

CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-S-2 - Compartment



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **33** questions. All questions are **compulsory**.
- (ii) This question paper is divided into **five** sections – **Section A, B, C, D** and **E**.
- (iii) **Section A** – questions number **1 to 16** are multiple choice type questions. Each question carries **1** mark.
- (iv) **Section B** – questions number **17 to 21** are very short answer type questions. Each question carries **2** marks.
- (v) **Section C** – questions number **22 to 28** are short answer type questions. Each question carries **3** marks.
- (vi) **Section D** – questions number **29** and **30** are case-based questions. Each question carries **4** marks.
- (vii) **Section E** – questions number **31 to 33** are long answer type questions. Each question carries **5** marks.
- (viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.
- (ix) Kindly note that there is a separate question paper for Visually Impaired candidates.
- (x) Use of calculators is not allowed.

Section A (16 marks)

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each.

1. The most stable complex among the following is :

[1 mark]

- (A) $\text{Na}_2[\text{Na}(\text{CN})_5(\text{NO})]$
- (B) $\text{K}_3[\text{Fe}(\text{CN})_6]$
- (C) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- (D) $\text{Na}_2[\text{Ni}(\text{EDTA})]$

Correct Answer: (D) $\text{Na}_2[\text{Ni}(\text{EDTA})]$

Solution:

Concept:

- A chelating ligand coordinates to the same metal ion through two or more donor atoms and forms rings.
- EDTA is hexadentate: its two nitrogen atoms and four carboxylate oxygen atoms can bind one metal ion. Chelation increases complex stability.

Step 1: Identify the chelating ligand In $\text{Na}_2[\text{Ni}(\text{EDTA})]$, EDTA surrounds the nickel ion through several donor atoms, forming a multidentate chelate complex. This favours retention of the ligand at the metal ion.

Step 2: Compare the listed complexes The cyanide, nitrosyl and ammonia ligands appearing in the other options do not provide the multidentate EDTA framework. Although some of these ligands form strong metal-ligand bonds, the distinguishing stabilising feature in the listed EDTA complex is the chelate effect. Thus the chelated nickel complex is the expected most stable choice.

Step 3: Conclusion The most stable complex is $\text{Na}_2[\text{Ni}(\text{EDTA})]$. Hence, the correct option is (D).

Quick Tip to Solve: For this comparison, identify the hexadentate EDTA ligand and use the chelate effect.

2. If amines are arranged in decreasing order of their basic strength in gaseous phase, then the correct order will be :

[1 mark]

- (A) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$
- (B) $\text{NH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$
- (C) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{NH}_3$
- (D) $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

Correct Answer: (A) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

Solution:

Concept:

- Amines are bases because the nitrogen lone pair accepts a proton.
- In the gaseous phase, the electron-releasing inductive effect of alkyl groups increases basic strength;

Quick Tip to Solve: Underline "gaseous phase": count methyl groups, since solvation does not reverse the inductive trend.

aqueous solvation effects do not determine this order.

Step 1: Compare electron donation to nitrogen Each methyl group supplies electron density towards nitrogen through its positive inductive effect. Increasing the number of methyl groups makes the nitrogen lone pair more available for proton acceptance and stabilises the protonated species.

Step 2: Arrange all four bases Trimethylamine has three methyl groups, dimethylamine has two, methylamine has one, and ammonia has none. Therefore the gaseous-phase order is

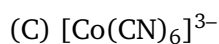
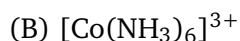
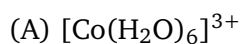


Option (B) reverses this trend. Options (C) and (D) incorrectly place a less substituted amine above trimethylamine; the familiar aqueous ordering must not be used here.

Step 3: Conclusion The decreasing basic-strength order is $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$. Hence, the correct option is (A).

Quick Tip to Solve: Underline "gaseous phase": count methyl groups, since solvation does not reverse the inductive trend.

3. Considering the strength of the ligand, the lowest excitation energy will be observed in : [1 mark]



Correct Answer: (D) $[\text{CoCl}_6]^{3-}$

Solution:

Concept:

- For an octahedral complex, the excitation energy between the two sets of metal d orbitals is the crystal field splitting energy, Δ_o .
- For the ligands listed, the spectrochemical order is $\text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$, from weaker to stronger field.

Step 1: Hold the metal and oxidation state fixed All four complexes contain cobalt in oxidation state +3 with six ligands. Therefore comparison of ligand field strengths directly identifies which complex has the smallest splitting between its d-orbital energy levels.

Step 2: Select the weakest ligand Chloride is weaker field than water, ammonia and cyanide. Thus $[\text{CoCl}_6]^{3-}$ has the smallest Δ_o and needs the least energy for the indicated d-orbital excitation. The water and ammonia complexes have larger splittings, while cyanide gives the largest splitting among these options.

Step 3: Conclusion The lowest excitation energy is observed in $[\text{CoCl}_6]^{3-}$. Hence, the correct option is (D).

Quick Tip to Solve: With the same metal, oxidation state and coordination number, choose the weakest ligand for lowest excitation energy.

4. The standard electrode potential for $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is + 0.15 V and for Cr^{3+}/Cr couple is – 0.73 V. These two couples are connected to make an electrochemical cell. The redox reaction is spontaneous. The cell potential will be : [1 mark]

- (A) + 0.88 V
- (B) + 0.58 V
- (C) – 0.88 V
- (D) – 0.58 V

Correct Answer: (A) + 0.88 V

Solution:

Concept:

- For a spontaneous cell reaction, $E_{\text{cell}}^{\circ} > 0$, since $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$. Here n is the number of electrons transferred and F is the Faraday constant.
- Using standard reduction potentials, $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$. Electrode potentials are not multiplied by balancing coefficients.

Step 1: Identify reduction and oxidation The more positive reduction potential, +0.15 V, makes $\text{Sn}^{4+} + 2\text{e}^{-} \rightarrow \text{Sn}^{2+}$ the cathode process. Chromium is oxidised at the anode: $\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^{-}$, with reduction potential –0.73 V for its couple.

Step 2: Calculate the cell potential

$$E_{\text{cell}}^{\circ} = 0.15 - (-0.73) = +0.88 \text{ V.}$$

The positive value is consistent with spontaneity. The value +0.58 V would result from adding the signed reduction potentials incorrectly; either negative option would describe the nonspontaneous reverse direction.

Step 3: Conclusion The cell potential is +0.88 V. Hence, the correct option is (A).

Quick Tip to Solve: Subtract the lower reduction potential from the higher one; keep the minus sign of chromium inside brackets.

5. The chemical test which can be used to distinguish between ethanamine and aniline is : [1 mark]

- (A) Haloform test
- (B) Tollens' test
- (C) Azo dye test
- (D) Hinsberg test

Correct Answer: (C) Azo dye test

Solution:

Concept:

- Primary aromatic amines form diazonium salts on treatment with nitrous acid at 273–278 K.

Quick Tip to Solve: Look for the aromatic primary amine: aniline forms a cold diazonium salt that couples to an azo dye.

- An aromatic diazonium salt couples with phenol in alkaline medium to form a coloured azo dye. Primary aliphatic diazonium salts decompose readily.

Step 1: Apply the azo dye test Aniline is diazotised using NaNO_2/HCl in the cold. Its benzenediazonium salt then couples with phenol in alkaline solution to give a coloured azo dye. Ethanamine instead forms an unstable aliphatic diazonium species, which decomposes with nitrogen evolution, so it does not give this azo dye.

Step 2: Eliminate the other tests Neither amine contains the required haloform-test structural group, and neither is an aldehyde giving the usual Tollens test. Both ethanamine and aniline are primary amines; both react with Hinsberg reagent to give sulphonamides soluble in alkali. Thus Hinsberg classification does not distinguish these two primary amines as reliably as the azo dye test.

Step 3: Conclusion The distinguishing test is the azo dye test. Hence, the correct option is (C).

Quick Tip to Solve: Look for the aromatic primary amine: aniline forms a cold diazonium salt that couples to an azo dye.

6. The geometry of diamagnetic nickel complex $[\text{Ni}(\text{CN})_4]^{2-}$ is :

[1 mark]

- (A) Tetrahedral
- (B) Octahedral
- (C) Square planar
- (D) Distorted octahedral

Correct Answer: (C) Square planar

Solution:

Concept:

- In $[\text{Ni}(\text{CN})_4]^{2-}$, nickel has oxidation state +2, so Ni^{2+} has a $3d^8$ configuration.
- CN^- is a strong-field ligand. A four-coordinate d^8 nickel complex can pair its electrons and use dsp^2 hybridisation, giving square planar geometry.

Step 1: Use the ligand strength and magnetic behaviour Four cyanide ions contribute charge -4 ; hence $x - 4 = -2$ gives $x = +2$ for nickel. The strong-field cyanide ligands cause pairing of the eight 3d electrons, leaving one 3d orbital available. All electrons are paired, consistent with the stated diamagnetism.

Step 2: Infer the geometry One 3d orbital, one 4s orbital and two 4p orbitals form four dsp^2 hybrid orbitals directed towards the corners of a square in one plane. A tetrahedral nickel(II) d^8 complex would have unpaired electrons. Octahedral and distorted octahedral geometries require six coordination positions, whereas this complex has four.

Step 3: Conclusion $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar. Hence, the correct option is (C).

Quick Tip to Solve: Combine four-coordinate Ni(II), strong-field cyanide and diamagnetism to identify square planar geometry.

7. Williamson's synthesis of preparing dimethyl ether is a/an :

[1 mark]

- (A) Electrophilic substitution
- (B) S_N1 reaction
- (C) Electrophilic addition
- (D) S_N2 reaction

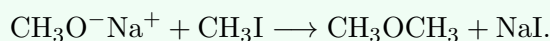
Correct Answer: (D) S_N2 reaction

Solution:

Concept:

- Williamson synthesis forms an ether by reaction of an alkoxide ion with a suitable alkyl halide.
- For a methyl halide, nucleophilic substitution is concerted: the nucleophile attacks as the leaving group departs, giving an S_N2 reaction.

Step 1: Identify the reacting species To prepare dimethyl ether, sodium methoxide reacts with a methyl halide, for example methyl iodide:



The methoxide ion is the nucleophile and iodide is the leaving group.

Step 2: Identify the mechanism The methoxide ion attacks the methyl carbon from the side opposite the leaving group. Bond formation and C-I bond breaking take place in the same step. A methyl carbocation is too unstable for an S_N1 pathway. No electrophile substitutes on an aromatic ring, and there is no multiple bond for electrophilic addition, so options (A), (B) and (C) do not apply.

Step 3: Conclusion Williamson synthesis of dimethyl ether is an S_N2 reaction. The correct option is (D).

Quick Tip to Solve: For Williamson synthesis, identify the alkoxide as the nucleophile and the methyl halide as the best S_N2 substrate.

8. Out of Fe^{2+} , Co^{2+} , Cr^{3+} , Ni^{2+} , the one which shows highest magnetic moment is :

[Atomic number : Cr = 24, Fe = 26, Co = 27, Ni = 28]

[1 mark]

- (A) Fe^{2+}
- (B) Co^{2+}
- (C) Cr^{3+}
- (D) Ni^{2+}

Correct Answer: (A) Fe^{2+}

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)} \mu_B$, where n is the number of unpaired electrons and μ_B is the Bohr magneton.

