

CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-S-1 - 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 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 galvanic cell, reduction occurs at the electrode with the higher standard reduction potential.
- The standard cell potential is $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$, using reduction potentials for both electrodes.

Step 1: Identify the cathode and anode Since $+0.15\text{ V} > -0.73\text{ V}$, Sn^{4+} is reduced to Sn^{2+} at the cathode. Chromium metal is oxidised to Cr^{3+} at the anode. This direction makes the cell potential positive, as required for spontaneity.

Step 2: Subtract the reduction potentials

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

Adding the two reduction potentials gives -0.58 V , which is not the cell-potential rule. Thus neither value of magnitude 0.58 V is valid. The value -0.88 V describes the reverse, non-spontaneous reaction. Electrode potentials are not multiplied when balancing electrons.

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

Quick Tip to Solve: Place the more positive reduction potential first, then subtract the other potential with its sign.

2. The most stable complex among the following is :

[1 mark]

- (A) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- (B) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
- (C) $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$
- (D) $\text{K}_4[\text{Fe}(\text{CN})_6]$

Correct Answer: (C) $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$

Solution:

Concept:

- A chelating ligand binds to the same metal ion through two or more donor atoms and forms a ring containing the metal.
- Ethane-1,2-diamine, abbreviated en, is a bidentate ligand. Chelation generally enhances the stability of a complex; this is the chelate effect.

Step 1: Identify the ring-forming ligand In $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$, each en ligand coordinates through both nitrogen atoms and forms a five-membered chelate ring with platinum. The two en ligands therefore supply four donor atoms and form two chelate rings.

Step 2: Compare the listed ligand arrangements The ammonia and chloride ligands in (A), and the ammonia ligands in (B), are monodentate and do not form chelate rings. Cyanide in (D) is also monodentate in this complex: six cyanide ligands give six metal–ligand bonds, but no chelate rings. On the chelate-effect criterion tested here, the en-containing platinum complex receives the additional stability associated with ring formation.

Step 3: Conclusion The most stable complex among the given choices is $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$. Hence, the correct option is (C).

Quick Tip to Solve: Look for en: its two nitrogen donors bind the same metal and produce a five-membered chelate ring.

3. 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:

- Oxidation state and ligand strength determine the electronic arrangement of a transition-metal complex.
- A diamagnetic species has no unpaired electrons. For Ni^{2+} , the strong-field ligand CN^- gives a paired $3d^8$ arrangement and dsp^2 hybridisation.

Quick Tip to Solve: For four-coordinate nickel(II), strong-field cyanide plus diamagnetism identifies square-planar geometry.

Step 1: Determine the nickel configuration Let the oxidation state of nickel be x . Since each cyanide ligand has charge -1 , $x + 4(-1) = -2$, giving $x = +2$. Nickel has atomic number 28, so Ni^{2+} has configuration $[\text{Ar}]3d^8$.

Step 2: Apply the ligand-field and magnetic information Cyanide is a strong-field ligand. Pairing of the eight $3d$ electrons leaves one $3d$ orbital vacant for dsp^2 hybridisation with the $4s$ and two $4p$ orbitals. The four hybrid orbitals point towards the corners of a square. A tetrahedral d^8 complex would have two unpaired electrons and would be paramagnetic. Octahedral and distorted-octahedral geometries require six donor positions, whereas this complex has four.

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

Quick Tip to Solve: For four-coordinate nickel(II), strong-field cyanide plus diamagnetism identifies square-planar geometry.

4. 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+}

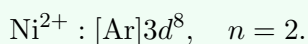
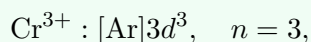
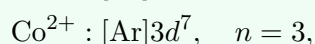
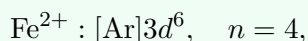
Correct Answer: (A) Fe^{2+}

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons and BM denotes Bohr magneton.
- Transition-metal cations lose the $4s$ electrons before the $3d$ electrons. Apply Hund's rule to the resulting d -electron configuration.

Step 1: Count the unpaired electrons The configurations and unpaired-electron counts for the listed ions are



For chromium, begin with $[\text{Ar}]3d^5 4s^1$; removing three electrons gives $3d^3$.

Step 2: Compare the spin-only moments The corresponding moments are $\sqrt{24} \approx 4.90$ BM for Fe^{2+} , $\sqrt{15} \approx 3.87$ BM for both Co^{2+} and Cr^{3+} , and $\sqrt{8} \approx 2.83$ BM for Ni^{2+} . Thus (B) and (C) each have fewer unpaired electrons than (A), while (D) has the fewest. The comparison is based on unpaired electrons, not atomic number.

Step 3: Conclusion Fe^{2+} shows the highest magnetic moment. Hence, the correct option is (A).

Quick Tip to Solve: Remove the $4s$ electrons first, then count unpaired d electrons; the largest count gives the largest spin-only moment.

5. If amines are arranged in increasing order of their basic strength in gaseous phase, then the correct order will be : [1 mark]

(A) $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_3\text{N} < (\text{CH}_3)_2\text{NH}$

(B) $\text{NH}_3 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2$

(C) $(\text{CH}_3)_3\text{N} < (\text{CH}_3)_2\text{NH} < \text{CH}_3\text{NH}_2 < \text{NH}_3$

(D) $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$

Correct Answer: (D) $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$

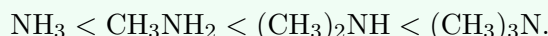
Solution:

Concept:

- An amine acts as a base by donating the nitrogen lone pair to a proton. Greater electron availability at nitrogen favours proton acceptance.
- Methyl groups exert a positive inductive effect, $+I$. In the gaseous phase, there is no aqueous solvation to modify the usual order of these methylamines.

Step 1: Compare the number of electron-releasing groups Ammonia has no methyl group, methylamine has one, dimethylamine has two, and trimethylamine has three. Increasing methyl substitution increases electron donation towards nitrogen and stabilises the corresponding protonated amine. Therefore, basic strength increases from ammonia through the primary and secondary methylamines to the tertiary methylamine in the gaseous phase.

Step 2: Check the direction of the printed orders The required increasing order is



Option (A) incorrectly puts dimethylamine above trimethylamine for the gaseous phase. Option (B) incorrectly makes methylamine strongest. Option (C) reverses the trend and makes ammonia strongest. Only (D) follows increasing electron donation with methyl substitution.

Step 3: Conclusion The correct order is $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$. Hence, the correct option is (D).

Quick Tip to Solve: Underline gaseous phase: for these methylamines, increase basic strength as the number of methyl groups rises.

6. 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:

- An aldehyde or ketone undergoes self-aldol condensation when it has at least one α -hydrogen, a hydrogen attached to the carbon next to the carbonyl carbon.
- Removal of an α -hydrogen forms an enolate, which attacks another carbonyl molecule. The initial aldol product can lose water to form an unsaturated carbonyl compound.

Step 1: Locate the alpha hydrogens in each aliphatic compound In CH_3CHO , the methyl group next to CHO has three α -hydrogens. In CH_3COCH_3 , both methyl groups provide α -hydrogens. In $\text{CH}_3\text{CH}_2\text{CHO}$, the adjacent CH_2 group has two α -hydrogens. Hence (A), (B) and (C) can undergo aldol condensation.

Step 2: Examine benzaldehyde In $\text{C}_6\text{H}_5\text{CHO}$, the carbon adjacent to the carbonyl carbon is the aromatic ring carbon directly bonded to CHO; it bears no hydrogen. The hydrogen in the CHO group is attached to the carbonyl carbon itself and is not an α -hydrogen. Benzaldehyde therefore cannot form the required enolate and does not undergo self-aldol condensation.

Step 3: Conclusion $\text{C}_6\text{H}_5\text{CHO}$, benzaldehyde, does not undergo aldol condensation by itself. Hence, the correct option is (D).

Quick Tip to Solve: Count hydrogens on the carbon beside $\text{C}=\text{O}$; the aldehydic hydrogen on the carbonyl carbon does not count.

7. 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:

- Select the longest continuous carbon chain as the parent hydrocarbon; side branches do not extend the chain through the same carbon twice.
- Number the parent to give the substituents the lowest set of locants, and arrange substituent names alphabetically, ignoring prefixes such as di-.

Quick Tip to Solve: Trace a chain from the brominated carbon through the central carbon to one methyl group before numbering this branched molecule.

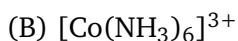
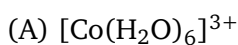
Step 1: Identify the parent and substituents In $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Br}$, the longest chain contains three carbons: $\text{CH}_3-\text{C}-\text{CH}_2\text{Br}$. Thus the parent is propane. The central carbon carries two remaining methyl groups, while the terminal carbon carries bromine.

Step 2: Number from the bromine end Starting at CH_2Br gives locants 1, 2, 2, which are lower than 2, 2, 3 from the other end. Write bromo before methyl alphabetically. Option (A) incorrectly puts bromine on the central carbon; options (B) and (C) select ethane even though a three-carbon chain exists.

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

Quick Tip to Solve: Trace a chain from the brominated carbon through the central carbon to one methyl group before numbering this branched molecule.

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



Correct Answer: (C) $[\text{Co}(\text{CN})_6]^{3-}$

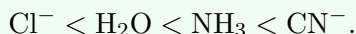
Solution:

Concept:

- In an octahedral complex, the ligand field separates the metal d orbitals into lower t_{2g} and higher e_g levels. The excitation energy is governed by the splitting Δ_o .
- For the same metal ion and geometry, a stronger-field ligand produces a larger Δ_o .

Step 1: Compare equivalent metal centres Water and ammonia are neutral, whereas cyanide and chloride carry charge -1 . Charge balance shows that cobalt has oxidation state $+3$ in all four six-coordinate complexes. We can therefore compare their ligand strengths directly.

Step 2: Apply the spectrochemical series The relevant ligand order is



Cyanide is the strongest-field ligand listed and gives the largest octahedral splitting. Chloride, water and ammonia in options (D), (A) and (B), respectively, produce smaller splittings and require less excitation energy.

Step 3: Conclusion $[\text{Co}(\text{CN})_6]^{3-}$ has the highest excitation energy. Hence, the correct option is (C).

Quick Tip to Solve: First confirm that all complexes contain cobalt(III), then select the strongest ligand from the spectrochemical series.

