

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-5-1

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 calculator is not allowed.

Section A (16 marks)

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

1. Which of the reactions is used in the conversion of a ketone into hydrocarbon ?

[1 mark]

- (A) Reimer-Tiemann reaction
- (B) Wolff-Kishner reduction
- (C) Aldol condensation
- (D) Stephen reaction

Correct Answer: (B) Wolff-Kishner reduction

Solution:

Concept:

- Wolff-Kishner reduction replaces the carbonyl group $>C=O$ of an aldehyde or ketone by $>CH_2$.
- Hydrazine NH_2NH_2 and strong base, usually KOH , are used on heating.

Step 1: Identify the required change A ketone has the general formula $RCOR'$. Conversion to the corresponding hydrocarbon requires removal of the carbonyl oxygen and replacement by two hydrogen atoms, giving RCH_2R' . The carbon skeleton is retained.

Step 2: Compare the named reactions Wolff-Kishner reduction performs exactly this change, through hydrazone formation followed by heating with base. Reimer-Tiemann introduces a formyl group into phenol, aldol condensation forms a carbon-carbon bond between suitable carbonyl compounds, and Stephen reduction converts a nitrile into an aldehyde. Thus none of those three matches the specified conversion.

Step 3: Conclusion The reaction is Wolff-Kishner reduction. Hence, the correct option is (B).

Quick Tip to Solve: For carbonyl-to-methylene conversion, look for hydrazine with base and heat.

2. Which of the following reagents are used to prepare primary amines by Hoffmann bromamide degradation reaction ?

(i) $R-CO-NH_2$ (ii) $NaOH$ (iii) Br_2 (iv) $CHCl_3$

[1 mark]

- (A) (i), (ii) and (iv)
- (B) (i) and (iii)
- (C) (i), (ii) and (iii)
- (D) (i), (iii) and (iv)

Correct Answer: (C) (i), (ii) and (iii)

Solution:

Concept:

- Hoffmann bromamide degradation converts a primary amide $RCONH_2$ into a primary amine RNH_2 .
- Bromine and aqueous sodium hydroxide are required; the product has one carbon atom fewer than

Quick Tip to Solve: Remember bromamide degradation as primary amide plus bromine and aqueous alkali.

the amide.

Step 1: Select the substrate and reagents The primary amide in (i) supplies the organic group. Bromine in (iii), together with sodium hydroxide in (ii), produces the alkaline brominating conditions needed for the rearrangement. The overall reaction is



Step 2: Reject the other combinations Chloroform in (iv) is not required in this degradation. It is associated with the carbylamine test of primary amines in alcoholic alkali. Options (A) and (D) unnecessarily include chloroform and omit a necessary reagent; option (B) omits sodium hydroxide. Only the set containing the amide, alkali and bromine is complete.

Step 3: Conclusion The required substances are (i), (ii) and (iii). Hence, the correct option is (C).

Quick Tip to Solve: Remember bromamide degradation as primary amide plus bromine and aqueous alkali.

3. The major product of carbylamine reaction is :

[1 mark]

- (A) Carboxylic acid
- (B) Aldehyde
- (C) Cyanide
- (D) Isocyanide

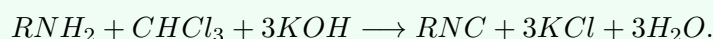
Correct Answer: (D) Isocyanide

Solution:

Concept:

- Only primary amines give the carbylamine reaction with chloroform and alcoholic potassium hydroxide on heating.
- The product is an isocyanide, $R - N \equiv C$, whose nitrogen is bonded to the organic group.

Step 1: Write the characteristic reaction For a primary amine, the reaction is



The organic product RNC is an isocyanide, also called a carbylamine, and has a characteristic offensive smell.

Step 2: Distinguish the alternatives A cyanide or nitrile has connectivity $R - C \equiv N$, which differs from the isocyanide connectivity $R - N \equiv C$. The carbylamine reaction does not produce this nitrile linkage. Carboxylic acid and aldehyde products contain oxygen and belong to other transformations; neither is the characteristic product of the given test.

Step 3: Conclusion The major product is isocyanide. Hence, the correct option is (D).

Quick Tip to Solve: Carbylamine means isocyanide: the organic group attaches to nitrogen, not carbon.

4. Actinoids show larger number of oxidation states :

[1 mark]

- (A) because they are radioactive in nature
- (B) because they have large atomic numbers
- (C) because they have large atomic masses
- (D) due to comparable energies of 5f, 6d and 7s orbitals

Correct Answer: (D) due to comparable energies of 5f, 6d and 7s orbitals

Solution:

Concept:

- Oxidation states depend on the electrons available for participation in bonding.
- In actinoids, the 5f, 6d and 7s orbitals have comparable energies.

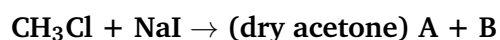
Step 1: Connect orbital energies to bonding Because the energies of these three subshells are close, different numbers of electrons from them can participate in bonding. Actinoids therefore exhibit a larger range of oxidation states, especially among the earlier members of the series.

Step 2: Test the proposed explanations Radioactivity concerns instability of the nucleus, whereas oxidation states describe electron loss or participation in chemical bonding. A large atomic number or atomic mass by itself does not explain the availability of different numbers of bonding electrons. The only option that identifies the relevant electronic reason is the comparable energy of the three subshells.

Step 3: Conclusion The cause is comparable energies of the 5f, 6d and 7s orbitals. Hence, the correct option is (D).

Quick Tip to Solve: For variable oxidation states, compare energies of bonding subshells rather than nuclear properties.

5. Consider the following reaction and identify A and B :



[1 mark]

- (A) A = CH₃I, B = NaCl
- (B) A = CH₃OH, B = NaCl
- (C) A = CH₃CHO, B = NaCl
- (D) A = C₂H₆, B = CH₃I

Correct Answer: (A) A = CH₃I, B = NaCl

Solution:

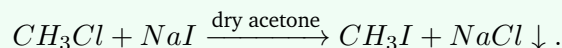
Concept:

- The Finkelstein reaction exchanges chlorine or bromine in an alkyl halide for iodine using sodium iodide in dry acetone.
- Sodium chloride is insoluble in acetone, so its precipitation drives the halogen exchange forward.

Step 1: Apply halide substitution Iodide replaces chloride in chloromethane without changing the

Quick Tip to Solve: Dry acetone with sodium iodide signals halogen exchange; keep the alkyl group unchanged.

methyl group. Thus



The organic product A is iodomethane, while the inorganic product B is sodium chloride.

Step 2: Check all proposed products Option (A) gives both products with the correct atom balance. Methanol in (B) would require replacement by hydroxide, which is absent. The aldehyde in (C) is not a halogen-exchange product. Formation of ethane in (D) would require coupling two methyl groups, as in a different reaction, and its proposed products do not match the sodium iodide substitution.

Step 3: Conclusion $A = CH_3I$ and $B = NaCl$. Hence, the correct option is (A).

Quick Tip to Solve: Dry acetone with sodium iodide signals halogen exchange; keep the alkyl group unchanged.

6. The correct formula of Hinsberg's reagent is :

[1 mark]

- (A) C_6H_5COCl
- (B) $C_6H_5SO_2Cl$
- (C) $C_6H_5CONHCH_3$
- (D) $C_6H_5CH_2NH_2$

Correct Answer: (B) $C_6H_5SO_2Cl$

Solution:

Concept:

- Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$.
- Its reaction with amines distinguishes primary, secondary and tertiary amines through sulphonamide formation and solubility behaviour.