Quick Tip to Solve: Count unpaired electrons first; comparing their counts is enough, so numerical square roots are unnecessary.

- For transition-metal cations, remove the 4s electrons before the 3d electrons; count unpaired electrons using Hund's rule.

Step 1: Find the ionic configurations The configurations are $\text{Fe}^{2+} : [\text{Ar}]3d^6$, $\text{Co}^{2+} : [\text{Ar}]3d^7$, $\text{Cr}^{3+} : [\text{Ar}]3d^3$, and $\text{Ni}^{2+} : [\text{Ar}]3d^8$. Their respective unpaired-electron counts are 4, 3, 3, 2.

Step 2: Compare the magnetic moments The corresponding spin-only moments are $\sqrt{24}$, $\sqrt{15}$, $\sqrt{15}$, and $\sqrt{8}$, in units of μ_B . Since $\sqrt{n(n+2)}$ increases with n , the ion with four unpaired electrons has the largest moment. The other three ions all have fewer unpaired electrons.

Step 3: Conclusion Fe^{2+} has the highest magnetic moment, approximately $4.90 \mu_B$. The correct option is (A).

Quick Tip to Solve: Count unpaired electrons first; comparing their counts is enough, so numerical square roots are unnecessary.

9. The IUPAC name of the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ is :

[1 mark]

- (A) Pentaamminenitrito-O-cobalt(III) chloride
- (B) Pentaamminenitrito-N-cobalt(III) chloride
- (C) Pentaamminenitro-cobalt(III) chloride
- (D) Pentaamminenitrito-cobalt(II) chloride

Correct Answer: (B) Pentaamminenitrito-N-cobalt(III) chloride

Solution:

Concept:

- Name ligands before the central metal, and indicate its oxidation state using a Roman numeral.
- The ambidentate ligand NO_2^- can bind through nitrogen or oxygen; nitrito-N specifies nitrogen coordination and nitrito-O specifies oxygen coordination.

Step 1: Calculate the cobalt oxidation state The two chloride ions are outside the coordination sphere, so the complex ion has charge +2. Ammonia is neutral and NO_2^- has charge -1 . If the cobalt oxidation state is x , then $x + 5(0) - 1 = +2$, giving $x = +3$.

Step 2: Name the ligands and select the option The five ammonia ligands give pentaammine. The ligand written as NO_2 is nitrogen-bound and is designated nitrito-N in the linkage-explicit nomenclature used here. The counter-ion is named chloride. Option (A) specifies oxygen binding, while (D) gives the wrong oxidation state and misspells ammine. The older nitro designation in (C) is replaced by the explicit nitrito-N designation in the requested IUPAC name.

Step 3: Conclusion The name is pentaamminenitrito-N-cobalt(III) chloride. The correct option is (B).

Quick Tip to Solve: Use the external chloride ions to find the complex charge, then check both the cobalt oxidation state and the nitrite donor atom.

10. Which of the following does not undergo Aldol condensation ?

[1 mark]

- (A) CH_3CHO
- (B) CH_3COCH_3
- (C) $\text{CH}_3\text{CH}_2\text{CHO}$
- (D) $\text{C}_6\text{H}_5\text{CHO}$

Correct Answer: (D) $\text{C}_6\text{H}_5\text{CHO}$

Solution:

Concept:

- Aldol condensation requires at least one α -hydrogen on a carbon adjacent to the carbonyl carbon.
- Base removes an α -hydrogen to generate an enolate, which attacks another carbonyl molecule.

Step 1: Test the aliphatic carbonyl compounds In CH_3CHO , the methyl group provides α -hydrogens. In CH_3COCH_3 , both methyl groups provide them. In $\text{CH}_3\text{CH}_2\text{CHO}$, the adjacent methylene group provides them. Hence options (A), (B) and (C) can undergo aldol condensation.

Step 2: Examine benzaldehyde In $\text{C}_6\text{H}_5\text{CHO}$, the carbonyl group is bonded directly to a benzene-ring carbon. That adjacent carbon carries no hydrogen, so benzaldehyde has no α -hydrogen and cannot form the required enolate for self-aldol condensation. The hydrogen attached to the aldehyde carbon itself is not an α -hydrogen.

Step 3: Conclusion $\text{C}_6\text{H}_5\text{CHO}$ does not undergo aldol condensation. The correct option is (D).

Quick Tip to Solve: Look on the carbon next to the carbonyl, not on the aldehyde carbon, when checking for an α -hydrogen.

11. For a chemical reaction, $\text{A} \rightarrow \text{B}$, it was observed that the rate of reaction doubles when the concentration of A is increased four times. The order of the reaction is :

[1 mark]

- (A) 2
- (B) 1
- (C) $1/2$
- (D) Zero

Correct Answer: (C) $1/2$

Solution:

Concept:

- For a reaction with rate law $r = k[\text{A}]^n$, n is the reaction order and k is the rate constant at fixed temperature.
- Comparing two rates eliminates k : $r_2/r_1 = ([\text{A}]_2/[\text{A}]_1)^n$.

Step 1: Apply the experimental ratios The concentration is increased fourfold, so $[\text{A}]_2/[\text{A}]_1 = 4$. The rate doubles, so $r_2/r_1 = 2$. Substituting these measured ratios gives

$$2 = 4^n.$$

Quick Tip to Solve: Convert the concentration and rate factors to powers of the same base, then compare exponents directly.

Step 2: Solve for the order and check alternatives Write $4 = 2^2$, so $2^1 = 2^{2n}$. Equating exponents gives $1 = 2n$, hence $n = 1/2$. A second-order reaction would increase its rate sixteenfold; a first-order reaction would increase it fourfold; a zero-order reaction would show no rate change. None of these agrees with the observed doubling.

Step 3: Conclusion The reaction is of order $\frac{1}{2}$. The correct option is (C).

Quick Tip to Solve: Convert the concentration and rate factors to powers of the same base, then compare exponents directly.

12. The correct IUPAC name of $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br}$ is :

[1 mark]

- (A) 2,2-Dimethyl-2-bromopropane
- (B) 1-Bromo-2,2,2-trimethylethane
- (C) 2-Bromo-1,1,1-trimethylethane
- (D) 1-Bromo-2,2-dimethylpropane

Correct Answer: (D) 1-Bromo-2,2-dimethylpropane

Solution:

Concept:

- Choose the longest continuous carbon chain as the parent, including the carbon bearing the halogen.
- Number the parent chain to give the lowest set of substituent locants, and list bromo before methyl alphabetically.

Step 1: Choose the parent chain In $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br}$, the longest continuous chain has three carbons: $\text{BrCH}_2-\text{C}-\text{CH}_3$. Thus the parent is propane. The two remaining methyl groups are substituents on its central carbon; an ethane parent in options (B) and (C) does not follow the longest-chain rule.

Step 2: Assign locants and assemble the name Numbering from the brominated end gives bromo at carbon 1 and the two methyl groups at carbon 2: the locants are 1, 2, 2. Numbering from the other end gives 2, 2, 3, which is higher at the first point of difference. Option (A) incorrectly places bromine at carbon 2, although it is attached to the terminal CH_2 carbon.

Step 3: Conclusion The correct IUPAC name is 1-bromo-2,2-dimethylpropane. The correct option is (D).

Quick Tip to Solve: Trace a three-carbon path through the central carbon, then start numbering from the CH_2Br end.

For Questions number 13 to 16, two statements are given — one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below.

- (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.

13. Assertion (A) : Rate constant increases with increase in temperature.

Reason (R) : Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than activation energy. [1 mark]

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

Solution:

Concept:

- For a reaction with positive activation energy, the Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy and T the absolute temperature.
- An effective collision requires sufficient energy to cross the activation-energy barrier.

Step 1: Judge the assertion Increasing T makes $-E_a/(RT)$ less negative, so the exponential factor and hence k increase. Thus Assertion (A) is true.

Step 2: Judge the reason At higher temperature the molecular energy distribution shifts so that a larger fraction of molecules possess energy greater than the activation energy. Consequently more collisions have the energy needed for reaction. Reason (R) is true.

Step 3: Check the explanatory link The increase in the fraction of sufficiently energetic collisions is precisely why the rate constant rises with temperature. Thus R explains A; option (B) misses the causal link, while (C) and (D) incorrectly reject a true statement.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is (A).

Quick Tip to Solve: Use the sign of the Arrhenius exponent: raising T makes it less negative and increases k .

14. Assertion (A) : Cu^{2+} iodide is not known.

Reason (R) : Cu^{2+} has strong tendency to oxidise I^- to iodine.

[1 mark]

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

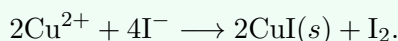
Solution:

Concept:

- Copper(II) ions oxidise iodide ions to iodine and are themselves reduced to copper(I). Copper(I) iodide precipitates because it is sparingly soluble.
- Oxidation is loss of electrons; reduction is gain of electrons. Both must occur together in a redox reaction.

Step 1: Judge the assertion A stable copper(II) iodide, CuI_2 , is not obtained when copper(II) ions meet iodide ions. Instead, copper(I) iodide and iodine form. Assertion (A) is therefore true.

Step 2: Judge the reason The reaction is



Each copper ion gains one electron, while two iodide ions lose two electrons to form iodine. The other two iodide ions form the precipitate. Thus Reason (R) is true.

Step 3: Check the explanatory link The ability of copper(II) to oxidise iodide destroys the copper(II)-iodide combination and produces copper(I) iodide. This directly explains the assertion. Option (B) denies this link, and (C) and (D) each wrongly call a true statement false.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is (A).

Quick Tip to Solve: With Cu^{2+} and iodide, write CuI plus I_2 , not stable CuI_2 .

15. Assertion (A) : Maltose is a reducing sugar.

Reason (R) : Maltose is composed of two glucose units in which C-1 of one glucose unit is linked to C-4 of another glucose unit.

[1 mark]

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

Solution:

Concept:

- A reducing disaccharide retains a free anomeric carbon as a hemiacetal. Its ring can open to give an aldehyde group that reduces suitable oxidising reagents.
- Maltose contains two glucose units joined by an $\alpha(1 \rightarrow 4)$ glycosidic linkage.

Step 1: Judge the assertion Maltose has a free anomeric carbon on its second glucose unit. This unit can open into the aldehydic form, so maltose can reduce reagents such as Tollens' reagent. Thus Assertion (A) is true.

Quick Tip to Solve: For a disaccharide, check whether both anomeric carbons are bonded; maltose leaves one C-1 free.

Step 2: Judge the reason The glycosidic bond joins C-1 of the first glucose unit to C-4 of the second. Therefore, the C-1 of the second glucose unit is not used in the glycosidic linkage. Reason (R) correctly describes maltose and is true.

Step 3: Check the explanatory link The stated C-1 to C-4 linkage leaves one anomeric C-1 free, which accounts for the reducing nature of maltose. Hence R explains A. Option (B) overlooks this consequence of the linkage; (C) and (D) reject statements that are both true.

