CBSE EXAMINATION PAPER-2023

CHEMISTRY

(Solved)

Time allowed : 3 hours | Maximum Marks : 78

General Instructions :

Read the following instructions carefully and follow them :

i. This question paper contains **41 questions.** All questions are **compulsory.**

ii. This question paper is divided into **5 sections.**

iii. **Section A** – questions number **1 to 3** are case based questions

iv. **Section B** – questions number **4 to 21** are multiple choice questions

v. **Section C** – questions number **22 to 30** are very short answer

vi. **Section D** – questions number **31 to 36** are short answer

vii. **Section E** – questions number **37 to 41** are long answer

viii. There is no overall choice given in the question paper. However, an internal choice has been provided in few questions.

ix. Use of calculator is NOT allowed.

Section A

Question 1. Nucleophilic Substitution reaction of haloalkane can be conducted according to both SN1 and SN2 mechanisms. SN1 is a two step reaction while SN2 is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent. Influences of solvent polarity: In SN1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction. In SN2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar

solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slowing down the reaction rate. For example, the decomposition rate (SN1) of tertiary chlorobutane at 25 °C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (SN2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence the level of solvent polarity has influence on both SN1 and SN2 reaction, but with different results. Generally speaking, weak polar solvent is favourable for SN2 reaction, while strong polar solvent is favourable for SN1. Generally speaking, the substitution reaction of tertiary haloalkane is based on SN1 mechanism in solvents with a strong polarity (for example ethanol containing water).

Question 2.

The following questions are case – based questions. Read the passage carefully and answer the questions that follow :

Nucleophilic Substitution

Nucleophilic Substitution reaction of haloalkane can be conducted according to both SN1 and SN2 mechanisms. SN1 is a two step reaction while SN2 is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent. Influences of solvent polarity : In SN1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction. In SN2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (SN1) of tertiary chlorobutane at 25 °C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (SN2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence the level of solvent polarity has influence on both SN1 and SN2 reaction, but with different results. Generally speaking weak polar solvent is favourable for SN2 reaction, while strong polar solvent is favourable for SN1. Generally speaking the substitution reaction of tertiary haloalkane is based on SN1 mechanism in solvents with a strong polarity (for example ethanol containing water).

(1)

Why racemisation occurs in SN1 ?

[1 Marks]

Answer: Racemisation occurs in SN1 reactions due to the formation of a planar carbocation intermediate, which allows the attacking nucleophile to approach from either side of the positively charged carbon atom. As a result, two different stereoisomers (enantiomers) are formed in equal amounts, leading to a racemic mixture.

Key Points: 1. Formation of a planar carbocation intermediate 2. Attacking nucleophile can approach from either side 3. Results in equal formation of enantiomers

(2)

Why is ethanol less polar than water ?

[1 Marks]

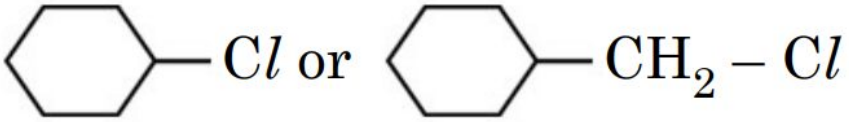
Answer: Ethanol is less polar than water primarily due to its molecular structure. Water has a highly polar O-H bond with a significant difference in electronegativity between oxygen and hydrogen, resulting in a strong dipole moment. Ethanol also has an O-H bond, but the presence of the hydrocarbon ethyl group (C2H5) makes the molecule less polar overall. The alkyl part of ethanol contributes to its non-polar characteristics, reducing the overall polarity compared to water, which has no non-polar groups.

Key Points: Difference in electronegativity between O and H in water is large; ethanol has a hydrocarbon (C2H5) that decreases polarity; water is a highly polar molecule, while ethanol has both polar and non-polar characteristics.

(3)

Which one of the following in each pair is more reactive towards SN2 reaction ?

(i) $CH_3 - CH_2 - I$ or $CH_3CH_2 - Cl$

(ii)  or

[2 Marks]

Answer: The substrate that has less steric hindrance and a better leaving group will be more reactive towards SN2 reactions. Therefore, generally, primary alkyl halides are more reactive than secondary, while tertiary alkyl halides are usually not reactive due to steric hindrance.

Key Points:

(i) $CH_3–CH_2–I$ or $CH_3–CH_2–Cl$

Both are primary alkyl halides, so steric factor is same.

But I^- is a better leaving group than Cl^- (weaker C–I bond, larger size).

More reactive: $CH_3–CH_2–I$

(ii) Cyclohexyl–Cl or Cyclohexyl–CH_2–Cl

Cyclohexyl–Cl → secondary halide (Cl attached directly to ring carbon → more steric hindrance)

Cyclohexyl–CH_2–Cl → primary halide (less steric hindrance)

SN2 prefers less hindered (primary) substrates.

More reactive: Cyclohexyl–CH_2–Cl

(4)

Arrange the following in the increasing order of their reactivity towards SN1 reactions :

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3 methylbutane

[2 Marks]

Answer: The increasing order of reactivity towards SN1 reactions is 1-Bromo-3-methylbutane < 2-Bromo-3-methylbutane < 2-Bromo-2-methylbutane. This is because 2-Bromo-2-methylbutane is the most reactive due to the formation of a more stable tertiary carbocation, while 1-Bromo-3-methylbutane forms a primary carbocation, which is the least stable.

Key Points: 1-Bromo-3-methylbutane has a primary carbocation; 2-Bromo-2-methylbutane forms a tertiary carbocation; stability of carbocation determines SN1 reactivity.

Question 3.

Rahul set-up an experiment to find resistance of aqueous KCl solution for different concentrations at 298 K using a conductivity cell connected to a Wheatstone bridge. He fed the Wheatstone bridge with a.c. power in the audio frequency range 550 to 5000 cycles per second. Once the resistance was calculated from null point he also calculated the conductivity K and molar conductivity $\wedge_m$ and recorded his readings in tabular form.

S.No.	Conc.(M)	k S cm^{-1}	$\wedge_m$ S cm^2 mol^{-1}
1.	1.00	111.3×10^{-3}	111.3
2.	0.10	12.9×10^{-3}	129.0
3.	0.01	1.41×10^{-3}	141.0

(1)

Why does conductivity decrease with dilution ?

[1 Marks]

Answer: Conductivity decreases with dilution because as the solution is diluted, the number of ions per unit volume decreases. This means fewer ions are available to carry electric current, leading to lower conductivity as mentioned in the case where Rahul observed resistance changes with concentration.

Key Points: Conductivity decreases with dilution - Fewer ions available to carry current - Conductivity depends on ion concentration

(2)

If Λ_m° of KCl is 150.0 S cm^2 mol^{-1}, calculate the degree of dissociation of 0.01 M KCl.