Step 1: Identify the functional group The reagent contains a phenyl group attached to the sulphonyl chloride group $-SO_2Cl$. Its formula is therefore $C_6H_5SO_2Cl$. Primary and secondary amines can react at this sulphonyl group to form sulphonamides.

Step 2: Compare the other formulas C_6H_5COCl is benzoyl chloride, an acyl chloride rather than a sulphonyl chloride. $C_6H_5CONHCH_3$ is an amide, while $C_6H_5CH_2NH_2$ is benzylamine. These are different functional classes and are not the reagent used in the Hinsberg test.

Step 3: Conclusion Hinsberg's reagent is $C_6H_5SO_2Cl$. Hence, the correct option is (B).

Quick Tip to Solve: Identify Hinsberg reagent by the sulphur-containing group SO_2Cl attached to a phenyl ring.

7. Half-life ($t_{1/2}$) of a first order reaction is 1386 s. The value of rate constant is :

[1 mark]

(A) $0.5 \times 10^4 \text{ s}^{-1}$

(B) $5.0 \times 10^{-4} \text{ s}^{-1}$

(C) $0.5 \times 10^{-5} \text{ s}^{-1}$

(D) $0.5 \times 10^{-2} \text{ s}^{-1}$

Correct Answer: (B) $5.0 \times 10^{-4} \text{ s}^{-1}$

Solution:

Concept:

- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant.
- When half-life is measured in seconds, the first-order rate constant has unit s^{-1} .

Step 1: Substitute the half-life Rearrange the first-order half-life relation and substitute $t_{1/2} = 1386 \text{ s}$:

$$k = \frac{0.693}{1386 \text{ s}} = 0.000500 \text{ s}^{-1} = 5.0 \times 10^{-4} \text{ s}^{-1}.$$

Step 2: Check the alternatives and scale Multiplying the result by the given half-life gives $kt_{1/2} = 0.693$, as required. Printed option (A), $0.5 \times 10^4 \text{ s}^{-1}$, is much too large. Option (C) is $5 \times 10^{-6} \text{ s}^{-1}$, a hundred times too small, and option (D) is $5 \times 10^{-3} \text{ s}^{-1}$, ten times too large. Only option (B) has the correct magnitude and unit.

Step 3: Conclusion $k = 5.0 \times 10^{-4} \text{ s}^{-1}$. Hence, the correct option is (B).

Quick Tip to Solve: Use $1386 = 2 \text{ times } 693$ to evaluate $0.693/1386$ quickly as 0.0005 .

8. Which of the following ligands forms a chelate complex ?

[1 mark]

(A) Ammonia

(B) Water

(C) NO_2^-

(D) Oxalate ion

Correct Answer: (D) Oxalate ion

Solution:

Concept:

- A chelating ligand coordinates to the same metal ion through two or more donor atoms, forming a ring.
- Denticity counts the donor atoms attached simultaneously to one metal centre.

Step 1: Identify the multidentate ligand Oxalate, $\text{C}_2\text{O}_4^{2-}$, has two oxygen donor atoms that bind simultaneously to the same metal ion. The metal and ligand atoms form a ring, so oxalate acts as a bidentate chelating ligand.

Step 2: Eliminate the other ligands Ammonia and water bind through one nitrogen and one oxygen

Quick Tip to Solve: Distinguish ambidentate from bidentate: chelation needs simultaneous bonding through two donor atoms.

atom, respectively, and are monodentate. Nitrite, NO_2^- , is ambidentate: it may bind through nitrogen or oxygen, but normally uses only one of these donor sites at a time. Ambidentate does not mean bidentate, so nitrite does not form the chelate intended here.

Step 3: Conclusion Oxalate ion forms a chelate complex. Hence, the correct option is (D).

Quick Tip to Solve: Distinguish ambidentate from bidentate: chelation needs simultaneous bonding through two donor atoms.

9. Primary, secondary and tertiary alcohols can be distinguished by :

[1 mark]

- (A) Lucas test
- (B) Fehling's test
- (C) Tollens' test
- (D) Hinsberg's test

Correct Answer: (A) Lucas test

Solution:

Concept:

- Lucas reagent is concentrated HCl with anhydrous ZnCl_2 .
- Alcohols form insoluble alkyl chlorides; the time taken for turbidity distinguishes their classes.

Step 1: Apply the Lucas test At room temperature, a tertiary alcohol produces turbidity immediately, a secondary alcohol produces turbidity after a few minutes, and an ordinary primary alcohol does not produce turbidity at room temperature. These different reaction rates distinguish the three classes of alcohols.

Step 2: Check the alternatives Fehling's and Tollens' tests chiefly detect aldehydes through reduction of the reagent. Hinsberg's test distinguishes primary, secondary and tertiary amines using benzenesulphonyl chloride. None of these is the standard classification test for the three classes of alcohols.

Step 3: Conclusion The required test is the Lucas test. Hence, the correct option is (A).

Quick Tip to Solve: For Lucas reagent at room temperature, remember: tertiary immediate, secondary delayed, primary no turbidity.

10. Consider the following compounds :

$\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, NH_3 , $\text{C}_6\text{H}_5\text{NH}_2$

The correct increasing order of the above compounds on the basis of their basic strength is : [1 mark]

(A) $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$

(B) $\text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$

(C) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2$

(D) $\text{C}_2\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$

Correct Answer: (A) $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$

Solution:

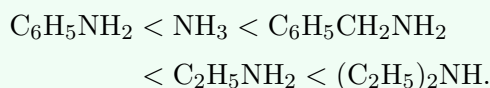
Concept:

- Basic strength depends on the availability of the nitrogen lone pair for accepting H^+ .
- Resonance, the inductive effect and solvation together determine the usual aqueous basicity order.

Step 1: Compare aniline, ammonia and benzylamine In aniline, $\text{C}_6\text{H}_5\text{NH}_2$, the nitrogen lone pair is delocalised into the benzene ring and is less available for protonation, making aniline weaker than ammonia. In benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, the intervening saturated CH_2 group prevents this direct resonance. Benzylamine is therefore stronger than ammonia.

Step 2: Compare the aliphatic amines and check the options Ethylamine has a stronger electron-releasing alkyl influence than benzylamine and is more basic. Diethylamine benefits from two ethyl groups and favourable solvation, making it stronger than ethylamine in the usual aqueous comparison. Thus aniline comes first and diethylamine last, with ammonia, benzylamine and ethylamine between them in that order. Option (B) wrongly places ammonia below aniline; (C) makes benzylamine the weakest; (D) makes ethylamine the weakest.

Step 3: Conclusion The increasing order is



Hence, the correct option is (A).

Quick Tip to Solve: First place aniline lowest because of resonance; then compare benzylamine and the ethylamines.

11. Identify the polysaccharide among the following :

[1 mark]

- (A) Fructose
- (B) Maltose
- (C) Glucose
- (D) Cellulose

Correct Answer: (D) Cellulose

Solution:

Concept:

- A monosaccharide is a single sugar unit; a disaccharide contains two monosaccharide units.
- A polysaccharide contains a large number of monosaccharide units joined by glycosidic bonds.

