

CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-S-3 - 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 Ni^{2+}/Ni couple is -0.25 V and for Ag^+/Ag couple is 0.80 V . These two couples are connected to make an electrochemical cell. The redox reaction is spontaneous. The cell potential will be : [1 mark]

- (A) $+1.05\text{ V}$
- (B) -1.05 V
- (C) $+0.55\text{ V}$
- (D) -0.55 V

Correct Answer: (A) $+1.05\text{ V}$

Solution:

Concept:

- Standard cell potential is $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$, where both tabulated values are reduction potentials.
- A spontaneous galvanic reaction has $E_{\text{cell}}^{\circ} > 0$, since $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$.

Step 1: Identify the electrodes The silver couple has the higher reduction potential, so silver ions are reduced at the cathode: $2\text{Ag}^+ + 2e^- \rightarrow 2\text{Ag}$. Nickel is oxidised at the anode: $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$. Thus the net reaction is $\text{Ni} + 2\text{Ag}^+ \rightarrow \text{Ni}^{2+} + 2\text{Ag}$.

Step 2: Calculate the potential

$$E_{\text{cell}}^{\circ} = 0.80 - (-0.25) = +1.05\text{ V}.$$

The negative alternatives correspond to a nonspontaneous direction. The value $+0.55\text{ V}$ results from adding the signed reduction potentials instead of subtracting them. Electrode potentials are not multiplied when half-reactions are balanced.

Step 3: Conclusion The cell potential is $+1.05\text{ V}$. Hence, the correct option is (A).

Quick Tip to Solve: Subtract the lower reduction potential from the higher one; retain the negative sign of nickel.

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

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

[1 mark]

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

Correct Answer: (D) Ni^{2+}

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)} \text{ BM}$, where n is the number of unpaired electrons.
- For transition-metal cations, remove the $4s$ electrons before the $3d$ electrons.

Step 1: Find the ionic configurations The configurations are $\text{Fe}^{2+} : 3d^6$, $\text{Co}^{2+} : 3d^7$, $\text{Cr}^{3+} : 3d^3$, and $\text{Ni}^{2+} : 3d^8$. In the usual spin-only comparison of these ions, Hund's rule gives respectively four, three, three and two unpaired electrons.

Step 2: Compare the magnetic moments The corresponding moments are $\sqrt{24} \approx 4.90 \text{ BM}$, $\sqrt{15} \approx 3.87 \text{ BM}$, $\sqrt{15} \approx 3.87 \text{ BM}$, and $\sqrt{8} \approx 2.83 \text{ BM}$. The function $n(n+2)$ increases with nonnegative n ; hence the ion with two unpaired electrons has the smallest moment. Neither cobalt nor chromium has fewer unpaired electrons than nickel.

Step 3: Conclusion Ni^{2+} has the lowest magnetic moment. Hence, the correct option is (D).

Quick Tip to Solve: For this comparison, count unpaired d electrons first; calculating every square root is optional.

3. The geometry of paramagnetic nickel complex $[\text{NiCl}_4]^{2-}$ is :

[1 mark]

- (A) tetrahedral
- (B) octahedral
- (C) square planar
- (D) distorted octahedral

Correct Answer: (A) tetrahedral

Solution:

Concept:

- The oxidation state of nickel in $[\text{NiCl}_4]^{2-}$ is +2; Ni^{2+} has a $3d^8$ configuration.
- Chloride is a weak-field ligand; a tetrahedral nickel(II) complex retains unpaired electrons.

Step 1: Use the ligand and magnetic behaviour From $x + 4(-1) = -2$, nickel has oxidation state $x = +2$. With weak-field chloride ligands, the four-coordinate complex has tetrahedral geometry and is paramagnetic. In the valence-bond description it uses sp^3 hybrid orbitals; two d electrons remain unpaired.

Quick Tip to Solve: For four-coordinate nickel(II), use both ligand strength and the stated magnetic behaviour.

Step 2: Eliminate the other geometries Octahedral and distorted octahedral geometries require six donor positions, whereas the formula contains four monodentate chloride ligands. The square-planar arrangement commonly obtained for strong-field d^8 nickel(II) complexes involves pairing and is diamagnetic. It is therefore incompatible with the stated paramagnetism of this chloride complex.

Step 3: Conclusion The geometry is tetrahedral. Hence, the correct option is (A).

Quick Tip to Solve: For four-coordinate nickel(II), use both ligand strength and the stated magnetic behaviour.

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

[1 mark]

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

Correct Answer: (A) HCHO

Solution:

Concept:

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

Step 1: Examine formaldehyde Formaldehyde, HCHO, has only the carbonyl carbon and no adjacent carbon atom. Thus it has no alpha hydrogen and cannot form the required enolate for self-aldol condensation. The hydrogens directly bonded to its carbonyl carbon are not alpha hydrogens.

Step 2: Check the other options Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, has two alpha hydrogens on its adjacent methylene group. Acetone, CH_3COCH_3 , has alpha hydrogens on both methyl groups. Ethanal, CH_3CHO , has three alpha hydrogens. Each of these can therefore undergo aldol condensation under suitable basic conditions.

Step 3: Conclusion HCHO does not undergo aldol condensation. Hence, the correct option is (A).

Quick Tip to Solve: Locate the carbon next to $\text{C}=\text{O}$; hydrogens attached directly to the carbonyl carbon do not count.

5. The IUPAC name of the complex $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ is :

[1 mark]

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

Correct Answer: (A) Pentaamminenitrito-O-cobalt(III) chloride

Solution:

Concept:

- NH_3 is a neutral ligand named ammine; ONO^- is an O-bonded nitrito ligand.
- The oxidation number of the central metal is stated in Roman numerals in the complex name.

Step 1: Find the cobalt oxidation state The two chloride counterions show that the complex ion has charge +2. If cobalt has oxidation state x , then $x + 5(0) - 1 = +2$, giving $x = +3$. The metal is therefore cobalt(III), ruling out the cobalt(II) option.

Step 2: Identify the donor atom and name The written ligand ONO is attached through oxygen, so it is designated nitrito-O. Five ammonia ligands give pentaammine. Combining the ligand names, metal oxidation state and counterion gives pentaamminenitrito-O-cobalt(III) chloride. The nitrito-N and nitro alternatives describe nitrogen coordination, inconsistent with the printed ONO linkage.

Step 3: Conclusion The name is Pentaamminenitrito-O-cobalt(III) chloride. Hence, the correct option is (A).

Quick Tip to Solve: Read ONO as oxygen-bonded nitrito, then use the two outside chlorides to find cobalt(III).

6. 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 multidentate ligand binds a metal through more than one donor atom and can form chelate rings.
- The chelate effect enhances stability compared with analogous complexes containing only monodentate ligands.

Step 1: Recognise the chelating ligand Ethylenediamine, abbreviated en, is a neutral bidentate ligand with two nitrogen donor atoms. Each en molecule can attach to the same platinum centre through both nitrogen atoms, forming a five-membered chelate ring. Thus $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ contains two such rings.

Quick Tip to Solve: Look for en: its two donor nitrogen atoms form chelate rings, the key stability clue here.

Step 2: Compare the listed ligand types The ammonia and chloride ligands in options (A) and (B) are monodentate and do not form chelate rings. Cyanide in $K_4[Fe(CN)_6]$ is a strong-field ligand, but each cyanide binds the iron through one donor atom and does not chelate that centre. In this standard CBSE comparison based on the chelate effect, the en-containing platinum complex is selected as the most stable.

Step 3: Conclusion The most stable complex in the given comparison is $[Pt(en)_2Cl_2]^{2+}$. Hence, the correct option is (C).

Quick Tip to Solve: Look for en: its two donor nitrogen atoms form chelate rings, the key stability clue here.

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

(A) $NH_3 < CH_3NH_2 < (CH_3)_3N < (CH_3)_2NH$

(B) $NH_3 < (CH_3)_2NH < (CH_3)_3N < CH_3NH_2$

(C) $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2 < NH_3$

(D) $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

Correct Answer: (D) $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$

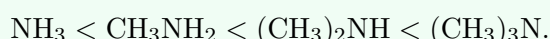
Solution:

Concept:

- Basicity measures the tendency of the nitrogen lone pair to accept a proton.
- In the gaseous phase, electron donation by alkyl groups increases nitrogen basicity through the positive inductive effect.

Step 1: Count the electron-donating groups Ammonia has no methyl group, methylamine has one, dimethylamine has two and trimethylamine has three. Each methyl group donates electron density towards nitrogen and stabilises the corresponding protonated amine.

Step 2: Apply the gaseous-phase order Without aqueous solvation effects, increasing alkyl substitution gives increasing basic strength:



Option (A) incorrectly places the tertiary amine below the secondary amine; (B) makes methylamine strongest; (C) reverses the electron-donation trend.

Step 3: Conclusion The correct increasing order is $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$. Hence, the correct option is (D).

Quick Tip to Solve: Check the phase first: for these methylamines in gas, count methyl groups to rank basicity.

8. 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 that can undergo azo coupling.
- Primary aliphatic diazonium salts decompose readily, releasing nitrogen.

Step 1: Compare reactions with nitrous acid Aniline reacts with nitrous acid, generated from sodium nitrite and hydrochloric acid at 273–278 K, to form benzenediazonium chloride. Ethanamine instead forms an unstable aliphatic diazonium species, which decomposes to ethanol with evolution of nitrogen.