[1 Marks]

Answer: The degree of dissociation (\u03b1) is calculated by the formula \u03b1 = \u2308m / \u2308m\u00b0. For 0.01 M KCl, if the molar conductivity \u2308m is known from readings, divide it by 150.0 S cm\u00b2 mol\u207b\u2071 as given in the case to find \u03b1. This shows how much KCl dissociates in solution.

Key Points: Degree of dissociation calculation - Use \u03b1 = \u2308m / \u2308m\u00b0 - Use given molar conductivity of KCl 150 S cm\u00b2 mol\u207b\u2071

(3)

Amit, a classmate of Rahul repeated the same experiment with CH_3COOH solution instead of KCl solution. Give one point that would be similar and one that would be different in his observations as compared to Rahul.

[2 Marks]

Answer: Similar point: Both Rahul and Amit would observe that conductivity increases with increasing concentration due to more ions in the solution.
Different point: Amit would find lower molar conductivity values for CH_3COOH compared to KCl because CH_3COOH is a weak electrolyte and partially ionizes, while KCl is a strong electrolyte that fully ionizes, leading to higher conductivity. This difference is due to the nature of the solute, as mentioned in Rahul's experiment with KCl solutions.

Key Points: Conductivity increases with concentration for both solutions - KCl is a strong electrolyte, CH3COOH is a weak electrolyte - Molar conductivity values differ due to ionization extent

(4)

If Rahul had used HCl instead to KCl then would you expect the Λ_m values to be more or less than those per KCl for a given concentration. Justify.

[2 Marks]

Answer: If Rahul used HCl instead of KCl, the molar conductivity \u2307\u2098 values would be more for HCl at the same concentration. This is because HCl is a strong acid that dissociates completely into H^+ and Cl^- ions, and H^+ ions have very high mobility due to the Grotthuss mechanism. In contrast, KCl dissociates into K^+ and Cl^-, where K^+ is less mobile than H^+. Hence, the overall molar conductivity of HCl solution is higher than that of KCl at the same concentration, as supported by the concept of ion mobility and conductivity in the given experiment.

Key Points: Molar conductivity of HCl is higher than KCl at same concentration - H^+ ion has higher mobility due to Grotthuss mechanism - Conductivity depends on ion mobility and concentration

Section B

Question 4.

Which of the following molecules has a chiral centre correctly labelled with an asterisk (*)?

[1 Marks]

(A) $CH_3C^*Br_2CH_3$

(B) $CH_3C^*HClCH_2Br$

(C) $CH_3C^*HBrCH_3$

(D) $HOCH_2C^*H(OH)CH_2OH$

Explanation:

The correct answer is $HOCH_2C^*H(OH)CH_2OH$. A chiral center is a carbon atom that is bonded to four different groups. In this molecule, the carbon atom marked with an asterisk is attached to four distinct substituents: a hydroxymethyl group ($HOCH_2$), a hydroxyl group (OH), a hydrogen (H), and a methylene group (CH_2OH), making it chiral. The other options do not present a carbon atom bonded to four different groups.

Question 5.

Which of the following alcohols will not undergo oxidation?

[1 Marks]

(A) 3-Methylbutan-2-ol

(B) 2-Methylbutan-2-ol

(C) Butan-2-ol

(D) Butanol

Explanation:

2-Methylbutan-2-ol is the correct answer because it is a tertiary alcohol. Tertiary alcohols are resistant to oxidation under normal conditions, unlike primary and secondary alcohols, which can be oxidized to aldehydes or ketones respectively. The context mentions that alkanes having tertiary hydrogen can be oxidized, but it must be noted that tertiary alcohols generally do not undergo oxidation readily.

Question 6.

A voltaic cell is made by connecting two half cells represented by half equations below: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $E° = – 0.14$ V $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E° = + 0.77$ V Which statement is correct about this voltaic cell?

[1 Marks]

(A) Fe^{2+} is oxidised and the voltage of the cell is 0.91 V

(B) Sn is oxidised and the voltage of the cell is 0.63 V

(C) Fe^{2+} is oxidised and the voltage of the cell is –0.91 V

(D) Sn is oxidised and the voltage of the cell is 0.91 V

Explanation:

The correct answer is 'Sn is oxidised and the voltage of the cell is 0.91 V.' In the voltaic cell, Sn is oxidised from Sn(s) to Sn^{2+}(aq), while Fe^{3+} is reduced to Fe^{2+}. To find the cell voltage, we subtract the standard reduction potential of the oxidised species (Sn, -0.14 V) from that of the reduced species (Fe^{3+}, +0.77 V): 0.77 V - (-0.14 V) = 0.91 V.

Question 7.

Four half reactions I to IV are shown below:

I. $2Cl^- \rightarrow Cl_2 + 2e^-$

II. $4OH^- \rightarrow O_2 + 2H_2O + 2e^-$

III. $Na^+ + e^- \rightarrow Na$

IV. $2H^+ + 2e^- \rightarrow H_2$ Which two of these reactions are most likely to occur when concentrated brine is electrolysed?

[1 Marks]

(A) I and III

(B) I and IV

(C) II and III

(D) II and IV

Explanation:

The correct answer is I and IV. During the electrolysis of concentrated brine, chlorine is generated at the anode (I: $2Cl^- \rightarrow Cl_2 + 2e^-$) and hydrogen is produced at the cathode (IV: $2H^+ + 2e^- \rightarrow H_2$). Reaction II ($4OH^- \rightarrow O_2 + 2H_2O + 2e^-$) is not preferred due to higher overpotential for oxygen generation compared to chlorine, and reaction III is not relevant in this context since sodium does not get reduced in the electrolysis of brine.

Question 8.

Which property of transition metals enables them to behave as catalysts?

[1 Marks]

(A) Alloy formation

(B) Variable oxidation states

(C) High ionisation enthalpy

(D) High melting point

Explanation:

The correct option is 'Variable oxidation states'. Transition metals are known for their ability to adopt multiple oxidation states, which allows them to participate in various chemical reactions and form intermediate complexes, making them effective catalysts.

Question 9.

In the two tetrahedral structures of dichromate ion,

[1 Marks]

(A) All Cr – O bonds are equivalent in length.

(B) All Cr – O bonds are non-equivalent.

(C) 6 Cr – O bonds are equivalent in length.

(D) 4 Cr – O bonds are equivalent in length.

Explanation:

All Cr – O bonds are non-equivalent. In the dichromate ion (Cr2O7^2-), the two tetrahedral structures result in Cr–O bonds that are not all the same in length due to the shared oxygen and the differing angles that arise from its structure, specifically the Cr–O–Cr bond angle of 126°. This creates a situation where some of the bonds behave differently due to the geometry and resonance in the molecule.

Question 10.