Step 1: Identify the polymeric carbohydrate Cellulose is a long-chain polysaccharide composed of many β -D-glucose units joined by $\beta(1 \rightarrow 4)$ glycosidic bonds. It serves as a structural component of plant cell walls.

Step 2: Classify the other choices Glucose and fructose are monosaccharides, so each is a single sugar unit. Maltose is a disaccharide consisting of two glucose units. Having two units does not make maltose a polysaccharide, which requires a large number of linked monosaccharide units.

Step 3: Conclusion Cellulose is the polysaccharide. Hence, the correct option is (D).

Quick Tip to Solve: Classify by number of sugar units: glucose and fructose one, maltose two, cellulose many.

12. The polypeptide chain in a protein has amino acids linked with each other in a specific sequence. This specific sequence of amino acids is called :

[1 mark]

- (A) Primary structure of protein
- (B) Secondary structure of protein
- (C) Tertiary structure of protein
- (D) Quaternary structure of protein

Correct Answer: (A) Primary structure of protein

Solution:

Concept:

- The primary structure of a protein is the specific sequence of amino acid residues in its polypeptide chain.
- Peptide bonds connect successive amino acids; higher structural levels describe folding or association.

Step 1: Match the wording to the structural level The question specifies the order in which amino acids are linked, rather than the shape of the chain. This exact amino acid sequence is the primary structure, conventionally described from the N-terminal end to the C-terminal end.

Step 2: Distinguish the other structures Secondary structure refers to local arrangements such as an α -helix or a β -pleated sheet. Tertiary structure is the overall three-dimensional folding of a

Quick Tip to Solve: When a question says sequence or order of amino acids, select primary structure.

polypeptide. Quaternary structure describes the arrangement of multiple polypeptide subunits. These levels do not name the amino acid sequence itself.

Step 3: Conclusion The specific sequence is the primary structure of protein. Hence, the correct option is (A).

Quick Tip to Solve: When a question says sequence or order of amino acids, select primary structure.

13. Assertion (A): D(+)-Glucose is dextrorotatory in nature.

Reason (R): (+) represents dextrorotatory nature and D represents the configuration.

[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 sign (+) denotes dextrorotation: rotation of plane-polarised light to the right.
- The prefix D denotes configuration relative to D-glyceraldehyde; it does not by itself specify the sign of optical rotation.

Step 1: Judge the assertion D(+)-glucose rotates plane-polarised light to the right. It is therefore dextrorotatory, and Assertion (A) is true.

Step 2: Judge the reason The (+) symbol indicates dextrorotatory behaviour, while D specifies the relative configuration. These are distinct kinds of information, so Reason (R) is also true. A D-configured substance need not always be dextrorotatory.

Step 3: Check the explanatory link The assertion names glucose explicitly as D(+)-glucose. The reason correctly explains that its (+) symbol indicates rightward optical rotation. Thus R explains the dextrorotatory nature stated in A. Option (B) incorrectly denies this link; (C) and (D) incorrectly declare a true statement false.

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

Quick Tip to Solve: Read D as configuration and the plus sign as rotation; use the plus sign to establish dextrorotation.

14. Assertion (A): Highest oxidation state of Mn is +7 in first series of transition elements.

Reason (R): Transition metals exhibit variable oxidation states.

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

Solution:

Concept:

- Manganese has electronic configuration $[\text{Ar}]3d^54s^2$, allowing a maximum oxidation state of +7.
- Transition metals show variable oxidation states because their outer s and inner d electrons can participate in bonding.

Step 1: Judge the assertion Manganese reaches oxidation state +7, for example in MnO_4^- : if the oxidation state of Mn is x , then $x + 4(-2) = -1$, giving $x = +7$. This is the highest oxidation state in the first transition series, so Assertion (A) is true.

Step 2: Judge the reason Transition metals commonly exhibit several oxidation states because electrons from both the outer s and the nearby d subshell may participate in bonding. Hence Reason (R) is true.

Step 3: Check whether the reason explains the maximum The general statement about variable oxidation states does not explain why Mn specifically reaches +7. The specific maximum follows from its five 3d and two 4s electrons being available for bonding. Thus R does not correctly explain A; option (A) overstates the explanatory link, whereas (C) and (D) wrongly label one statement false.

Step 4: Conclusion Both A and R are true, but R is not the correct explanation of A. Hence, the correct option is (B).

Quick Tip to Solve: A general statement about variable oxidation states does not explain the specific maximum of manganese.

15. Assertion (A): *p*-nitrophenol is more acidic than phenol.

Reason (R): Nitro group is an electron-withdrawing group, it stabilises phenoxide ion by dispersal of negative charge. [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:

- An acid is stronger when its conjugate base is more stable. Phenol loses H^+ to form the phenoxide ion.
- The para nitro group has electron-withdrawing inductive and resonance effects; these disperse negative charge in the conjugate base.

Step 1: Judge Assertion (A) Phenol and *p*-nitrophenol both undergo acid dissociation. The conjugate base of *p*-nitrophenol has additional stabilisation because the para NO_2 group withdraws electron density. Loss of a proton is therefore favoured more strongly than in phenol, so Assertion (A) is true.

Step 2: Judge Reason (R) The nitro group is electron withdrawing. At the para position its resonance effect allows the negative charge of the phenoxide system to be dispersed towards the nitro group. This lowers the energy of the conjugate base, so Reason (R) is true.

Step 3: Check the explanatory connection The stabilisation described in Reason (R) is precisely why *p*-nitrophenol is more acidic. Thus the reason directly explains the assertion. Option (B) misses this connection; (C) and (D) wrongly declare one of the two true statements false.

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

Quick Tip to Solve: For phenol acidity comparisons, compare the stability of the phenoxide ions after removal of H^+ .

16. Assertion (A): All aliphatic aldehydes give a positive Fehling's test.

Reason (R): Aliphatic aldehydes are reduced by Fehling's reagent.

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

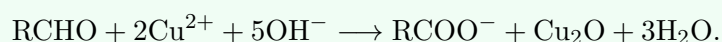
Solution:

Concept:

- Fehling's reagent contains complexed copper(II) ions in alkaline solution. A positive test produces a brick-red precipitate of Cu_2O .
- In this reaction the aldehyde is oxidised to a carboxylate ion, while copper(II) is reduced to copper(I).

Step 1: Judge Assertion (A) Aliphatic aldehydes reduce Fehling's reagent on warming, producing the characteristic brick-red copper(I) oxide precipitate. This is the positive Fehling's test stated in the question. Assertion (A) is therefore true.

Step 2: Judge Reason (R) Reason (R) reverses the direction of the change in the aldehyde. The aldehyde is oxidised, not reduced, by Fehling's reagent. An illustrative balanced ionic equation is



Copper is reduced from oxidation state +2 to +1. Hence Reason (R) is false.

Step 3: Choose the matching option Because A is true and R is false, only option (C) matches. Options (A) and (B) incorrectly treat R as true, and option (D) incorrectly treats A as false. The observed precipitate belongs to the reduced copper product, not to a reduced aldehyde.

Step 4: Conclusion The assertion is true, but the reason is false. Hence, the correct option is (C).

Quick Tip to Solve: In Fehling's test, remember the pair: aldehyde is oxidised and Cu^{2+} is reduced.

Section B (10 marks)

17(a). 1.00 molal aqueous solution of trichloroacetic acid is heated to its boiling point. Boiling point of this solution was found to be 100.18°C . Calculate the van't Hoff factor for trichloroacetic acid.