Step 2: Use the characteristic dye formation Benzenediazonium chloride couples with phenol in alkaline medium to produce a coloured azo dye; ethanamine does not give this characteristic dye. The haloform and Tollens' tests do not distinguish this pair. Both are primary amines and react with Hinsberg reagent to give sulphonamides soluble in alkali, so the standard Hinsberg classification does not separate them.

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

Quick Tip to Solve: For an aliphatic versus aromatic primary amine, use cold diazotisation followed by azo coupling.

9. 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:

- The IUPAC parent is the longest continuous carbon chain; halogens are named as prefixes.
- Number the parent chain to give the substituents the lowest set of locants.

Step 1: Identify and number the parent In $(\text{CH}_3)_3\text{C} - \text{CH}_2\text{Br}$, the longest chain contains three carbon atoms: $\text{BrCH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_3$. Thus the parent is propane, with two methyl substituents on carbon 2. Numbering from the brominated end gives the locants 1, 2, 2, instead of 2, 2, 3.

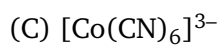
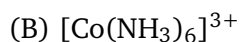
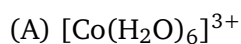
Quick Tip to Solve: Trace the longest continuous chain through the central carbon before numbering the brominated end.

Step 2: Assemble the name and reject alternatives Bromo precedes methyl alphabetically; the multiplicative prefix di does not affect alphabetisation. The name therefore has bromo at carbon 1 and dimethyl at carbon 2. Option (A) locates bromine on the wrong carbon. Options (B) and (C) incorrectly choose ethane despite the available three-carbon parent chain.

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

Quick Tip to Solve: Trace the longest continuous chain through the central carbon before numbering the brominated end.

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



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

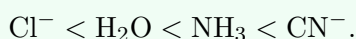
Solution:

Concept:

- In an octahedral complex, excitation from t_{2g} to e_g requires crystal-field splitting energy Δ_o .
- For a fixed metal ion and oxidation state, a stronger-field ligand produces a larger Δ_o .

Step 1: Compare the same metal ion Each complex contains cobalt in the +3 oxidation state: water and ammonia are neutral, whereas each cyanide or chloride ligand has charge -1 . All four complexes have six ligands, so the decisive comparison here is the ligand field strength.

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



Cyanide produces the largest separation between the two sets of cobalt d orbitals and hence needs the greatest excitation energy. Water, ammonia and chloride are all weaker-field ligands than cyanide; none of their listed complexes has the maximum splitting.

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

Quick Tip to Solve: When metal, oxidation state and geometry match, rank excitation energy directly by ligand field strength.

11. 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:

- For a single-reactant rate law, $r = k[A]^n$, where n is the reaction order and k is constant at a fixed temperature.
- Taking a ratio of two rates eliminates the rate constant.

Step 1: Form the rate ratio Let the initial concentration be $[A]_1 = a$ and initial rate be $r_1 = ka^n$. The new concentration is $[A]_2 = 4a$ and the observed rate is $r_2 = 2r_1$. Therefore

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

Step 2: Determine and check the exponent Since $4 = 2^2$, the equation becomes $2^{2n} = 2^1$, giving $2n = 1$ and $n = \frac{1}{2}$. An order of 2 would increase the rate sixteenfold, an order of 1 would increase it fourfold, and zero order would leave it unchanged. Only half-order gives the observed doubling.

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

Quick Tip to Solve: Express the concentration and rate factors as powers of the same base to read off the order.

12. Williamson's synthesis of preparing dimethyl ether is a/an : [1 mark]

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

Correct Answer: (D) S_N2 reaction

Solution:

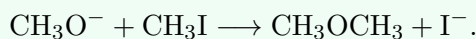
Concept:

- Williamson ether synthesis uses an alkoxide nucleophile and an alkyl halide.
- An S_N2 reaction is a concerted nucleophilic substitution with simultaneous bond making and bond breaking.

Step 1: Write the ether-forming reaction Methoxide ion attacks a methyl halide, for example methyl

Quick Tip to Solve: For Williamson synthesis, identify alkoxide attack on an unhindered alkyl halide as a single-step substitution.

iodide:



The oxygen of methoxide supplies the electron pair, and iodide acts as the leaving group.

Step 2: Identify the substitution mechanism The attack occurs at the methyl carbon in a single step, from the side opposite the leaving group. The rate depends on both methoxide and methyl halide concentrations, as expected for $\text{S}_{\text{N}}2$. An $\text{S}_{\text{N}}1$ mechanism would require a highly unstable methyl carbocation. Electrophilic substitution and electrophilic addition are excluded because the reacting species is a nucleophile and it replaces a leaving group rather than adding across a multiple bond.

Step 3: Conclusion Williamson synthesis of dimethyl ether is an $\text{S}_{\text{N}}2$ reaction. Hence, the correct option is (D).

Quick Tip to Solve: For Williamson synthesis, identify alkoxide attack on an unhindered alkyl halide as a single-step substitution.

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

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

- (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 rate constant, A frequency factor, E_a activation energy, R gas constant and T absolute temperature.
- An effective collision requires sufficient energy to cross the activation-energy barrier.

Step 1: Judge the assertion For positive activation energy, increasing T makes the exponent $-E_a/(RT)$ less negative. The exponential factor and hence k increase. Assertion A is true.

Step 2: Judge the reason At higher temperature a larger fraction of molecules has energies greater than the activation energy. Thus more collisions have the necessary energy for reaction. Reason R is true.

Step 3: Check the explanation This increased fraction of sufficiently energetic collisions explains the increase in the rate constant. Option (B) incorrectly denies the explanation; (C) and (D) incorrectly reject a true statement.

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

Quick Tip to Solve: For positive activation energy, increasing T makes $-E_a/(RT)$ less negative and increases k .

(A).

Quick Tip to Solve: For positive activation energy, increasing T makes $-E_a/(RT)$ less negative and increases k .

14. Assertion (A) : Cu^{2+} iodide is 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: (D) Assertion (A) is false, but Reason (R) is true.

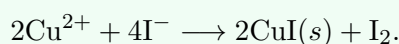
Solution:

Concept:

- Copper(II) ions oxidise iodide to iodine and are reduced to copper(I).
- Copper(I) iodide, CuI , precipitates; stable copper(II) iodide is not obtained under ordinary conditions.

Step 1: Judge the assertion Copper(II) iodide is unstable. Mixing a copper(II) salt with iodide gives copper(I) iodide and iodine instead. Hence the assertion that copper(II) iodide is known is false.

Step 2: Judge the reason The overall reaction is



Copper is reduced from +2 to +1, and some iodide is oxidised from -1 to zero. Thus R is true.

Step 3: Choose the code The reason explains why copper(II) iodide is unstable and contradicts the assertion as written. Options (A), (B) and (C) all require a true assertion, so all three are excluded.

Step 4: Conclusion A is false, but R is true. Hence, the correct option is (D).

Quick Tip to Solve: Remember that iodide produces CuI , with copper in the +1 state, along with iodine.

15. Assertion (A) : Maltose is a non-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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- A reducing sugar retains a free anomeric hemiacetal group that can open to a carbonyl form.
- Maltose contains two glucose units joined through an $\alpha(1 \rightarrow 4)$ glycosidic linkage.

Step 1: Judge the assertion Maltose is a reducing sugar. Its second glucose residue retains a free anomeric carbon and can open to an aldehydic form that reduces Tollens reagent or Fehling solution. Hence A is false.

Step 2: Judge the reason C-1 of one glucose unit is linked through oxygen to C-4 of the second glucose unit. Therefore the linkage stated in R is correct and R is true.

Step 3: Check the reducing end Only the first anomeric C-1 is involved in the glycosidic bond. The second C-1 remains free, making maltose reducing. Options (A), (B) and (C) are excluded because all require a true assertion.

Step 4: Conclusion A is false, but R is true. Hence, the correct option is (D).

Quick Tip to Solve: Check whether both anomeric carbons are bonded: maltose retains one free anomeric carbon.

16. Assertion (A) : Acetanilide is more 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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- Basicity depends on the availability of the nitrogen lone pair to accept a proton.
- Acetylation converts aniline, $\text{C}_6\text{H}_5\text{NH}_2$, to the amide acetanilide, $\text{C}_6\text{H}_5\text{NHCOCH}_3$.

Step 1: Judge the assertion Acetanilide is less basic than aniline. Its nitrogen lone pair is strongly delocalised towards the carbonyl group and is less available to accept a proton. Thus the assertion, which claims greater basicity, is false.

Step 2: Judge the reason After acetylation nitrogen is part of an amide group. Donation of its lone pair towards the carbonyl oxygen through resonance gives nitrogen partial positive character and decreases available electron density on it. Hence R is true.

Step 3: Check the relationship The decrease in electron density explains a decrease in basicity, opposing the increase claimed in A. Options (A) and (B) require both statements to be true, while (C) incorrectly calls A true and R false; they are excluded.

Step 4: Conclusion A is false, but R is true. Hence, the correct option is (D).

Quick Tip to Solve: Acetylation produces an amide: check lone-pair delocalisation into $\text{C}=\text{O}$ when comparing basicity.

Section B (10 marks)

17(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:

- HCN addition involves nucleophilic attack by CN^- at the electrophilic carbonyl carbon, followed by protonation.
- Electron donation and steric hindrance reduce carbonyl reactivity. Stronger intermolecular attractions raise boiling point.