1 mole of liquid A and 2 moles of liquid B make a solution having a total vapour pressure 40 torr. The vapour pressure of pure A and pure B are 45 torr and 30 torr respectively. The above solution

[1 Marks]

(A) shows positive deviation.

(B) is a maximum boiling azeotrope.

(C) shows negative deviation.

(D) is an ideal solution.

Explanation:

The correct option is 'shows positive deviation.' The total vapour pressure (40 torr) is lower than what would be expected based on Raoult's law for an ideal solution, which indicates that the interactions between the molecules of A and B are weaker than those in the pure components. Thus, the solution exhibits positive deviation from Raoult's law.

Question 11.

Which of the following would not be a good choice for reducing nitrobenzene to aniline?

[1 Marks]

(A) H_2/Ni

(B) Sn and HCl

(C) $LiAlH_4$

(D) Fe and HCl

Explanation:

The correct option is $LiAlH_4$. While H_2/Ni, Sn and HCl, and Fe and HCl are effective methods for reducing nitrobenzene to aniline, $LiAlH_4$ is a strong reducing agent that would more likely reduce nitro compounds to amines but is generally not preferred for this specific reduction, as it can lead to over-reduction or undesired side reactions.

Question 12.

If molality of a dilute solution is doubled, the value of the molal elevation constant (Kb) will be

[1 Marks]

(A) unchanged

(B) halved

(C) doubled

(D) tripled

Explanation: The molal elevation constant (Kb) is a characteristic property of the solvent, meaning it depends only on the solvent itself and not on the amount of solute or the molality of the solution. When the molality is doubled, the boiling point elevation (ΔTb) will double, but Kb remains the same.

Question 13.

Hydrolysis of sucrose is called

[1 Marks]

(A) saponification

(B) hydration

(C) esterification

(D) inversion

Explanation:

The correct answer is 'inversion' because hydrolysis of sucrose involves the breakdown of sucrose into its component monosaccharides, glucose and fructose, resulting in a mixture that is sweeter and has different optical rotation compared to the original disaccharide. This process is specifically referred to as 'inversion'.

Question 14.

Which one of the following has lowest pK_a value?

[1 Marks]

(A) $Cl–CH_2–COOH$

(B) $O_2N–CH_2–COOH$

(C) $HCOOH$

(D) $CH_3–COOH$

Explanation:

The compound with the lowest pK_a value is $O_2N–CH_2–COOH$ (Nitroacetic acid). The presence of the electron-withdrawing nitro group ($-NO_2$) increases the acidity of the carboxylic acid, resulting in a lower pK_a compared to the other options which have less electron-withdrawing substituents.

Question 15.

Which of the following cell was used in Apollo space programme?

[1 Marks]

(A) H_2–O_2 Fuel cell

(B) Daniel cell

(C) Mercury cell

(D) Dry cell

Explanation:

The correct answer is H_2–O_2 Fuel cell, as it directly produces electricity from the reaction of hydrogen and oxygen, which was a key technology utilized during the Apollo space program for powering spacecraft.

Question 16.

The following experimental rate data were obtained for a reaction carried out at 25 °C:

[1 Marks]

$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$

Initial $[A_{(g)}]$/mol dm^{-3}	Initial $[B_{(g)}]$/mol dm^{-3}	Initial rate/mol $dm^{-3}s^{-1}$
3.0×10^{-2}	2.0×10^{-2}	1.89×10^{-4}
3.0×10^{-2}	4.0×10^{-2}	1.89×10^{-4}
6.0×10^{-2}	4.0×10^{-2}	7.56×10^{-4}

(A) Second, First

(B) Zero, Second

(C) First, Zero

(D) Second, Zero

Explanation:

Let the rate law be:
Rate = $k [A]^m [B]^n$

Compare experiments 1 and 2:
[A] is same (3.0×10^{-2}), [B] doubles ($2.0 \times 10^{-2} \rightarrow 4.0 \times 10^{-2}$), but rate remains the same (1.89×10^{-4}).
So, order with respect to B = 0.

Compare experiments 2 and 3:
[B] is same (4.0×10^{-2}), [A] doubles ($3.0 \times 10^{-2} \rightarrow 6.0 \times 10^{-2}$), and rate increases 4 times ($1.89 \times 10^{-4} \rightarrow 7.56 \times 10^{-4}$).
So, order with respect to A = 2.

Answer:

- Order w.r.t. A = Second
- Order w.r.t. B = Zero

Question 17.

The magnetic moment of $[NiCl_4]^{2-}$ is [Atomic number : Ni = 28]

[1 Marks]

(A) 1.82 BM

(B) 5.46 BM

(C) 4.42 BM

(D) 2.82 BM

Explanation: The correct option is 2.82 BM. The $[NiCl_4]^{2-}$ complex has two unpaired electrons, which gives n = 2. Using the formula $\mu = \sqrt{n(n+2)}$, we have $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ BM, rounded to 2.82 BM. This matches the trend indicating that the magnetic moment will increase with unpaired electrons, confirming it is paramagnetic.

Question 18.

Assertion (A) : Proteins are polymers of α-amino acids connected by a peptide bond.

Reason (R) : A tetrapeptide contains 4 amino acids linked by 4 peptide bonds

[1 Marks]

(A) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(C) Assertion (A) is false, but Reason (R) is true.

(D) Assertion (A) is true, but Reason (R) is false.

Explanation:

Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A). Proteins are indeed polymers of amino acids linked by peptide bonds, and in a tetrapeptide, which consists of 4 amino acids, there are 3 peptide bonds connecting them, which confirms the relationship stated in Reason (R).

Question 19.

Assertion (A) : For a zero order reaction the unit of rate constant and rate of reaction are same.

Reason (R) : Rate of reaction for zero order reaction is independent of concentration of reactant.

[1 Marks]

(A) Assertion (A) is true, but Reason (R) is false.

(B) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(C) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(D) Assertion (A) is true, but Reason (R) is false.

Explanation: In a zero order reaction, the rate of reaction is independent of the concentration of reactant, meaning the rate remains constant. Therefore, the unit of the rate constant is the same as the unit of the rate of reaction, which is concentration/time (e.g., mol L^{-1} s^{-1}). Hence, both the assertion and reason are true, and the reason correctly explains the assertion.

Question 20.

Assertion (A) : Acetic acid but not formic acid can be halogenated in presence of red P and Cl_2.

Reason (R) : Acetic acid is a weaker acid than formic acid.

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Explanation:

Assertion (A) is true, but Reason (R) is false. Acetic acid can be halogenated due to its structure and the presence of the methyl group which facilitates the free radical halogenation process. However,

formic acid is actually a stronger acid than acetic acid, which contradicts Reason (R). Therefore, while the assertion is correct, the reason provided does not support it.

Question 21.