(Given : K_b for water = $0.512 \text{ K kg mol}^{-1}$)

[2 marks]

Solution:

Concept:

- The elevation in boiling point is $\Delta T_b = T_b(\text{solution}) - T_b(\text{pure solvent})$. A temperature difference has the same numerical value in kelvin and degrees Celsius.

Quick Tip to Solve: Subtract 100.00°C first, then divide the elevation by $K_b m$; i has no units.

- For a solution with van't Hoff factor i , $\Delta T_b = iK_b m$, where K_b is the ebullioscopic constant and m is molality.

Step 1: Find the boiling-point elevation The boiling point of pure water is 100.00°C , while the stated solution boils at 100.18°C . Thus

$$\Delta T_b = 100.18 - 100.00 = 0.18 \text{ K}.$$

Use this elevation in the colligative-property formula, rather than the absolute boiling point.

Step 2: Substitute the given molality and constant Rearranging the equation gives

$$i = \frac{\Delta T_b}{K_b m} = \frac{0.18 \text{ K}}{(0.512 \text{ K kg mol}^{-1})(1.00 \text{ mol kg}^{-1})} = 0.3515625.$$

The units cancel, as required for the dimensionless van't Hoff factor. The numerical factor here is obtained directly from the measured elevation and the printed values; it must not be replaced by an expected dissociation value.

Step 3: Conclusion The van't Hoff factor calculated from the given data is $i \approx 0.352$.

Quick Tip to Solve: Subtract 100.00°C first, then divide the elevation by $K_b m$; i has no units.

OR

17(b). State Henry's law. Calculate the mole fraction of CO_2 in water at 298 K under 760 mm Hg.
(Given : K_H for CO_2 in H_2O at 298 K = 1.25×10^6 mm Hg) [2 marks]

Solution:

Concept:

- Henry's law relates the partial pressure p of a gas above a solution to its mole fraction x in the liquid at a fixed temperature: $p = K_H x$.
- The Henry's law constant K_H and gas pressure must be expressed in the same pressure unit. Mole fraction is dimensionless.

Step 1: State Henry's law At constant temperature, the partial pressure of a gas in equilibrium with a solution is directly proportional to the mole fraction of that gas in the solution. Mathematically,

$$p = K_H x.$$

Here p is the pressure of carbon dioxide, x is its mole fraction in water, and K_H is the Henry's law constant for this gas-solvent pair at 298 K.

Step 2: Calculate the dissolved carbon dioxide mole fraction The pressure and the constant are both given in mm Hg, so no pressure conversion is needed. Rearranging Henry's law and substituting,

$$x_{\text{CO}_2} = \frac{p}{K_H} = \frac{760 \text{ mm Hg}}{1.25 \times 10^6 \text{ mm Hg}} = 6.08 \times 10^{-4}.$$

Quick Tip to Solve: When p and K_H are both in mm Hg, use their ratio directly; do not convert only one to atm.

The pressure units cancel. This small value is the fraction of all molecules in the liquid solution that are carbon dioxide molecules.

Step 3: Conclusion Henry's law is $p = K_H x$ at constant temperature, and $x_{\text{CO}_2} = 6.08 \times 10^{-4}$.

Quick Tip to Solve: When p and K_H are both in mm Hg, use their ratio directly; do not convert only one to atm.

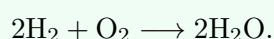
18. (a) Name the cell which was used in the Apollo space programme for providing electrical power.
(b) Define limiting molar conductivity. [2 marks]

Solution:

Concept:

- A fuel cell converts the chemical energy of continuously supplied reactants into electrical energy through separate electrode reactions.
- Molar conductivity Λ_m measures conductivity per molar concentration. Its limiting value Λ_m° is reached as concentration tends to zero.

Step 1: (a) Identify the Apollo power cell The Apollo space programme used the hydrogen-oxygen fuel cell for electrical power. Hydrogen acts as the fuel and oxygen as the oxidant. Their overall reaction is



The electrode reactions transfer electrons through the external circuit, producing electrical energy. The water formed was also useful to the astronauts. Thus the required cell is the hydrogen-oxygen fuel cell.

Step 2: (b) Define limiting molar conductivity Limiting molar conductivity is the molar conductivity of an electrolyte at infinite dilution, when its concentration approaches zero. It is denoted by Λ_m° :

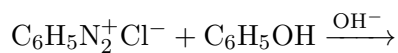
$$\Lambda_m^\circ = \lim_{c \rightarrow 0} \Lambda_m.$$

At this limit interionic interactions become negligible and the ions contribute independently to conduction. A commonly used unit is $\text{S cm}^2 \text{mol}^{-1}$. It is a limiting conductivity per mole, rather than the conductivity of an empty solvent sample.

Step 3: Conclusion (a) Hydrogen-oxygen fuel cell. (b) Limiting molar conductivity is the molar conductivity of an electrolyte at infinite dilution, denoted by Λ_m° .

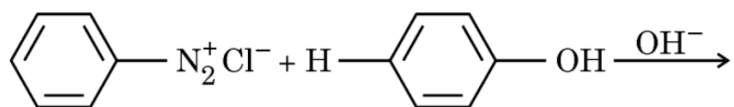
Quick Tip to Solve: Link Apollo to H_2/O_2 fuel cells; in the conductivity definition always state infinite dilution.

19. (a) Complete the following equation :



(b) How will you convert nitromethane to methyl isocyanide ?

[2 marks]

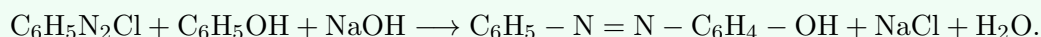


Solution:

Concept:

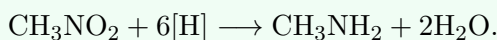
- Diazonium salts couple with phenols in alkaline medium to form coloured azo compounds containing the $-\text{N}=\text{N}-$ group.
- Reduction converts a nitro compound into a primary amine. Primary amines give isocyanides with chloroform and alcoholic potassium hydroxide (carbylamine reaction).

Step 1: (a) Couple the diazonium salt with phenol The phenol ring is activated in alkaline medium. Coupling occurs mainly at the para position relative to its hydroxyl group, producing *p*-hydroxyazobenzene, an orange azo dye. A balanced molecular equation is

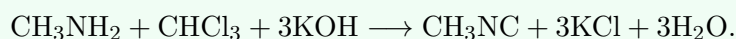


The azo group and $-\text{OH}$ occupy para positions on the second benzene ring.

Step 2: (b) Convert nitromethane through methylamine First reduce nitromethane with Sn/HCl , then add alkali to liberate methylamine:



Heat the methylamine with chloroform and alcoholic KOH:



The carbon of the isocyanide group is supplied by chloroform; the methyl group remains attached to nitrogen.

Step 3: Conclusion (a) The product is *p*-hydroxyazobenzene, $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{OH}$. (b) $\text{CH}_3\text{NO}_2 \xrightarrow{\text{Sn}/\text{HCl}} \text{CH}_3\text{NH}_2 \xrightarrow[\Delta]{\text{CHCl}_3, \text{ alcoholic KOH}} \text{CH}_3\text{NC}$, with alkali work-up after reduction.

Quick Tip to Solve: Reduce the nitro group to a primary amine first; only then apply the carbylamine reaction to obtain the isocyanide.