Step 1: (i) Compare electronic and steric effects Acetaldehyde, CH_3CHO , has one methyl group and one hydrogen at its carbonyl carbon, whereas acetone, CH_3COCH_3 , has two methyl groups. The additional methyl group in acetone exerts a positive inductive effect, reducing the partial positive charge at the carbonyl carbon and making attack by CN^- less favourable. Moreover, two methyl groups cause greater steric hindrance to the incoming nucleophile than one methyl group and a small hydrogen. Therefore acetaldehyde reacts more readily with HCN for both electronic and steric reasons.

Step 2: (ii) Compare intermolecular association Carboxylic acids contain an O–H hydrogen-bond donor and a carbonyl oxygen acceptor. They associate through strong intermolecular hydrogen bonds, commonly forming cyclic dimers containing two hydrogen bonds. Aldehydes and ketones lack an O–H group, so they cannot form such hydrogen bonds with each other in their pure liquids. More energy is required to separate the associated acid molecules into the vapour phase. Thus carboxylic acids have higher boiling points than aldehydes and ketones of comparable molecular mass.

Step 3: Conclusion (i) Acetaldehyde is more reactive towards HCN because its carbonyl carbon is more electrophilic and less hindered. (ii) Carboxylic acids boil higher owing to intermolecular hydrogen bonding and dimerisation.

Quick Tip to Solve: For carbonyl addition compare electron donation and crowding; for boiling point compare intermolecular hydrogen bonding.

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

(i) Propanal and Propanone

(ii) Benzaldehyde and Benzoic acid

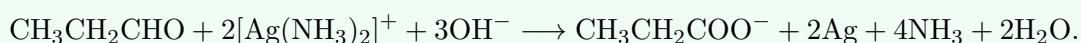
[2 marks]

Solution:

Concept:

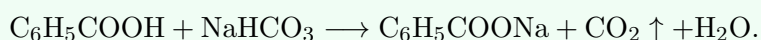
- Tollens' reagent, ammoniacal silver nitrate, oxidises an aldehyde group to carboxylate while silver(I) is reduced to metallic silver. Ordinary ketones do not give this test.
- Carboxylic acids react with aqueous sodium hydrogencarbonate to release carbon dioxide; an aldehyde has no carboxylic acid group and does not do so.

Step 1: (i) Propanal and propanone Warm separate samples gently with freshly prepared Tollens' reagent. Propanal produces a silver mirror on the test tube, whereas propanone gives no silver mirror. The reaction for propanal is



This distinguishes the aldehyde from the ketone by a positive observation.

Step 2: (ii) Benzaldehyde and benzoic acid Add aqueous sodium hydrogencarbonate to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide; benzaldehyde does not. The gas turns limewater milky.



The effervescence is caused by neutralisation of the carboxylic acid group, which benzaldehyde lacks.

Step 3: Conclusion Propanal: positive Tollens' test; propanone: negative. Benzoic acid: effervescence with NaHCO_3 ; benzaldehyde: no effervescence.

Quick Tip to Solve: For each pair state the reagent and both observations; bicarbonate identifies the acid directly.

18. Write the reaction involved in the following :

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

[2 marks]

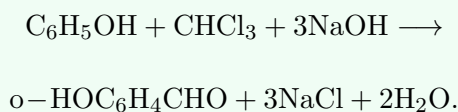
Solution:

Concept:

- Reimer-Tiemann reaction introduces a formyl group, $-\text{CHO}$, mainly at the ortho position of phenol using chloroform and aqueous alkali, followed by acidification.
- Kolbe's reaction of phenol is carboxylation of sodium phenoxide with carbon dioxide under pressure, followed by acidification to give salicylic acid.

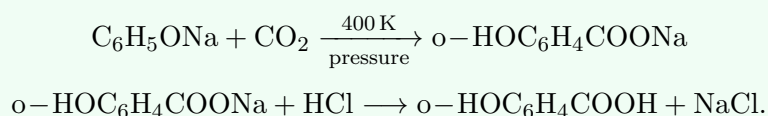
Quick Tip to Solve: Remember the introduced group: chloroform gives CHO , whereas carbon dioxide gives COOH after acidification.

Step 1: (a) Reimer–Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, and then acidify. The major product is 2-hydroxybenzaldehyde (salicylaldehyde). The overall reaction, with acid work-up understood, is



The formyl group replaces an ortho hydrogen of the aromatic ring; the phenolic group remains present.

Step 2: (b) Kolbe's reaction Sodium phenoxide is heated with carbon dioxide at about 400 K under 4–7 atm pressure. Sodium salicylate is formed; acidification gives salicylic acid (2-hydroxybenzoic acid).



Thus this reaction introduces a carboxyl group adjacent to the hydroxyl group.

Step 3: Conclusion Reimer–Tiemann gives salicylaldehyde, o–HOC₆H₄CHO; Kolbe's reaction gives salicylic acid, o–HOC₆H₄COOH, after acidification.

Quick Tip to Solve: Remember the introduced group: chloroform gives CHO, whereas carbon dioxide gives COOH after acidification.

19. Write the reaction of glucose with :

(a) HI

(b) Br₂ water

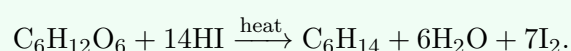
[2 marks]

Solution:

Concept:

- Prolonged heating with excess hydrogen iodide reduces glucose to *n*-hexane, retaining its straight chain of six carbon atoms.
- Bromine water is a mild oxidising reagent: it oxidises the aldehyde group of open-chain glucose to a carboxylic acid without oxidising the terminal primary alcohol group.

Step 1: (a) Reaction with HI On prolonged heating with excess HI, all oxygen-containing groups of glucose are removed by reduction and *n*-hexane is obtained. The balanced overall equation is

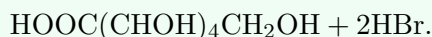


The product is the unbranched hydrocarbon CH₃(CH₂)₄CH₃. Formation of this six-carbon straight-chain product is evidence that the carbon atoms in glucose are arranged in an unbranched chain.

Step 2: (b) Reaction with bromine water Bromine water oxidises the –CHO group of glucose to

Quick Tip to Solve: HI removes oxygen groups; bromine water changes only the aldehyde end into COOH in this reaction.

–COOH, forming gluconic acid.



Bromine water is decolourised as bromine is consumed. The terminal –CH₂OH group remains unchanged because bromine water is a mild oxidant; therefore the product is gluconic acid, not the dicarboxylic acid.

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

Quick Tip to Solve: HI removes oxygen groups; bromine water changes only the aldehyde end into COOH in this reaction.

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

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

[2 marks]

Solution:

Concept:

- For a first-order reaction, $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$, where $[A]_0$ is the initial concentration, $[A]_t$ is the concentration remaining at time t , and k is the rate constant.
- The concentration ratio must use the fraction remaining, not the fraction decomposed. A first-order fractional-life calculation does not need the initial quantity.

Step 1: Find the fraction of acid remaining Three-fourths of the initial acid has decomposed, so the fraction left is $1 - \frac{3}{4} = \frac{1}{4}$. Thus

$$[A]_t = \frac{[A]_0}{4}, \quad \frac{[A]_0}{[A]_t} = 4.$$

The given rate constant is $k = 2.3 \times 10^{-3} \text{ s}^{-1}$. Using three-fourths as the remaining fraction would describe a different stage of the reaction.

Step 2: Apply the integrated first-order rate law Substitute the remaining-concentration ratio and the given value $\log 4 = 0.6021$:

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

As a check, one-fourth remains after two half-lives, so $t = 2(0.693/k)$, consistent with approximately 603 s.

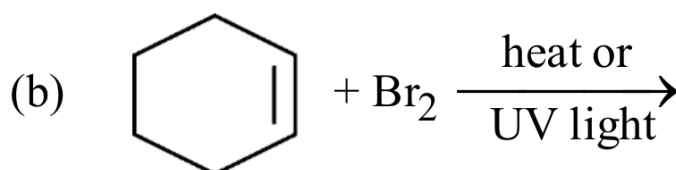
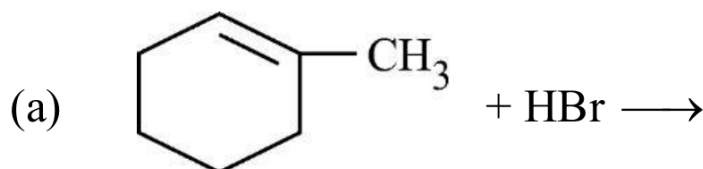
Step 3: Conclusion The acid takes approximately $6.03 \times 10^2 \text{ s}$, or 10.05 min, for three-fourths to

Quick Tip to Solve: Convert the decomposed fraction to the remaining fraction first: 3/4 decomposed means a ratio of 4 in the logarithm.

decompose.

Quick Tip to Solve: Convert the decomposed fraction to the remaining fraction first: $3/4$ decomposed means a ratio of 4 in the logarithm.