9. For a chemical reaction, $A \rightarrow B$, 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:

- The rate law for the stated reaction is $r = k[A]^n$, where r is the rate, k the rate constant and n the order with respect to the sole reactant.
- At a fixed temperature, taking a ratio of rates cancels k and relates the rate multiplier to the concentration multiplier.

Step 1: Form the ratio of rates Let the original concentration be c . After increasing it fourfold, the rate changes from r_1 to $r_2 = 2r_1$. Therefore,

$$\frac{r_2}{r_1} = \frac{k(4c)^n}{kc^n} = 4^n = 2.$$

Step 2: Solve for the order and check the choices Since $4 = 2^2$, the relation becomes $2^{2n} = 2^1$, so $2n = 1$ and $n = \frac{1}{2}$. A second-order reaction would show a sixteenfold rate increase, a first-order reaction a fourfold increase, and a zero-order reaction no increase. Only the half-order law gives the observed doubling.

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

Quick Tip to Solve: Use $n = \log(\text{rate multiplier}) / \log(\text{concentration multiplier})$; here the multipliers are 2 and 4.

10. 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) Pentaaminenitrito-cobalt(II) chloride

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

Solution:

Concept:

- Name ligands before the central metal and specify its oxidation state using a Roman numeral. Neutral NH_3 is named ammine.
- Nitrite is an ambidentate ligand: N-bonded NO_2^- is named nitrito-N, whereas O-bonded ONO^- is

Quick Tip to Solve: Use the two external chlorides to find cobalt(III), then distinguish NO_2 (N-bound) from ONO (O-bound).

named nitrito-O in the systematic convention used here.

Step 1: Calculate the oxidation state of cobalt The two chloride counterions show that the complex ion has charge +2. Each ammine is neutral and nitrite has charge -1. If cobalt's oxidation state is x ,

$$x + 5(0) - 1 = +2, \quad x = +3.$$

Step 2: Name the ligands and distinguish the linkage Five ammine ligands give pentaammine. The written NO_2 ligand denotes N attachment, giving nitrito-N, followed by cobalt(III) chloride. Option (A) names the O-linked isomer. Option (C) uses the older name nitro for the N-linked ligand; the explicit systematic linkage name requested here is nitrito-N. Option (D) has both an incorrect ammine spelling and the wrong cobalt oxidation state.

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

Quick Tip to Solve: Use the two external chlorides to find cobalt(III), then distinguish NO_2 (N-bound) from ONO (O-bound).

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

[1 mark]

- (A) Electrophilic substitution
- (B) $\text{S}_{\text{N}}1$ reaction
- (C) Electrophilic addition
- (D) $\text{S}_{\text{N}}2$ reaction

Correct Answer: (D) $\text{S}_{\text{N}}2$ reaction

Solution:

Concept:

- Williamson ether synthesis is a nucleophilic substitution in which an alkoxide ion attacks an alkyl halide to form an ether.
- A methyl halide reacts by the concerted $\text{S}_{\text{N}}2$ mechanism: bond formation and leaving-group departure occur in the same step.

Step 1: Write the reaction for dimethyl ether Methoxide ion attacks the methyl carbon of a methyl halide, for example methyl bromide:



The electron-rich methoxide is the nucleophile, and bromide is the leaving group.

Step 2: Identify the substitution mechanism The methyl carbon is readily accessible to backside attack, so methoxide displaces bromide in one concerted step. An $\text{S}_{\text{N}}1$ route would require the highly unstable methyl carbocation. Electrophilic substitution is excluded because the attacking species is a nucleophile, while electrophilic addition is excluded because this is replacement of a leaving group rather than addition across a multiple bond.

Quick Tip to Solve: An alkoxide plus a methyl halide points directly to backside attack and $\text{S}_{\text{N}}2$, with no carbocation intermediate.

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

Quick Tip to Solve: An alkoxide plus a methyl halide points directly to backside attack and S_N2 , with no carbocation intermediate.

12. 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 with nitrous acid at 273–278 K; these salts undergo coupling to give coloured azo compounds.
- Primary aliphatic diazonium salts are unstable and decompose with nitrogen evolution, so they do not give the corresponding azo dye test.

Step 1: Compare the azo dye test results Treat each amine with NaNO_2 and dilute HCl in the cold, then couple with phenol in alkaline solution. Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, forms benzenediazonium chloride and then an orange azo dye. Ethanamine, $\text{C}_2\text{H}_5\text{NH}_2$, instead evolves N_2 and forms ethanol on treatment with nitrous acid; it does not produce the azo dye.

Step 2: Exclude the other listed tests Both compounds are primary amines and show the same primary-amine classification in the Hinsberg test: their sulphonamide products dissolve in alkali. Haloform testing concerns suitable carbonyl compounds and alcohols, while Tollens' reagent primarily detects aldehydes. Neither supplies the required characteristic distinction between these two amines.

Step 3: Conclusion The azo dye test distinguishes aniline from ethanamine. Hence, the correct option is (C).

Quick Tip to Solve: To distinguish a primary aromatic amine from a primary aliphatic amine, test for diazotisation followed by coloured azo coupling.

13. 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]

- (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.

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 sugar has a free anomeric carbon whose cyclic hemiacetal can open to a carbonyl form.
- In maltose, an $\alpha(1 \rightarrow 4)$ glycosidic bond joins two glucose units, leaving one anomeric carbon free.

Step 1: Evaluate the assertion Maltose reduces Tollens' and Fehling's reagents because one glucose residue can open to its aldehyde form. Thus, the assertion is true.

Step 2: Evaluate the reason The glycosidic linkage connects C-1 of the first glucose unit to C-4 of the second through oxygen. This is the actual structure of maltose, so the reason is true.

Step 3: Connect the linkage to reducing behaviour Since the second unit contributes C-4, its C-1 remains a free hemiacetal centre. Ring opening at this centre provides the aldehyde group needed for reduction. The reason therefore explains the assertion; the option claiming no explanatory connection is inappropriate, and the options declaring either statement false are also excluded.

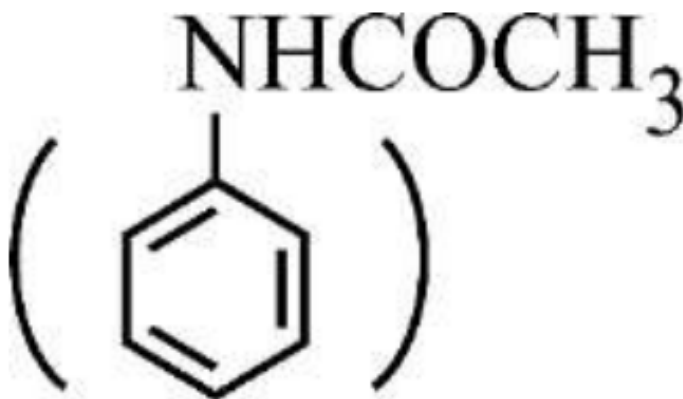
Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is (A).

Quick Tip to Solve: Inspect both anomeric carbons: one free C-1 is enough to make maltose a reducing sugar.

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

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

[1 mark]



- (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.

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 a nitrogen lone pair to accept a proton.
- Acetylation converts aniline, $C_6H_5NH_2$, into the amide acetanilide, $C_6H_5NHCOCH_3$.

Step 1: Evaluate the assertion The nitrogen lone pair in acetanilide is less available for proton acceptance than that in aniline. Acetanilide is therefore less basic, and the assertion is true.

Step 2: Evaluate the reason The acetyl group introduces a carbonyl group directly attached to nitrogen. The nitrogen lone pair becomes delocalised towards this carbonyl group by resonance, decreasing electron density and lone-pair availability at nitrogen. Thus, the reason is true.

Step 3: Test the explanatory connection The reduced availability of the nitrogen lone pair is precisely why acetylation lowers basicity. Although aniline also shows resonance with its benzene ring, acetanilide has the stronger amide delocalisation towards the carbonyl group. Thus, the option stating that R does not explain A is excluded, as are the options declaring either 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: When an amino group is acetylated, identify the new amide linkage and the loss of nitrogen lone-pair availability.

15. 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]

- (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.

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

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For a reaction with positive activation energy, heating increases the fraction of molecules with sufficient energy for effective collisions.

Step 1: Evaluate the assertion As T increases, the exponent $-E_a/(RT)$ becomes less negative. With the other Arrhenius parameters treated as constant over the temperature interval, the exponential factor and hence k increase. The assertion is true.

Step 2: Evaluate the reason Raising temperature shifts the molecular energy distribution so that a larger fraction of molecules has energy above the activation-energy threshold. Therefore, a larger fraction of collisions can lead to reaction. The reason is true.

Step 3: Relate molecular energy to the rate constant The increased fraction of energetically effective collisions gives the molecular explanation for the increase in the rate constant. Thus, R explains A, excluding the option that both are true without an explanatory connection; neither statement is 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: In the Arrhenius exponential, increasing temperature makes the negative exponent smaller in magnitude, so the rate constant rises.

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

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

[1 mark]

- (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.

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).
- The formation of insoluble copper(I) iodide, CuI , favours this redox reaction.

Step 1: Evaluate the assertion Copper(II) iodide, CuI_2 , is not obtained as a stable ordinary iodide salt. When copper(II) ions meet iodide ions, copper(I) iodide and iodine form instead. The assertion is true.

Step 2: Evaluate the reason Iodide loses electrons to form iodine while copper(II) gains electrons to form copper(I). The overall balanced ionic equation is



Two iodide ions are oxidised, while the other two combine with copper(I) to form the precipitate. The reason is true.

Step 3: Test the explanatory connection The redox incompatibility of copper(II) and iodide prevents stable copper(II) iodide from forming. The reason directly explains the assertion, so the option denying an explanatory link is excluded. The options declaring either statement false are also incorrect.

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 copper(II) with iodide, write copper(I) iodide precipitate plus iodine, then balance both charge and iodine atoms.