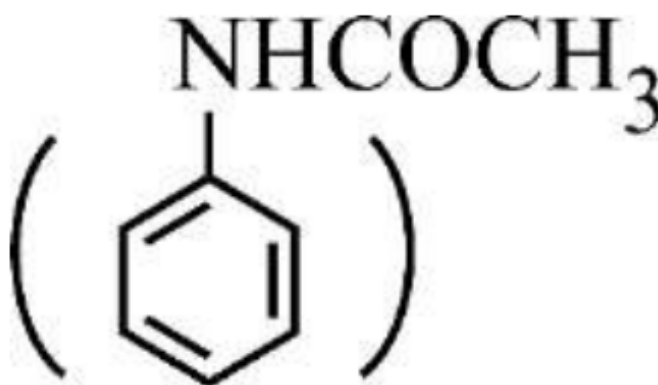
Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is (A).

Quick Tip to Solve: For a disaccharide, check whether both anomeric carbons are bonded; maltose leaves one C-1 free.

16. Assertion (A) : Acetanilide is less basic than aniline.

Reason (R) : Acetylation of aniline results in decrease of electron density on nitrogen.

[1 mark]



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

Solution:

Concept:

- Basicity depends on the availability of the nitrogen lone pair for accepting a proton.
- Acetylation changes aniline, $C_6H_5NH_2$, into the amide acetanilide, $C_6H_5NHCOCH_3$. In an amide the nitrogen lone pair is delocalised towards the carbonyl group.

Step 1: Judge the assertion The lone pair on the nitrogen of acetanilide is less available for protonation than that of aniline. Hence acetanilide is less basic, and Assertion (A) is true.

Step 2: Judge the reason In acetanilide, resonance donation of the nitrogen lone pair into the carbonyl group gives a contributing form with positive charge on nitrogen and negative charge on oxygen. The acetyl group therefore decreases the electron density available on nitrogen. Reason (R) is true.

Quick Tip to Solve: When an amine becomes an amide, check lone-pair delocalisation towards $C=O$ before comparing basicity.

Step 3: Check the explanatory link The decrease in electron density and lone-pair availability on nitrogen is the cause of the reduced basicity on acetylation. Thus R correctly explains A. Option (B) ignores this causal relation, while (C) and (D) each misclassify a true statement.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is (A).

Quick Tip to Solve: When an amine becomes an amide, check lone-pair delocalisation towards $C=O$ before comparing basicity.

Section B (10 marks)

17. Write the reactions of glucose with :

(a) HCN

(b) Conc. HNO_3

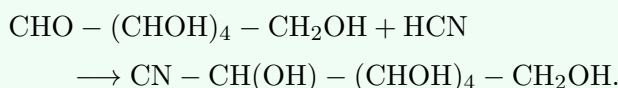
[2 marks]

Solution:

Concept:

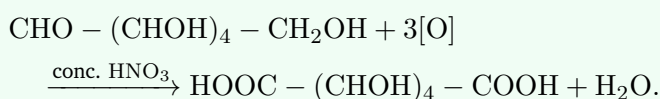
- Open-chain glucose has an aldehyde group at C-1 and a primary alcohol group at C-6: $CHO - (CHOH)_4 - CH_2OH$.
- HCN adds across an aldehydic carbonyl to give a cyanohydrin. Concentrated nitric acid is a strong oxidising agent and oxidises both terminal groups of glucose to carboxyl groups.

Step 1: (a) Reaction with HCN The carbonyl carbon undergoes nucleophilic addition by cyanide, followed by protonation of oxygen. The aldehyde group becomes $CH(OH)CN$:



The product is glucose cyanohydrin. The terminal primary alcohol group remains unchanged in this addition reaction.

Step 2: (b) Reaction with concentrated nitric acid Concentrated HNO_3 oxidises the aldehyde group as well as the terminal CH_2OH group, forming the dicarboxylic acid saccharic acid (glucaric acid):



Here $[O]$ denotes oxygen supplied by the oxidising agent. The four internal $CHOH$ groups retain the glucose configuration.

Step 3: Conclusion With HCN, glucose forms glucose cyanohydrin. With concentrated nitric acid, it forms saccharic acid.

Quick Tip to Solve: HCN adds at the aldehyde; concentrated nitric acid oxidises both ends of the glucose chain.

18(a). Account for the following :

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN .

(ii) Carboxylic acids are higher boiling liquids than aldehydes and ketones.

[2 marks]

Solution:

Concept:

- Addition of HCN is a nucleophilic addition: the cyanide ion attacks the electrophilic carbonyl carbon.
- Reactivity depends on both the electron density at the carbonyl carbon and steric hindrance. Intermolecular hydrogen bonding raises the boiling point.

Step 1: (i) Compare the carbonyl groups In acetaldehyde, CH_3CHO , the carbonyl carbon has one methyl group and one hydrogen; acetone, CH_3COCH_3 , has two methyl groups. Methyl groups donate electron density by their $+I$ effect. Thus acetone has a less positively polarised carbonyl carbon, so attack by CN^- is less favourable. Its two methyl groups also hinder the approach of the nucleophile more than the methyl group and small hydrogen in acetaldehyde do. Both electronic and steric effects therefore favour addition of HCN to acetaldehyde.

Step 2: (ii) Compare intermolecular forces Carboxylic acids contain both a hydrogen-bond donor, the $\text{O}-\text{H}$ group, and a hydrogen-bond acceptor, the carbonyl oxygen. They associate as hydrogen-bonded dimers, with two hydrogen bonds between the molecules. Aldehydes and ketones have no $\text{O}-\text{H}$ group and cannot form such hydrogen bonds among their own molecules. More energy is needed to overcome the stronger intermolecular attractions in carboxylic acids, so their boiling points are higher than those of comparable aldehydes and ketones.

Step 3: Conclusion (i) Acetaldehyde reacts faster with HCN because it has lower steric hindrance and a more electrophilic carbonyl carbon. (ii) Carboxylic acids have higher boiling points because of strong intermolecular hydrogen bonding and dimer formation.

Quick Tip to Solve: For carbonyl addition, check both alkyl donation and crowding; for boiling points, check whether molecules can hydrogen-bond to one another.

OR

18(b). Give chemical tests to distinguish between the following pair of compounds :

(i) Propanal and Propanone

(ii) Benzaldehyde and Benzoic acid

[2 marks]

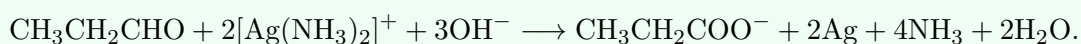
Solution:

Concept:

- Tollens' reagent oxidises an aldehyde and is reduced to metallic silver; an ordinary ketone gives no silver mirror.
- A carboxylic acid reacts with aqueous sodium hydrogen carbonate to liberate carbon dioxide; a neutral aldehyde does not.

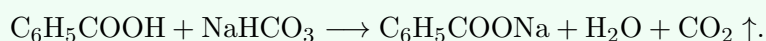
Quick Tip to Solve: Choose a test for the differing functional group, and always state the observable result for both compounds.

Step 1: (i) Propanal and propanone: Tollens test Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Propanal gives a silver mirror, whereas propanone gives no silver mirror. The aldehyde group of propanal is oxidised to propanoate, while silver(I) is reduced to silver:



Propanone is a ketone and does not undergo this mild oxidation.

Step 2: (ii) Benzaldehyde and benzoic acid: hydrogen carbonate test Add aqueous NaHCO_3 to separate samples. Benzoic acid gives brisk effervescence of CO_2 , whereas benzaldehyde gives no effervescence. The reaction is



The gas can be confirmed by passing it through limewater, which turns milky. Benzoic acid is sufficiently acidic to release carbon dioxide from hydrogen carbonate; benzaldehyde has no carboxyl group and does not show this reaction.

Step 3: Conclusion (i) Propanal gives a silver mirror with Tollens' reagent; propanone does not. (ii) Benzoic acid releases CO_2 with aqueous NaHCO_3 ; benzaldehyde does not.

Quick Tip to Solve: Choose a test for the differing functional group, and always state the observable result for both compounds.

19. Write the reaction involved in the following :

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

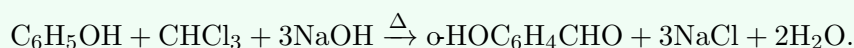
[2 marks]

Solution:

Concept:

- Phenoxide activates the aromatic ring towards substitution, mainly at the ortho and para positions.
- The Reimer-Tiemann reaction introduces a formyl group; Kolbe's reaction of sodium phenoxide introduces a carboxyl group after acidification.

Step 1: (a) Reimer-Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide, followed by acidification. The major product is *o*-hydroxybenzaldehyde (salicylaldehyde). The overall equation is



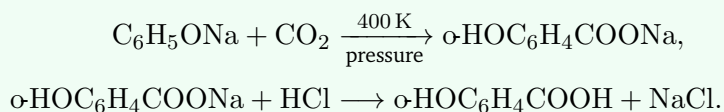
Acid work-up gives the free phenolic product. In alkaline medium chloroform generates dichlorocarbene, which brings about substitution predominantly ortho to the hydroxyl group; a small amount of the para isomer also forms.

Quick Tip to Solve: Remember the introduced group: Reimer-Tiemann gives ortho CHO, while Kolbe carboxylation gives ortho COOH after acidification.

Step 2: (b) Kolbe reaction First convert phenol to sodium phenoxide using sodium hydroxide:



Heat sodium phenoxide with carbon dioxide under pressure at about 400 K, then acidify:



The final product is salicylic acid, or 2-hydroxybenzoic acid. In this phenol context, Kolbe's reaction is the carboxylation of sodium phenoxide.

Step 3: Conclusion Reimer–Tiemann: phenol gives salicylaldehyde using $\text{CHCl}_3/\text{NaOH}$ and acid work-up. Kolbe: sodium phenoxide gives salicylic acid using CO_2 , heat and pressure, followed by acidification.

Quick Tip to Solve: Remember the introduced group: Reimer–Tiemann gives ortho CHO, while Kolbe carboxylation gives ortho COOH after acidification.

20. The thermal decomposition of an acid is a first order reaction with a rate constant of $2.3 \times 10^{-3} \text{ s}^{-1}$ at a certain temperature. Calculate how long it will take for three-fourths of the initial quantity of acid to decompose.

($\log 4 = 0.6021$, $\log 2 = 0.301$)

[2 marks]

Solution:

Concept:

- For a first order reaction, $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_t$ is the concentration remaining at time t .
- The fraction decomposed must first be subtracted from one to obtain the fraction remaining.

Step 1: Identify the amount remaining Let the initial quantity of acid be a . The quantity decomposed is $3a/4$, so the quantity still present is

$$a - x = a - \frac{3a}{4} = \frac{a}{4}.$$

At constant volume this gives $[A]_0/[A]_t = 4$. The time does not depend on the numerical initial amount because it cancels in this ratio. Here $k = 2.3 \times 10^{-3} \text{ s}^{-1}$.

Step 2: Substitute into the integrated rate equation Using common logarithms and the supplied value $\log 4 = 0.6021$,

$$\begin{aligned}t &= \frac{2.303}{2.3 \times 10^{-3}} \log 4 \\ &= \frac{2.303 \times 0.6021}{2.3 \times 10^{-3}} \\ &= 602.9 \text{ s} \approx 603 \text{ s}.\end{aligned}$$

Quick Tip to Solve: Three-fourths decomposed means one-fourth remains: use a concentration ratio of 4, or simply two half-lives.

