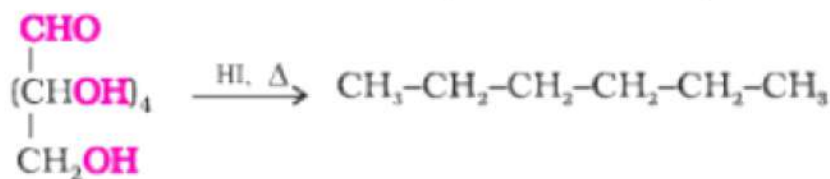
   ii. Chemical reaction to show that open structure of D-glucose contains five alcohol groups:
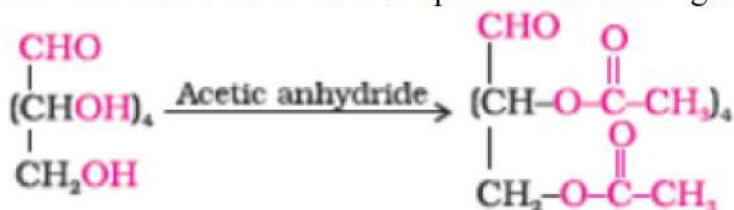
   iii. Chemical reaction to show that open structure of D-glucose contains the aldehyde as carbonyl group:

Section D

31. **Read the text carefully and answer the questions:**

Transition metal oxides are generally formed by the reaction of metals with oxygen at high temperatures. The highest oxidation number in the oxides coincides with the group number. In vanadium, there is a gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give VO^{2+} salts. Potassium dichromate is a very important chemical used in the leather industry and as an oxidant for the preparation of many azo compounds. Dichromates are generally prepared from chromate. Sodium dichromate is more soluble than potassium dichromate. The latter is, therefore, prepared by treating the solution of sodium dichromate with potassium chloride. Sodium and potassium dichromates are strong oxidising agents; sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis.

(i) Manganese (Z = 25) shows maximum number of O.S. This is because its outer EC is $3d^54s^2$. As 3d and 4s are close in energy, it has maximum number of e-1 s to loose or share. Hence, it shows O.S. from +2 to +7 which is the maximum number.

(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are highly electronegative elements, small in size and strongest oxidising agents.

(iii)This is due to the increasing stability of the lower species to which they are reduced.

OR

When a metal is in a high oxidation state, its oxide is acidic and when a metal is in a low oxidation state its oxide is basic.

32. **Read the text carefully and answer the questions:**

Vapour pressure of a liquid or a solution is the pressure exerted by the vapour in equilibrium with the liquid or solution at a particular temperature. It depends upon the nature of the liquid and temperature. The non-volatile solute in solution reduces the escaping tendency of the solvent molecules in the vapour phase because some of the solute particles occupy the positions of the solvent molecules on the liquid surface. The relative lowering of the vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution. This is also known as Raoult's law. However, for solutions of volatile solutes, the vapour pressure of a component in a solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that pure component. The solutions in which each component obeys Raoult's law is called an ideal solution. For ideal solutions ΔH_{mixing} and ΔV_{mixing} are also zero. Practically no solution is ideal. A non-ideal solution is that solution in which solute and solvent molecules interact with one another with a different force than the forces of interaction between the molecules of the pure components. There are two types of non-ideal solutions, showing positive deviations and negative deviations from ideal behaviour. If for the two components A and B, the forces of interaction between A and B molecules are less than the A-A and B-B interactions, the non-ideal solutions have positive deviations. On the other hand, if the forces of interaction between A and B molecules are more than the A-A and B-B interactions, the non-ideal solutions have negative deviations.

(i) $P_A = x_A \times P_A^\circ$

$32 = x_A \times 40$

$x_A = \frac{32}{40}$

$x_A = 0.8$

(ii) For pure octane, x = 0

∴ p(sol.)(mm Hg) = P (octane) = 35 + 65 × 0 = 35 mm of Hg

(iii)The value of ΔV_{mixing} and ΔH_{mixing} is negative.