20. (a) What are the products obtained on hydrolysis of sucrose ?

(b) What are essential amino acids ?

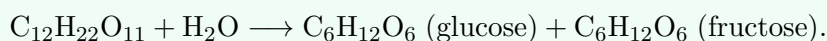
[2 marks]

Solution:

Concept:

- Hydrolysis breaks the glycosidic linkage of a disaccharide by addition of water, giving its constituent monosaccharides.
- An essential amino acid must be supplied in the diet because the human body cannot synthesise it in sufficient amounts.

Step 1: (a) Hydrolyse sucrose Sucrose contains one glucose unit and one fructose unit joined through their anomeric carbons. On hydrolysis with dilute acid, or the enzyme invertase, its glycosidic linkage breaks:



Thus one mole of sucrose gives one mole each of D-glucose and D-fructose. The products are monosaccharides, rather than two molecules of the same sugar.

Step 2: (b) Define essential amino acids Essential amino acids are amino acids that the human body cannot synthesise in adequate quantities and must therefore obtain from food. For example, valine and lysine are essential amino acids. They are required for protein synthesis, but the word essential refers specifically to their dietary requirement; it does not mean that other amino acids have no biological importance.

Step 3: Conclusion (a) Hydrolysis of sucrose gives an equimolar mixture of D-glucose and D-fructose. (b) Essential amino acids must be obtained from the diet because the body cannot make sufficient amounts of them.

Quick Tip to Solve: For sucrose remember glucose plus fructose; for essential amino acids state the dietary requirement, not merely their importance.

21. (a) Write any two fat soluble vitamins.

(b) How will you confirm the presence of five -OH groups in a glucose molecule, which are attached to different carbon atoms ?

[2 marks]

Solution:

Concept:

- Fat-soluble vitamins dissolve in fats and oils; vitamins A, D, E and K belong to this group.
- Acetylation converts each free hydroxyl group –OH into an acetate ester –OCOCH₃. The number of acetyl groups introduced counts the hydroxyl groups.

Step 1: (a) Name two fat-soluble vitamins Vitamins A and D are two fat-soluble vitamins. Either E or K is also an acceptable example from the same group. In contrast, vitamins B and C are water-soluble, so they are not suitable answers to this part.

Step 2: (b) Use acetylation of glucose Treat glucose with acetic anhydride. It forms glucose

Quick Tip to Solve: Use the prefix penta- to count five hydroxyl groups, and mention product stability to justify their attachment to different carbons.

pentaacetate, containing five acetate ester groups:



Formation of the pentaacetate establishes the presence of five hydroxyl groups, since each hydroxyl group is acetylated once. Glucose pentaacetate is a stable compound. Its stability supports the inference that these hydroxyl groups are attached to different carbon atoms: structures having two hydroxyl groups on the same carbon (geminal diols) are generally unstable in this context. Thus acetylation and the stability of its product supply the required evidence.

Step 3: Conclusion (a) Vitamins A and D. (b) Glucose forms a stable pentaacetate with acetic anhydride, confirming five hydroxyl groups attached to different carbon atoms.

Quick Tip to Solve: Use the prefix penta- to count five hydroxyl groups, and mention product stability to justify their attachment to different carbons.

Section C (21 marks)

22. Calculate emf of the following cell at 298 K :



(Given : $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$, $[\log 10 = 1]$)

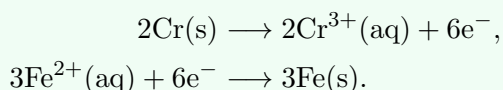
[3 marks]

Solution:

Concept:

- For a galvanic cell, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify and balance the electrode reactions The iron reduction potential, -0.44 V , is more positive than that of chromium, -0.74 V . Hence chromium is oxidised at the anode and iron ions are reduced at the cathode:



Adding gives $2\text{Cr(s)} + 3\text{Fe}^{2+}(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Fe(s)}$. Therefore $n = 6$; it is neither 2 nor 3 because the electrons must cancel in the balanced overall reaction.

Step 2: Calculate the standard emf and reaction quotient The standard cell potential is

$$E^\circ_{\text{cell}} = (-0.44) - (-0.74) = 0.30 \text{ V}.$$

Electrode potentials are intensive quantities and are not multiplied by stoichiometric coefficients. Omitting the pure metals from the quotient and using the given molar concentrations,

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} = \frac{(0.1)^2}{(0.01)^3} = 10^4.$$

Quick Tip to Solve: Balance the chromium and iron half-reactions first: six electrons fix the Nernst denominator, while coefficients 2 and 3 fix the powers in Q .

Thus $\log Q = 4$, since $\log 10 = 1$.

Step 3: Apply the Nernst equation Substituting the balanced electron count and reaction quotient,

$$\begin{aligned}E_{\text{cell}} &= 0.30 - \frac{0.0591}{6} \log(10^4) \\&= 0.30 - \frac{0.0591 \times 4}{6} \\&= 0.30 - 0.0394 = 0.2606 \text{ V}.\end{aligned}$$

Since $Q > 1$, the concentration correction lowers the potential below its standard value; the positive result is consistent with the stated galvanic direction.

Step 4: Conclusion The emf of the cell at 298 K is $E_{\text{cell}} = 0.2606 \text{ V} \approx 0.261 \text{ V}$.

Quick Tip to Solve: Balance the chromium and iron half-reactions first: six electrons fix the Nernst denominator, while coefficients 2 and 3 fix the powers in Q .

23. (a) Define order of a reaction.

(b) The rate for the following reaction is given by : $A + B \rightarrow C$, $\text{Rate} = k[A][B]^2$

(i) How is the rate of reaction affected if we double the concentration of B ?

(ii) Write the overall order of a reaction if 'A' is present in large excess.

[3 marks]

Solution:

Concept:

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- For $r = k[A]^m[B]^n$, the order with respect to A is m , with respect to B is n , and the overall order is $m + n$.
- A reactant present in large excess has an effectively constant concentration during the reaction; its factor can be included in an observed rate constant.

Step 1: Define order of reaction For part (a), order refers to the exponents in the experimentally established rate expression. It need not equal the sum of the stoichiometric coefficients in the balanced chemical equation. Here the given law is $r = k[A][B]^2$, so its individual orders are 1 in A and 2 in B; when both concentrations vary appreciably, the overall order is $1 + 2 = 3$.

Step 2: Double the concentration of B For part (b)(i), keep the temperature and concentration of A unchanged. Let the initial rate be $r = k[A][B]^2$. On doubling B,

$$r' = k[A](2[B])^2 = 4k[A][B]^2 = 4r.$$

Thus the rate becomes four times its initial value. The square on B makes the factor 4, although its stoichiometric coefficient is 1.

Step 3: Treat A as a reactant in large excess For part (b)(ii), the fractional change in $[A]$ is negligible

Quick Tip to Solve: Raise the concentration-change factor to its rate-law exponent; absorb an excess reactant into the observed rate constant.

when A is in large excess. Put $k' = k[A]$, which is effectively constant under these conditions. Then

$$r = k'[B]^2.$$

The measurable rate depends on the square of the changing concentration of B, giving an observed or pseudo-second-order reaction. The original full rate law remains third order; it is the effective order under excess-A conditions that is 2.