This is about 10.05 min. As a check, one-quarter remaining corresponds to two successive half-lives, since $1 \rightarrow 1/2 \rightarrow 1/4$. Hence the calculated time is also $2(0.693/k)$, consistent with the integrated equation within rounding.

Step 3: Conclusion The time required for three-fourths of the acid to decompose is $t \approx 6.03 \times 10^2 \text{ s}$, or approximately 10.05 min.

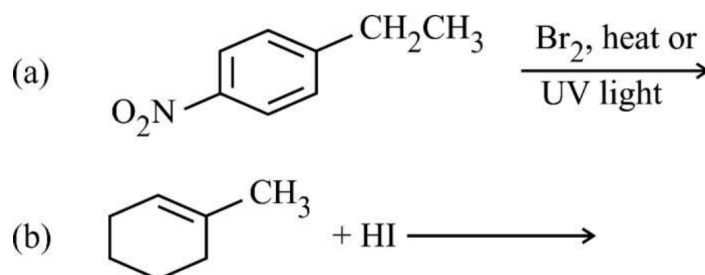
Quick Tip to Solve: Three-fourths decomposed means one-fourth remains: use a concentration ratio of 4, or simply two half-lives.

21. Draw the structures of major monohalo products in each of the following reactions :

(a) 1-Ethyl-4-nitrobenzene treated with Br_2 , heat or UV light

(b) 1-Methylcyclohex-1-ene treated with HI

[2 marks]



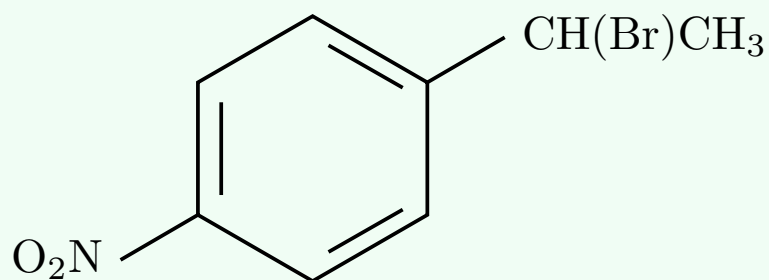
Solution:

Concept:

- With Br_2 under heat or UV light, an alkylbenzene undergoes free-radical substitution preferentially at the benzylic carbon, whose radical is resonance-stabilised.
- Addition of HI to an unsymmetrical alkene follows Markovnikov orientation: protonation favours the more stable carbocation, which is then attacked by I^- .

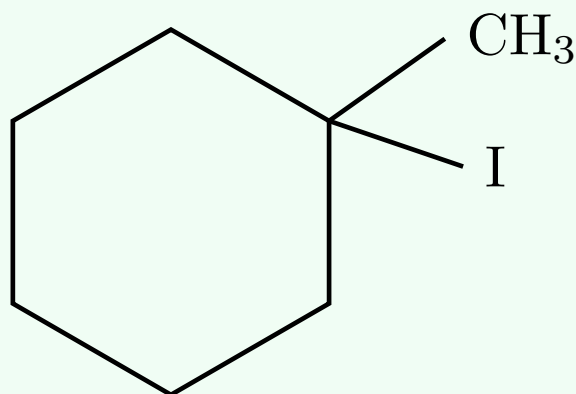
Step 1: (a) Identify the position for side-chain bromination The starting compound has an ethyl group para to the nitro group. Its benzylic carbon is the CH_2 carbon directly attached to the benzene ring. Replacing one hydrogen at this carbon by bromine gives $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}(\text{Br})\text{CH}_3$. The benzene ring and the terminal methyl group remain unchanged. The heat/UV condition initiates a radical chain reaction, so bromination occurs in the side chain; ordinary electrophilic ring bromination is not the reaction indicated here.

Quick Tip to Solve: Use the reagent condition first: bromine with UV targets a benzylic hydrogen, while HI places iodine on the more substituted alkene carbon.



(a) Benzylic monobromination product

Step 2: (b) Apply Markovnikov addition across the double bond In 1-methylcyclohex-1-ene, the double-bond carbon carrying the methyl group has no hydrogen, whereas the other double-bond carbon has one hydrogen. The proton from HI adds to the latter carbon, forming the more stable tertiary carbocation on the methyl-bearing carbon. Iodide then attacks that carbon. The double bond becomes a single bond and the product is 1-iodo-1-methylcyclohexane, with iodine and methyl attached to the same ring carbon.



(b) 1-Iodo-1-methylcyclohexane

Step 3: Conclusion The major monohalo products are (a) $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH(Br)CH}_3$, 1-(1-bromoethyl)-4-nitrobenzene, and (b) 1-iodo-1-methylcyclohexane, with the structures shown above.

Quick Tip to Solve: Use the reagent condition first: bromine with UV targets a benzylic hydrogen, while HI places iodine on the more substituted alkene carbon.

Section C (21 marks)

22. What happens when : (any three)

(a) CH_3MgBr is treated with cyclohexanone followed by hydrolysis.

(b) Phenol is treated with Br_2 in the presence of CS_2 .

(c) Benzene diazonium chloride is treated with H_2O .

(d) Anisole is treated with HI .

[3 marks]

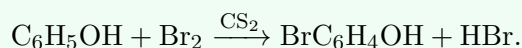
Solution:

Concept:

- A Grignard reagent adds an alkyl group to the carbonyl carbon; hydrolysis of the resulting magnesium alkoxide gives an alcohol.
- Phenol activates its ortho and para positions toward electrophilic substitution. A non-polar solvent such as CS_2 favours controlled monobromination.
- Aryl diazonium salts hydrolyse to phenols. In anisole, HI cleaves the alkyl–oxygen bond rather than the aryl–oxygen bond.

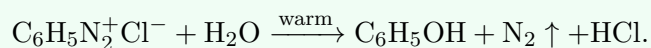
Step 1: (a) Methylmagnesium bromide and cyclohexanone The methyl group from CH_3MgBr adds to the carbonyl carbon of cyclohexanone in dry ether. Hydrolysis protonates the alkoxide to give 1-methylcyclohexan-1-ol, a tertiary alcohol. The original carbonyl carbon bears both OH and CH_3 , and remains bonded to its two neighbouring ring carbons.

Step 2: (b) Phenol with bromine in carbon disulphide In the non-polar solvent CS_2 , phenol gives a mixture of 2-bromophenol and 4-bromophenol, with the para product predominating because it is less sterically crowded:



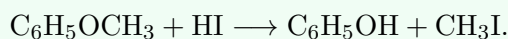
Here $\text{BrC}_6\text{H}_4\text{OH}$ represents the ortho and para isomers. Bromine water instead gives 2,4,6-tribromophenol.

Step 3: (c) Hydrolysis of benzenediazonium chloride On warming with water, benzenediazonium chloride forms phenol with evolution of nitrogen gas:



The diazonium group is replaced by a hydroxyl group.

Step 4: (d) Cleavage of anisole by hydrogen iodide Anisole gives phenol and iodomethane:

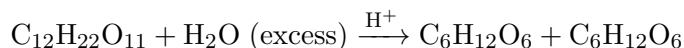


After protonation of the ether oxygen, iodide attacks the methyl carbon by the $\text{S}_{\text{N}}2$ mechanism. The aryl–oxygen bond has partial double-bond character through resonance and does not undergo this displacement; consequently iodobenzene and methanol are not the products.

Step 5: Conclusion The products are (a) 1-methylcyclohexan-1-ol; (b) ortho- and predominantly para-bromophenol; (c) phenol and nitrogen; (d) phenol and iodomethane.

Quick Tip to Solve: For anisole cleavage, attach iodine to the methyl group; for phenol bromination, check whether the solvent is water or carbon disulphide.

23. Hydrolysis of sucrose takes place by the chemical reaction :



Based on the above reaction, write :

(a) Rate law equation

(b) Molecularity and order of reaction

(c) What do you call such reactions ?

[3 marks]

Solution:

Concept:

- For sucrose hydrolysis at fixed acid concentration, the rate depends on sucrose and water: $r = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}]$. The catalyst dependence is included in k .
- When a reactant is present in large excess, its concentration changes negligibly. It can be absorbed into an observed rate constant, reducing the observed order.

Step 1: (a) Write the observed rate law Water is present in excess, so the amount consumed during hydrolysis is very small compared with the initial amount of water. Thus $[\text{H}_2\text{O}]$ is effectively constant. At fixed acid concentration, put $k_{\text{obs}} = k[\text{H}_2\text{O}]$. The rate law then becomes

$$r = -\frac{d[\text{C}_{12}\text{H}_{22}\text{O}_{11}]}{dt} = k_{\text{obs}}[\text{C}_{12}\text{H}_{22}\text{O}_{11}].$$

Therefore, doubling the sucrose concentration doubles the rate under otherwise identical conditions.

Step 2: (b) Distinguish molecularity from observed order The hydrolysis equation involves one molecule of sucrose and one molecule of water, so the molecularity assigned to this hydrolysis in the usual school-level description is two (bimolecular). Its observed order is one, since the exponent of the only varying reactant concentration in the effective rate law is one. Water still participates chemically; its concentration has been incorporated into k_{obs} . Strictly, molecularity describes an elementary step, whereas reaction order is established from the rate law, not merely from a balanced overall equation.

Step 3: (c) Name this kinetic behaviour Such a reaction is called a pseudo-first-order reaction. Although two reactants participate, a large excess of one reactant makes its concentration effectively constant. Consequently, the measured kinetics have the mathematical form of a first-order reaction. The prefix pseudo records this experimental simplification; it does not mean water has ceased to be a reactant.

Step 4: Conclusion $r = k_{\text{obs}}[\text{sucrose}]$; the conventional molecularity is 2 and the observed order is 1. This is a pseudo-first-order reaction.

Quick Tip to Solve: When water is labelled excess, absorb its constant concentration into the rate constant before identifying the observed order.

24. Account for the following :

(a) *n*-butyl bromide has higher boiling point than *t*-butyl bromide.

(b) Alkyl halides are insoluble in water.

(c) Cyclohexyl chloride possesses higher dipole moment than chlorobenzene.

[3 marks]

Solution:

Concept:

- Boiling points of isomeric haloalkanes depend on intermolecular attractions: a larger surface area gives stronger London dispersion forces.
- Dissolution in water requires new solute–water attractions to compensate for the hydrogen bonds broken between water molecules.
- The dipole moment measures charge separation. Hybridisation and resonance both influence the polarity of the carbon–chlorine bond.

Step 1: (a) Compare the shapes and intermolecular forces *n*-Butyl bromide and *t*-butyl bromide are isomers with the same molar mass. The straight-chain *n*-butyl bromide molecule has a larger surface area available for contact with neighbouring molecules. The highly branched *t*-butyl bromide molecule is more compact. Consequently, London dispersion forces are stronger between *n*-butyl bromide molecules, and more heat is needed to separate them into the vapour phase.