Section B (10 marks)

17. Write the reaction involved in the following :

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

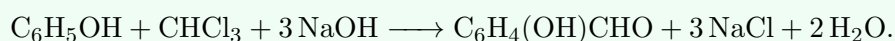
[2 marks]

Solution:

Concept:

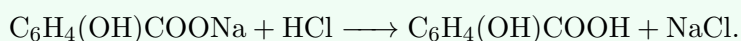
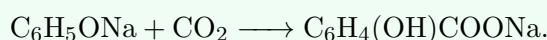
- The hydroxyl group activates the benzene ring of phenol and directs electrophilic substitution mainly to its ortho and para positions.
- Reimer-Tiemann formylation introduces $-\text{CHO}$; Kolbe's reaction introduces $-\text{COOH}$ after acidification.

Step 1: Write the Reimer-Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. The major product is 2-hydroxybenzaldehyde (salicylaldehyde), with the formyl group ortho to the hydroxyl group. The overall reaction, showing the product after work-up, is



Here $\text{C}_6\text{H}_4(\text{OH})\text{CHO}$ denotes the ortho isomer. The electrophile is dichlorocarbene, $:\text{CCl}_2$, generated from chloroform in alkaline medium.

Step 2: Write Kolbe's reaction Sodium phenoxide reacts with carbon dioxide at about 400 K under 4–7 atm pressure to give sodium salicylate. Acidification yields 2-hydroxybenzoic acid (salicylic acid):

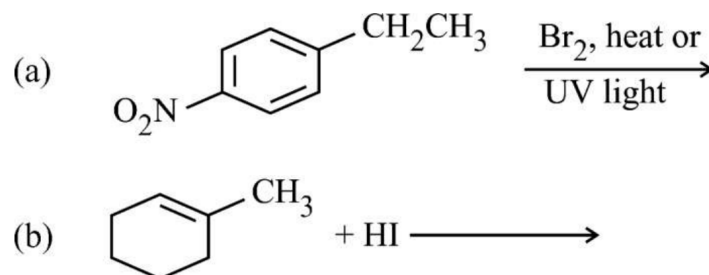


The hydroxyl and carboxyl groups are adjacent in these salicylate products. The alkaline phenoxide makes the ring reactive enough for carboxylation.

Step 3: Conclusion (a) Reimer-Tiemann reaction gives salicylaldehyde from phenol. (b) Kolbe's reaction gives salicylic acid through sodium phenoxide and carbon dioxide, followed by acidification.

Quick Tip to Solve: Remember the reagent-product pair: chloroform gives an ortho aldehyde; carbon dioxide gives an ortho carboxylic acid after acidification.

18. Draw the structures of major monohalo products in each of the following reactions : [2 marks]



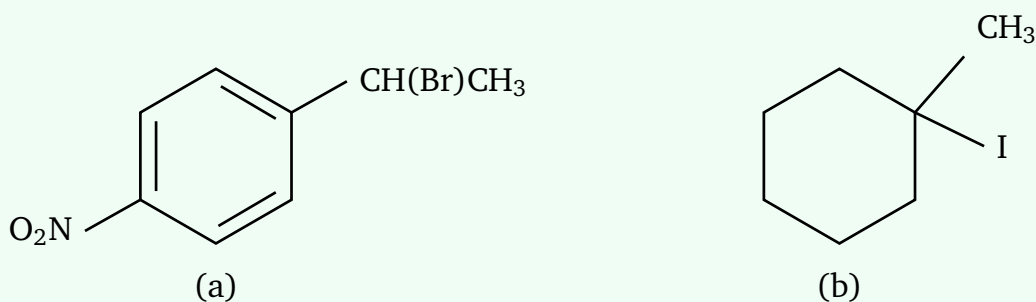
Solution:

Concept:

- In heat or ultraviolet light, Br_2 brominates an alkylbenzene by a free-radical substitution at the benzylic carbon, the carbon directly attached to the benzene ring.
- Addition of HI to an unsymmetrical alkene follows Markovnikov's rule: protonation proceeds through the more stable carbocation, which is then attacked by I^- .

Step 1: Locate the benzylic substitution in (a) The side chain is $-\text{CH}_2\text{CH}_3$. A hydrogen on its benzylic CH_2 group is replaced by bromine because the intermediate benzylic radical is resonance-stabilised. The para nitro group and the aromatic ring remain intact. Thus the side chain becomes $-\text{CH}(\text{Br})\text{CH}_3$; bromination of the terminal methyl group is not the major pathway under these conditions.

Step 2: Apply Markovnikov addition in (b) In 1-methylcyclohex-1-ene, the methyl-bearing double-bond carbon has no hydrogen, whereas the other double-bond carbon has one. Addition of H^+ to the latter produces a tertiary carbocation at the methyl-bearing carbon. Attack by I^- places iodine on that same carbon. The double bond becomes a single bond, and the product is a saturated cyclohexane ring.



Major products: (a) benzylic bromide; (b) 1-iodo-1-methylcyclohexane.

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

Quick Tip to Solve: For (a), mark the carbon next to benzene; for (b), put iodine on the double-bond carbon already bearing the methyl group.

19. 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:

- A first-order reaction obeys $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$, where $[A]_0$ is the initial concentration, $[A]_t$ is the concentration remaining at time t , and k is the rate constant.
- The integrated rate equation uses the amount remaining, not the amount decomposed. For a fixed volume, the ratio of concentrations equals the ratio of the corresponding quantities of acid.

Step 1: Convert the fraction decomposed to the fraction remaining Let the initial quantity of acid be a . When three-fourths decomposes, the undecomposed quantity is

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

Therefore $[A]_0/[A]_t = a/(a/4) = 4$. The initial quantity cancels, as expected for a specified fractional conversion in a first-order reaction.

Step 2: Substitute into the first-order rate equation Using $k = 2.3 \times 10^{-3} \text{ s}^{-1}$ and the supplied $\log 4 = 0.6021$,

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

The unit is seconds because the logarithm is dimensionless and the rate constant has unit s^{-1} . A remaining fraction of $1/4$ also corresponds to two half-lives, providing a check on the result.

Step 3: Conclusion Three-fourths of the acid decomposes in approximately 603 s, or 10.05 min.

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

20(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:

- Nucleophilic addition to a carbonyl group begins with attack on its electrophilic carbon. Electron-donating alkyl groups reduce the positive character of this carbon and also hinder the nucleophile sterically.

Quick Tip to Solve: For carbonyl addition, compare both methyl-group donation and crowding; for acid boiling points, identify the O–H donor that enables hydrogen-bonded dimers.

- Boiling requires separation of molecules against intermolecular attractions. Strong intermolecular hydrogen bonding increases the energy needed for this separation and hence raises the boiling point.

Step 1: Compare the two carbonyl compounds towards HCN In the reaction with HCN, CN^- attacks the carbonyl carbon, followed by protonation of the oxygen. Acetaldehyde, CH_3CHO , has one methyl group and one small hydrogen attached to the carbonyl carbon. Acetone, CH_3COCH_3 , has two methyl groups. Their combined positive inductive effect decreases the electrophilicity of the carbonyl carbon more in acetone. Its two methyl groups also present greater steric hindrance to the approaching nucleophile. Both electronic and steric effects therefore favour faster addition to acetaldehyde.

Step 2: Compare intermolecular association and boiling points Carboxylic acids contain both a hydrogen-bond donor, the O–H group, and an acceptor, the carbonyl oxygen. Two acid molecules can form a cyclic dimer held by two intermolecular hydrogen bonds. Aldehydes and ketones lack an O–H bond and cannot form such hydrogen-bonded dimers with themselves in their pure liquids. Their principal polar attraction is dipole–dipole interaction. More energy is therefore required to separate associated acid molecules than aldehyde or ketone molecules of comparable molar mass.

Step 3: Conclusion (i) CH_3CHO reacts more readily with HCN because its carbonyl carbon is more electrophilic and less sterically hindered. (ii) Carboxylic acids have higher boiling points because of strong intermolecular hydrogen bonding and dimer formation.

Quick Tip to Solve: For carbonyl addition, compare both methyl-group donation and crowding; for acid boiling points, identify the O–H donor that enables hydrogen-bonded dimers.

OR

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

(i) Propanal and Propanone

(ii) Benzaldehyde and Benzoic acid

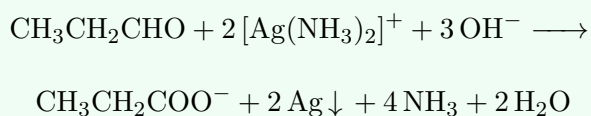
[2 marks]

Solution:

Concept:

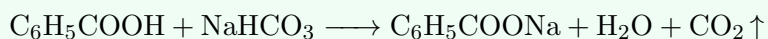
- Tollens' reagent, containing $[\text{Ag}(\text{NH}_3)_2]^+$, oxidises an aldehyde to a carboxylate ion while silver ions are reduced to metallic silver. An ordinary ketone does not respond.
- A carboxylic acid reacts with aqueous sodium hydrogen carbonate, NaHCO_3 , to release carbon dioxide. An aldehyde lacks this acidic carboxyl group.

Step 1: (i) Apply Tollens' test Warm separate samples with freshly prepared Tollens' reagent in a water bath. Propanal gives a silver mirror on the test-tube wall because its aldehyde group is oxidised; propanone gives no silver mirror under these conditions.



Quick Tip to Solve: Use Tollens' reagent for an aldehyde versus a ketone, and bicarbonate effervescence for an acid versus an aldehyde; always state both observations.

Step 2: (ii) Add sodium hydrogen carbonate solution Add aqueous NaHCO_3 separately to benzaldehyde and benzoic acid. Benzoic acid gives brisk effervescence of CO_2 , which turns limewater milky, whereas benzaldehyde gives no effervescence.



The evolution of gas distinguishes the acid without requiring oxidation of either compound.

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

Quick Tip to Solve: Use Tollens' reagent for an aldehyde versus a ketone, and bicarbonate effervescence for an acid versus an aldehyde; always state both observations.

21. Write the reaction of glucose with :

(a) HI

(b) Br_2 water

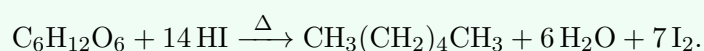
[2 marks]

Solution:

Concept:

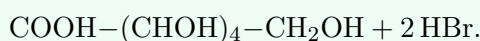
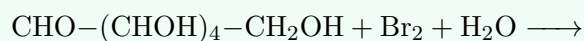
- Open-chain glucose has the structure $\text{CHO}-(\text{CHOH})_4-\text{CH}_2\text{OH}$. It contains six carbon atoms in an unbranched chain, one aldehyde group and five hydroxyl groups.
- Prolonged heating with hydrogen iodide reduces glucose to a hydrocarbon, whereas bromine water is a mild oxidising agent that selectively oxidises the aldehyde group to a carboxyl group.