Assertion (A) : Trans $[Cr\ Cl2(ox)_2]^{3-}$ shows optical isomerism.

Reason (R) : Optical isomerism is common in octahedral complexes involving didentate ligands.

[1 Marks]

(A) Assertion (A) is false, but Reason (R) is true.

(B) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(C) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(D) Assertion (A) is true, but Reason (R) is false.

Explanation: Optical isomerism is common in octahedral complexes involving bidentate ligands, as the chelate rings create chirality. However, the trans isomer of [CrCl2(ox)2]3- does not show optical isomerism because it is symmetrical. Only the cis isomer of this complex exhibits optical isomerism. Thus, the assertion is false while the reason is true.

Section C

Question 22.

(i) What should be the signs (positive/negative) for E°Cell and ΔG° for a spontaneous redox reaction occurring under standard conditions?

(ii) State Faraday's first law of electrolysis.

[2 Marks]

Answer: (i) For a spontaneous redox reaction under standard conditions, the standard electrode potential, E°Cell, should be positive and the standard Gibbs free energy change, ΔG°, should be negative. This means the reaction can produce electrical energy and occurs spontaneously.
(ii) Faraday's first law of electrolysis states that the mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.

Key Points: E°Cell positive for spontaneity - ΔG° negative for spontaneity - Faraday's

first law relates mass deposited to charge passed

Question 23.

What happens to the rate constant k and activation energy E_a as the temperature of a chemical reaction is increased? Justify.

[2 Marks]

Answer: As the temperature of a chemical reaction increases, the rate constant k increases because more molecules have enough energy to overcome the activation energy barrier. However, the activation energy E_a itself remains constant since it depends on the nature of the reaction and the reactants involved, not on temperature. According to the Arrhenius equation, $k = A * \exp(-E_a / (R * T))$, increasing temperature T increases k exponentially while E_a stays unchanged.

Key Points: rate constant k increases with temperature - activation energy E_a remains constant - Arrhenius equation explains the relation

Question 24.

a) Which of the following species cannot act as a ligand? Give reason.
OH^-, NH_4^+, CH_3NH_2, H_2O

(b) The complex $[Co(NH_3)_5(NO_2)]Cl_2$ is red in colour. Give IUPAC name of its linkage isomer.

[2 Marks]

Answer: (a) NH_4^+ cannot act as a ligand because it has no lone pair of electrons to donate for coordinate bond formation. OH^-, CH_3NH_2, and H_2O have lone pairs and can donate them to the central metal ion.
(b) The linkage isomer of $[Co(NH_3)_5(NO_2)]Cl_2$ has the nitrite ligand bonded through oxygen as -ONO. Its IUPAC name is pentaammine nitrito-O-cobalt(III) chloride.

Key Points: NH4+ cannot act as ligand - No lone pair on NH4+ - IUPAC name of linkage isomer is pentaammine nitrito-O-cobalt(III) chloride

Question 25. Why is boiling point of o-dichlorobenzene higher than p-dichlorobenzene but melting point of para isomer is higher than ortho isomer?

[2 Marks]

Answer: The boiling point of o-dichlorobenzene is higher than p-dichlorobenzene because the ortho isomer has a polar molecular structure due to the closer position of chlorine atoms, causing stronger intermolecular dipole-dipole interactions and thus requiring more heat to boil.
However, the melting point of the para isomer is higher because p-dichlorobenzene molecules are

more symmetrical and pack more efficiently in the solid state, resulting in a more stable crystalline structure and higher melting point.

Key Points: o-dichlorobenzene has stronger dipole-dipole interactions - p-dichlorobenzene is more symmetrical - p-isomer packs better in solid state leading to higher melting point

Question 26.

For the pair phenol and cyclohexanol, answer the following:

(a) Why is phenol more acidic than cyclohexanol?

(b) Give one chemical test to distinguish between the two.

[2 Marks]

Answer: (a) Phenol is more acidic than cyclohexanol because the negative charge on phenoxide ion formed after losing H^+ is stabilized by resonance in the aromatic ring, whereas in cyclohexanol the alkoxide ion does not have resonance stabilization. This makes phenol release H^+ more easily, increasing its acidity.
(b) To distinguish, perform the neutral $FeCl_3$ test. Phenol gives a violet colour with $FeCl_3$ indicating the presence of phenol, while cyclohexanol shows no colour change.

Key Points: Phenol acidity due to resonance - Cyclohexanol no resonance stabilization - FeCl3 test distinguishes phenol by violet colour

Question 27.

(i) Draw the zwitter ion structure for sulphanilic acid.

(ii) How can the activating effect of $–NH_2$ group in aniline be controlled?

[2 Marks]

Answer: (i) The zwitterion structure of sulphanilic acid has the amino group NH_2 protonated to NH_3^+ and the sulfonic acid group SO_3H deprotonated to SO_3^- resulting in a molecule with both positive and negative charges but overall neutral.
(ii) The activating effect of the $–NH_2$ group in aniline can be controlled by protecting it through acetylation using acetic anhydride to form an acetanilide. This reduces the electron donating effect of $–NH_2$ making substitution reactions more selective. After the substitution, hydrolysis of the amide group regenerates the free $–NH_2$ group.

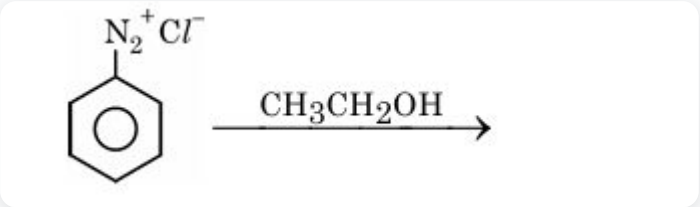
Key Points: Zwitterion of sulphanilic acid has NH_3^+ and SO_3^- groups - Protect NH_2 by acetylation with acetic anhydride - Hydrolyze substituted amide to recover NH_2 group

Question 28.

(i) Complete the reaction with the main product formed :

(ii) Convert Bromoethane to Propanamine.

[2 Marks]



Answer:

(i) The given compound is benzenediazonium chloride reacting with ethanol (CH_3CH_2OH).

In alcoholic medium, diazonium salts are reduced and the $–N_2^+$ group is replaced by H.

So, the main product is benzene.

Reaction:

$C_6H_5–N_2^+Cl^- + CH_3CH_2OH \rightarrow C_6H_6 + N_2 + CH_3CHO + HCl$

Main product: Benzene (C_6H_6)

Reason (straight): Ethanol acts as a reducing agent, replacing the diazonium group by hydrogen.

(ii) To convert bromoethane (CH3-CH2-Br) to propanamine, first react bromoethane with excess ammonia (NH3) in ethanolic solution. This causes nucleophilic substitution replacing bromine with amine group forming ethylamine (CH3-CH2-NH2). For propanamine, extend the carbon chain by first converting bromoethane to propyl bromide and then reacting with ammonia to get propanamine (CH3-CH2-CH2-NH2).