Step 2: (b) Compare the interactions involved in dissolution Although alkyl halides have polar carbon–halogen bonds, they cannot form sufficiently strong hydrogen bonds with water. To dissolve them, some strong water–water hydrogen bonds and some solute–solute attractions must be broken. The relatively weak attractions formed between alkyl halide and water molecules do not compensate for this energy requirement. Hence their solubility in water is very low.

Step 3: (c) Compare the carbon–chlorine bonds In cyclohexyl chloride, chlorine is bonded to an sp^3 -hybridised carbon. In chlorobenzene it is bonded to an sp^2 -hybridised carbon, which has greater *s*-character and is more electronegative. Thus the electronegativity difference across the bond is smaller in chlorobenzene. Also, donation of a chlorine lone pair into the benzene ring gives the bond partial double-bond character and opposes its ordinary inductive polarity. These effects reduce the dipole moment of chlorobenzene relative to cyclohexyl chloride.

Step 4: Conclusion (a) Stronger dispersion forces give *n*-butyl bromide the higher boiling point. (b) Weak alkyl-halide–water interactions account for their very low water solubility. (c) The carbon hybridisation and resonance in chlorobenzene give it a lower dipole moment than cyclohexyl chloride.

Quick Tip to Solve: Compare branching for boiling points, hydrogen bonding for water solubility, and hybridisation plus resonance for aryl-halide dipole moments.

25. Give plausible explanation for the following :

(a) Diazonium salts of aromatic amines are stable.

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

(c) Aniline on nitration gives a substantial amount of meta product.

[3 marks]

Solution:

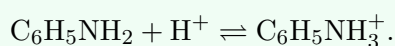
Concept:

- Resonance delocalisation stabilises an aromatic diazonium ion, ArN_2^+ , relative to an aliphatic diazonium ion.
- The amino-group lone pair makes aniline basic and activates its ring, but reaction with an acid or Lewis acid removes that activating influence.
- The anilinium group, $-\text{NH}_3^+$, is strongly electron-withdrawing and directs electrophilic substitution mainly to the meta position.

Step 1: (a) Stability of aromatic diazonium salts In an aromatic diazonium ion, the diazonium group is conjugated with the benzene ring. Resonance allows delocalisation of the positive charge, lowering the energy of the ion. Aliphatic diazonium ions lack this stabilisation and readily lose nitrogen. Aromatic diazonium salts therefore have sufficient stability in cold aqueous solution, normally at 273–278 K, to be prepared and used in further reactions; this does not imply that they are indefinitely stable on heating.

Step 2: (b) Failure of the Friedel–Crafts reaction The Lewis-acid catalyst AlCl_3 accepts the nitrogen lone pair of aniline, forming a Lewis acid–base complex. This ties up the lone pair that would otherwise be donated into the ring and gives nitrogen a positive character. The ring becomes strongly deactivated towards electrophilic substitution, so aniline does not undergo the usual Friedel–Crafts alkylation or acylation.

Step 3: (c) Formation of the meta product on nitration The strongly acidic nitrating mixture protonates a substantial fraction of aniline:



The resulting anilinium ion has no available nitrogen lone pair to donate to the ring. Its positively charged $-\text{NH}_3^+$ group withdraws electron density and is meta-directing. Nitration of this ion therefore produces the meta isomer. The presence of anilinium ions explains the substantial meta product even though unprotonated aniline is ortho/para-directing.

Step 4: Conclusion Aromatic diazonium ions are resonance-stabilised; aniline complexes with the Friedel–Crafts Lewis acid and becomes deactivated; and protonation to the meta-directing anilinium ion explains the substantial meta product during nitration.

Quick Tip to Solve: Before applying the ortho/para-directing rule for aniline, check whether the reagent binds or protonates its nitrogen lone pair.

26. Calculate elevation of the boiling point of solution when 2 g of MgSO_4 (molar mass = 120 g/mol) was dissolved in 100 g of water, assuming MgSO_4 undergoes complete dissociation.

$[K_b \text{ for water} = 0.52 \text{ K kg mol}^{-1}]$

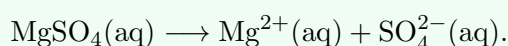
[3 marks]

Solution:

Concept:

- Elevation of boiling point is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b is the ebullioscopic constant and m is the molality.
- Molality is the number of moles of solute formula units per kilogram of solvent. Complete dissociation into two ions gives $i = 2$.

Step 1: Identify the number of particles after dissociation Magnesium sulphate dissociates completely as stipulated:



Each formula unit produces two independently moving solute ions. Thus the van't Hoff factor is $i = 2$. The magnitudes of the ionic charges do not change the number of particles: there are two ions, not four.

Step 2: Calculate the molality using the solvent mass The amount of magnesium sulphate and mass of water in kilograms are

$$n = \frac{2 \text{ g}}{120 \text{ g mol}^{-1}} = \frac{1}{60} \text{ mol},$$
$$w_{\text{water}} = 100 \text{ g} = 0.100 \text{ kg}.$$

Therefore,

$$m = \frac{1/60}{0.100} = \frac{1}{6} \text{ mol kg}^{-1}.$$

The denominator is the mass of water alone, because molality uses solvent mass rather than total solution mass.

Step 3: Apply the boiling-point elevation formula Substituting the given constant gives

$$\begin{aligned}\Delta T_b &= iK_b m \\ &= 2 \times 0.52 \text{ K kg mol}^{-1} \times \frac{1}{6} \text{ mol kg}^{-1} \\ &= 0.1733 \text{ K}.\end{aligned}$$

The units kg and mol cancel, leaving kelvin. Dissociation doubles the elevation compared with the same formula-unit molality of a non-electrolyte.

Step 4: Conclusion The elevation of the boiling point is $\Delta T_b \approx 0.173 \text{ K}$, equivalent to a temperature rise of 0.173°C .

Quick Tip to Solve: Count ions to obtain the van't Hoff factor, and convert the water mass to kilograms before calculating molality.

27. The electrical resistance of a column of 0.05 M KOH solution of cell constant 60 cm^{-1} is $5.4 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity and molar conductivity. [3 marks]

Solution:

Concept:

- The cell constant is $G^* = l/A$, where l is electrode separation and A is the cross-sectional area. Resistance and resistivity are related by $R = \rho l/A$.
- Conductivity is $\kappa = 1/\rho = G^*/R$. For concentration C in mol L^{-1} , molar conductivity is $\Lambda_m = 1000\kappa/C$ when κ is in S cm^{-1} .

Step 1: Identify the data and calculate resistivity The resistance is $R = 5.4 \times 10^3 \Omega$, the cell constant is $G^* = 60 \text{ cm}^{-1}$, and the concentration is $C = 0.05 \text{ mol L}^{-1}$. Since $R = \rho G^*$, divide the resistance by the cell constant:

$$\rho = \frac{R}{G^*} = \frac{5.4 \times 10^3 \Omega}{60 \text{ cm}^{-1}} = 90 \Omega \text{ cm}.$$

The length unit in resistivity is cm because the supplied cell constant is expressed in inverse centimetres.

Step 2: Calculate conductivity Take the reciprocal of resistivity, or equivalently divide the cell constant by resistance:

$$\kappa = \frac{1}{90 \Omega \text{ cm}} = 1.11 \times 10^{-2} \text{ S cm}^{-1}.$$

Conductance alone would be $1/R$; multiplication by the cell constant is essential to obtain conductivity.

Step 3: Calculate molar conductivity The conversion factor 1000 changes concentration from mol L^{-1} to mol cm^{-3} . Therefore,

$$\Lambda_m = \frac{1000\kappa}{C} = \frac{1000(1/90)}{0.05} = 222.2 \text{ S cm}^2 \text{ mol}^{-1}.$$

Retaining the unrounded value $\kappa = 1/90$ during substitution avoids rounding error.

Step 4: Conclusion $\rho = 90 \Omega \text{ cm}$, $\kappa = 1.11 \times 10^{-2} \text{ S cm}^{-1}$, $\Lambda_m = 222.2 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: First use $\rho = R/(l/A)$; use the factor 1000 in Λ_m only when conductivity is in S cm^{-1} .

28. (a) Draw the geometrical isomers of the complex $[\text{Mn}(\text{Br})_2(\text{Cl})_2]^{2-}$.

(b) Give the electronic configuration of d^4 ion when $\Delta_o < P$.

(c) Solution of $[\text{CoF}_6]^{3-}$ is coloured whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Explain. [Atomic number : Co = 27, Ni = 28] [3 marks]

Solution:

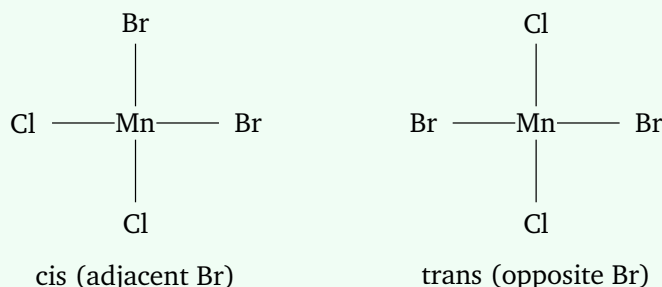
Concept:

- Square-planar $[\text{MA}_2\text{B}_2]$ has cis/trans forms; tetrahedral $[\text{MA}_2\text{B}_2]$ does not.
- When octahedral splitting Δ_o is less than pairing energy P , a high-spin configuration results. Colour requires absorption in the visible region.

Quick Tip to Solve: For part (a), check geometry before naming cis/trans isomers; for part (c), connect colour to visible-light absorption, not only unpaired electrons.

Step 1: (a) Examine the printed complex and draw the formal layouts In $[\text{MnBr}_2\text{Cl}_2]^{2-}$, $x - 4 = -2$ gives Mn(II), $3d^5$. With four weak-field halide ligands this is tetrahedral; all pairs of ligand positions are equivalent, so the printed complex has no geometrical isomers. The formal square-planar layouts below place Br ligands adjacent (cis) or opposite (trans). These are conditional square-planar layouts, not two actual isomers of the tetrahedral Mn(II) complex.

Square-planar layouts only; not tetrahedral isomers



Formal cis and trans layouts, conditional on square-planar geometry

Step 2: (b) Fill the orbitals for the weak-field d-four ion Because $\Delta_o < P$, the fourth electron enters an e_g orbital instead of pairing in t_{2g} . Thus



There are four unpaired electrons.

Step 3: (c) Compare the cobalt and nickel complexes In $[\text{CoF}_6]^{3-}$, Co(III) is $3d^6$; weak-field fluoride gives high-spin $t_{2g}^4 e_g^2$, with four unpaired electrons. Visible-light $d-d$ absorption makes the solution coloured. In $[\text{Ni}(\text{CN})_4]^{2-}$, Ni(II) is $3d^8$. Strong-field cyanide gives a square-planar dsp^2 complex with paired electrons and an empty highest $d_{x^2-y^2}$ orbital. Its large relevant splitting places absorption outside the visible region, making it colourless; electron pairing alone is not a universal colour criterion.

Step 4: Conclusion (a) The printed tetrahedral Mn(II) complex has no geometrical isomers; cis/trans applies conditionally to square-planar geometry. (b) $t_{2g}^3 e_g^1$. (c) Only the cobalt complex absorbs visible light.