Step 1: (a) Heat glucose with hydrogen iodide On prolonged heating with excess HI, the oxygen-containing groups are reduced and glucose forms *n*-hexane. The six-carbon skeleton is retained. The overall balanced reaction is



Formation of the straight-chain hydrocarbon supports the presence of an unbranched chain of six carbon atoms in glucose.

Step 2: (b) Treat glucose with bromine water Bromine water oxidises the terminal aldehyde group of glucose to a carboxyl group, giving gluconic acid. Under these mild conditions the terminal primary alcohol group remains unchanged:



The bromine colour disappears as bromine is consumed. This reaction establishes the aldehydic nature of the carbonyl group of glucose.

Step 3: Conclusion Glucose gives *n*-hexane on prolonged heating with HI, and gluconic acid on oxidation with bromine water.

Quick Tip to Solve: Remember the contrast: hot excess HI removes oxygen to give hexane, while bromine water changes only CHO to COOH, giving gluconic acid.

Section C (21 marks)

22. (a) Draw the geometrical isomers of the complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

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

(c) Solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green in colour whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Give reason. [Atomic number : Ni = 28]

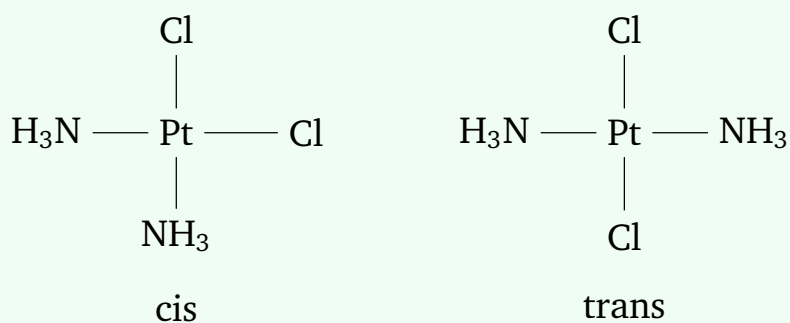
[3 marks]

Solution:

Concept:

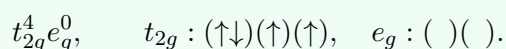
- A square-planar complex of the type $[\text{MA}_2\text{B}_2]$ has cis and trans geometrical isomers: identical ligands occupy adjacent and opposite positions, respectively.
- In an octahedral field, the t_{2g} set lies below the e_g set. When the splitting energy Δ_o exceeds the pairing energy P , electrons pair in the lower set before entering the upper set.
- The colour of a coordination compound depends on the energy gap between its split d orbitals and whether its electronic transitions absorb visible light.

Step 1: (a) Arrange the ligands around platinum Platinum(II) forms a square-planar complex. In the cis isomer the chloride ligands are adjacent, with a 90° Cl–Pt–Cl angle; in the trans isomer they are opposite, with a 180° angle. All four ligands lie in the plane of the drawing.



Cis and trans geometrical isomers of square-planar $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Step 2: (b) Fill the octahedral d orbitals Place the first three electrons singly in the lower t_{2g} orbitals. Since $\Delta_o > P$, the fourth electron pairs in this set rather than entering e_g . The low-spin configuration is



It contains two unpaired electrons.

Step 3: (c) Compare the ligand fields of the nickel complexes Nickel (atomic number 28) loses its two 4s electrons to give Ni^{2+} , $[\text{Ar}]3d^8$, in both complexes. Weak-field water gives octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, with $t_{2g}^6 e_g^2$ and two unpaired electrons. Its d–d transitions absorb visible light, so the solution appears green. Strong-field cyanide gives square-planar dsp^2 $[\text{Ni}(\text{CN})_4]^{2-}$, with all electrons paired. Its larger relevant energy gap places absorption outside the visible region, so it is colourless. Pairing accounts for diamagnetism; colour depends on the absorption energy.

Step 4: Conclusion (a) The complex has cis and trans square-planar isomers as drawn. (b) The configuration is $t_{2g}^4 e_g^0$. (c) The aqua complex absorbs visible light and appears green; the strong-field

Quick Tip to Solve: Draw both Pt isomers in one plane, pair the fourth d electron when splitting exceeds pairing energy, and connect nickel's colour to visible-light absorption.

square-planar cyanide complex has no appreciable visible absorption and is colourless.

Quick Tip to Solve: Draw both Pt isomers in one plane, pair the fourth d electron when splitting exceeds pairing energy, and connect nickel's colour to visible-light absorption.

23. The electrical resistance of a column of 0.05 M NaOH solution of cell constant 50 cm^{-1} is $4.5 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity and molar conductivity. [3 marks]

Solution:

Concept:

- For a solution column of length l and area A , resistance is $R = \rho l/A$, where ρ is resistivity. The cell constant is $G^* = l/A$, so $\rho = R/G^*$.
- Conductivity is the reciprocal of resistivity: $\kappa = 1/\rho = G^*/R$. With the cell constant in cm^{-1} , conductivity is obtained in S cm^{-1} .
- Molar conductivity is $\Lambda_m = 1000\kappa/c$, where c is concentration in mol L^{-1} ; the factor 1000 converts litres into cubic centimetres.

Step 1: Calculate the resistivity The given resistance is $R = 4.5 \times 10^3 \Omega$, the cell constant is $G^* = 50 \text{ cm}^{-1}$, and the concentration of NaOH is $c = 0.05 \text{ mol L}^{-1}$. Divide the resistance by the cell constant, since resistance contains the geometrical factor l/A :

$$\rho = \frac{R}{G^*} = \frac{4.5 \times 10^3}{50} = 90 \Omega \text{ cm}.$$

Step 2: Determine the conductivity Take the reciprocal of the resistivity. Equivalently, divide the cell constant by the resistance:

$$\kappa = \frac{G^*}{R} = \frac{50}{4.5 \times 10^3} = 1.11 \times 10^{-2} \text{ S cm}^{-1}.$$

Conductance alone is $1/R$; multiplication by the cell constant is essential to obtain conductivity, a property of the solution at the stated concentration and temperature.

Step 3: Convert conductivity into molar conductivity A litre contains 0.05 mole of the solute, so use the molarity directly with the centimetre-based formula:

$$\Lambda_m = \frac{1000\kappa}{c} = \frac{1000 \times (50/4500)}{0.05} = 222.2 \text{ S cm}^2 \text{ mol}^{-1}.$$

The unrounded value of conductivity is used here to avoid accumulating rounding error.

Step 4: Conclusion The resistivity is $90 \Omega \text{ cm}$, conductivity is $1.11 \times 10^{-2} \text{ S cm}^{-1}$, and molar conductivity is $222.2 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: First divide the cell constant by resistance to get κ ; then use $1000\kappa/c$ only when conductivity is in S cm^{-1} and concentration is in molarity.

24. Calculate elevation of the boiling point of the solution when 4 g of MgSO_4 (molar mass = 120 g/mol) was dissolved in 100 g of water, assuming MgSO_4 undergoes complete ionisation.

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

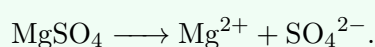
[3 marks]

Solution:

Concept:

- Boiling-point elevation is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b is the molal elevation constant and m is molality.
- Molality is the number of moles of solute per kilogram of solvent: $m = n/w$, where w is the solvent mass in kilograms. Use solvent mass, not the total solution mass.
- Under the stated complete-ionisation assumption, the van't Hoff factor equals the number of ions formed from one formula unit of the electrolyte.

Step 1: Find the van't Hoff factor Magnesium sulphate ionises as follows:



Each formula unit produces one magnesium ion and one sulphate ion. Hence there are two solute particles per original formula unit, so $i = 2$. The magnitude of the ionic charge does not change this particle count.

Step 2: Calculate the molality Divide the mass of MgSO_4 by its given molar mass to find the number of moles:

$$n = \frac{4 \text{ g}}{120 \text{ g mol}^{-1}} = \frac{1}{30} \text{ mol}.$$

The solvent is $100 \text{ g} = 0.100 \text{ kg}$ of water. Therefore,

$$m = \frac{1/30}{0.100} = \frac{1}{3} \text{ mol kg}^{-1}.$$

The solute mass is not added to the water mass because molality is defined using the solvent alone.

Step 3: Apply the boiling-point elevation relation Substitute $i = 2$, $K_b = 0.52 \text{ K kg mol}^{-1}$, and $m = 1/3 \text{ mol kg}^{-1}$:

$$\Delta T_b = 2 \times 0.52 \times \frac{1}{3} = 0.3467 \text{ K}.$$

The kilogram and mole units cancel, leaving a temperature difference in kelvin. The positive change indicates that the solution boils at a higher temperature than pure water at the same pressure.

Step 4: Conclusion The elevation in boiling point is $\Delta T_b \approx 0.347 \text{ K}$, or approximately 0.35 K to two significant figures.

Quick Tip to Solve: Count the two ions from MgSO_4 before substituting, and convert the 100 g of water to 0.100 kg; both factors are essential here.

25. Account for the following :

(a) The dipole moment of chlorobenzene is lower than that of cyclohexylchloride.

(b) Alkyl halides are immiscible in water.

(c) t-butyl bromide has lower boiling point than n-butyl bromide.

[3 marks]

Solution:

Concept:

- Bond dipole moment depends on both the magnitude of separated charge and the separation: $\mu = qr$. Carbon hybridisation and resonance affect the polarity and length of the carbon–halogen bond.
- Dissolution requires replacement of solute–solute and solvent–solvent attractions by sufficiently favourable solute–solvent interactions.
- Among isomeric haloalkanes of the same molar mass, increased branching reduces molecular surface contact and weakens London dispersion forces, lowering the boiling point.