Step 4: Conclusion (a) Order is the sum of concentration exponents in the rate law. (b)(i) The rate becomes $4r$. (b)(ii) The observed overall order is $\boxed{2}$ (pseudo-second order).

Quick Tip to Solve: Raise the concentration-change factor to its rate-law exponent; absorb an excess reactant into the observed rate constant.

24. The rate of the chemical reaction doubles when the temperature is raised from 298 K to 308 K. Calculate activation energy (E_a) for this reaction assuming that it does not change with temperature. (Given : $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $\log 2 = 0.30$) [3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, R is the gas constant and T is absolute temperature.
- For the same reaction and fixed concentrations, the rate ratio equals k_2/k_1 . The two-temperature form is $\log(k_2/k_1) = E_a(1/T_1 - 1/T_2)/(2.303R)$.

Step 1: Use the temperature and rate ratio The temperature increases from $T_1 = 298 \text{ K}$ to $T_2 = 308 \text{ K}$, and the rate doubles. Therefore $k_2/k_1 = 2$, with the concentrations held fixed. Taking common logarithms of the Arrhenius equations at the two temperatures and subtracting eliminates the pre-exponential factor A:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

The reciprocal-temperature difference is positive because the hotter temperature is in the second denominator.

Step 2: Rearrange and substitute the supplied values Solving for activation energy gives

$$\begin{aligned} E_a &= \frac{2.303R \log(k_2/k_1) T_1 T_2}{T_2 - T_1} \\ &= \frac{2.303(8.314)(0.30)(298)(308)}{308 - 298} \text{ J mol}^{-1} \\ &= 52722.0 \text{ J mol}^{-1}. \end{aligned}$$

Here the supplied value $\log 2 = 0.30$ is used directly. The temperatures must be in kelvin; their product is 91784 K^2 , and their difference is 10 K .

Step 3: Convert to the usual activation-energy unit Dividing the energy in joules per mole by 1000

Quick Tip to Solve: For a rate-doubling calculation use the given $\log 2$, and combine the reciprocal temperatures as $(T_2 - T_1)/(T_1 T_2)$.

gives $E_a = 52.7220 \text{ kJ mol}^{-1}$, or approximately 52.7 kJ mol^{-1} . Its positive sign is consistent with a larger rate constant at higher temperature: the Boltzmann factor increases as $E_a/(RT)$ decreases.

Step 4: Conclusion

$$E_a \approx 5.27 \times 10^4 \text{ J mol}^{-1} = 52.7 \text{ kJ mol}^{-1}$$

Quick Tip to Solve: For a rate-doubling calculation use the given $\log 2$, and combine the reciprocal temperatures as $(T_2 - T_1)/(T_1 T_2)$.

25(a). Write the IUPAC name of the following complex : $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$

[1 mark]

Solution:

Concept:

- Oxalato, $\text{C}_2\text{O}_4^{2-}$, is a bidentate ligand with charge -2 .
- Name the cation before the complex anion; an anionic chromium complex uses the metal name chromate with its oxidation state.

Step 1: Determine the oxidation state Three potassium ions require the complex ion to have charge -3 . If chromium has oxidation state x , then $x + 3(-2) = -3$, so $x = +3$. The six donor atoms arise from three bidentate ligands, not six separate oxalato ligands.

Step 2: Assemble the coordination name The three oxalato ligands are named tris(oxalato), followed by chromate(III) for the anionic coordination entity. Potassium is named first as the counter-cation. The ligand count determines the prefix tris; the oxidation-state numeral describes chromium.

Step 3: Conclusion The IUPAC name is potassium tris(oxalato)chromate(III).

Quick Tip to Solve: Count oxalato ligands, then use their -2 charge to find chromium(III); the anion requires chromate.

25(b). Differentiate between homoleptic complex and heterolyptic complex.

[1 mark]

Solution:

Concept:

- Ligands are ions or molecules bonded directly to the central metal through donor atoms.
- The homoleptic or heteroleptic classification counts different kinds of coordinated ligands, not their total number.

Step 1: State the homoleptic criterion A homoleptic complex contains only one kind of ligand attached to the central metal. For example, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is homoleptic because all six coordinated ligands are ammonia. Multiple identical ligands still represent one ligand type.

Step 2: State the heteroleptic criterion A heteroleptic complex contains more than one kind of ligand attached to the central metal. For example, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has both ammonia and chlorido ligands

Quick Tip to Solve: Look only inside the coordination brackets and count ligand types, not the number of ligand molecules.

and is heteroleptic. Counter-ions outside the coordination sphere do not enter this classification.

Step 3: Conclusion Homoleptic: one kind of coordinated ligand. Heteroleptic (called heterolyptic in the question): two or more kinds of coordinated ligands.

Quick Tip to Solve: Look only inside the coordination brackets and count ligand types, not the number of ligand molecules.

25(c). Which type of isomerism is exhibited by the following complex : $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

[1 mark]

Solution:

Concept:

- Platinum(II) forms a square-planar complex in $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.
- Geometrical isomerism arises when the same ligands occupy different relative positions around the metal.

Step 1: Identify the coordination arrangement Ammonia is neutral and each chlorido ligand has charge -1 . The neutral complex therefore contains platinum in the $+2$ oxidation state. Its four ligands occupy a square-planar arrangement, allowing two distinct relative positions for the identical ligand pairs.

Step 2: Compare the two possible configurations In the cis isomer the two chlorido ligands are adjacent, at 90° to each other. In the trans isomer they are opposite, at 180° . These arrangements have the same formula and metal-ligand connectivity but differ in spatial geometry; hence they are geometrical isomers.

Step 3: Conclusion $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ exhibits geometrical (cis-trans) isomerism.

Quick Tip to Solve: A square-planar complex with two identical pairs of ligands has adjacent cis and opposite trans arrangements.

26(a). A coordination compound $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is mixed with excess of AgNO_3 solution, two moles of AgCl are precipitated per mole of the compound. Write the structural formula of the coordination compound.

[1 mark]

Solution:

Concept:

- Only ionisable chloride ions outside the coordination sphere react with excess AgNO_3 to give AgCl . Chromium(III) has coordination number six in these hydrated complexes.

Step 1: Count the outside chloride ions Two moles of AgCl per mole of compound show that two of its three chloride ions are outside the coordination sphere. The remaining chloride ion acts as a ligand bonded to chromium.

Step 2: Complete the coordination sphere The six ligand positions are occupied by one chloride and five water molecules. Of the six waters in the formula, the sixth is water of crystallisation outside the

Quick Tip to Solve: Use the moles of AgCl to count external chlorides first, then fill six ligand positions.

sphere. The complex ion has charge +2, balanced by the two external chloride ions.

Step 3: Conclusion The structural formula is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Quick Tip to Solve: Use the moles of AgCl to count external chlorides first, then fill six ligand positions.

26(b). Write the oxidation state and hybridisation of the central metal in the following complex : $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ [Atomic number of Fe = 26] [1 mark]

Solution:

Concept:

- Water is a neutral ligand. Weak-field ligands give a high-spin complex; octahedral outer-orbital complexes use sp^3d^2 hybridisation.

Step 1: Determine the oxidation state Let the oxidation state of iron be x . Since each of the six water ligands has zero charge, $x + 6(0) = +3$, so iron is in the +3 oxidation state. Neutral Fe is $[\text{Ar}]3d^64s^2$, giving $\text{Fe}^{3+} : [\text{Ar}]3d^5$.