Quick Tip to Solve: For part (a), check geometry before naming cis/trans isomers; for part (c), connect colour to visible-light absorption, not only unpaired electrons.

Section D (8 marks)

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

29(a). Case: The cause for deviation from Raoult's law in the colligative properties of non-ideal solutions lie in the nature of interactions at the molecular level. These properties show deviations from Raoult's law due to difference in interactions between solute – solvent, solute – solute and solvent – solvent. Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope.

(a) Pure ethanol cannot be prepared by fractional distillation of ethanol – water mixture. Comment.

[1 mark]

Solution:

Concept:

- An azeotrope is a constant-boiling mixture whose equilibrium vapour and liquid have the same composition.
- Fractional distillation enriches a component only while the vapour composition differs from the liquid composition.

Step 1: Identify the ethanol-water azeotrope Ethanol and water form a minimum-boiling azeotrope owing to positive deviation from Raoult's law. On repeated fractional distillation, the distillate approaches this constant-boiling composition.

Step 2: Explain why distillation stops separating them At the azeotropic composition, ethanol and water pass into the vapour in the same ratio as in the liquid. Condensing and redistilling this vapour therefore gives the same mixture, with water still present. Further fractionation cannot yield pure ethanol.

Step 3: Conclusion Pure ethanol cannot be obtained by fractional distillation because the ethanol-water mixture forms a minimum-boiling azeotrope.

Quick Tip to Solve: Connect the failure of fractionation to equal liquid and vapour compositions at the azeotrope, not merely to close boiling points.

29(b). Why does a mixture of chloroform and acetone show deviation from ideal behaviour ? [1 mark]

Solution:

Concept:

- An ideal solution obeys Raoult's law because interactions between unlike molecules are comparable to those between like molecules.
- Stronger unlike-molecule attractions lower the escaping tendency and cause negative deviation from Raoult's law.

Step 1: Identify the new interaction The hydrogen atom of chloroform, CHCl_3 , is attracted to

Quick Tip to Solve: Look for the acidic H of chloroform and the carbonyl O of acetone to identify the new hydrogen bond.

the carbonyl oxygen atom of acetone, $(\text{CH}_3)_2\text{CO}$. Hydrogen bonds form between the two unlike molecules.

Step 2: Relate attraction to vapour pressure These intermolecular hydrogen bonds make the chloroform–acetone attractions stronger than the average attractions in the separate liquids. The molecules escape less readily into the vapour, so the observed vapour pressure is lower than that predicted for an ideal solution.

Step 3: Conclusion The mixture shows **negative deviation** from ideal behaviour due to hydrogen bonding between chloroform and acetone.

Quick Tip to Solve: Look for the acidic H of chloroform and the carbonyl O of acetone to identify the new hydrogen bond.

29(c). The vapour pressure of pure benzene at a certain temperature is 1.25 atm. When 1.2 g of non-volatile, non-electrolyte solute is added to 60 g of benzene ($M = 78 \text{ g mol}^{-1}$), the vapour pressure of the solution becomes 1.237 atm. Calculate the molar mass of the non-volatile solute. [2 marks]

Solution:

Concept:

- For a non-volatile solute, only the solvent contributes to the vapour pressure: $p = x_1 p^0$, where p^0 is the pure-solvent vapour pressure.
- For a dilute solution, $(p^0 - p)/p^0 \simeq n_2/n_1 = w_2 M_1 / (M_2 w_1)$. Here w , M and n denote mass, molar mass and amount; subscripts 1 and 2 denote solvent and solute.

Step 1: Calculate the relative lowering The solute is non-volatile and non-electrolytic, so no ionisation factor is needed. The lowering of vapour pressure is

$$p^0 - p = 1.250 - 1.237 = 0.013 \text{ atm.}$$

Hence,

$$\frac{p^0 - p}{p^0} = \frac{0.013}{1.25} = 0.0104.$$

Step 2: Use the dilute-solution relation With $w_2 = 1.2 \text{ g}$, $w_1 = 60 \text{ g}$ and $M_1 = 78 \text{ g mol}^{-1}$,

$$M_2 \simeq \frac{w_2 M_1 p^0}{w_1 (p^0 - p)} = \frac{1.2 \times 78 \times 1.25}{60 \times 0.013} = 150 \text{ g mol}^{-1}.$$

The relative lowering is small, supporting the usual dilute-solution approximation. If the exact mole-fraction expression is retained, $n_2/n_1 = (p^0 - p)/p$, giving $M_2 = 148.44 \text{ g mol}^{-1}$; the slight difference is due to the approximation.

Step 3: Conclusion The molar mass is approximately 150 g mol^{-1} using the standard dilute-solution formula.

Quick Tip to Solve: Use the vapour-pressure lowering 0.013 atm, not the solution pressure, in the dilute relative-lowering formula.

29(c). The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K_b for benzene is $2.53 \text{ K kg mol}^{-1}$. [2 marks]

Solution:

Concept:

- For a dilute solution of a non-volatile solute, the boiling-point elevation is $\Delta T_b = K_b m$, with m the molality.
- Molality is moles of solute per kilogram of solvent: $m = (w_2/M_2)/(w_1/1000)$, where masses w_1, w_2 are in grams and M_2 is the solute molar mass.

Step 1: Find the temperature elevation The pure solvent boils at 353.23 K, whereas the solution boils at 354.11 K. Therefore,

$$\Delta T_b = 354.11 - 353.23 = 0.88 \text{ K}.$$

The solvent mass is $90 \text{ g} = 0.090 \text{ kg}$.

Step 2: Calculate molality and molar mass Using $K_b = 2.53 \text{ K kg mol}^{-1}$,

$$m = \frac{0.88}{2.53} = 0.3478 \text{ mol kg}^{-1}.$$

Thus the amount of dissolved solute is

$$n_2 = 0.3478 \times 0.090 = 0.03130 \text{ mol}.$$

Its molar mass is

$$M_2 = \frac{1.80}{0.03130} = 57.5 \text{ g mol}^{-1}.$$

Equivalently, substitute directly into $M_2 = 1000K_b w_2 / (\Delta T_b w_1)$.

Step 3: Conclusion The molar mass of the non-volatile solute is 57.5 g mol^{-1} .

Quick Tip to Solve: Subtract the pure boiling point first, and convert only the solvent mass from grams into kilograms.

30(a). Case: The particles in the nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids. These are mainly of two types, DNA and RNA. Nucleic acids on hydrolysis yield a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compound. Nucleic acids have a very diverse set of functions, such as cell creation, the storage and processing of genetic information, protein synthesis and the generation of energy cells. Although their functions may differ, the structure of DNA and RNA are very similar, with only a few fundamental differences in their molecular make-up.

(a) Write two functions of DNA.

[1 mark]

Solution:

Concept:

- DNA is the hereditary material: its nucleotide-base sequence stores genetic information.
- DNA can replicate and its sequence directs RNA formation, which in turn directs protein synthesis.

Step 1: Transmission of hereditary information DNA stores genetic information and replicates before cell division. Copies pass this information to daughter cells and from parents to offspring, maintaining hereditary continuity.

Step 2: Direction of protein synthesis DNA provides the template for the formation of RNA. The genetic message carried by messenger RNA determines the amino-acid sequence of proteins. Thus DNA controls protein synthesis and thereby many cellular functions.

Step 3: Conclusion Two functions of DNA are **storage and transmission of hereditary information** and **control of protein synthesis**.

Quick Tip to Solve: Recall one function involving inheritance and one involving expression of the genetic message as proteins.

30(b). What products will be formed when a nucleotide from DNA containing Adenine is hydrolyzed ?

[1 mark]

Solution:

Concept:

- A nucleotide consists of a nitrogenous base, a pentose sugar and a phosphate group.
- The pentose sugar in DNA is 2-deoxy-D-ribose; complete hydrolysis separates all three nucleotide components.

Step 1: Identify the base and sugar The question specifies adenine as the nitrogenous base. Since the nucleotide belongs to DNA, the sugar obtained is 2-deoxy-D-ribose, rather than the ribose present in RNA.

Step 2: Account for the phosphate group Complete hydrolysis also releases the phosphate component as phosphoric acid, H_3PO_4 . Hence all three constituents of the nucleotide must be included. A nucleoside would yield only the base and sugar, but the given species is a nucleotide.

Step 3: Conclusion The products are adenine, 2-deoxy-D-ribose and phosphoric acid.

Quick Tip to Solve: For complete nucleotide hydrolysis, list base, sugar and phosphoric acid; DNA selects deoxyribose as the sugar.

30(c)(i). What are nucleic acids ? What is the difference between nucleotide and nucleoside ?

[2 marks]

Solution:

Concept:

- Nucleic acids are biological macromolecules made of repeating nucleotide units. Their two principal types are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).
- Each nucleotide contains a nitrogenous base, a pentose sugar and a phosphate group; a nucleoside contains only the base and the sugar.

Step 1: Define nucleic acids Nucleic acids are long-chain polynucleotides in which nucleotide units are joined through phosphodiester linkages. DNA stores and transmits hereditary information, while RNA participates in its expression, including protein synthesis. Hydrolysis of nucleic acids yields a pentose sugar, phosphoric acid and nitrogenous bases.

Step 2: Distinguish the two building units In a nucleoside, a nitrogenous base is attached to a pentose sugar through a glycosidic linkage. Addition of a phosphate group to the sugar gives a nucleotide. Thus, a nucleotide has a phosphate group, whereas a nucleoside does not. For example, adenosine is a nucleoside, while adenosine monophosphate is a nucleotide.

Step 3: Conclusion Nucleic acids are polynucleotides, principally DNA and RNA. A nucleoside is base + sugar; a nucleotide is base + sugar + phosphate.

Quick Tip to Solve: To distinguish the two terms, check for phosphate: its presence makes the unit a nucleotide.

OR

30(c)(ii). Give one similarity and one difference between DNA and RNA.

[2 marks]

Solution:

Concept:

- DNA and RNA are both nucleic acids: each is a polymer of nucleotides containing a pentose sugar, phosphate and a nitrogenous base.
- Their sugar components differ: DNA contains 2-deoxyribose, whereas RNA contains ribose.

Step 1: State one similarity Both DNA and RNA are polynucleotides. In each, successive nucleotide units are linked by phosphodiester bonds to form a sugar-phosphate backbone. Each nucleotide also carries a nitrogenous base. This common nucleotide-based organisation is a structural similarity between the two nucleic acids.

Step 2: State one difference The pentose sugar in DNA is 2-deoxyribose, whereas that in RNA is ribose. At the 2'-carbon, deoxyribose has a hydrogen atom in place of the hydroxyl group present in ribose. This distinguishes their sugar components even though both are five-carbon sugars.

Step 3: Conclusion Similarity: both are polynucleotides with phosphodiester-linked nucleotide units. Difference: DNA contains 2-deoxyribose sugar, while RNA contains ribose sugar.

Quick Tip to Solve: For one clear difference, compare the sugars directly: deoxyribose in DNA and ribose in RNA.

Section E (15 marks)

31(a)(i). Explain with the help of chemical reaction when :

(I) Acetone is treated with semicarbazide.

(II) Two molecules of benzaldehyde are treated with conc. NaOH.