OR

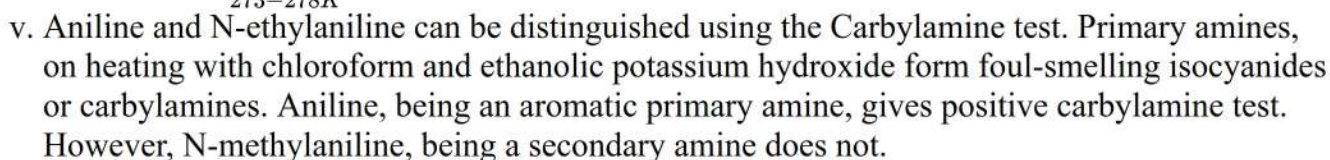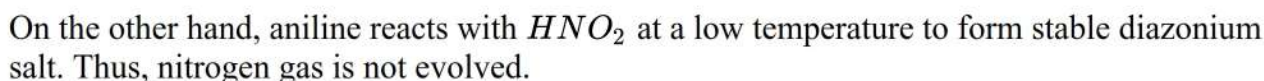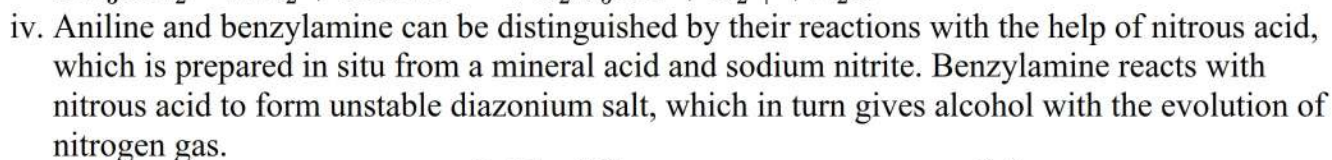It is an example of Non-ideal solution.

Section E

33. i. Methylamine and dimethylamine can be distinguished by the carbylamine test. Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

ii. Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).

Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N - diethylamine reacts with Hinsberg's reagent to form N, N - diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.

iii. Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with $HNO_2\,(NaNO_2 + dil.\ HCl)$ at $0 - 5°C$ followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour.

Aliphatic amines give a brisk effervescence due to the evolution of N_2 gas under similar conditions.

$$CH_3CH_2 - NH_2 + HONO \xrightarrow{0-5°} C_2H_5OH + N_2 \uparrow + H_2O$$

iv. Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite. Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.

$$C_6H_5CH_2 - NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [C_6H_5CH_2 - N_2^+Cl^-] \xrightarrow{H_2O} N_2 \uparrow + C_6H_5{}_6CH_2$$
$$\underset{Benzyla\,min\,e}{} \qquad \underset{Unstable}{} \qquad \underset{Benzyl\,alcohol}{}$$

$$- OH + HCl$$

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

$$C_6H_5NH_2 \xrightarrow[273-278K]{NaNO_2 + HCl} C_6H_5 - \overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$$

v. Aniline and N-ethylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.

<div align="center">OR</div>

a. i. Since the compound C of molecular formula C₆H₇N is formed B on treatment with Br₂ and KOH (Hoffmann bromamide reaction), therefore, the compound 'B' must be an amide and 'C' must be an amine. The only aromatic amine having molecular formula C₆H₇N is C₆H₅NH₂ (aniline).

ii. Since 'C' is aniline, the amide from which is formed by must be benzamide (C₆H₅CONH₂).

$$\underset{Aniline\,(C)}{C_6H_5NH_2} \xleftarrow{Br_2,\ KOH} \underset{Benzamide\,(B)}{C_6H_5CONH_2}$$

Thus, B is benzamide.

iii. Since B is formed from A with aqueous ammonia and heating, therefore, compound 'A' must be benzoic acid.

$$\underset{Benzoic\,acid\,(A)}{C_6H_5COOH} \xrightarrow[Heat]{aq.NH_3} \underset{Benzamide\,(B)}{C_6H_5CONH_2}$$

Thus, A = C₆H₅COOH, B = C₆H₅CONH₂, C = C₆H₅NH₂.

b. i. C₆H₅NH₂ + CHCl₃ + 3KOH → $\underset{Phenyl\,isocyanide}{C_6H_5NC}$ + 3KCl + 3H₂O
$\qquad \qquad \qquad \underset{(alc)}{}$

ii. C₆H₅N₂Cl + H₃PO₂ + H₂O → $\underset{Benzene}{C_6H_6}$ + N₂ + H₃PO₃ + HCl

34. i. $E^{\ominus}{}_{Cr^{3+}/Cr} = 0.74V$

$E^{\ominus}{}_{Cd^{2+}/Cd} = 0.40V$

The galvanic cell of the given reaction is depicted as: $Cr_{(s)}|Cr^{3+}{}_{(aq)}||Cd^{2+}{}_{(aq)}|Cd_{(s)}$