Step 2: Determine the hybridisation Water is a weak-field ligand and does not pair the five electrons in the 3d orbitals. No pair of vacant inner 3d orbitals is available. One 4s, three 4p and two 4d orbitals form six sp^3d^2 hybrid orbitals directed octahedrally.

Step 3: Conclusion The central iron has oxidation state $+3$ and hybridisation sp^3d^2 .

Quick Tip to Solve: For Fe(III), start with the half-filled d5 configuration before checking ligand strength.

26(c). Why is $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ coloured ? [Atomic number of Ni = 28] [1 mark]

Solution:

Concept:

- In an octahedral ligand field, the metal d orbitals split into lower-energy t_{2g} and higher-energy e_g sets. Absorption of visible light can cause a $d-d$ transition.

Step 1: Find the d-electron configuration Nickel has atomic number 28 and configuration $[\text{Ar}]3d^84s^2$. Removal of two 4s electrons gives $\text{Ni}^{2+} : [\text{Ar}]3d^8$, so the complex contains partially filled d orbitals.

Step 2: Explain the absorption of light The six water ligands split the d orbitals. Electrons absorb light of an appropriate visible wavelength and move from lower to higher energy d levels. The remaining transmitted or reflected light gives the observed complementary colour.

Step 3: Conclusion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is coloured because its d^8 metal ion undergoes $d-d$ transitions by absorbing visible light.

Quick Tip to Solve: Check the metal ion configuration: partially filled d orbitals permit visible d-d absorption.

27. How do you convert the following ?

(a) Acetophenone to Benzoic acid

(b) Acetonitrile to Acetone

(c) Benzoic acid to Benzene

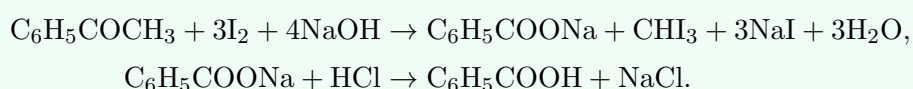
[3 marks]

Solution:

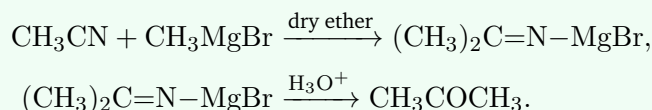
Concept:

- Methyl ketones undergo the haloform reaction to form a carboxylate with one fewer carbon. Acidification gives the carboxylic acid.
- A nitrile reacts with one equivalent of a Grignard reagent in dry ether; hydrolysis of the intermediate gives a ketone. Sodium carboxylates undergo soda-lime decarboxylation.

Step 1: Convert acetophenone to benzoic acid Treat acetophenone with iodine and aqueous sodium hydroxide, then acidify the sodium benzoate formed. The methyl group is removed as iodoform:

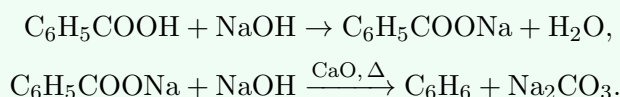


Step 2: Convert acetonitrile to acetone React acetonitrile with methylmagnesium bromide in dry ether. Addition to the nitrile gives an imine magnesium salt; acidic hydrolysis replaces its nitrogen group by oxygen:



Dry ether is needed because water would destroy the Grignard reagent before its addition.

Step 3: Convert benzoic acid to benzene First neutralise benzoic acid with sodium hydroxide to obtain sodium benzoate. Heat the dry salt with soda lime, a mixture of NaOH and CaO:



The carboxyl carbon is removed and replaced by hydrogen.

Step 4: Conclusion The required routes are haloform reaction followed by acidification; CH_3MgBr addition followed by hydrolysis; and sodium salt formation followed by soda-lime decarboxylation, respectively.

Quick Tip to Solve: Count carbons: haloform removes the methyl carbon, Grignard adds one, and soda lime removes COOH .

28(a). (i) Arrange the following compounds in increasing order of their acidic strengths : $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-COOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$

(ii) Why is CH_3CHO more reactive than acetone towards reaction with HCN ?

(iii) Complete the equation : $(\text{CH}_3)(\text{H})\text{C}=\text{O} + \text{NH}_2\text{-NH}_2 \rightarrow (\text{H}^+)$

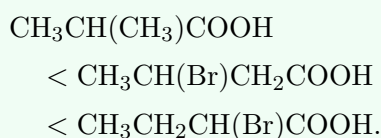
[3 marks]

Solution:

Concept:

- An electron-withdrawing group stabilises a carboxylate ion by its $-I$ effect and increases acidity; this effect falls with distance. Alkyl groups show a $+I$ effect.
- Carbonyl nucleophilic addition is favoured by a more electrophilic and less crowded carbonyl carbon. Hydrazine condenses with an aldehyde to form a hydrazone and water.

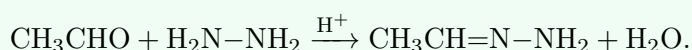
Step 1: Arrange the acids in increasing strength The branched alkyl acid has electron-donating methyl groups and no electron-withdrawing bromine. Bromine stabilises the carboxylate, with the stronger effect when located on the carbon adjacent to COOH . Thus



The second compound has bromine at the beta position, whereas the third has it at the alpha position.

Step 2: Compare ethanal and acetone towards HCN The nucleophile CN^- attacks the carbonyl carbon. Ethanal has one methyl group and one hydrogen, while acetone has two methyl groups. The two methyl groups in acetone donate more electron density by the $+I$ effect, reducing the positive character of its carbonyl carbon. They also create greater steric hindrance to the attacking nucleophile. Ethanal is therefore more reactive for both electronic and steric reasons.

Step 3: Complete the hydrazine reaction In the presence of acid, the carbonyl compound condenses with hydrazine. The oxygen is removed as water and the carbon forms a double bond to nitrogen:



The organic product is ethanal hydrazone; the carbon retains its original methyl and hydrogen substituents.

Step 4: Conclusion (i) Branched alkyl acid $<$ beta-bromo acid $<$ alpha-bromo acid. (ii) Ethanal is less hindered and more electrophilic. (iii) The product is $\text{CH}_3\text{CH=N-NH}_2$, with water.

Quick Tip to Solve: For acidity compare the position of Br; for HCN compare both crowding and alkyl electron donation.

28(b). An organic compound with the molecular formula C_8H_8O forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation it gives Benzene-1,2-dicarboxylic acid. Identify the compound and write the reactions of the compound with 2,4-DNP and when it undergoes Cannizzaro reaction. [3 marks]

Solution:

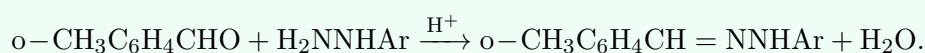
Concept:

- A 2,4-dinitrophenylhydrazine (2,4-DNP) derivative establishes a carbonyl group. Reduction of Tollens' reagent identifies an aldehyde in this problem.
- An aldehyde without an α -hydrogen undergoes Cannizzaro disproportionation: one molecule is oxidised to carboxylate and another is reduced to alcohol.
- Vigorous oxidation converts both an aromatic methyl group and an aldehyde group into carboxyl groups; their relative positions on the ring are preserved.