Key Points: 2-bromopropane is main product - Markovnikov's rule explains product formation - Bromoethane reacts with NH3 to form ethylamine/propanamine

Question 29.

Give the reaction of glucose with hydrogen cyanide. Presence of which group is confirmed by this reaction ?

[2 Marks]

Answer: Glucose reacts with hydrogen cyanide (HCN) to form a cyanohydrin. In this reaction, HCN adds across the carbonyl group (>C=O) of glucose resulting in the formation of a cyanohydrin compound. This reaction confirms the presence of the carbonyl group, specifically the aldehyde group (-CHO), in glucose.

Key Points: Glucose reacts with HCN to form cyanohydrin - Reaction confirms presence of carbonyl group - Specifically indicates aldehyde group in glucose

Question 30.

Calculate the emf of the following cell at 298 K:

$Fe(s) \mid Fe^{2+}(0.01\ M) \parallel H^{+}(1\ M) \mid H_2(g)\ (1\ bar), Pt(s)$

Given: $E°_{cell} = 0.44\ V$

[2 Marks]

Answer: Given: $E°_{cell} = 0.44\ V$, $T = 298\ K$, $[Fe^{2+}] = 0.01\ M$, $[H^{+}] = 1\ M$, $pH_2 = 1\ bar$
Step 1: Write the cell reaction: $Fe(s) \rightarrow Fe^{2+} + 2e^{-}$ and $2H^{+} + 2e^{-} \rightarrow H_2(g)$
Step 2: Number of electrons, $n = 2$
Step 3: Use Nernst equation to calculate emf:
$E = E° - (RT/nF) * lnQ$, where
$R = 8.314\ J/mol\ K$, $T = 298\ K$, $F = 96485\ C/mol$, $Q = [Fe^{2+}]/[H^{+}]^2 = 0.01/1 = 0.01$
Step 4: Calculate $(RT/nF) = (8.314*298)/(2*96485) \approx 0.0128\ V$
Step 5: Calculate $lnQ = ln(0.01) = -4.605$
Step 6: Calculate $E = 0.44 - 0.0128 * (-4.605) = 0.44 + 0.059 = 0.499\ V$
Answer: The emf of the cell at 298 K is approximately 0.50 V.

Key Points: Identify cell reaction - Use Nernst equation - Calculate reaction quotient Q - Calculate emf using given concentrations and constants

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Section D

Question 31.

(a) For the reaction
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ at 318 K,
calculate the rate of reaction if rate of disappearance of $N_2O_5(g)$ is 1.4×10^{-3} mol m^{-3} s^{-1}.

(b) For a first order reaction, derive the relationship
$t_{99}\% = 2t_{90}\%$

[3 Marks]

Answer: (a) Given reaction: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, rate of disappearance of $N_2O_5 = 1.4 * 10^{-3}$ mol m^{-3} s^{-1}.
Rate of reaction = (1/2) * rate of disappearance of N_2O_5 because 2 moles of N_2O_5 react.
$= (1/2) * 1.4 * 10^{-3} = 0.7 * 10^{-3}$ mol m^{-3} s^{-1}.

(b) For first order reaction, rate = k[A]. The integrated rate law is $\ln([A]_0/[A]) = kt$.
For $t_{90\%}$, 90% react means 10% left: $[A] = 0.1\ [A]_0$.
So, $\ln(1/0.1) = k\ t_{90\%} \Rightarrow \ln 10 = k\ t_{90\%}$.
For $t_{99\%}$, 99% react means 1% left: $[A] = 0.01\ [A]_0$.
$\ln(1/0.01) = k\ t_{99\%} \Rightarrow \ln 100 = k\ t_{99\%}$.
Divide both: $t_{99\%}/t_{90\%} = \ln 100/\ln 10 = 2$, hence $t_{99\%} = 2\ t_{90\%}$.

> **Key Points: Calculate rate using stoichiometric ratio - Use integrated rate law for first order reaction - Derive time relation using logarithms**

Question 32.

(a) On the basis of crystal field theory, write the electronic configuration for d^5 ion with a strong field ligand for which $\Delta_0 > P$.

(b) $[Ni(CO)_4]$ has tetrahedral geometry while $[Ni(CN)_4]^{2-}$ has square planar, yet both exhibit diamagnetism. Explain.

[Atomic number: Ni = 28]

[3 Marks]

Answer: (a) For a d5 ion with a strong field ligand where crystal field splitting energy Δ0 > pairing energy P, the complex exhibits low spin configuration. The five d electrons will pair up in the lower energy t2g orbitals before occupying the eg orbitals. Therefore, the electronic configuration is $(t2g)^5(eg)^0$ with all electrons paired except one; but since Δ0 > P, pairing occurs to minimize energy leading to $(t2g)^6$ (if possible), here for d5, the low spin arrangement has one unpaired electron less than high spin.

(b) [Ni(CO)4] has tetrahedral geometry and is diamagnetic because Ni is in oxidation state zero with electronic configuration 3d8 4s2. CO is a strong field ligand causing pairing of electrons, leading to no unpaired electrons.
$[Ni(CN)4]^{2-}$ has a square planar geometry due to strong field ligand CN^- which causes pairing of d electrons and dsp2 hybridization. Ni is in +2 oxidation state (d8). The electrons pair up, making the complex low spin and diamagnetic. Tetrahedral complexes are usually high spin, but strong ligand CO can cause pairing even in tetrahedral geometry.

Thus, both complexes are diamagnetic due to electron pairing induced by strong field ligands, despite having different geometries.

Key Points: d5 ion low spin configuration - Δ0 greater than pairing energy causes electron pairing - Ni oxidation states in complexes - CO and CN as strong field ligands causing pairing - geometry influences hybridization dsp2 square planar and tetrahedral - diamagnetism due to paired electrons

Question 33.

(a) Illustrate Sandmeyer's reaction with an equation.

(b) Explain why $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in aqueous solution.

[3 Marks]

Answer: (a) **Sandmeyer's reaction:** It is used to prepare aryl halides from aryl diazonium salts using copper salts. For example:
$C_6H_5N_2^+Cl^- + CuCl \rightarrow C_6H_5Cl + N_2 + Cu^+$
Here, benzenediazonium chloride reacts with cuprous chloride to give chlorobenzene.

(b) **Basicity of $(CH_3)_2NH$ vs $(CH_3)_3N$:**
$(CH_3)_2NH$ (dimethylamine) is more basic than $(CH_3)_3N$ (trimethylamine) in aqueous solution because in $(CH_3)_3N$ the lone pair on nitrogen is more sterically hindered and less available for protonation. Also, in aqueous medium, the bulky methyl groups repel water molecules, reducing solvation of the protonated species. In contrast, dimethylamine has less steric hindrance and better solvation of its conjugate acid, making it more basic.