Step 1: Explain the lower dipole moment of chlorobenzene In chlorobenzene, chlorine is bonded to an sp^2 -hybridised carbon, whereas in cyclohexyl chloride it is bonded to an sp^3 -hybridised carbon. The sp^2 carbon has greater s-character and is more electronegative, reducing the electronegativity difference between carbon and chlorine and hence the bond polarity. Also, donation of a chlorine lone pair into the benzene ring gives the carbon–chlorine bond partial double-bond character and shortens it. Resonance opposes the charge separation produced by chlorine's inductive withdrawal. These effects account for chlorobenzene having the smaller dipole moment.

Step 2: Explain the immiscibility of alkyl halides in water Water molecules are strongly associated through intermolecular hydrogen bonding. To dissolve an alkyl halide, some water–water hydrogen bonds must be broken and the alkyl halide molecules must be separated. Alkyl halides do not form sufficiently strong hydrogen bonds with water; the new attractions between alkyl halide and water molecules do not adequately compensate for the attractions disrupted. Their hydrocarbon groups also interact poorly with water. Thus alkyl halides are only sparingly soluble and are described as immiscible with water despite having polar carbon–halogen bonds.

Step 3: Compare the boiling points of the butyl bromides Both compounds have the same molecular formula, C_4H_9Br , and hence the same molar mass. However, tert-butyl bromide, $(CH_3)_3CBr$, is branched and more compact, while n-butyl bromide, $CH_3CH_2CH_2CH_2Br$, has an extended, unbranched chain. The compact molecules have less effective surface contact and weaker intermolecular dispersion forces. Less thermal energy is therefore required to separate tert-butyl bromide molecules into the vapour phase, so its boiling point is lower.

Step 4: Conclusion (a) Chlorobenzene has a less polar, shorter carbon–chlorine bond influenced by resonance. (b) Alkyl halides cannot adequately replace water's hydrogen-bonding interactions. (c) Branching weakens intermolecular attractions in tert-butyl bromide, giving it a lower boiling point than n-butyl bromide.

Quick Tip to Solve: Match each comparison to its cause: hybridisation and resonance for dipole moment, hydrogen bonding for water solubility, and branching with surface contact for isomeric boiling points.

26. What happens when : (any three)

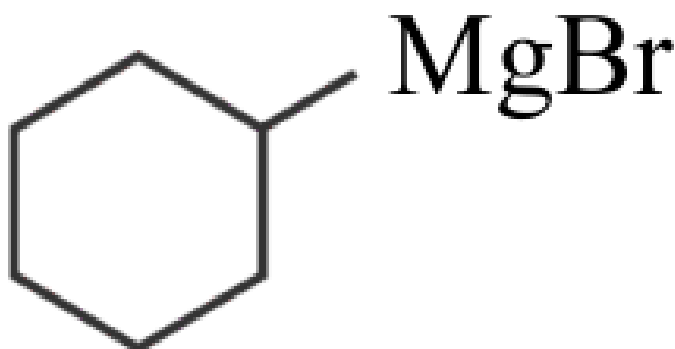
(a) The Grignard reagent shown below is treated with CH_3CHO followed by hydrolysis.

(b) Phenol is treated with conc. ($\text{HNO}_3 + \text{H}_2\text{SO}_4$).

(c) Anisole is treated with CH_3COCl in the presence of anhydrous AlCl_3 .

(d) Propan-2-ol is heated with Cu at 573 K.

[3 marks]

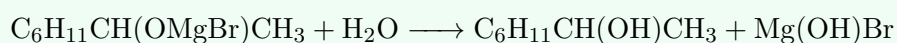


Solution:

Concept:

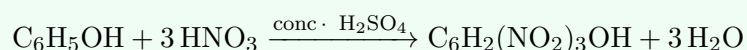
- A Grignard reagent RMgBr adds its R group to a carbonyl carbon; hydrolysis of the magnesium alkoxide gives an alcohol.
- The $-\text{OH}$ and $-\text{OCH}_3$ groups activate an aromatic ring and direct electrophilic substitution mainly to ortho and para positions.
- A secondary alcohol loses hydrogen over heated copper to form a ketone, retaining its carbon skeleton.

Step 1: (a) Add the cyclohexyl group to ethanal The printed ring represents cyclohexylmagnesium bromide, $\text{C}_6\text{H}_{11}\text{MgBr}$. In dry ether, its cyclohexyl group attacks the electrophilic carbonyl carbon of ethanal. Hydrolysis then protonates the oxygen:



The product is the secondary alcohol 1-cyclohexylethan-1-ol. Here C_6H_{11} denotes the saturated cyclohexyl ring, not a phenyl group.

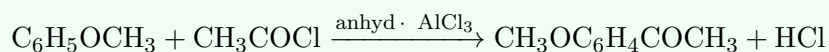
Step 2: (b) Nitrate phenol with the concentrated mixture The strongly activating hydroxyl group allows nitration at both ortho positions and the para position. Concentrated nitrating mixture therefore forms 2,4,6-trinitrophenol, commonly called picric acid:



The three nitro groups occupy positions 2, 4 and 6 relative to the hydroxyl group.

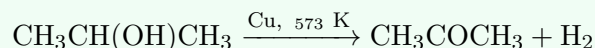
Quick Tip to Solve: Read the Grignard reagent's ring carefully: attach the intact cyclohexyl group to ethanal's carbonyl carbon, then change the carbonyl oxygen into OH on hydrolysis.

Step 3: (c) Acylate the anisole ring Acetyl chloride and anhydrous AlCl_3 carry out Friedel–Crafts acylation. The methoxy group directs the incoming acetyl group to ortho and para positions:



This gives 2-methoxyacetophenone and 4-methoxyacetophenone; the para isomer is the major product because it has less steric crowding. The acetyl group substitutes a ring hydrogen while the methoxy group is retained.

Step 4: (d) Dehydrogenate propan-2-ol Passing propan-2-ol over copper at 573 K removes one hydrogen from the hydroxyl group and one from the carbon bearing it. Propanone and hydrogen are formed:



Step 5: Conclusion (a) 1-Cyclohexylethan-1-ol. (b) Picric acid.

(c) The ortho and para isomers of methoxyacetophenone, with para major.

(d) Propanone and hydrogen. Any three reactions may be presented as required.

Quick Tip to Solve: Read the Grignard reagent's ring carefully: attach the intact cyclohexyl group to ethanal's carbonyl carbon, then change the carbonyl oxygen into OH on hydrolysis.

27. 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:

- Conjugation delocalises charge and stabilises an aromatic diazonium ion. Aromatic diazonium salts can be maintained in cold solution at 273–278 K.
- The amino group's lone pair normally activates the benzene ring, but coordination to a Lewis acid or protonation removes its availability for donation.
- The anilinium group, $-\text{NH}_3^+$, withdraws electron density and is meta directing in electrophilic aromatic substitution.

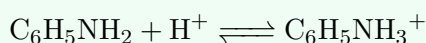
Step 1: (a) Relate diazonium stability to resonance In an aromatic diazonium salt, the diazonium group is directly bonded to an aromatic ring. Its conjugation with the ring permits resonance delocalisation of the positive charge, stabilising the diazonium ion. Aliphatic diazonium ions lack this aromatic resonance stabilisation and readily lose N_2 . Thus aromatic diazonium salts are comparatively stable in cold aqueous solution, especially at 273–278 K; this does not imply stability on strong heating.

Step 2: (b) Account for interaction with the Friedel–Crafts catalyst Friedel–Crafts alkylation and acylation normally use anhydrous AlCl_3 , a Lewis acid. Aniline is a Lewis base because nitrogen has a lone pair. Nitrogen coordinates to AlCl_3 , producing a salt-like Lewis acid–base complex. The lone pair

Quick Tip to Solve: Before applying the directing effect of an amino group, check the medium: strong acid gives $-\text{NH}_3^+$, while AlCl_3 binds its lone pair.

is then unavailable for donation into the benzene ring, and nitrogen acquires electron-withdrawing character. The ring is strongly deactivated and does not undergo the normal Friedel–Crafts reaction.

Step 3: (c) Identify the directing group in nitrating mixture Concentrated nitric and sulphuric acids provide a strongly acidic medium. Much of the aniline is therefore protonated:

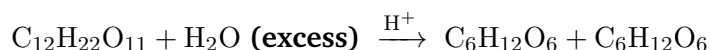


The anilinium ion has no free nitrogen lone pair to donate to the ring. Its positively charged $-\text{NH}_3^+$ group withdraws electrons and directs nitration to the meta position. Consequently, direct nitration gives a substantial amount of meta-nitroaniline after work-up, even though unprotonated aniline itself is ortho/para directing. Any remaining free aniline accounts for ortho and para substitution.

Step 4: Conclusion Aromatic diazonium salts are resonance stabilised; aniline's complex formation with AlCl_3 prevents Friedel–Crafts substitution; protonation to the meta-directing anilinium ion explains substantial meta nitration.

Quick Tip to Solve: Before applying the directing effect of an amino group, check the medium: strong acid gives $-\text{NH}_3^+$, while AlCl_3 binds its lone pair.

28. 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:

- The observed order follows the concentration dependence of the rate law. A reactant present in large excess has an effectively constant concentration during the reaction.
- For sucrose hydrolysis at fixed acid concentration, the water factor can be included in an observed rate constant: $k_{\text{obs}} = k[\text{H}_2\text{O}]$.
- Molecularity counts reacting species in an elementary step; the conventional molecularity assigned to the written hydrolysis reaction is two, one sucrose molecule and one water molecule.

Step 1: (a) Write the effective rate law Let S represent sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. For the usual treatment of its hydrolysis, write the concentration dependence as

$$r = k[S][\text{H}_2\text{O}].$$

Water is present in large excess, so the small amount consumed causes a negligible fractional change in its concentration. At constant temperature and acid concentration, combine the constant water

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

factor with k :

$$k_{\text{obs}} = k[\text{H}_2\text{O}], \quad r = -\frac{d[S]}{dt} = k_{\text{obs}}[S].$$

Thus the measured rate changes with sucrose concentration alone. The catalytic acid is held fixed in this comparison, and its effect is included in the rate constant.

Step 2: (b) Distinguish molecularity from observed order The written hydrolysis consumes one molecule of sucrose and one molecule of water, giving the expected molecularity of 2, or bimolecular character. However, the effective rate law contains only one variable concentration, raised to the first power. Its observed order is therefore 1. The excess water has not disappeared from the reaction; its concentration dependence has been absorbed into k_{obs} . Strictly, molecularity describes an elementary step, while this count is the textbook description of the overall hydrolysis shown.