(III) Butan-2-one is treated with Zn/Hg and conc. HCl.

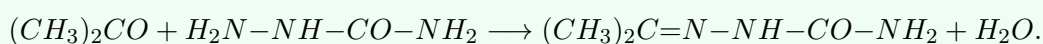
[3 marks]

Solution:

Concept:

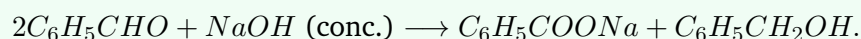
- Carbonyl compounds condense with semicarbazide, $H_2N-NH-CO-NH_2$, to form semicarbazones with elimination of water.
- Aldehydes without an alpha-hydrogen undergo the Cannizzaro disproportionation in concentrated alkali. Clemmensen reduction converts a carbonyl group into a methylene group using $Zn(Hg)$ and concentrated HCl .

Step 1: (I) Acetone with semicarbazide The terminal $-NH_2$ group of semicarbazide reacts with the carbonyl group of acetone. Condensation eliminates one molecule of water and forms acetone semicarbazone:



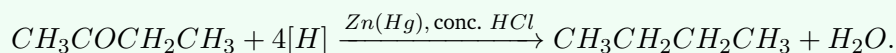
The nitrogen bonded to the carbonyl carbon in the product belongs to the terminal amino group of semicarbazide.

Step 2: (II) Benzaldehyde with concentrated sodium hydroxide Benzaldehyde has no alpha-hydrogen and therefore undergoes the Cannizzaro reaction. One molecule is oxidised to sodium benzoate and another is reduced to benzyl alcohol:



The acid product remains as its sodium salt in the alkaline reaction mixture; benzoic acid would be obtained only after acidification.

Step 3: (III) Butan-2-one with zinc amalgam and concentrated hydrochloric acid These are the reagents for Clemmensen reduction. The ketonic $>C=O$ group is reduced to $>CH_2$, without changing the carbon skeleton:



Thus the four-carbon ketone gives the corresponding four-carbon alkane.

Step 4: Conclusion Products: (I) acetone semicarbazone, (II) sodium benzoate and benzyl alcohol, and (III) butane.

Quick Tip to Solve: For concentrated alkali, check for an alpha-hydrogen first: benzaldehyde has none, so choose Cannizzaro rather than aldol condensation.

31(a)(ii). Arrange the following in the increasing order of their acidic strength :

(I) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CHBrCH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{CHBrCOOH}$

(II) Benzoic acid, 4-Methoxybenzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid

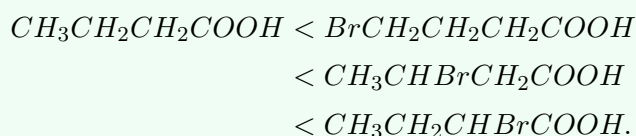
[2 marks]

Solution:

Concept:

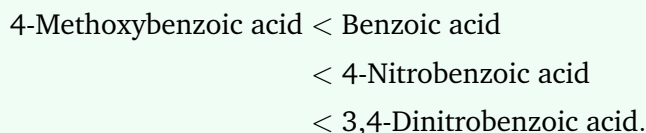
- Acidity increases when an electron-withdrawing substituent stabilises the carboxylate ion formed by loss of H^+ . The inductive effect decreases with distance from the $-\text{COOH}$ group.
- Nitro groups withdraw electrons and increase aromatic carboxylic-acid strength. A para-methoxy group donates electrons by resonance and decreases acidity relative to benzoic acid.

Step 1: (I) Compare the position of bromine Unsubstituted butanoic acid has no electron-withdrawing bromine substituent and is the weakest acid of the four. Bromine exerts a negative inductive effect. Its stabilising effect on the carboxylate ion is weakest at the gamma carbon, stronger at the beta carbon and strongest at the alpha carbon. The increasing acidic strength is therefore



Here alpha denotes the carbon directly next to the carboxyl group, so the last compound has the closest bromine substituent.

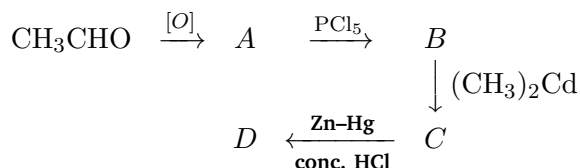
Step 2: (II) Compare substituent effects on benzoic acid At the para position, the methoxy group has a net electron-donating resonance effect, which destabilises the carboxylate ion relative to benzoate. The nitro group withdraws electrons and stabilises the anion. Two nitro groups provide stronger electron withdrawal than one. Hence the increasing order is



Step 3: Conclusion In (I), acidity increases from the unsubstituted acid through gamma-bromo and beta-bromo to alpha-bromo acid. In (II), the order is 4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

Quick Tip to Solve: Locate the substituent relative to COOH before ranking: nearer halogens strengthen acidity more, while para-methoxy weakens benzoic acid.

31(b)(i). Identify the products A, B, C and D in the following sequence of reactions:



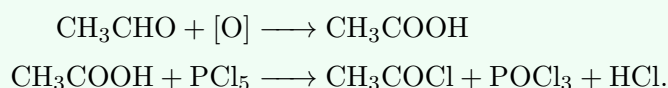
[2 marks]

Solution:

Concept:

- Oxidation converts an aldehyde into the corresponding carboxylic acid without changing its carbon skeleton. Phosphorus pentachloride then replaces the acid's hydroxyl group by chlorine to form an acyl chloride.
- A dialkylcadmium reagent converts an acyl chloride into a ketone. Clemmensen reduction, using zinc amalgam and concentrated hydrochloric acid, replaces the ketone's carbonyl group by a methylene group.

Step 1: Identify the acid and its acyl chloride Ethanal is oxidised to ethanoic acid, so A is CH_3COOH . The acid then reacts with PCl_5 to give ethanoyl chloride B:

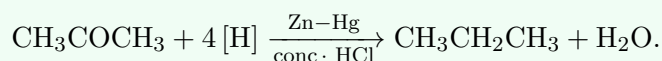


Thus the first two transformations retain the original two-carbon framework.

Step 2: Form the ketone and reduce it Dimethylcadmium transfers a methyl group to the acyl chloride, giving propanone C. This step introduces one additional carbon atom into each organic product molecule:



In the printed sequence, the final arrow runs from C towards D. Clemmensen reduction gives propane D:



The carbonyl carbon is retained and becomes the middle methylene carbon of propane.

Step 3: Conclusion A = ethanoic acid, CH_3COOH ; B = ethanoyl chloride, CH_3COCl ; C = propanone, CH_3COCH_3 ; D = propane, $\text{CH}_3\text{CH}_2\text{CH}_3$.

Quick Tip to Solve: Track the carbon count: oxidation and acyl chloride formation retain two carbons, dimethylcadmium adds a methyl group, and Clemmensen reduction retains all three carbons.

31(b)(ii). How will you bring about the following conversions ?

(I) Propanone to Propene

(II) Benzoic acid to Benzaldehyde

(III) Ethanal to But-2-enal

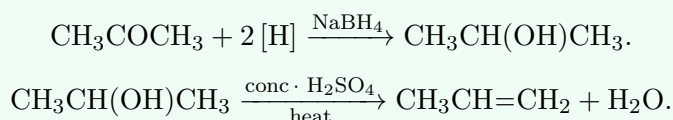
[3 marks]

Solution:

Concept:

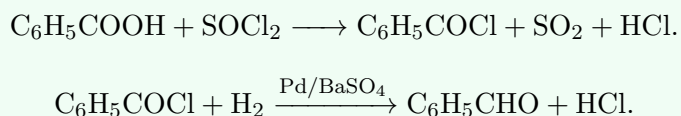
- Reduce a ketone to a secondary alcohol and then dehydrate the alcohol to obtain an alkene. The carbon skeleton remains unchanged in these two steps.
- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen over poisoned palladium on barium sulphate, limiting further reduction.
- An aldehyde containing an alpha hydrogen undergoes aldol addition with dilute alkali. Heating the aldol eliminates water to give an alpha,beta-unsaturated aldehyde.

Step 1: Convert propanone into propene First reduce propanone with NaBH_4 , followed by aqueous work-up, to form propan-2-ol. Heat this secondary alcohol with concentrated sulphuric acid to eliminate water:



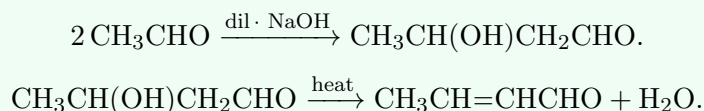
Reduction supplies the alcohol needed for dehydration; the three-carbon chain is preserved throughout.

Step 2: Convert benzoic acid into benzaldehyde Treat benzoic acid with thionyl chloride to prepare benzoyl chloride. Subject the acyl chloride to Rosenmund reduction:



The poisoned catalyst allows the product to be isolated at the aldehyde stage. Direct reduction with a strong hydride would instead tend to give benzyl alcohol and would not achieve the requested conversion.

Step 3: Convert ethanal into but-2-enal Ethanal has alpha hydrogens and undergoes self-aldol addition with dilute sodium hydroxide. Two molecules form 3-hydroxybutanal, which loses water on heating:



Numbering from the aldehyde carbon places the double bond between carbons 2 and 3, confirming the product as but-2-enal.

Step 4: Conclusion (I) Propanone $\rightarrow$ propan-2-ol $\rightarrow$ propene; (II) benzoic acid $\rightarrow$ benzoyl chloride $\rightarrow$ benzaldehyde; (III) ethanal $\rightarrow$ 3-hydroxybutanal $\rightarrow$ but-2-enal, using the reagents and conditions shown above.

Quick Tip to Solve: For these conversions, choose the intermediate by the target group: an alcohol before an alkene, an acyl chloride before an aldehyde, and a beta-hydroxy aldehyde before an enal.

32. Attempt any five of the following :

- (a) Cu^+ is not stable in aqueous solution. Comment.
- (b) Out of Cr^{2+} and Fe^{2+} , which one is a stronger reducing agent and why ?
- (c) Actinoid contraction is greater from element to element than lanthanoid contraction. Why ?
- (d) KMnO_4 acts as an oxidising agent in acidic medium. Write the ionic equation to support this.
- (e) Name the metal in the first transition series which exhibits +1 oxidation state most frequently.
- (f) Transition metals and their compounds are good catalysts. Justify.
- (g) Scandium forms no coloured ions, yet it is regarded as a transition element. Why ? [5 marks]

Solution:

Concept:

- A transition element has a partially filled d subshell in its atom or in at least one of its ions. Electronic configurations help explain its oxidation states and colour.
- The stability of aqueous ions depends on hydration as well as electronic configuration; disproportionation converts one oxidation state into two different oxidation states.
- Poor shielding by f electrons increases effective nuclear attraction across a series. Variable oxidation states and adsorption on metal surfaces help explain catalytic activity.

Step 1: (a) Instability of aqueous copper(I) In water, Cu^+ undergoes disproportionation:

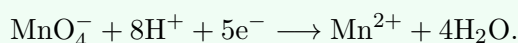


The much more negative hydration enthalpy of Cu^{2+} , compared with Cu^+ , compensates for the energy required to remove the second electron. Thus hydration stabilises copper(II), making copper(I) unstable in aqueous solution.