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



Solution:

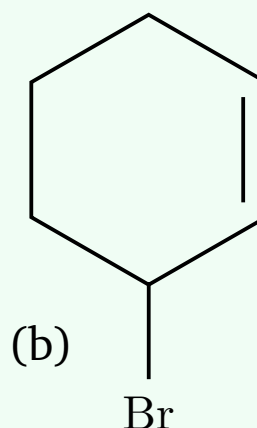
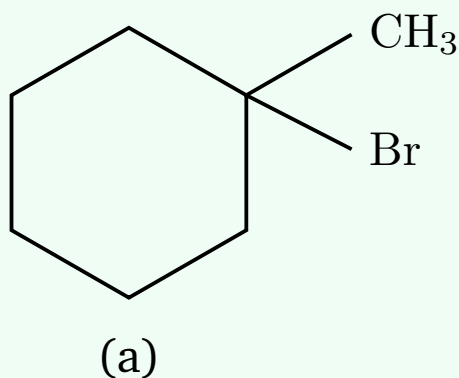
Concept:

- Without peroxide, HBr adds to an unsymmetrical alkene by Markovnikov's rule through the more stable carbocation.
- Heat or UV light initiates free-radical bromination. The requested monohalo product forms by allylic substitution, retaining the double bond.

Step 1: (a) Add HBr across the double bond In 1-methylcyclohex-1-ene, H adds to the double-bond carbon bearing a hydrogen. This puts the positive charge on the carbon bearing the methyl group, giving the more stable tertiary carbocation. Attack by Br⁻ places Br and CH₃ on the same ring carbon. The product is 1-bromo-1-methylcyclohexane; its structure is shown in (a).

Step 2: (b) Replace an allylic hydrogen Heat or UV light causes homolytic cleavage of Br₂. A bromine radical abstracts an allylic hydrogen, giving a resonance-stabilised allylic radical. Reaction with Br₂ then replaces this hydrogen by bromine. The equivalent allylic positions give the same constitutional monohalo product, 3-bromocyclohex-1-ene, shown in (b). Its double bond remains intact. The specified radical conditions and monohalo requirement distinguish this substitution from ordinary bromine addition, which would give a vicinal dibromide.

Quick Tip to Solve: Check conditions first: HBr gives Markovnikov addition, whereas bromine with heat or light gives the requested allylic substitution.



Structures of the major monohalo products (a) and (b)

Step 3: Conclusion The products are (a) 1-bromo-1-methylcyclohexane and (b) 3-bromocyclohex-1-ene, with structures shown above.

Quick Tip to Solve: Check conditions first: HBr gives Markovnikov addition, whereas bromine with heat or light gives the requested allylic substitution.

Section C (21 marks)

22. Give plausible explanation for the following :

- (a) Diazonium salts of aromatic amines are stable.
- (b) Aniline does not undergo Friedel-Crafts reaction.
- (c) Aniline on nitration gives a substantial amount of meta product.

[3 marks]

Solution:

Concept:

- Resonance delocalisation stabilises aromatic diazonium ions, ArN_2^+ , relative to aliphatic diazonium ions.
- The amino nitrogen lone pair can accept a proton or coordinate to a Lewis acid, changing the reactivity and directing effect of aniline.

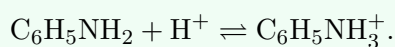
Step 1: (a) Stability of aromatic diazonium salts The diazonium group is directly attached to the aromatic ring. Conjugation permits delocalisation of charge between the diazonium group and the ring, so the aromatic diazonium ion is resonance-stabilised. Aliphatic diazonium ions lack this stabilisation and readily lose nitrogen. Aromatic diazonium salts are therefore comparatively stable and can be handled in cold aqueous solution at 273–278 K; this does not imply indefinite stability on heating.

Step 2: (b) Failure of the Friedel–Crafts reaction The lone pair on the nitrogen of aniline coordinates strongly to the Lewis acid catalyst, such as anhydrous AlCl_3 , forming a salt-like Lewis acid–base complex. This ties up the nitrogen lone pair and withdraws electron density from the ring, strongly de-

Quick Tip to Solve: Before applying the usual ortho/para directing effect of amino groups, check whether the reaction conditions protonate or coordinate the nitrogen lone pair.

activating it towards electrophilic substitution. The catalyst is also bound by the amine. Consequently, aniline does not undergo the usual Friedel–Crafts alkylation or acylation.

Step 3: (c) Formation of a substantial meta product on nitration In the strongly acidic nitrating mixture, aniline is protonated:



The anilinium group, $-\text{NH}_3^+$, is electron-withdrawing and meta-directing. Nitration of this protonated species therefore produces meta-nitroaniline after work-up. The unprotonated aniline present directs substitution towards ortho and para positions, explaining why direct nitration gives a mixture with a substantial meta component.

Step 4: Conclusion Aromatic diazonium salts are resonance-stabilised; aniline binds the Friedel–Crafts Lewis acid catalyst; and protonation to meta-directing anilinium ions accounts for the meta nitration product.

Quick Tip to Solve: Before applying the usual ortho/para directing effect of amino groups, check whether the reaction conditions protonate or coordinate the nitrogen lone pair.

23. 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:

- The bond dipole depends on the separated charge and the bond length: $\mu = q r$. Hybridisation and resonance alter the carbon–halogen bond.
- Dissolution depends on the energy needed to break existing intermolecular attractions compared with that released on forming new ones.
- For isomeric alkyl halides, increased branching reduces effective contact area and weakens London dispersion attractions.

Step 1: (a) Compare the two carbon–chlorine bonds In chlorobenzene, a chlorine lone pair is conjugated with the aromatic ring, giving the C–Cl bond partial double-bond character. The carbon attached to chlorine is sp^2 -hybridised and has more s-character than the sp^3 carbon in cyclohexyl chloride. It is therefore more electronegative, reducing the electronegativity difference between carbon and chlorine. The aryl C–Cl bond is also shorter. Reduced bond polarity and bond length account for the lower dipole moment of chlorobenzene compared with cyclohexyl chloride.

Step 2: (b) Explain immiscibility with water To dissolve an alkyl halide, water–water hydrogen bonds and alkyl halide–alkyl halide attractions must be disrupted. Alkyl halides cannot form sufficiently strong hydrogen bonds with water. The new solute–water attractions do not release enough energy to compensate for breaking the strong hydrogen bonds between water molecules. Consequently, ordinary

Quick Tip to Solve: For boiling-point comparisons between isomers with the same halogen, compare branching and molecular contact area before considering molecular mass.

alkyl halides have very low solubility in water and are described as immiscible, despite having polar carbon–halogen bonds.

Step 3: (c) Compare the boiling points of the butyl bromides Tert-butyl bromide and n-butyl bromide have the same molecular formula and molar mass. However, tert-butyl bromide is more branched and compact, whereas n-butyl bromide has a longer, less-branched shape. The compact molecules offer less surface area for effective intermolecular contact, so their London dispersion forces are weaker. Less thermal energy is needed to separate tert-butyl bromide molecules into the vapour phase, and its boiling point is therefore lower.

Step 4: Conclusion The differences arise from (a) the shorter, less polar aryl C–Cl bond, (b) insufficient compensation for disruption of water hydrogen bonding, and (c) weaker dispersion forces in the more branched isomer.

Quick Tip to Solve: For boiling-point comparisons between isomers with the same halogen, compare branching and molecular contact area before considering molecular mass.

24. (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]

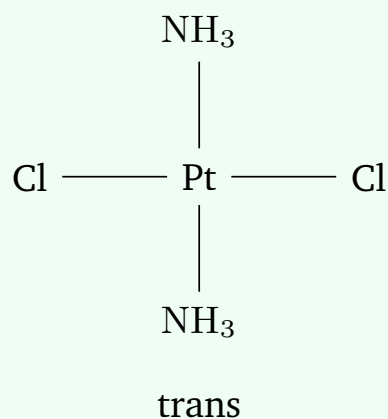
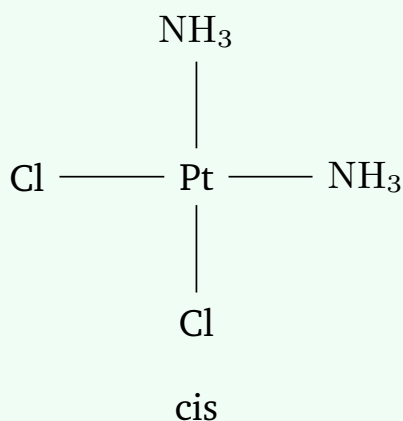
Solution:

Concept:

- A square-planar complex $[\text{MA}_2\text{B}_2]$ has cis and trans isomers, with identical ligands adjacent and opposite respectively.
- Octahedral splitting places three t_{2g} orbitals below two e_g orbitals. When $\Delta_o > P$, pairing costs less energy than promotion to e_g .
- Colour depends on absorption of visible light by electronic transitions between ligand-field levels.

Step 1: (a) Draw the two geometrical isomers The platinum(II) complex is square planar. In the cis form the two ammine ligands occupy adjacent positions and make an angle of 90° at Pt. In the trans form they occupy opposite positions and make an angle of 180° . The chloride ligands occupy the remaining positions in each drawing. Rotation of the entire complex gives no additional isomer.

Quick Tip to Solve: Identify the d count, geometry and ligand strength before explaining colour: diamagnetism alone does not imply colourlessness.



Square-planar cis and trans isomers

Step 2: (b) Fill the orbitals for a strong field The first three d electrons singly occupy the three lower t_{2g} orbitals. Since $\Delta_o > P$, the fourth electron pairs in a t_{2g} orbital rather than entering the higher e_g level. Thus the configuration is $t_{2g}^4 e_g^0$, a low-spin configuration with two unpaired electrons.