Now, the standard cell potential is $E^{\ominus}_{cell} = E^{\ominus}_R - E^{\ominus}_L$

= 0.40 - (-0.74)

= +0.34 V

$\Delta_r G^\Theta = -nFE^\Theta_{cell}$

In the given equation,

n = 6

F = 96487 C mol^{-1}

E^Θ_{cell} = +0.34 V

Then, $\Delta_r G^\Theta = -6 \times 96487 C mol^{-1} \times 0.34V$

= -196833.48 CV mol^{-1}

= -196833.48 J mol^{-1}

= -196.86 kJ mol^{-1}

Again, $\Delta_r G^\Theta = -RT \ln K$

$\Delta_r G^\Theta = -2.303 RT \ln K$

$\log K = -\frac{\Delta_r G}{2.303 RT}$

$= \frac{196.83 \times 10^3}{2.303 \times 8.314 \times 298}$

= 34.496

Therefore, K = antilog (34.496)

$= 3.13 \times 10^{34}$

ii. $E^\Theta_{Fe^{3+}/Fe^{2+}} = 0.77\,V$

$E^\Theta_{Ag^+/Ag} = 0.80\,V$

The galvanic cell of the given reaction is depicted as: $Fe^{2+}_{(aq)}|Fe^{3+}_{(aq)}||Ag^+_{(aq)}|Ag_{(s)}$

Now, the standard cell potential is $E^\Theta_{cell} = E^\Theta_R - E^\Theta_L$

= 0.80 - 0.77

= 0.03 V

Here, n = 1.

Then, $\Delta_r G^\Theta = -nFE^\Theta_{cell}$

$= -1 \times 96487 C mol^{-1} \times 0.03V$

= -2894.61 J mol^{-1}

= -2.89 kJ mol^{-1}

Again, $\Delta_r G^\Theta = 2.303 RT \ln K$

$\log K = -\frac{\Delta_r G}{2.303 RT}$

$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$

= 0.5073

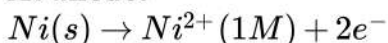Therefore, K = antilog (0.5073)

= 3.2 (approximately)

<div align="center">OR</div>
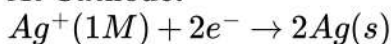
Reactions involved for the electrochemical cells are
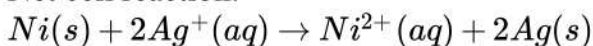
At anode:

$Ni(s) \rightarrow Ni^{2+}(1M) + 2e^-$

At Cathode:

$Ag^+(1M) + 2e^- \rightarrow 2Ag(s)$

Net cell reaction:

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

For this reaction, n=-2 moles of electrons.

For standard emf of the cell, we have

$E^\Theta_{cell} = E^\Theta_{cathode} - E^\Theta_{anode}$

= 0.80 - (-0.25)

= 1.05 V

To find the emf of the cell, we use Nernst equation.

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.059}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$
$$E_{Cell} = 1.05 - \frac{0.059}{2} \log\left(\frac{1}{1}\right)$$
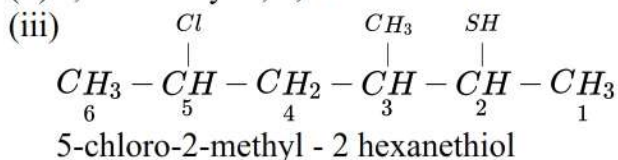$$= 1.05 - \frac{0.059}{2}(0)$$
$$= 1.05V$$
$$\therefore E_{cell} = 1.05\ V$$

35. Answer the following questions:

(i) It is first order with respect to N_2O_5.

(ii) 2, 2- Dihexyl 1, 1, 1-Trichloro ethane

(iii)

$$\underset{6}{CH_3} - \underset{5}{\overset{\overset{Cl}{|}}{CH}} - \underset{4}{CH_2} - \underset{3}{\overset{\overset{CH_3}{|}}{CH}} - \underset{2}{\overset{\overset{SH}{|}}{CH}} - \underset{1}{CH_3}$$

5-chloro-2-methyl - 2 hexanethiol

(iv) HNO_3 acts as a base in the nitrating mixture and provides the electrophile, NO_2^+ (nitronium ion).

(v) Much larger third ionisation energy of (Manganese) Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.