Key Points: Sandmeyer reaction converts aryl diazonium salts to aryl halides - Use of copper(I) salts in Sandmeyer reaction - Dimethylamine is more basic due to less steric hindrance and better solvation than trimethylamine

Question 34.

Give reasons for any three of the following observations:

(a) Penta-acetate of glucose does not react with hydroxylamine.

(b) Amino acids behave like salts.

(c) Water-soluble vitamins must be taken regularly in diet.

(d) The two strands in DNA are complementary to each other.

[3 Marks]

Answer: (a) Penta-acetate of glucose does not react with hydroxylamine because the aldehyde group (—CHO) of glucose is involved in forming acetal bonds with acetic anhydride, thus it is not free to react.
(b) Amino acids behave like salts because they contain both acidic (—COOH) and basic ($—NH_2$) functional groups. In aqueous solution, they exist as zwitterions having both positive and negative charges, which is characteristic of salts.
(c) Water-soluble vitamins must be taken regularly in the diet because they are not stored in the body and are easily excreted through urine, so a regular supply is necessary.
(d) The two strands in DNA are complementary because the nitrogenous bases on one strand form specific hydrogen bonds with bases on the opposite strand; adenine pairs with thymine and guanine pairs with cytosine. This complementarity helps in accurate replication and maintaining the DNA structure.

Key Points: Penta-acetate glucose lacks free aldehyde group - Amino acids are zwitterions behaving like salts - Water soluble vitamins are not stored in body - DNA strands are complementary due to base pairing

Question 35.

(i) Why is the C–O bond length in phenols less than that in methanol?

(ii) Arrange the following in order of increasing boiling point:
Ethoxyethane, Butanal, Butanol, n-butane

(iii) How can phenol be prepared from anisole? Give reaction.

[3 Marks]

Answer: (i) The C–O bond length in phenols is less than that in methanol because in phenol the lone pair of electrons on oxygen is delocalised into the aromatic ring through resonance. This partial double bond character shortens the C–O bond length. In methanol, there is no such resonance effect and the bond remains purely single bond, so it is longer.

(ii) Order of increasing boiling point based on intermolecular forces and molecular structure is: n-butane < ethoxyethane < butanal < butanol.
- n-butane is non-polar with weak van der Waals forces.
- Ethoxyethane is an ether with dipole-dipole interactions but no hydrogen bonding.
- Butanal is an aldehyde with dipole interactions and slightly higher boiling than ethoxyethane.
- Butanol is an alcohol with hydrogen bonding which gives it the highest boiling point.

(iii) Phenol can be prepared from anisole by acidic hydrolysis. Under acidic conditions, anisole undergoes cleavage of the methoxy group to produce phenol.

$C_6H_5OCH_3$ + HBr (acidic hydrolysis) → C_6H_5OH + CH_3Br

> **Key Points: C-O bond shorter in phenol due to resonance - Boiling point order: n-butane < ethoxyethane < butanal < butanol - Phenol prepared by acidic hydrolysis of anisole**

Question 36.

(i) Give mechanism of the following reaction :

(ii) Illustrate hydroboration – oxidation reaction with an example.

[3 Marks]

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} CH_3CH_2 - O - CH_2CH_3 + H_2O$$

Answer:

(i) This is the **acid-catalysed dehydration of ethanol** to form **diethyl ether** at **413 K**. The mechanism is as follows:

Step 1: Protonation of ethanol

CH3CH2OH+H+ ⟶ CH3CH2OH2+

Ethanol gets protonated, making **water a good leaving group**.

Step 2: Nucleophilic attack by another ethanol molecule (SN2)

CH3CH2OH+CH3CH2OH2+ ⟶ CH3CH2OCH2CH3++H2O

Another ethanol molecule attacks the ethyl group, forming a **protonated ether**.

Step 3: Deprotonation

CH3CH2OCH2CH3+ ⟶ CH3CH2OCH2CH3+H+

Loss of a proton gives **diethyl ether** and regenerates the acid catalyst.

Overall reaction:

$2\,CH3CH2OH\ (413\,K\ ,conc.\ H2SO4) \rightarrow CH3CH2OCH2CH3+H2O2$

This is the **intermolecular dehydration of ethanol** to form an ether.

(ii) Hydroboration-oxidation reaction: This reaction converts an alkene into an alcohol by adding water across the double bond without rearrangement.
Step 1 (Hydroboration): The alkene reacts with diborane (B2H6) to form trialkylborane; boron adds to the less substituted carbon and hydrogen to the more substituted carbon.
Step 2 (Oxidation): The trialkylborane is treated with hydrogen peroxide (H2O2) in basic medium (NaOH), converting it into corresponding alcohol.
Example: $CH2=CH2 + B2H6 \rightarrow CH3CH2\text{-}B$
Then, $CH3CH2\text{-}B + H2O2/NaOH \rightarrow CH3CH2OH + B(OH)3$
This reaction provides anti-Markovnikov addition of water to the alkene.

Key Points: Two-step mechanism involving peroxide and iodide ions - Hydroboration adds boron to less substituted carbon - Oxidation converts trialkylborane to alcohol - Anti-Markovnikov addition in hydroboration-oxidation

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Section E

Question 37.

(i) Why is boiling point of 1 M NaCl solution more than that of 1 M glucose solution?

(ii) A non-volatile solute 'X' (molar mass = 50 g mol^{-1}) when dissolved in 78 g of benzene reduced its vapour pressure to 90%. Calculate the mass of X dissolved in the solution.

(iii) Calculate the boiling point elevation for a solution prepared by adding 10 g of $MgCl_2$ to 200 g of water assuming $MgCl_2$ is completely dissociated.
(K_β for water = 0.512 K kg mol^{-1}, Molar mass of $MgCl_2$ = 95 g mol^{-1})

[5 Marks]

Answer: (i) The boiling point of 1 M NaCl solution is more than that of 1 M glucose solution because NaCl is an ionic compound and dissociates completely into ions (Na^+ and Cl^-) in solution. This increases the number of solute particles, thus increasing the boiling point elevation according to colligative properties. Glucose, being a non-electrolyte, does not dissociate and produces fewer particles.

(ii) Given:

Vapour pressure of pure benzene, P_0; vapour pressure of solution, $P = 0.90\ P_0$

Mass of solvent (benzene), $m_{solvent} = 78\ g = 0.078\ kg$

Molar mass of solute X = 50 g mol^{-1}

Using Raoult's law:

$P = X_{solvent} * P_0 \Rightarrow X_{solvent} = P / P_0 = 0.90$

Mole fraction of solvent, $X_{solvent}$ = moles of solvent / (moles of solvent + moles of solute) = 0.90

Let mass of X = m g, moles of X = m / 50

Moles of benzene = 78 / 78 = 1 mol

So, $0.90 = 1 / (1 + m / 50) \Rightarrow 1 + m / 50 = 1 / 0.90 = 1.111$

$m / 50 = 0.111$

$m = 0.111 * 50 = 5.55\ g$

Therefore, mass of X dissolved is 5.55 g.