Step 3: (c) Compare the electronic transitions Nickel has configuration $[\text{Ar}]3d^8 4s^2$, giving Ni^{2+} the configuration $3d^8$ in both complexes. Water is a weak-field ligand. Octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ has configuration $t_{2g}^6 e_g^2$; its partly filled d levels permit d–d absorption in the visible range and the solution appears green. Cyanide is a strong-field ligand, producing a much larger splitting in square-planar $[\text{Ni}(\text{CN})_4]^{2-}$. Its d electrons pair, and the relevant excitation needs higher-energy radiation outside the visible range, so the solution is colourless. The transition energy, rather than pairing alone, explains the absence of visible absorption.

Step 4: Conclusion (a) The geometrical isomers are cis and trans, shown below the first step. (b) The configuration is $t_{2g}^4 e_g^0$. (c) Visible d–d absorption makes the aqua complex green; the larger splitting in the cyanide complex makes its solution colourless.

Quick Tip to Solve: Identify the d count, geometry and ligand strength before explaining colour: diamagnetism alone does not imply colourlessness.

25. 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 conductivity cell, resistance $R = \rho l/A$, where ρ is resistivity and l/A is the cell constant. Thus conductivity $\kappa = 1/\rho = (l/A)/R$.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity is in S cm^{-1} and concentration c is in mol L^{-1} . The factor 1000 converts litres to cubic centimetres.

Step 1: Identify the given cell quantities Here $R = 4.5 \times 10^3 \Omega$, cell constant $l/A = 50 \text{ cm}^{-1}$, and $c = 0.05 \text{ mol L}^{-1}$. Conductance $G = 1/R$ belongs to this particular cell, while conductivity includes

Quick Tip to Solve: First divide the cell constant by resistance to find conductivity, then use $1000\kappa/c$ with concentration in molarity.

the cell-geometry correction. Keep the centimetre unit of the cell constant throughout the calculation.

Step 2: Calculate resistivity Rearranging $R = \rho(l/A)$,

$$\rho = \frac{R}{l/A} = \frac{4.5 \times 10^3 \Omega}{50 \text{ cm}^{-1}} = 90 \Omega \text{ cm}.$$

Dividing by the cell constant gives resistivity; multiplying resistance by it would give the wrong dimensions.

Step 3: Calculate conductivity Conductivity is the reciprocal of resistivity:

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

Equivalently, $\kappa = 50/(4.5 \times 10^3) \text{ S cm}^{-1}$. The reciprocal relation provides a direct check on the first result.

Step 4: Convert to molar conductivity A solution of concentration 0.05 mol L^{-1} contains one mole in $1000/0.05 = 20000 \text{ cm}^3$. Therefore,

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

The concentration must be in moles per litre for this form of the formula; omitting the factor 1000 would make the answer a thousand times too small.

Step 5: 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 find conductivity, then use $1000\kappa/c$ with concentration in molarity.

26. 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 = $0.52 \text{ K kg mol}^{-1}$)

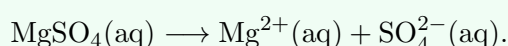
[3 marks]

Solution:

Concept:

- Elevation of boiling point is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the molal elevation constant and m the molality.
- Molality is the amount of solute in moles per kilogram of solvent. Complete ionisation increases the number of independently moving solute particles.

Step 1: Determine the particle factor Magnesium sulphate ionises according to



One formula unit produces two ions. Since complete ionisation is assumed, the number of solute

Quick Tip to Solve: Count ions first, then use kilograms of solvent: complete ionisation of magnesium sulphate gives $i = 2$.

particles doubles, so $i = 2$. The ionic charges do not multiply this factor further; it counts particles, not charge.

Step 2: Calculate the molality The amount of magnesium sulphate is

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

The mass of water is $100 \text{ g} = 0.100 \text{ kg}$. Hence

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

Use the solvent mass, not the total solution mass, in this calculation.

Step 3: Substitute in the boiling point relation Using the given constant and the ionisation factor,

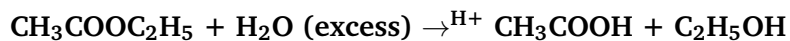
$$\Delta T_b = 2 \times 0.52 \text{ K kg mol}^{-1} \times \frac{1}{3} \text{ mol kg}^{-1} = 0.3467 \text{ K}.$$

The kilograms and moles cancel, leaving kelvin. The positive change is an elevation because the dissolved nonvolatile salt lowers the vapour pressure of water.

Step 4: Conclusion The elevation in boiling point is $\Delta T_b \simeq 0.347 \text{ K}$.

Quick Tip to Solve: Count ions first, then use kilograms of solvent: complete ionisation of magnesium sulphate gives $i = 2$.

27. Hydrolysis of ethyl ethanoate takes place by the chemical reaction :



Based on the above reaction, write :

(a) What do you call such reactions ?

(b) Rate law equation

(c) Molecularity and order of reaction

[3 marks]

Solution:

Concept:

- A pseudo first order reaction has an observed rate proportional to one reactant concentration because another reactant is present in large excess and its concentration is effectively constant.
- Order is obtained from the concentration powers in the rate law. In the school-level description here, molecularity counts the two reacting species, ester and water.

Step 1: (a) Identify the reaction The acid-catalysed hydrolysis of ethyl ethanoate is a pseudo first order reaction. Water is present in such large excess that the small amount consumed during hydrolysis has negligible effect on its concentration. The acid acts as a catalyst, with its concentration held fixed in the kinetic description.

Step 2: (b) Write the rate law Writing the usual concentration dependence for ester hydrolysis at

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

fixed acid concentration,

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

Since $[\text{H}_2\text{O}]$ is effectively constant, define $k_{\text{obs}} = k[\text{H}_2\text{O}]$. Thus the experimentally used rate equation is

$$r = -\frac{d[\text{CH}_3\text{COOC}_2\text{H}_5]}{dt} = k_{\text{obs}}[\text{CH}_3\text{COOC}_2\text{H}_5].$$

Any fixed catalyst contribution is included in the rate constant.

Step 3: (c) State molecularity and observed order For the reaction as described in this question, the reacting species are one ester molecule and one water molecule, so the expected molecularity is two (bimolecular). The observed order is one because only the ester concentration varies appreciably. Strictly, molecularity belongs to an elementary step; this school-level bimolecular description is not a claim that the acid-catalysed mechanism occurs in a single step.

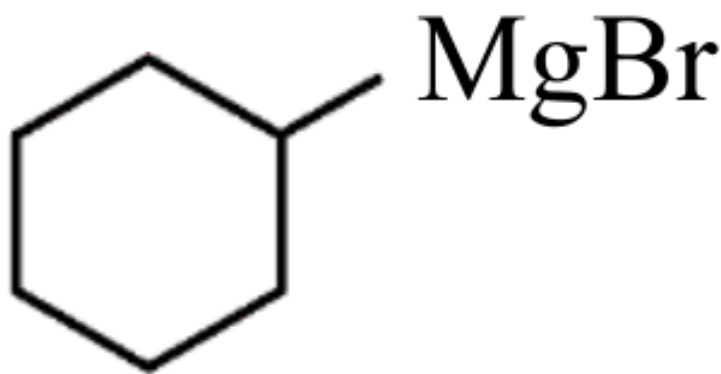
Step 4: Conclusion (a) Pseudo first order reaction. (b) $r = k_{\text{obs}}[\text{CH}_3\text{COOC}_2\text{H}_5]$. (c) Molecularity: 2; observed order: 1.

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

28. What happens when : (any three)

- (a) Cyclohexylmagnesium bromide 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]



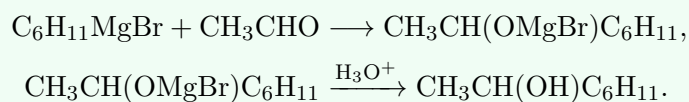
Solution:

Concept:

- A Grignard reagent adds its carbon group to the carbonyl carbon; hydrolysis of the magnesium alkoxide gives an alcohol.
- The hydroxyl and methoxy groups activate an aromatic ring and direct electrophilic substitution to the ortho and para positions.
- Passing a secondary alcohol over heated copper at 573 K removes hydrogen to give a ketone.

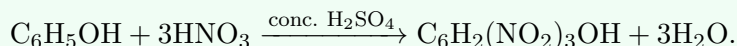
Quick Tip to Solve: For each conversion, identify the reaction first: Grignard addition, nitration, acylation or copper-catalysed dehydrogenation.

Step 1: (a) Addition to ethanal followed by hydrolysis Let C_6H_{11} denote the cyclohexyl group. Its Grignard reagent adds to ethanal, forming a magnesium alkoxide. Hydrolysis protonates the oxygen:



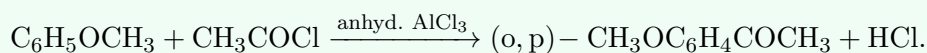
The product is the secondary alcohol 1-cyclohexylethan-1-ol; the original aldehyde hydrogen remains on the alcohol carbon.

Step 2: (b) Nitration of phenol Concentrated nitrating mixture gives extensive substitution at both ortho positions and the para position. Phenol forms 2,4,6-trinitrophenol (picric acid):



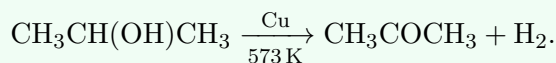
The strongly activating hydroxyl group explains why all three directed positions can be nitrated.