Step 3: (c) Name the kinetic behaviour A reaction whose rate behaves as first order because another reactant is maintained effectively constant is called a pseudo-first-order reaction. Here the excess solvent water produces precisely this condition. The adjective “pseudo” distinguishes the experimentally observed first-order form from the participation of both sucrose and water in hydrolysis.

Step 4: Conclusion (a) $r = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}] = k_{\text{obs}}[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$; (b) molecularity 2, observed order 1; (c) a pseudo-first-order reaction.

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

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 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 genetic material whose sequence of nitrogenous bases carries hereditary information.
- Replication copies this information, while gene expression uses it to direct protein synthesis.

Step 1: Identify the hereditary function DNA stores genetic information and transmits it from parents to offspring. Before cell division, replication produces copies of DNA so that daughter cells receive the hereditary instructions.

Quick Tip to Solve: For two DNA functions, recall inheritance through replication and protein synthesis through RNA.

Step 2: Identify the role in protein synthesis DNA provides the coded instructions for synthesis of proteins. Its base sequence is transcribed into RNA, and the message is used to determine the amino-acid sequence of a protein.

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

Quick Tip to Solve: For two DNA functions, recall inheritance through replication and protein synthesis through RNA.

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

[1 mark]

Solution:

Concept:

- A nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group.
- DNA contains 2-deoxy-D-ribose as its sugar; complete hydrolysis separates the nucleotide into its constituent components.

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

Step 2: Include the phosphate component Complete hydrolysis cleaves the linkages connecting the base, sugar and phosphate. Thus, besides adenine and 2-deoxy-D-ribose, phosphoric acid, H_3PO_4 , is obtained. A nucleoside alone would not supply this phosphate component.

Step 3: Conclusion The products are adenine, 2-deoxy-D-ribose and phosphoric acid, H_3PO_4 .

Quick Tip to Solve: Expand a DNA nucleotide as base + deoxyribose + phosphate before naming its hydrolysis products.

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

[2 marks]

Solution:

Concept:

- Nucleic acids are biological macromolecules built from repeating nucleotide units; DNA and RNA are the two major types.
- A nucleoside contains a pentose sugar and a nitrogenous base. Adding a phosphate group gives a nucleotide.

Step 1: Define nucleic acids Nucleic acids are long-chain polymers of nucleotides, also called polynucleotides. Their nucleotide units are joined through phosphodiester linkages in the sugar-phosphate backbone. They store, transmit or help express genetic information. DNA is deoxyribonucleic acid and RNA is ribonucleic acid.

Quick Tip to Solve: Check for phosphate: sugar plus base is a nucleoside; phosphate makes it a nucleotide.

Step 2: Distinguish the two building blocks A nucleoside consists of a nitrogenous base linked to a pentose sugar through a glycosidic linkage; it contains no phosphate group. A nucleotide is the phosphate ester of a nucleoside and therefore contains a base, a pentose sugar and phosphate. For example, adenosine is a nucleoside, whereas adenosine monophosphate is a nucleotide.

$$\begin{aligned}\text{Nucleoside} &= \text{base} + \text{pentose sugar}, \\ \text{Nucleotide} &= \text{nucleoside} + \text{phosphate}.\end{aligned}$$

Step 3: Conclusion Nucleic acids are polynucleotides. A nucleotide has a phosphate group in addition to the sugar and base present in a nucleoside.

Quick Tip to Solve: Check for phosphate: sugar plus base is a nucleoside; phosphate makes it a nucleotide.

OR

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

[2 marks]

Solution:

Concept:

- DNA and RNA are nucleic acids consisting of nucleotide units, each containing a sugar, a phosphate group and a nitrogenous base.
- Their sugars differ at the second carbon atom: DNA has 2-deoxyribose, whereas RNA has ribose.

Step 1: State a common structural feature Both DNA and RNA are polynucleotides. In each, nucleotide units are connected by phosphodiester linkages to form a sugar-phosphate backbone, with nitrogenous bases attached to the sugars. Thus both have the same general type of repeating building unit even though the identities of some components differ.

Step 2: Compare the pentose sugars DNA contains 2-deoxy-D-ribose, while RNA contains D-ribose. The distinction is at the 2' carbon of the sugar: RNA has a hydroxyl group there, whereas DNA has hydrogen in its place. Hence the DNA sugar contains one fewer oxygen atom than the corresponding RNA sugar; this is the meaning of “deoxy” in its name.

Step 3: Conclusion Similarity: both DNA and RNA are polynucleotides with a sugar-phosphate backbone. Difference: DNA contains 2-deoxyribose, whereas RNA contains ribose.

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

30(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:

- Fractional distillation separates liquids because their equilibrium vapour generally differs in composition from the liquid.
- An azeotrope boils at a constant temperature with identical compositions of its liquid and vapour phases.

Step 1: Recognise the ethanol-water azeotrope Ethanol and water show positive deviation from Raoult's law and form a minimum-boiling azeotrope. Thus repeated distillation can approach an azeotropic composition instead of giving completely pure ethanol.

Step 2: Apply the equal-composition condition At the azeotropic composition, the vapour has the same ethanol-water ratio as the boiling liquid. Condensing and redistilling this vapour does not further enrich it in ethanol, so fractional distillation cannot remove the remaining water.

Step 3: Conclusion Pure ethanol cannot be obtained by fractional distillation of ethanol-water because the mixture forms a minimum-boiling azeotrope with identical liquid and vapour compositions.

Quick Tip to Solve: When a distillation stops improving purity, check whether equal liquid and vapour compositions form an azeotrope.

30(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: each component's partial vapour pressure is its mole fraction multiplied by its pure vapour pressure.
- Stronger attractions between unlike molecules lower their escaping tendency and produce negative deviation from Raoult's law.

Step 1: Identify the intermolecular attraction On mixing, the hydrogen of chloroform, CHCl_3 , forms a hydrogen bond with the carbonyl oxygen of acetone, CH_3COCH_3 . The three electron-withdrawing chlorine atoms make this hydrogen capable of hydrogen bonding to oxygen.

Step 2: Relate the attraction to vapour pressure The chloroform–acetone attractions are stronger than the average attractions in the separate pure liquids. Molecules are held more firmly in the liquid

Quick Tip to Solve: Locate the chloroform hydrogen and the acetone oxygen: their hydrogen bond predicts stronger attraction and negative deviation.

and escape less readily into the vapour. Consequently, the observed vapour pressure is below the value predicted for an ideal mixture.

Step 3: Conclusion Chloroform and acetone show negative deviation from ideal behaviour because hydrogen bonding between their molecules strengthens the intermolecular attractions.

Quick Tip to Solve: Locate the chloroform hydrogen and the acetone oxygen: their hydrogen bond predicts stronger attraction and negative deviation.

30(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, Raoult's law gives the relative lowering $(p^0 - p)/p^0 = x_2$, where x_2 is the mole fraction of solute.
- For a dilute solution, $x_2 \simeq n_2/n_1 = w_2M_1/(M_2w_1)$. Here w_1, w_2 are solvent and solute masses, and M_1, M_2 are their molar masses.

Step 1: Calculate the relative lowering The solute is non-volatile, so only benzene contributes to the vapour pressure. It is also a non-electrolyte, so no dissociation factor is required. The pressure lowering is

$$\Delta p = 1.25 - 1.237 = 0.013 \text{ atm.}$$

Therefore,

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

The small solute mole fraction permits the usual dilute-solution approximation.

Step 2: Substitute in the molar-mass relation Rearranging the dilute-solution relation and using masses in the same units gives

$$\begin{aligned} M_2 &\simeq \frac{w_2 M_1 p^0}{w_1 \Delta p} \\ &= \frac{1.2 \times 78 \times 1.25}{60 \times 0.013} \\ &= 150 \text{ g mol}^{-1}. \end{aligned}$$

For comparison, retaining the exact mole-fraction expression $x_2 = n_2/(n_1 + n_2)$ gives

$$M_2 = \frac{w_2 M_1 p}{w_1 (p^0 - p)} = \frac{1.2 \times 78 \times 1.237}{60 \times 0.013} = 148.44 \text{ g mol}^{-1}.$$

The small difference is due to neglecting the solute moles in the total moles in the dilute approximation.

Step 3: Conclusion The molar mass is approximately 150 g mol^{-1} by the standard dilute-solution method; the exact Raoult-law calculation gives $148.44 \text{ g mol}^{-1}$.

Quick Tip to Solve: Use the pressure difference 0.013 atm in the denominator; use pure-solvent pressure for the dilute formula and solution pressure for the exact molar-mass formula.

30(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:

- A non-volatile solute raises the boiling point of a solvent. For a dilute solution, the elevation is $\Delta T_b = K_b m$, where K_b is the molal elevation constant and m is the molality.
- Molality means moles of solute per kilogram of solvent: $m = (w_2/M_2)/(w_1/1000)$, when solvent mass w_1 and solute mass w_2 are in grams and solute molar mass M_2 is in g mol^{-1} .

Step 1: Find the elevation and solvent mass Subtract the boiling point of pure benzene from that of the solution:

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

The solvent is 90 g of benzene, so its mass is 0.090 kg. Use the solvent mass, rather than the combined mass of benzene and solute, in the molality.

Step 2: Calculate the amount and molar mass of solute First use the measured temperature elevation to determine the molality:

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

Thus the amount dissolved in 0.090 kg of benzene is

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

Dividing the solute mass by this amount gives

$$M_2 = \frac{w_2}{n_2} = \frac{1.80}{0.03130} = 57.5 \text{ g mol}^{-1}.$$

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

Quick Tip to Solve: Subtract the two boiling points first, then use 0.090 kg of benzene; molality always uses kilograms of solvent.

Section E (15 marks)

31. 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:

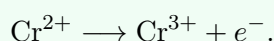
- The stability of a metal ion in water depends on both its electronic configuration and hydration enthalpy; an especially favourable hydration enthalpy can stabilise a higher charge.
- A reducing agent loses electrons. The ease of oxidation to the next stable oxidation state determines its reducing strength.
- Poor shielding by f electrons causes a progressive increase in effective nuclear charge and contraction. Variable oxidation states and adsorption help transition metals catalyse reactions.