Step 2: (b) Compare the reducing agents Cr^{2+} is the stronger reducing agent. It readily loses an electron to form Cr^{3+} , with the particularly stable $3d^3$ configuration (t_{2g}^3 in an octahedral field). The standard reduction potential for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative, whereas that for $\text{Fe}^{3+}/\text{Fe}^{2+}$ is positive. Hence oxidation of Cr^{2+} is more favourable than oxidation of Fe^{2+} , even though Fe^{3+} has a half-filled $3d^5$ subshell.

Step 3: (c) Compare the contractions Across the actinoid series, added electrons enter the 5f subshell. The 5f electrons shield the increasing nuclear charge less effectively than the 4f electrons do in the lanthanoid series. The effective nuclear attraction therefore increases more strongly, producing a greater element-to-element decrease in size in the actinoids.

Step 4: (d) Reduction of permanganate in acidic medium Permanganate accepts five electrons and is reduced from manganese(VII) to manganese(II):



Its acceptance of electrons causes oxidation of the other reactant, so KMnO_4 acts as an oxidising agent. Both atoms and total charge balance in this ionic equation.

Step 5: (e) Metal frequently exhibiting the +1 state The metal is copper, Cu. Removal of its 4s electron gives Cu^+ with a filled $3d^{10}$ subshell. This accounts for the occurrence of the +1 oxidation

Quick Tip to Solve: Distinguish the configuration of the neutral atom from that of its common ion: Sc is a transition element because its atom is d1, whereas Sc^{3+} is colourless because it is d0.

state in many copper compounds, although the aqueous ion disproportionates as explained in part (a).

Step 6: (f) Catalytic behaviour Transition metals and their compounds can adopt different oxidation states and form intermediate compounds with reactants. These intermediates provide a reaction pathway of lower activation energy, with the catalyst regenerated. Metal surfaces also adsorb reactants, bringing them together and weakening bonds before reaction. These properties explain their effectiveness as catalysts.

Step 7: (g) Scandium as a transition element The scandium atom has configuration $[\text{Ar}]3d^14s^2$, so its atom contains an incompletely filled d subshell and satisfies the definition of a transition element. Its usual ion, Sc^{3+} , is $[\text{Ar}]3d^0$. It has no d electrons for d-d transitions and is therefore colourless; the colour of this ion does not exclude scandium from the transition elements.

Step 8: Conclusion Any five parts may be attempted. The answers are: (a) aqueous Cu^+ disproportionates; (b) Cr^{2+} is the stronger reducing agent; (c) poorer shielding by 5f electrons gives greater contraction; (d) acidic permanganate accepts five electrons to form Mn^{2+} ; (e) copper; (f) variable oxidation states, intermediates and adsorption assist catalysis; (g) the scandium atom has a partially filled d subshell, while its usual ion is d^0 .

Quick Tip to Solve: Distinguish the configuration of the neutral atom from that of its common ion: Sc is a transition element because its atom is d1, whereas Sc^{3+} is colourless because it is d0.

33(a)(i). What type of battery is the lead storage battery ? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it. [3 marks]

Solution:

Concept:

- A secondary battery can be recharged by passing an external current in the reverse direction. A lead storage battery uses lead and lead dioxide electrodes in sulphuric acid.
- During discharge, oxidation occurs at the negative anode and reduction occurs at the positive cathode. The overall cell reaction is obtained by adding the balanced electrode reactions and cancelling electrons.

Step 1: Identify the battery and the discharge anode A lead storage battery is a secondary, rechargeable battery. When current is drawn, the lead electrode acts as the anode. Lead is oxidised from oxidation state zero to +2 and forms insoluble lead sulphate:

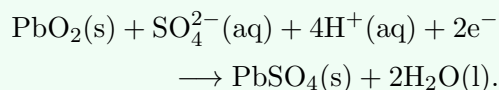


The two electrons released flow through the external circuit from the lead electrode to the lead dioxide electrode, supplying electrical energy to the connected load.

Step 2: Write the cathode reaction Lead dioxide, PbO_2 , is reduced at the cathode. Lead changes

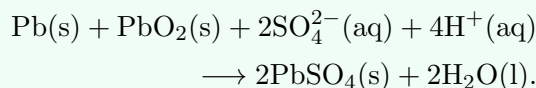
Quick Tip to Solve: Both electrodes become PbSO_4 on discharge: write the anode as oxidation of Pb and the cathode as reduction of PbO_2 , then cancel two electrons to obtain the overall equation.

from +4 to +2, consuming the two electrons released at the anode:

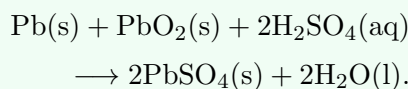


Thus lead sulphate is produced on both electrodes during discharge. The hydrogen ions balance oxygen as water, and the ionic charge on each side of the half-reaction is zero.

Step 3: Add the electrode reactions Cancelling the two electrons gives the net ionic reaction:



Combining hydrogen and sulphate ions as sulphuric acid gives the usual molecular form:



Sulphuric acid is consumed during discharge, so its concentration decreases. Charging reverses this overall chemical change and restores lead, lead dioxide and sulphuric acid.

Step 4: Conclusion The lead storage battery is a secondary battery. On discharge the Pb anode is oxidised and the PbO₂ cathode is reduced, both forming PbSO₄. The overall reaction is $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$.

Quick Tip to Solve: Both electrodes become PbSO₄ on discharge: write the anode as oxidation of Pb and the cathode as reduction of PbO₂, then cancel two electrons to obtain the overall equation.

33(a)(ii). Calculate the time to deposit 1.5 g of silver at cathode when a current of 1.5 A was passed through the solution of AgNO₃. [Molar mass of Ag = 108 g mol⁻¹, 1 F = 96500 C mol⁻¹] [2 marks]

Solution:

Concept:

- Faraday's law of electrolysis relates deposited mass to charge: $m = \frac{MIt}{nF}$, where M is molar mass, I is current, t is time, and n is the number of electrons required per metal ion.
- At the silver cathode, $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$, so one mole of silver requires one faraday of charge and $n = 1$.

Step 1: Find the charge needed for silver deposition The amount of silver to be deposited is $m/M = 1.5/108$ mol. Each mole consumes 96500 C, hence

$$Q = \frac{m}{M}nF = \frac{1.5 \times 1 \times 96500}{108} = 1340.28 \text{ C}.$$

The nitrate ion is a spectator; the electron requirement follows from the charge of Ag⁺.

Step 2: Use the current to calculate the deposition time Current is charge transferred per second,

Quick Tip to Solve: Write the cathode half-reaction first: silver is monovalent, so use $n = 1$ in Faraday's law.

$I = Q/t$. Therefore,

$$t = \frac{Q}{I} = \frac{1340.28}{1.5} = 893.52 \text{ s} = 14.89 \text{ min.}$$

Equivalently, direct substitution into $t = mnF/(MI)$ gives the same value. Using grams for both the deposited mass and molar mass keeps their ratio in moles.

Step 3: Conclusion The required time is $t \approx 894 \text{ s} \approx 14.9 \text{ min}$.

Quick Tip to Solve: Write the cathode half-reaction first: silver is monovalent, so use $n = 1$ in Faraday's law.

OR

33(b)(i). State Kohlrausch's law of independent migration of ions. Molar conductivity at infinite dilution for NH_4Cl , NaOH and NaCl solution at 298 K are 110, 100 and 105 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the molar conductivity of NH_4OH solution. [3 marks]

Solution:

Concept:

- Kohlrausch's law states that at infinite dilution each ion contributes independently to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present.
- For an electrolyte, $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$, where ν_+ and ν_- are the numbers of cations and anions per formula unit and λ° denotes an ionic molar conductivity at infinite dilution.

Step 1: Express the given electrolytes in terms of ionic contributions All three given electrolytes have one cation and one anion per formula unit. At the stated temperature, Kohlrausch's law gives

$$\begin{aligned}\Lambda_m^\circ(\text{NH}_4\text{Cl}) &= \lambda^\circ(\text{NH}_4^+) + \lambda^\circ(\text{Cl}^-), \\ \Lambda_m^\circ(\text{NaOH}) &= \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{OH}^-), \\ \Lambda_m^\circ(\text{NaCl}) &= \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-).\end{aligned}$$

Step 2: Cancel the unwanted ions and calculate the required conductivity Add the first two expressions and subtract the third. The sodium-ion and chloride-ion contributions cancel, leaving exactly the ammonium-ion and hydroxide-ion contributions required for NH_4OH :

$$\begin{aligned}\Lambda_m^\circ(\text{NH}_4\text{OH}) &= \Lambda_m^\circ(\text{NH}_4\text{Cl}) + \Lambda_m^\circ(\text{NaOH}) \\ &\quad - \Lambda_m^\circ(\text{NaCl}) \\ &= 110 + 100 - 105 \\ &= 105 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

This combination yields the limiting molar conductivity. It does not represent the molar conductivity of the weak electrolyte at an arbitrary finite concentration, where its degree of ionisation also matters.

Quick Tip to Solve: Add a strong electrolyte supplying each desired ion, then subtract the electrolyte formed by their two unwanted ions.

Step 3: Conclusion At 298 K, the limiting molar conductivity is

$$\Lambda_m^\circ(\text{NH}_4\text{OH}) = 105 \text{ S cm}^2 \text{ mol}^{-1}.$$

Quick Tip to Solve: Add a strong electrolyte supplying each desired ion, then subtract the electrolyte formed by their two unwanted ions.

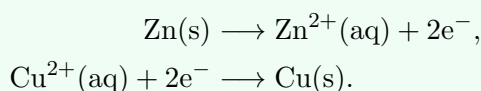
33(b)(ii). Calculate ΔG° of the following cell at 25°C : $\text{Zn (s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu (s)}$. Given : $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, $1 \text{ F} = 96500 \text{ C mol}^{-1}$ [2 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using both tabulated values as reduction potentials.
- Standard Gibbs energy and cell potential are related by $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of moles of electrons transferred per mole of the balanced cell reaction and F is the Faraday constant.

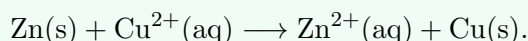
Step 1: Identify the electrode reactions and cell potential In the cell as written, zinc is oxidised at the anode and copper ions are reduced at the cathode:



Thus $n = 2$. From the given reduction potentials,

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10 \text{ V}.$$

Step 2: Calculate the standard Gibbs energy change The overall reaction is



Substitute the cell potential and electron transfer number:

$$\begin{aligned}\Delta G^\circ &= -2 \times 96500 \times 1.10 \\ &= -212300 \text{ J mol}^{-1} \\ &= -212.3 \text{ kJ mol}^{-1}.\end{aligned}$$

The unit follows from $\text{C} \times \text{V} = \text{J}$. The negative sign agrees with the positive standard cell potential and indicates that the reaction as written is spontaneous under standard conditions.

Step 3: Conclusion The standard Gibbs energy change at 25°C is $\Delta G^\circ = -212.3 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Subtract reduction potentials as cathode minus anode, and obtain n from the balanced electron transfer before using the Gibbs energy formula.