Step 3: (c) Friedel–Crafts acylation of anisole Anisole reacts with ethanoyl chloride in the presence of anhydrous aluminium chloride to form ortho- and para-methoxyacetophenone, with the para product predominant owing to lower steric crowding:



The methoxy group remains attached through oxygen and directs the incoming acetyl group to ortho and para positions.

Step 4: (d) Dehydrogenation of propan-2-ol Heated copper converts the secondary alcohol to propanone by removing two hydrogen atoms, one from oxygen and one from the carbon bearing the hydroxyl group:



Thus a ketone forms without changing the three-carbon skeleton.

Step 5: Conclusion (a) 1-Cyclohexylethan-1-ol; (b) picric acid; (c) the ortho/para acylation products (para major); (d) propanone and hydrogen. Any three of these transformations may be written.

Quick Tip to Solve: For each conversion, identify the reaction first: Grignard addition, nitration, acylation or copper-catalysed dehydrogenation.

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 three types of RNA molecules.

[1 mark]

Solution:

Concept:

- RNA is ribonucleic acid. Its three major classes participate together in protein synthesis, but perform different tasks.
- The standard names distinguish messenger RNA, ribosomal RNA and transfer RNA according to their functions.

Step 1: Name the information carrier Messenger RNA (mRNA) carries genetic information copied from DNA to the site of protein synthesis. Its sequence acts as the template for assembling the amino-acid sequence.

Step 2: Name the other two classes Ribosomal RNA (rRNA) forms an essential component of ribosomes. Transfer RNA (tRNA) brings the appropriate amino acids to the ribosome by recognizing the corresponding codons on mRNA.

Step 3: Conclusion The three types are messenger RNA (mRNA), ribosomal RNA (rRNA) and transfer RNA (tRNA).

Quick Tip to Solve: Remember the roles in order: mRNA carries the message, rRNA forms the ribosome and tRNA transfers amino acids.

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

[1 mark]

Solution:

Concept:

- A nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group; a nucleoside lacks the phosphate group.
- In DNA the pentose sugar is 2-deoxyribose, and the base specified in this question is thymine.

Step 1: Identify the sugar and base Because the nucleotide is from DNA, its sugar component is 2-deoxyribose rather than ribose. The stated nitrogenous base remains thymine on complete hydrolysis.

Quick Tip to Solve: First distinguish nucleotide from nucleoside: only the nucleotide contributes phosphoric acid on complete hydrolysis.

Step 2: Account for the phosphate component Complete hydrolysis cleaves the linkages connecting the sugar, base and phosphate. Thus the phosphate component gives phosphoric acid along with the sugar and the base; thymine alone is not the complete list of products.

Step 3: Conclusion Complete hydrolysis yields 2-deoxyribose, thymine and phosphoric acid.

Quick Tip to Solve: First distinguish nucleotide from nucleoside: only the nucleotide contributes phosphoric acid on complete hydrolysis.

29(c). Give two differences between DNA and RNA.

[2 marks]

Solution:

Concept:

- DNA means deoxyribonucleic acid, whereas RNA means ribonucleic acid. Both are polynucleotides containing a pentose sugar, phosphate and nitrogenous bases.
- Two independent chemical differences are the identity of the sugar and one of the pyrimidine bases; the shared components should not be listed as differences.

Step 1: Compare the pentose sugars DNA contains 2-deoxyribose sugar, whereas RNA contains ribose sugar. At the 2-prime carbon, deoxyribose has a hydrogen atom in place of the hydroxyl group present in ribose. This is the structural distinction indicated by the prefix deoxy.

Step 2: Compare the nitrogenous bases DNA contains adenine, guanine, cytosine and thymine. RNA contains adenine, guanine, cytosine and uracil. Therefore thymine in DNA is replaced by uracil in RNA; adenine, guanine and cytosine occur in both and do not provide the requested distinction.

Step 3: Conclusion DNA contains 2-deoxyribose and thymine; RNA contains ribose and uracil. These give the two required differences.

Quick Tip to Solve: Use the paired differences sugar and base: deoxyribose/thymine for DNA, ribose/uracil for RNA.

OR

29(c)(I). Why are the two strands of DNA complementary ?

[1 mark]

Solution:

Concept:

- The two strands of a DNA double helix are held together by hydrogen bonds between specific pairs of nitrogenous bases.
- Complementary base pairing permits adenine with thymine and guanine with cytosine.

Step 1: Identify the specific base pairs Adenine (A) on one strand pairs with thymine (T) on the other through two hydrogen bonds. Guanine (G) pairs with cytosine (C) through three hydrogen bonds. Each permitted pair combines one purine with one pyrimidine.

Step 2: Explain why this makes the strands complementary The identity of a base on one strand

Quick Tip to Solve: To construct a complementary DNA sequence, replace A by T, T by A, G by C and C by G.

therefore fixes the base at the corresponding position on the other strand. Consequently the sequence of either strand uniquely determines that of its partner; the two sequences are complementary rather than identical.

Step 3: Conclusion The strands are complementary because specific A–T and G–C hydrogen-bonded pairing makes the base sequence of one strand determine the other.

Quick Tip to Solve: To construct a complementary DNA sequence, replace A by T, T by A, G by C and C by G.

29(c)(II). What type of linkage joins two nucleotides ?

[1 mark]

Solution:

Concept:

- Nucleotides within a nucleic-acid strand are joined covalently through their sugar and phosphate groups.
- A phosphodiester group forms two ester bonds, connecting the sugars of adjacent nucleotides.

Step 1: Locate the groups that join The phosphate group bridges the 3-prime hydroxyl position of one pentose sugar and the 5-prime position of the next sugar. Repeated connections produce the sugar-phosphate backbone of the polynucleotide strand.

Step 2: Distinguish this bond from base pairing Since the phosphate makes ester connections with two sugar residues, the linkage is called a phosphodiester linkage. Hydrogen bonds instead join complementary bases between the two DNA strands and are not the linkage joining successive nucleotides along one strand.

Step 3: Conclusion Two adjacent nucleotides in a nucleic-acid chain are joined by a 3-prime,5-prime phosphodiester linkage.

Quick Tip to Solve: For bonds along a strand write phosphodiester; reserve hydrogen bonds for complementary bases between DNA strands.

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:

- An azeotrope boils at constant temperature and has the same composition in its liquid and vapour phases.
- Fractional distillation separates components by producing a vapour with a composition different from that of the liquid.

Step 1: Identify the mixture formed The ethanol–water system shows positive deviation from Raoult's law and forms a minimum-boiling azeotrope at about 95.6 percent ethanol by mass. Its boiling point is lower than that of either pure component.

Step 2: Apply the condition for fractional distillation At the azeotropic composition, the vapour contains the same proportions of ethanol and water as the boiling liquid. Condensing that vapour therefore reproduces the same mixture, so further fractionation cannot remove the remaining water to obtain pure ethanol.

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

Quick Tip to Solve: When a separation question mentions an azeotrope, connect equal liquid/vapour compositions directly to the failure of further enrichment.

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 because unlike-molecule attractions are comparable to those between like molecules.
- Negative deviation occurs when unlike-molecule attractions are stronger, reducing the escaping tendency and vapour pressure.

Step 1: Identify the new attraction On mixing, the hydrogen of chloroform, CHCl_3 , forms a hydrogen bond with the carbonyl oxygen of acetone, $(\text{CH}_3)_2\text{CO}$. The three chlorine atoms make the chloroform hydrogen sufficiently electron deficient for this attraction.

Step 2: Relate attraction to vapour pressure These chloroform–acetone interactions are stronger than

Quick Tip to Solve: For this pair, identify the bond as chloroform H to acetone carbonyl O; stronger attraction means lower vapour pressure.

the interactions present in the separate pure liquids. Molecules are consequently held more strongly in the liquid, so fewer escape into the vapour at the same temperature. The observed vapour pressure is lower than the ideal value.

Step 3: Conclusion The mixture shows **negative deviation from Raoult's law** because hydrogen bonding strengthens the attraction between chloroform and acetone molecules.

Quick Tip to Solve: For this pair, identify the bond as chloroform H to acetone carbonyl O; stronger attraction means lower vapour pressure.

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 dilute solution containing a non-volatile solute, relative lowering of vapour pressure is $\frac{p^0 - p}{p^0} \simeq \frac{n_2}{n_1} = \frac{w_2 M_1}{M_2 w_1}$.
- Here p^0 and p are pure-solvent and solution vapour pressures; w_1, M_1 refer to benzene and w_2, M_2 to the solute. A non-electrolyte does not dissociate.

Step 1: Calculate the relative lowering The solute has negligible vapour pressure, so the observed lowering is due to the reduced mole fraction of benzene. The pressure difference and its relative value are

$$\Delta p = 1.250 - 1.237 = 0.013 \text{ atm}, \quad \frac{\Delta p}{p^0} = \frac{0.013}{1.25} = 0.0104.$$

Step 2: Substitute the masses and determine molar mass Using the dilute-solution expression,

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

The solvent and solute masses are both in grams, so no kilogram conversion is required in this mass ratio. For completeness, retaining the exact mole-fraction denominator in Raoult's law gives $M_2 = \frac{1.2 \times 78 \times 1.237}{60 \times 0.013} = 148.44 \text{ g mol}^{-1}$; the small difference is the dilute-solution approximation.

Step 3: Conclusion The molar mass of the solute is approximately 150 g mol⁻¹ by the standard dilute-solution formula.