Step 1: (a) Explain the instability of aqueous copper(I) In aqueous solution, Cu^+ undergoes disproportionation: one ion is oxidised and the other is reduced.



The hydration enthalpy of Cu^{2+} is much more negative than that of Cu^+ . This stabilisation compensates for the energy needed to remove a second electron, so Cu^+ is unstable in water even though it has a $3d^{10}$ configuration.

Step 2: (b) Compare chromium(II) and iron(II) Cr^{2+} is the stronger reducing agent. It is readily oxidised from $3d^4$ to the more stable Cr^{3+} , with a $3d^3$ configuration:



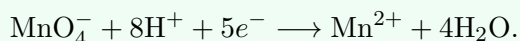
In an octahedral environment the $3d^3$ configuration has the stable t_{2g}^3 arrangement. Although Fe^{2+} can be oxidised to half-filled $3d^5$ Fe^{3+} , it is much less readily oxidised than Cr^{2+} ; hence it is the weaker reducing agent.

Step 3: (c) Explain the greater actinoid contraction The 5f electrons shield the increasing nuclear charge less effectively than the 4f electrons do. Consequently, the effective attraction of the nucleus for the outer electrons increases more strongly across the actinoids, producing a greater contraction from element to element than across the lanthanoids.

Step 4: (d) Write the acidic permanganate reduction half-reaction In acidic medium, manganese in

Quick Tip to Solve: For each reason, first write the relevant d-electron count; for aqueous copper(I), also consider hydration, and balance acidic permanganate using water, hydrogen ions and electrons.

permanganate is reduced from oxidation state +7 to +2 by accepting five electrons:



Acceptance of electrons from another species explains the oxidising action of KMnO_4 . Oxygen, hydrogen and total charge are balanced in this ionic equation.

Step 5: (e) Identify the first-series metal Copper, Cu , exhibits the +1 oxidation state most frequently among first-transition-series metals. Loss of its 4s electron gives Cu^+ the completely filled $3d^{10}$ configuration. Copper(I) compounds can exist even though the free aqueous ion disproportionates as described in part (a).

Step 6: (f) Account for catalytic activity Transition metals show variable oxidation states, allowing them to form intermediates and undergo reversible changes in oxidation state during a reaction. These processes provide a pathway with lower activation energy. Their surfaces can also adsorb reactant molecules, bringing them together and weakening their bonds. For example, iron catalyses ammonia formation and V_2O_5 catalyses the oxidation of SO_2 to SO_3 .

Step 7: (g) Apply the definition of a transition element A transition element has a partly filled d subshell in its atom or in at least one of its ions. The scandium atom has configuration $[\text{Ar}] 3d^1 4s^2$, so it satisfies the definition. Its usual ion, Sc^{3+} , is $[\text{Ar}] 3d^0$; with no d electron available for a d–d transition, this ion is colourless.

Step 8: Conclusion (a) Aqueous Cu^+ disproportionates; (b) Cr^{2+} is the stronger reducing agent; (c) weaker shielding by 5f electrons gives greater actinoid contraction; (d) acidic permanganate accepts five electrons to form Mn^{2+} ; (e) the metal is copper; (f) variable oxidation states and adsorption explain catalysis; (g) atomic scandium has an incomplete 3d subshell. Any five of these responses may be attempted.

Quick Tip to Solve: For each reason, first write the relevant d-electron count; for aqueous copper(I), also consider hydration, and balance acidic permanganate using water, hydrogen ions and electrons.

32(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:

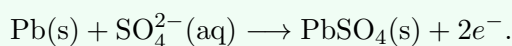
Concept:

- A secondary battery is rechargeable: an external electrical source can reverse the chemical reaction that occurs during discharge.
- When a battery supplies current, oxidation occurs at its anode and reduction at its cathode. The lead storage battery uses lead, lead dioxide and aqueous sulphuric acid.

Step 1: Identify the battery type and discharge electrodes The lead storage battery is a secondary (rechargeable) battery. When current is drawn, it operates as a galvanic cell: the lead plate is the negative anode, and the plate carrying lead dioxide, PbO_2 , is the positive cathode. Sulphuric acid provides the electrolyte.

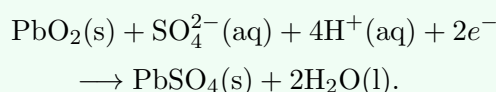
Quick Tip to Solve: For discharge, remember that both plates become lead sulphate; balance the cathode oxygen with two water molecules and then add four hydrogen ions and two electrons.

Step 2: Write the oxidation reaction at the anode Lead metal is oxidised from oxidation state zero to +2, releasing two electrons. In the sulphate-containing electrolyte it forms insoluble lead(II) sulphate:



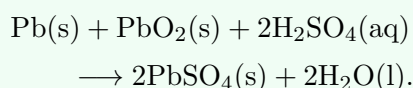
These electrons flow through the external circuit towards the cathode while the battery supplies electrical energy.

Step 3: Write the reduction reaction at the cathode Lead in PbO_2 is reduced from +4 to +2. Hydrogen ions convert its oxygen into water, and sulphate ions form lead(II) sulphate:



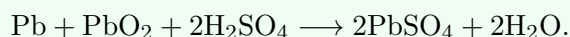
Thus both electrodes acquire a coating of PbSO_4 during discharge.

Step 4: Add the half-reactions The two electrons released at the anode equal the two consumed at the cathode and cancel. Combining the hydrogen and sulphate ions as sulphuric acid gives



Sulphuric acid is consumed and water is produced, so the acid concentration decreases as current is drawn. On charging, an external source reverses this overall reaction.

Step 5: Conclusion The lead storage battery is a secondary, rechargeable battery. During discharge, lead is oxidised at the anode and lead dioxide is reduced at the cathode, both forming PbSO_4 . Its overall reaction is



Quick Tip to Solve: For discharge, remember that both plates become lead sulphate; balance the cathode oxygen with two water molecules and then add four hydrogen ions and two electrons.

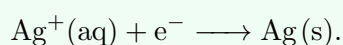
32(a)(ii). Calculate the time to deposit 1.5 g of silver at cathode when a current of 1.5 A was passed through the solution of AgNO_3 . [Molar mass of $\text{Ag} = 108 \text{ g mol}^{-1}$, $1 \text{ F} = 96500 \text{ C mol}^{-1}$] [2 marks]

Solution:

Concept:

- Faraday's law of electrolysis gives $m = MQ/(nF)$, where m is the deposited mass, M is molar mass, n is the number of electrons required per metal ion and F is the Faraday constant.
- For constant current, charge is $Q = It$, with I in amperes and t in seconds. Hence the deposition time is $t = mnF/(MI)$.

Step 1: Determine the electron requirement Silver ions are reduced at the cathode according to



Quick Tip to Solve: For silver deposition use $n = 1$; here the equal numerical values of mass and current cancel in $t = mnF/(MI)$.

Thus $n = 1$: depositing one mole of silver requires one mole of electrons, or 96500 C. The amount of silver to deposit is

$$\frac{m}{M} = \frac{1.5}{108} \text{ mol.}$$

Its charge requirement therefore follows directly from the one-to-one ratio of silver atoms to electrons.

Step 2: Calculate the charge and deposition time Using $M = 108 \text{ g mol}^{-1}$ and $F = 96500 \text{ C mol}^{-1}$,

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

Since the current supplies 1.5 C each second,

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

Dividing by 60 converts this time to 14.89 min. The use of grams is consistent because both the deposited mass and the molar mass use grams.

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

Quick Tip to Solve: For silver deposition use $n = 1$; here the equal numerical values of mass and current cancel in $t = mnF/(MI)$.

OR

32(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:

- At infinite dilution, the ions of an electrolyte migrate independently. Each ion contributes a definite amount to the limiting molar conductivity, irrespective of the nature of the other ion present.
- Kohlrausch's law is $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$, where λ_+° and λ_-° are limiting ionic molar conductivities and ν_+ , ν_- are their stoichiometric coefficients.

Step 1: Express each limiting conductivity as an ionic sum Every electrolyte here gives one cation and one anion per formula unit, so all ionic coefficients equal one. At the same temperature, Kohlrausch's law gives

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

For NH_4OH , the required sum is the contribution of NH_4^+ plus that of OH^- . Infinite dilution is essential: the law refers to limiting conductivities, where interionic effects are negligible.

Step 2: Cancel the unwanted ions and substitute Add the first two electrolyte conductivities and

Quick Tip to Solve: Combine a salt supplying NH_4^+ with a base supplying OH^- , then subtract the salt containing the two unwanted ions.

subtract the third. This cancels one contribution each from Na^+ and Cl^- , leaving exactly the required ionic sum:

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

Although NH_4OH is a weak electrolyte, its limiting value can therefore be obtained from the given strong-electrolyte data. No finite-concentration conductivity is inferred without additional information about dissociation.

Step 3: Conclusion By Kohlrausch's law, the molar conductivity of NH_4OH at infinite dilution and 298 K is $105 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: Combine a salt supplying NH_4^+ with a base supplying OH^- , then subtract the salt containing the two unwanted ions.

32(b)(ii). Calculate ΔG° of the following cell at 25°C :



Given: $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}$, $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.34 \text{ V}$, $1 \text{ F} = 96500 \text{ C mol}^{-1}$.

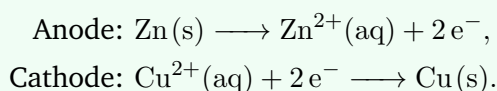
[2 marks]

Solution:

Concept:

- Using tabulated reduction potentials, the standard cell potential is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$.
- The standard Gibbs energy change is $\Delta G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons exchanged per balanced cell reaction and $F = 96500 \text{ C mol}^{-1}$.

Step 1: Identify the electrodes and electron transfer In the given cell, zinc at the left electrode is oxidised and copper ions at the right electrode are reduced:



Adding these gives $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$. Two electrons are transferred, so $n = 2$, not four; the same electrons produced at the anode are consumed at the cathode.