(iii) Given:

Mass of $MgCl_2$ = 10 g

Mass of water = 200 g = 0.2 kg

Molar mass of $MgCl_2$ = 95 g mol^{-1}

K_b for water = 0.512 K kg mol^{-1}

Moles of $MgCl_2 = 10 / 95 = 0.105$ mol

$MgCl_2$ dissociates into Mg^{2+} and $2Cl^-$ ions; number of particles = 3

Van't Hoff factor, i = 3

Molality, m = moles of solute / mass of solvent in kg = 0.105 / 0.2 = 0.525 mol/kg

Boiling point elevation, $\Delta T_b = i * K_b * m = 3 * 0.512 * 0.525 = 0.806\ K$

Thus, the boiling point elevation is approximately 0.81 K.

Key Points: Boiling point elevation depends on number of solute particles - NaCl dissociates increasing particles whereas glucose does not - Use of Raoult's law to find mass of solute from vapour pressure lowering - Calculation of boiling point elevation using van't Hoff factor and molality

Question 38.

(i) Why is the value of Van't Hoff factor for ethanoic acid in benzene close to 0.5?

(ii) Determine the osmotic pressure of a solution prepared by dissolving 2.32×10^{-2} g of K_2SO_4 in 2 L of solution at 25 °C, assuming that K_2SO_4 is completely dissociated.
(R = 0.082 L atm K^{-1} mol^{-1}, Molar mass of K_2SO_4 = 174 g mol^{-1})

(iii) When 25.6 g of sulphur was dissolved in 1000 g of benzene, the freezing point lowered by 0.512 K. Calculate the formula of sulphur (S_x).
(Kf for benzene = 5.12 K kg mol^{-1}, Atomic mass of sulphur = 32 g mol^{-1})

[5 Marks]

Answer: (i) The Van't Hoff factor for ethanoic acid in benzene is close to 0.5 because ethanoic acid molecules form dimers through hydrogen bonding in benzene, which is a non-polar solvent. These dimers behave as a single particle in solution, so the number of particles is roughly half the number of original molecules, making the factor about 0.5.

(ii) Given data:
Mass of K_2SO_4 = 2.32×10^{-2} g = 0.0232 g, Volume of solution = 2 L, Temperature (T) = 25 °C = 298 K, R = 0.082 L atm K^{-1} mol^{-i}, Molar mass of K_2SO_4 = 174 g mol^{-1}.
Calculate moles of K_2SO_4 = mass / molar mass = 0.0232 / 174 = 1.33×10^{-ă} mol.
K_2SO_4 dissociates into $2K^+$ and SO_4^{2-}, total 3 ions, so i = 3.
Osmotic pressure π = i * (n / V) * R * T = 3 * (1.33×10^{-ă} / 2) * 0.082 * 298 = 3 * $6.65 \times 10^{-ˆ□}$ * 0.082 * 298 = 3 * 0.162 = 0.486 atm.

(iii) Given:
Mass of sulphur (solute), m = 25.6 g; Mass of benzene (solvent), w = 1000 g = 1 kg; Freezing point depression, ΔT = 0.512 K; Kf for benzene = 5.12 K kg mol^{-i}; Atomic mass of sulphur = 32 g mol^{-1}.
Using freezing point depression formula: ΔT = Kf * molality => molality = ΔT / Kf = 0.512 / 5.12 = 0.1 mol kg^{-1}.
Molality = moles of solute / kg of solvent => moles = molality * kg solvent = 0.1 * 1 = 0.1 mol.
Molar mass of sulphur molecule = mass / moles = 25.6 / 0.1 = 256 g mol^{-1}.
Number of sulphur atoms in molecule x = molar mass / atomic mass = 256 / 32 = 8.
Therefore, the formula of sulphur is S_8.

Key Points: Van't Hoff factor of ethanoic acid is about 0.5 due to dimer formation in benzene - Osmotic pressure calculated using π = i * (n/V) * R * T with i = 3 for K_2SO_4 - Formula of sulphur (S_8) found using freezing point depression and molality calculation

Question 39.

(i) Write the reaction involved in Cannizzaro's reaction.

(ii) Why are the boiling points of aldehydes and ketones lower than that of the corresponding carboxylic acids?

(iii) An organic compound ‘A’ with molecular formula $C_5H_8O_2$ is reduced to n-pentane with hydrazine followed by heating with NaOH and glycol. ‘A’ forms a dioxime with hydroxylamine and gives a positive Iodoform and Tollen’s test. Identify ‘A’ and give its reactions for Iodoform and Tollen’s test.

[5 Marks]

Answer:

(i) **Cannizzaro’s reaction:** Aldehydes without an alpha-hydrogen atom undergo Cannizzaro reaction on heating with concentrated alkali. In this reaction, one molecule of aldehyde is oxidized to carboxylic acid ion and another molecule is reduced to alcohol.
Example: 2 C6H5CHO + NaOH \u2192 C6H5CH2OH + C6H5COONa

(ii) **Reason for lower boiling points of aldehydes and ketones than carboxylic acids:** Aldehydes and ketones have polar carbonyl groups (C=O) which exhibit dipole-dipole interactions. However, carboxylic acids have both carbonyl and hydroxyl groups that form hydrogen bonds between molecules. Hydrogen bonding is stronger than dipole-dipole interaction, so carboxylic acids have higher boiling points than corresponding aldehydes and ketones.

(iii) **Identification of compound A (C5H8O2):** Compound A gives positive iodoform and Tollen’s test and forms dioxime with hydroxylamine.
This indicates that A is methyl ketone with two carbonyl groups making it a diketone. Since it reduces to n-pentane with hydrazine followed by heating with NaOH and glycol (Wolff-Kishner reduction), the compound is pentane-2,4-dione (CH3COCH2COCH3).

Reactions:
Iodoform test: Pentane-2,4-dione reacts with I2 and NaOH to give yellow precipitate of iodoform (CHI3), confirming the presence of methyl ketone.
CH3COCH2COCH3 + 3I2 + 4NaOH \u2192 CHI3 (yellow ppt) + other products

Tollen’s test: Pentane-2,4-dione contains a keto group that can show positive Tollen’s test due to enolisation.
R-CO-CH3 + 2[Ag(NH3)2]+ + 3OH- \u2192 R-COO- + 2Ag (silver mirror) + 2NH3 + 2H2O

Thus, compound A is pentane-2,4-dione which shows positive iodoform and Tollen’s tests and forms dioxime with hydroxylamine.