Quick Tip to Solve: Subtract the pressures first, and use pure benzene pressure in the standard relative-lowering 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:

- Elevation of boiling point is $\Delta T_b = K_b m$, where m is the number of moles of solute per kilogram of solvent.
- For solute mass w_2 , solvent mass w_1 in grams and solute molar mass M_2 , $m = \frac{1000w_2}{M_2w_1}$. The non-volatile solute raises the boiling point by lowering solvent vapour pressure.

Step 1: Find the boiling-point elevation The solution boils at a higher temperature than pure benzene. The relevant temperature difference is

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

This difference, rather than the final boiling temperature, is used in the colligative-property equation.

Step 2: Calculate molality and molar mass The solvent mass is 90 g = 0.090 kg. Hence

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

The amount of solute is $n_2 = 0.3478 \times 0.090 = 0.03130 \text{ mol}$. Thus

$$M_2 = \frac{1.80}{0.03130} = \frac{2.53 \times 1.80 \times 1000}{0.88 \times 90} = 57.5 \text{ g mol}^{-1}.$$

The mass in the molality denominator is the solvent mass alone, not the mass of the solution.

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

Quick Tip to Solve: Use the rise of 0.88 K and convert the 90 g of benzene into 0.090 kg before calculating molality.

Section E (15 marks)

31(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:

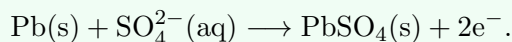
Concept:

- A secondary battery is rechargeable: an external source can reverse its discharge reaction. A lead storage battery is a secondary battery.
- During discharge, oxidation occurs at the lead anode and reduction at the lead dioxide cathode.

Quick Tip to Solve: Remember that both plates become lead sulfate on discharge; put electrons on the product side only at the lead anode.

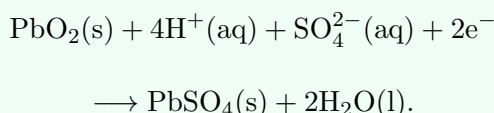
Both electrodes form PbSO_4 in sulfuric acid electrolyte.

Step 1: State the battery type and anode reaction The lead storage battery is a rechargeable secondary battery. When current is drawn, metallic lead is oxidised from oxidation state 0 to +2 at the negative anode. Its half-reaction is



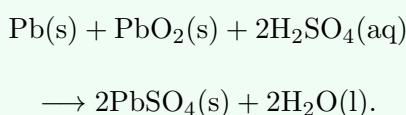
Sulfate ions from the electrolyte combine with the oxidised lead to form solid lead sulfate. The released electrons travel through the external circuit to the positive electrode.

Step 2: Write the cathode reaction At the positive cathode, lead in lead dioxide is reduced from oxidation state +4 to +2. In the acidic electrolyte, the balanced half-reaction is



Two electrons are consumed, equal to the number released by the anode. Hydrogen ions balance the oxygen atoms as water, and total charge is conserved.

Step 3: Add the half-reactions Cancel the two electrons and combine 4H^+ with 2SO_4^{2-} as $2\text{H}_2\text{SO}_4$. The overall discharge reaction is



Thus sulfuric acid is consumed during discharge and the electrolyte becomes less concentrated. Charging drives the reverse overall reaction, regenerating lead, lead dioxide and sulfuric acid.

Step 4: Conclusion Lead storage is a **secondary (rechargeable) battery**. During discharge, Pb is oxidised at the anode and PbO_2 is reduced at the cathode; both form PbSO_4 , with the overall reaction given above.

Quick Tip to Solve: Remember that both plates become lead sulfate on discharge; put electrons on the product side only at the lead anode.

31(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 Ag = 108 g mol^{-1} , $1 \text{ F} = 96500 \text{ C mol}^{-1}$] [2 marks]

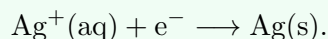
Solution:

Concept:

- Faraday's first law relates deposited mass to charge: $m = \frac{MIt}{nF}$, where M is molar mass, I is current, t is time and n is the number of electrons needed per metal ion.
- Silver ions undergo reduction at the cathode. Since Ag^+ accepts one electron, deposition of one mole of silver requires one faraday of charge.

Quick Tip to Solve: Write $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ first: silver needs one electron, so use $n = 1$ in $t = mnF/(MI)$.

Step 1: Identify the cathode process and charge The cathode reaction is



Hence $n = 1$. The amount of silver to be deposited is $m/M = 1.5/108 \text{ mol}$. Therefore the required charge is

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

Step 2: Convert the required charge into time For a constant current, $Q = It$. Substituting the current specified in the question,

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

Equivalently, $t = mnF/(MI)$. The units are consistent because $\text{C/A} = \text{s}$; nitrate ions do not change the one-electron stoichiometry of silver deposition.

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

Quick Tip to Solve: Write $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ first: silver needs one electron, so use $n = 1$ in $t = mnF/(MI)$.

OR

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

Solution:

Concept:

- Kohlrausch's law states that at infinite dilution each ion contributes independently to the total molar conductivity of an electrolyte, irrespective of the other ion present.
- The limiting molar conductivity is $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$, where λ_i° is an ion's limiting molar ionic conductivity and ν_i is its stoichiometric coefficient.

Step 1: State the independent ionic contributions For these 1:1 electrolytes at the same temperature,

$$\Lambda_m^\circ(\text{NH}_4\text{Cl}) = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{Cl}^-}^\circ,$$

$$\Lambda_m^\circ(\text{NaOH}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{OH}^-}^\circ,$$

$$\Lambda_m^\circ(\text{NaCl}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ.$$

At infinite dilution, ionic interactions become negligible, so the same ionic contribution can be used in each electrolyte.

Step 2: Form the required combination and substitute Add the first two equations and subtract the

Quick Tip to Solve: Add the salts carrying NH_4^+ and OH^- , then subtract NaCl to cancel the unwanted ions.

third. This cancels the contributions of Na^+ and Cl^- , leaving only NH_4^+ and OH^- :

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

This combination determines the limiting value for weakly ionised ammonium hydroxide without extrapolating its finite-concentration conductivity directly.

Step 3: Conclusion The molar conductivity of NH_4OH at infinite dilution at 298 K is $105 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: Add the salts carrying NH_4^+ and OH^- , then subtract NaCl to cancel the unwanted ions.

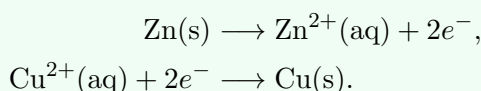
31(b)(ii). Calculate ΔG° of the following cell at 25°C : $\text{Zn (s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu (s)}$. Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, $1 \text{ F} = 96500 \text{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

Solution:

Concept:

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

Step 1: Balance the cell reaction and determine its potential The left-hand zinc electrode is the anode and copper is the cathode:



The net reaction is $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$, so $n = 2$. The standard potential is

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

Step 2: Calculate the standard Gibbs energy change Use the electron count from the balanced reaction:

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

Here $\text{C} \times \text{V} = \text{J}$. The negative sign agrees with the positive standard cell potential: the stated cell reaction is spontaneous under standard conditions at the given temperature.

Step 3: Conclusion For the cell reaction as written, $\Delta G^\circ = -212.3 \text{ kJ mol}^{-1}$.

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

32(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.

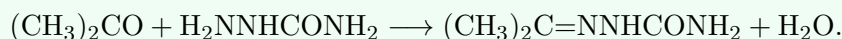
[3 marks]

Solution:

Concept:

- Semicarbazide, $\text{H}_2\text{NNHCONH}_2$, condenses with a carbonyl compound through its terminal amino group to form a semicarbazone and water.
- An aldehyde with no α hydrogen undergoes Cannizzaro disproportionation in concentrated alkali. Clemmensen reduction converts a carbonyl group to a methylene group using zinc amalgam and concentrated hydrochloric acid.

Step 1: I. Acetone with semicarbazide Acetone undergoes condensation with semicarbazide. The oxygen of the carbonyl group and two hydrogens of the terminal amino group are eliminated as water:



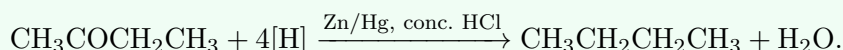
The product is acetone semicarbazone. The terminal amino nitrogen reacts because its lone pair is available for nucleophilic attack; the amino group attached directly to the carbonyl in semicarbazide is resonance-deactivated.

Step 2: II. Benzaldehyde with concentrated NaOH Benzaldehyde has no α hydrogen and therefore undergoes the Cannizzaro reaction instead of aldol condensation. One molecule is oxidised to sodium benzoate while the other is reduced to benzyl alcohol:



The carboxylate salt, rather than free benzoic acid, is obtained in the alkaline reaction mixture.

Step 3: III. Butan-2-one with zinc amalgam and hydrochloric acid Clemmensen reduction removes the carbonyl oxygen and replaces the carbonyl group by a methylene group without changing the carbon skeleton:



Thus butan-2-one gives butane; it does not stop at the secondary alcohol under these reduction conditions.

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

Quick Tip to Solve: Check for α hydrogen before choosing Cannizzaro; Zn/Hg with concentrated HCl converts $\text{C}=\text{O}$ directly into CH_2 .