Step 2: Calculate the standard cell potential and Gibbs energy The supplied values are reduction potentials. Subtract the zinc reduction potential from the copper reduction potential:

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

Quick Tip to Solve: Use $n = 2$ for this zinc-copper cell, and subtract the negative zinc reduction potential before applying $-nFE^\circ$.

Therefore, at the stated temperature,

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

Here $C \times V = J$, giving energy per mole of the balanced cell reaction. The negative sign agrees with the positive cell potential and indicates a spontaneous forward reaction under standard conditions.

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

Quick Tip to Solve: Use $n = 2$ for this zinc-copper cell, and subtract the negative zinc reduction potential before applying $-nFE^\circ$.

33(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.

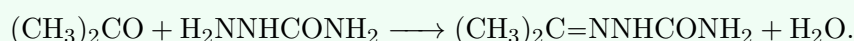
[3 marks]

Solution:

Concept:

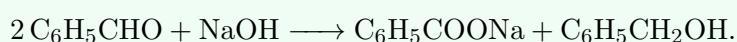
- A carbonyl compound condenses with semicarbazide, $\text{H}_2\text{NNHCONH}_2$, through its terminal amino group to form a semicarbazone with elimination of water.
- An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction in concentrated alkali: one molecule is oxidised to carboxylate and another is reduced to alcohol.
- Clemmensen reduction uses zinc amalgam, Zn-Hg , and concentrated HCl to replace a carbonyl oxygen by two hydrogen atoms.

Step 1: Form the semicarbazone of acetone The terminal $-\text{NH}_2$ nitrogen of semicarbazide attacks the carbonyl carbon. Elimination of water replaces the C=O bond by C=N , producing acetone semicarbazone:



The other amino group is attached to the carbonyl of semicarbazide; resonance reduces its nucleophilicity, so it does not form the new double bond.

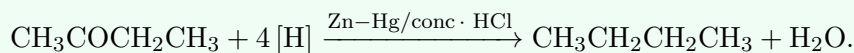
Step 2: Apply the Cannizzaro reaction to benzaldehyde Benzaldehyde has no alpha hydrogen and therefore undergoes disproportionation with concentrated NaOH, rather than aldol condensation. Two molecules give one molecule each of sodium benzoate and benzyl alcohol:



The acid product remains as its sodium salt because the medium is strongly alkaline; benzoic acid would require subsequent acidification.

Quick Tip to Solve: Match the reagent first: semicarbazide gives a carbonyl derivative, concentrated alkali disproportionates benzaldehyde, and Zn-Hg/HCl replaces C=O by CH_2 .

Step 3: Reduce butan-2-one by the Clemmensen method Zinc amalgam and concentrated hydrochloric acid reduce the ketonic carbonyl group to a methylene group without changing the four-carbon skeleton:



Here [H] represents reducing equivalents. The product is butane, not butan-2-ol, because Clemmensen reduction removes the carbonyl oxygen completely.

Step 4: Conclusion (I) Acetone forms acetone semicarbazone. (II) Benzaldehyde forms sodium benzoate and benzyl alcohol. (III) Butan-2-one forms butane.

Quick Tip to Solve: Match the reagent first: semicarbazide gives a carbonyl derivative, concentrated alkali disproportionates benzaldehyde, and Zn–Hg/HCl replaces C=O by CH₂.

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

(I) CH₃CH₂CH₂COOH, BrCH₂CH₂CH₂COOH, CH₃CHBrCH₂COOH, CH₃CH₂CHBrCOOH

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

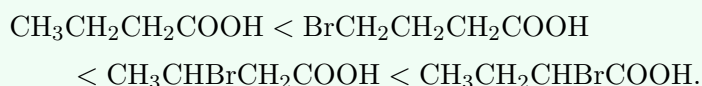
[2 marks]

Solution:

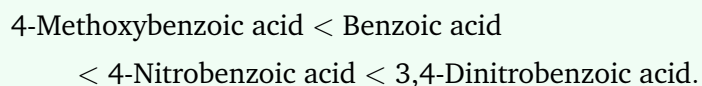
Concept:

- A carboxylic acid is stronger when its conjugate base, the carboxylate ion RCOO[–], is more stable. Electron-withdrawing groups stabilise this anion and increase acidity.
- The negative inductive effect of bromine decreases rapidly with its distance from –COOH. In aromatic acids, both inductive and resonance effects of ring substituents influence acidity.

Step 1: Compare bromine positions in the aliphatic acids Unsubstituted butanoic acid has no electron-withdrawing bromine. In the three substituted acids, bromine is at the gamma, beta and alpha positions, respectively, measured from –COOH. Moving it closer strengthens its negative inductive effect and stabilises the carboxylate ion more. Thus the increasing order is



Step 2: Compare the aromatic substituents At the para position, the methoxy group donates electrons by resonance; this effect outweighs its electron-withdrawing inductive effect and lowers acidity relative to benzoic acid. A nitro group withdraws electrons by both induction and resonance, increasing acidity. Adding another nitro group at the meta position adds an electron-withdrawing inductive effect, so the dinitro acid is still stronger.



Step 3: Conclusion In (I), acidity increases from butanoic acid through gamma-bromo and beta-bromo to alpha-bromobutanoic acid. In (II), it increases from 4-methoxybenzoic acid through benzoic acid

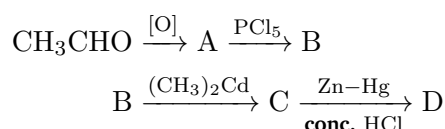
Quick Tip to Solve: For the bromo acids count distance from –COOH; for the aromatic acids remember that para methoxy donates by resonance, whereas nitro withdraws electrons.

and 4-nitrobenzoic acid to 3,4-dinitrobenzoic acid.

Quick Tip to Solve: For the bromo acids count distance from $-\text{COOH}$; for the aromatic acids remember that para methoxy donates by resonance, whereas nitro withdraws electrons.

OR

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



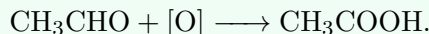
[2 marks]

Solution:

Concept:

- Oxidation converts an aldehyde RCHO into the corresponding carboxylic acid RCOOH ; PCl_5 then replaces the acid hydroxyl group by chlorine to give an acyl chloride.
- Dialkylcadmium reacts with an acyl chloride to form a ketone. Clemmensen reduction with Zn-Hg and concentrated HCl converts its carbonyl group to a methylene group.

Step 1: Identify A by oxidising ethanal The aldehyde group is oxidised without changing the carbon skeleton:



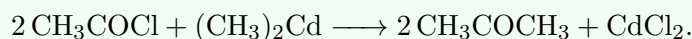
Thus A is ethanoic acid, CH_3COOH .

Step 2: Convert the acid to B Phosphorus pentachloride replaces the hydroxyl group of the carboxylic acid by chlorine:



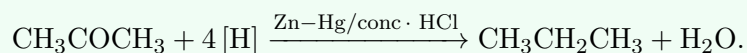
Therefore B is ethanoyl chloride, CH_3COCl .

Step 3: Use dimethylcadmium to obtain C A methyl group replaces the chlorine of ethanoyl chloride, producing a ketone. Dialkylcadmium stops at the ketone stage:



Hence C is propanone, CH_3COCH_3 . Its extra carbon comes from a methyl group of the reagent.

Step 4: Reduce C to D The final arrow converts C into D. Zinc amalgam and concentrated hydrochloric acid remove the carbonyl oxygen and replace it by two hydrogen atoms:



Thus D is propane, $\text{CH}_3\text{CH}_2\text{CH}_3$; no carbon atoms are lost in this step.

Step 5: Conclusion A = ethanoic acid (CH_3COOH); B = ethanoyl chloride (CH_3COCl); C =

Quick Tip to Solve: Track the functional group as aldehyde, acid, acyl chloride, ketone, alkane; the methylcadmium step alone increases the carbon count from two to three.

propanone (CH_3COCH_3); D = propane ($\text{CH}_3\text{CH}_2\text{CH}_3$).

Quick Tip to Solve: Track the functional group as aldehyde, acid, acyl chloride, ketone, alkane; the methylcadmium step alone increases the carbon count from two to three.

33(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

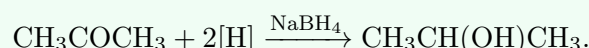
[3 marks]

Solution:

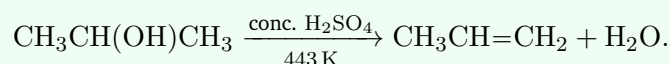
Concept:

- Reduction of a ketone gives a secondary alcohol; dehydration of the alcohol gives an alkene without changing the carbon skeleton.
- An acid chloride undergoes Rosenmund reduction with hydrogen over poisoned palladium supported on barium sulphate to form an aldehyde.
- An aldehyde containing alpha-hydrogen undergoes aldol addition in dilute alkali. Heating the aldol removes water to give an alpha,beta-unsaturated aldehyde.

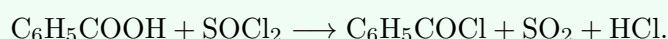
Step 1: (I) Convert propanone into propene Reduce propanone with sodium borohydride, followed by aqueous work-up, to give propan-2-ol:



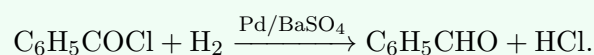
Heat with concentrated sulphuric acid to eliminate water and form propene:



Step 2: (II) Convert benzoic acid into benzaldehyde Treat benzoic acid with thionyl chloride to prepare benzoyl chloride:



Now carry out Rosenmund reduction using hydrogen and poisoned palladium on barium sulphate:



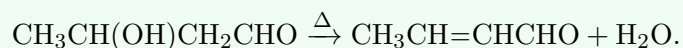
The poisoned catalyst limits further reduction of the aldehyde.

Step 3: (III) Convert ethanal into but-2-enal Ethanal has alpha-hydrogen. Dilute aqueous sodium hydroxide joins two molecules to give 3-hydroxybutanal:



Quick Tip to Solve: Match the carbon count first: retain three carbons by reduction/dehydration, retain the benzoyl skeleton by Rosenmund reduction, and join two ethanal molecules by aldol condensation.

Heating dehydrates this aldol to the conjugated aldehyde, 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: Match the carbon count first: retain three carbons by reduction/dehydration, retain the benzoyl skeleton by Rosenmund reduction, and join two ethanal molecules by aldol condensation.