Key Points: Cannizzaro reaction involves aldehydes without alpha-hydrogen undergoing disproportionation - Aldehydes and ketones have lower boiling points due to weaker dipole interactions compared to hydrogen bonding in carboxylic acids - Compound A is

pentane-2,4-dione identified by positive iodoform, Tollen's tests and Wolff-Kishner reduction

Question 40.

(i) Give a chemical test to distinguish between ethanal and ethanoic acid.

(ii) Why are the α-hydrogens of aldehydes and ketones acidic in nature?

(iii) An organic compound 'A' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds 'B' and 'C'. Oxidation of 'C' with acidified potassium permanganate also produces 'B'. Sodium salt of 'B' on heating with soda lime gives methane.

(1) Identify 'A', 'B', and 'C'.
(2) Out of 'B' and 'C', which will have higher boiling point? Give reason.

[5 Marks]

Answer: (i) Chemical test to distinguish ethanal and ethanoic acid: Tollens' test - When ethanal is treated with Tollens' reagent (ammoniacal silver nitrate) and warmed, a silver mirror is formed due to reduction of Ag^+ to metallic silver. Ethanoic acid does not give this test as it is not easily oxidized.

(ii) Acidity of α-hydrogens in aldehydes and ketones: α-hydrogens are acidic because the adjacent carbonyl group (C=O) stabilizes the carbanion formed after deprotonation through resonance. This resonance delocalizes the negative charge onto oxygen, increasing acidity.

(iii) (1) Identification of compounds: Given molecular formula $C_4H_8O_2$, compound 'A' is an ester which on acid hydrolysis gives an acid 'B' and an alcohol 'C'.
- Since oxidation of 'C' with acidified $KMnO_4$ forms 'B', 'C' is a primary alcohol and 'B' is a carboxylic acid.
- Sodium salt of 'B' on heating with soda lime gives methane, indicating 'B' is ethanoic acid (CH_3COOH).
- Therefore, 'B' is ethanoic acid, 'C' is ethanol (CH_3CH_2OH) and 'A' is ethyl ethanoate ($CH_3COOCH_2CH_3$).

(2) Boiling point comparison: Ethanoic acid ('B') has higher boiling point than ethanol ('C') because ethanoic acid molecules form strong hydrogen-bonded dimers due to their carboxyl groups, leading to higher intermolecular forces and boiling point compared to ethanol which forms hydrogen bonds but not dimers as strong as acids.

Key Points: Tollens test distinguishes ethanal by silver mirror formation - α-hydrogens acidic due to resonance stabilization of carbanion - Compound A is ethyl ethanoate

ester, B is ethanoic acid, C is ethanol - Ethanoic acid has higher boiling point due to hydrogen bonded dimers

Question 41.

(i) Why is chemistry of actinoids complicated as compared to lanthanoids ?

(ii) Complete the following reaction and justify that it is a disproportionation reaction :

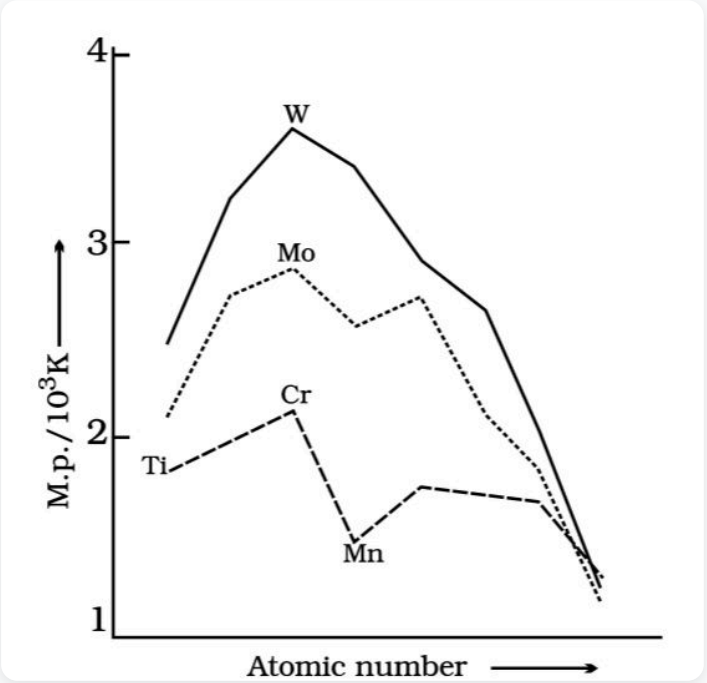
$3MAnO4^{2-}{}_4- + 4H^+ \rightarrow$_____ + _____ + 2 H2O.

(iii) The given graph shows the trends in melting points of transition metals :Explain the reason why Cr has highest melting point and manganese (Mn) a lower melting point.

Explain the reason why Cr has highest melting point and manganese

(Mn) a lower melting point.

[5 Marks]



Answer:

(a) The chemistry of actinoids is more complicated than that of lanthanoids because actinoids show a wide range of oxidation states from +3 to +6, whereas lanthanoids mainly exhibit +3 oxidation state. This variety in oxidation states leads to complex chemistry. Also, actinoids have 5f orbitals which are more extended and can participate in bonding, whereas lanthanoids have more buried 4f orbitals that do not participate much in bonding. Moreover, actinoids are radioactive, which presents additional experimental challenges.

(b) The reaction is: 3MnO42- + 4H+ → 2MnO4- + MnO2 + 2H2O.
This is a disproportionation reaction because the manganese in MnO42- is in +6 oxidation state and it

undergoes simultaneous oxidation to MnO_4^- (+7 oxidation state) and reduction to MnO_2 (+4 oxidation state). Thus the same species is both oxidized and reduced.

(c) Chromium (Cr) has a high melting point because:

- Cr has electronic configuration [Ar] $3d^5\ 4s^1$.
- It has a large number of unpaired d-electrons (6).
- More unpaired electrons → stronger metal–metal bonding (strong metallic bonding).
- Strong metallic bonding requires more energy to break → high melting point.

Manganese (Mn) has a lower melting point because:

- Mn has configuration [Ar] $3d^5\ 4s^2$.
- Though it has half-filled d-orbitals, its metallic bonding is comparatively weaker due to:
  - Stable half-filled $3d^5$ configuration
  - Less effective overlap between orbitals
- Therefore, metallic bonds are weaker → lower melting point.

Key Points: Actinoids show variable oxidation states - 5f orbitals participate in bonding - Actinoids are radioactive - Disproportionation reaction involves simultaneous oxidation and reduction - Reaction: $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$ - Cr has half-filled d orbitals leading to strong metallic bonding - Mn has weaker bonding due to paired electrons resulting in lower melting point

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