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

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

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

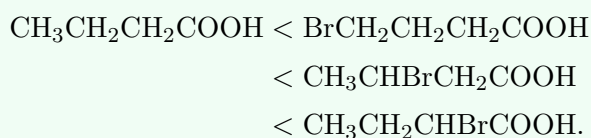
[2 marks]

Solution:

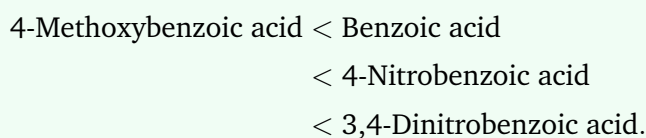
Concept:

- Acid strength increases when the conjugate carboxylate ion is stabilised. Electron-withdrawing groups stabilise its negative charge, whereas electron-donating groups destabilise it.
- The negative inductive effect of bromine decreases rapidly as its distance from the carboxyl group increases. Nitro groups withdraw electrons; a para methoxy group donates by resonance.

Step 1: I. Compare the bromine positions Relative to the carboxyl carbon, bromine is at the gamma position in $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{COOH}$, the beta position in $\text{CH}_3\text{CHBrCH}_2\text{COOH}$, and the alpha position in $\text{CH}_3\text{CH}_2\text{CHBrCOOH}$. Its electron-withdrawing inductive effect is strongest at the alpha position and weakest at the gamma position. Unsubstituted butanoic acid lacks this stabilising bromine substituent. Hence the increasing acidic strength is



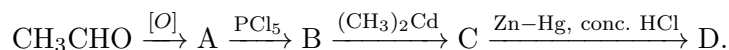
Step 2: II. Compare substituent effects on benzoic acid At the para position, methoxy donates electron density by resonance; its net effect decreases acidity relative to benzoic acid. A nitro group withdraws electrons and increases acidity. Two nitro groups in 3,4-dinitrobenzoic acid provide greater electron withdrawal than the single para nitro group. Therefore the increasing order is



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

Quick Tip to Solve: For halo acids count the distance from COOH first; for aromatic acids compare net electron donation or withdrawal.

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



[2 marks]

Solution:

Concept:

- Oxidation converts an aldehyde to a carboxylic acid. Phosphorus pentachloride converts a carboxylic acid to its acyl chloride.
- Dialkylcadmium converts an acyl chloride to a ketone. Clemmensen reduction with zinc amalgam and concentrated HCl converts the ketone carbonyl group to a methylene group.

Step 1: Identify A and B The starting compound is ethanal. Oxidation adds oxygen to the aldehyde group without altering the number of carbon atoms:



Thus A is ethanoic acid. Reaction with phosphorus pentachloride replaces the hydroxyl group of the acid by chlorine:

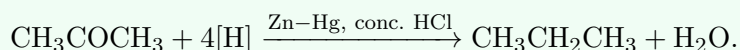


Therefore B is ethanoyl chloride (acetyl chloride).

Step 2: Identify C and D Dimethylcadmium transfers a methyl group to the acyl chloride, producing a ketone:



Hence C is propanone (acetone). In the printed sequence the final arrow goes from C to D. Clemmensen reduction then changes the carbonyl group to a methylene group:



Thus D is propane. The methyl group introduced by dimethylcadmium accounts for the increase from two carbon atoms in B to three in C and D.

Step 3: Conclusion A = CH₃COOH (ethanoic acid), B = CH₃COCl (ethanoyl chloride), C = CH₃COCH₃ (propanone), and D = CH₃CH₂CH₃ (propane).

Quick Tip to Solve: Follow each arrow from its tail: dimethylcadmium adds one methyl group and Clemmensen reduction preserves the carbon skeleton.

32(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

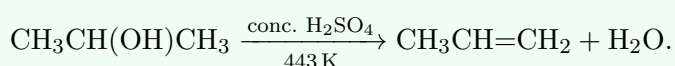
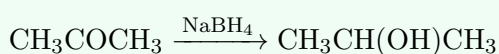
[3 marks]

Solution:

Concept:

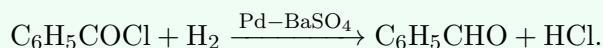
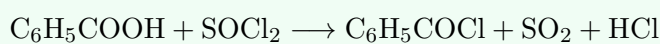
- Reduction of a ketone with NaBH_4 gives a secondary alcohol; dehydration of that alcohol gives an alkene.
- Rosenmund reduction converts an acid chloride into an aldehyde using $\text{H}_2/\text{Pd} - \text{BaSO}_4$. Aldehydes with an alpha hydrogen undergo aldol condensation.

Step 1: (I) Propanone to propene First reduce the carbonyl group of propanone to form propan-2-ol. Then heat the alcohol with concentrated sulphuric acid to eliminate water:



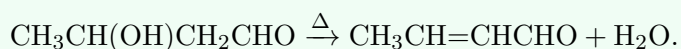
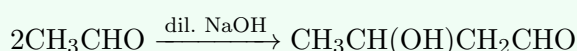
Reduction alone cannot yield propene: the subsequent dehydration introduces the carbon-carbon double bond.

Step 2: (II) Benzoic acid to benzaldehyde Convert benzoic acid to benzoyl chloride using thionyl chloride. Then carry out controlled catalytic hydrogenation by Rosenmund reduction:



The poisoned catalyst controls reduction at the aldehyde stage; a strong hydride reagent would reduce the acid derivative further to an alcohol.

Step 3: (III) Ethanal to but-2-enal Treat ethanal with dilute aqueous sodium hydroxide to form the aldol, 3-hydroxybutanal, and then heat it to eliminate water:



Ethanal has alpha hydrogen, so it undergoes aldol addition. Dehydration of the beta-hydroxy aldehyde gives the conjugated aldehyde but-2-enal.

Step 4: Conclusion The required routes are propanone $\rightarrow$ propan-2-ol $\rightarrow$ propene; benzoic acid $\rightarrow$ benzoyl chloride $\rightarrow$ benzaldehyde; and ethanal $\rightarrow$ 3-hydroxybutanal $\rightarrow$ but-2-enal.

Quick Tip to Solve: For each conversion, identify the needed functional-group change first: reduction then dehydration, Rosenmund reduction, or aldol condensation.

33. 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:

- Stability of oxidation states depends on electronic configuration and hydration enthalpy; a reducing agent loses electrons and is itself oxidised.
- Poor shielding by f electrons causes contraction across an f-block series. Variable oxidation states and surface adsorption help transition elements catalyse reactions.
- A transition element has an incomplete d subshell in its atom or in one of its cations; colour commonly arises from d-d electronic transitions.

Step 1: (a) Instability of aqueous copper(I) In aqueous solution, Cu^+ disproportionates:



The much more negative hydration enthalpy of Cu^{2+} , compared with Cu^+ , compensates for the energy required to remove the second electron. Thus the hydrated divalent ion is favoured and copper(I) is unstable in water.

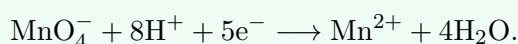
Step 2: (b) Comparing reducing strength Cr^{2+} is the stronger reducing agent. It readily loses an electron to form Cr^{3+} , with the stable $3d^3$ configuration (t_{2g}^3 in an octahedral field). The standard reduction potentials are approximately

$$E^\circ(\text{Cr}^{3+}/\text{Cr}^{2+}) = -0.41 \text{ V}, \quad E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}.$$

The more negative potential for the chromium couple confirms that chromium(II) is more readily oxidised, even though iron(III) also has a stable $3d^5$ configuration.

Step 3: (c) Greater actinoid contraction The 5f electrons shield the increasing nuclear charge less effectively than 4f electrons. Consequently, across the actinoid series, the effective nuclear attraction rises more strongly and pulls the electron cloud inward. The decrease in size from one element to the next is therefore greater than in the lanthanoid series.

Step 4: (d) Permanganate in acidic medium The reduction half-equation is



Manganese changes from oxidation state +7 to +2. Acceptance of five electrons per permanganate ion shows that it oxidises another species. Both atoms and charge are balanced: the net charge on each side is +2.

Quick Tip to Solve: Distinguish the atom's configuration from the common ion's configuration: scandium is a transition element even though scandium(III) is colourless.

Step 5: (e) Frequent +1 oxidation state The metal is copper, Cu. Its atomic configuration is $[\text{Ar}]3d^{10}4s^1$; loss of the 4s electron gives Cu^+ with a filled $3d^{10}$ subshell. The +1 state is common in its compounds, although the free aqueous ion disproportionates as explained in part (a).

Step 6: (f) Catalytic activity Transition metals and their compounds can adopt different oxidation states and form intermediate compounds with reactants, providing a pathway of lower activation energy. Metal surfaces also adsorb reactants, bringing them together and weakening their bonds. For example, iron catalyses ammonia synthesis, while V_2O_5 catalyses oxidation of SO_2 to SO_3 .

Step 7: (g) Scandium as a transition element The scandium atom has configuration $[\text{Ar}]3d^14s^2$. Its incomplete d subshell makes it a transition element. Its usual ion, Sc^{3+} , has configuration $[\text{Ar}]3d^0$, so no d-d transition is possible and it is colourless. Colour of the common ion is not a requirement for classifying the element as a transition element.

Step 8: Conclusion Any five parts may be attempted. The answers to all seven are given above: aqueous Cu^+ disproportionates; Cr^{2+} is the stronger reductant; poor 5f shielding causes greater contraction; acidic permanganate accepts five electrons; copper commonly shows +1; variable oxidation states and adsorption explain catalysis; and scandium has a partially filled d subshell in its atom.

Quick Tip to Solve: Distinguish the atom's configuration from the common ion's configuration: scandium is a transition element even though scandium(III) is colourless.