Step 1: Identify the functional group The formula is C_8H_8O . The positive 2,4-DNP test requires a carbonyl group, while the positive Tollens test selects an aldehyde rather than an ordinary ketone. A methyl-substituted benzaldehyde fits the formula: $CH_3C_6H_4CHO$. Its aldehydic carbon is attached directly to an aromatic ring, so it has no enolisable α -hydrogen and can undergo Cannizzaro reaction.

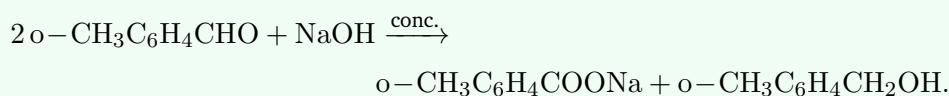
Step 2: Locate the methyl group Vigorous oxidation gives benzene-1,2-dicarboxylic acid (phthalic acid). Therefore the methyl and aldehyde groups must occupy adjacent positions. The compound is 2-methylbenzaldehyde, also called *o*-tolualdehyde. Oxidation of its $-CH_3$ and $-CHO$ groups produces the two adjacent $-COOH$ groups.

Step 3: Reaction with 2,4-DNP The carbonyl oxygen is replaced by the hydrazone linkage in an acid-catalysed condensation. With $Ar = C_6H_3(NO_2)_2$, where the nitro groups are at positions 2 and 4 relative to the hydrazine group,



The product is the 2,4-dinitrophenylhydrazone of 2-methylbenzaldehyde.

Step 4: Cannizzaro reaction Concentrated aqueous alkali causes disproportionation:



The products are sodium 2-methylbenzoate and 2-methylbenzyl alcohol. The ring methyl group remains unchanged in this reaction.

Step 5: Conclusion The compound is 2-methylbenzaldehyde (*o*-tolualdehyde); its 2,4-DNP and Cannizzaro reactions are given above.

Quick Tip to Solve: Use the positions of the two carboxyl groups after oxidation to locate the original methyl and aldehyde groups.

Section D (8 marks)

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

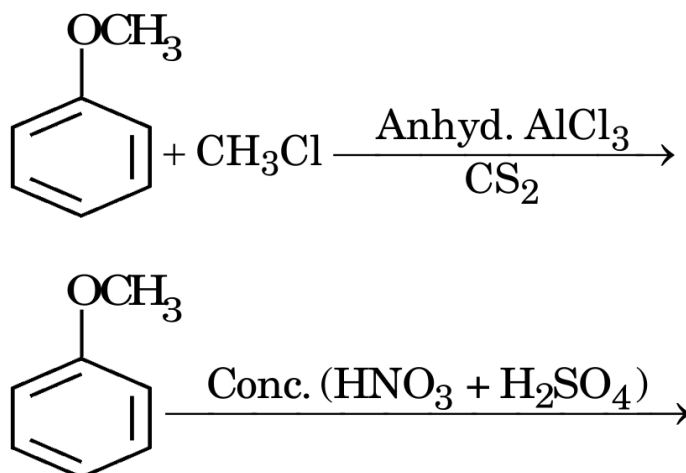
29(a). Case Study: Ethers are prepared by the dehydration of alcohols in presence of protic acids at 413 K. Symmetrical and unsymmetrical ethers can also be prepared by Williamson synthesis. This reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide. If a tertiary alkyl halide is used, elimination reaction occurs and an alkene is formed, no ether is formed. C-O bond in ethers are cleaved under drastic conditions with excess of HI. When unsymmetrical ethers react with HI, the alkyl halide is formed from smaller alkyl group. If one of the alkyl group is tertiary, the alkyl halide is formed from the tertiary alkyl group because tertiary alkyl carbocation is more stable than the primary carbocation. Cleavage of alkyl aryl ethers takes place at the alkyl-oxygen bond due to more stable aryl-oxygen bond. The order of reactivity of hydrogen halides is $HI > HBr > HCl$. Aromatic ethers undergo electrophilic substitution reactions. The alkoxy group attached to the aromatic ring activates the ring towards electrophilic substitution and directs the incoming group to ortho- and para-positions.

Answer the following questions :

Complete the following equations :



[2 marks]



Solution:

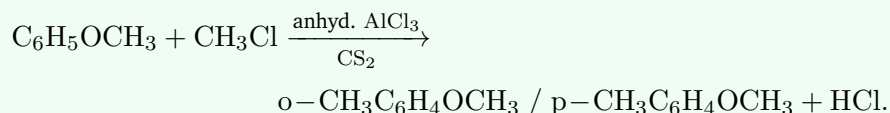
Concept:

- The $-OCH_3$ group donates electron density to the aromatic ring by resonance and directs electrophilic substitution to the ortho and para positions.
- Friedel-Crafts alkylation introduces a methyl group; nitration introduces a nitro group. Para substitution is usually favoured because it has less steric crowding.

Step 1: Complete the Friedel-Crafts reaction Anisole reacts with methyl chloride in anhydrous $AlCl_3$,

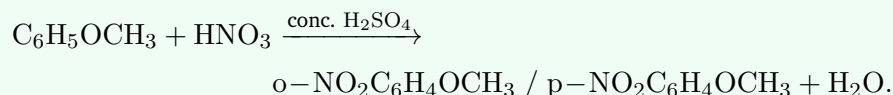
Quick Tip to Solve: Keep the methoxy group fixed at carbon 1 and put the incoming methyl or nitro group at carbon 2 or carbon 4.

with CS₂ as solvent. The products are 2-methylanisole and 4-methylanisole (the para isomer is major):



The slash indicates alternative products in the mixture; each substitution releases one molecule of hydrogen chloride.

Step 2: Complete the nitration reaction The concentrated nitric acid–sulphuric acid mixture provides the nitronium electrophile. Substitution occurs at the activated ortho and para positions:



These products are 2-nitroanisole and 4-nitroanisole, with the para isomer major. The methoxy group remains attached to the ring in both reactions.

Step 3: Conclusion (i) *o*- and *p*-methylanisole; (ii) *o*- and *p*-nitroanisole. The para isomer is the major product in each case.

Quick Tip to Solve: Keep the methoxy group fixed at carbon 1 and put the incoming methyl or nitro group at carbon 2 or carbon 4.

29(b). Write the names of alkyl halide and sodium alkoxide used to prepare tert-butyl ethyl ether.

[1 mark]

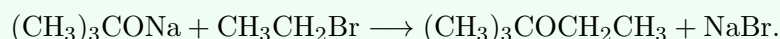
Solution:

Concept:

- Williamson ether synthesis is an S_N2 reaction of an alkoxide with a primary alkyl halide.
- Use the less hindered ethyl group as the halide and the tertiary group as the alkoxide to avoid elimination.

Step 1: Choose the alkyl halide Choose ethyl bromide (bromoethane), CH₃CH₂Br. Its primary carbon permits backside attack by the alkoxide. A tert-butyl halide would favour elimination instead of the required substitution.

Step 2: Choose the sodium alkoxide Use sodium tert-butoxide (sodium 2-methylpropan-2-olate), (CH₃)₃CONa:



The oxygen belongs to the tert-butoxide ion, which attacks the ethyl carbon to form tert-butyl ethyl ether.

Step 3: Conclusion The reagents are ethyl bromide and sodium tert-butoxide.

Quick Tip to Solve: For an ether containing a tertiary group, assign that group to the alkoxide and the primary group to the halide.

29(b). Anisole on reaction with HI gives phenol and $\text{CH}_3\text{-I}$ and not methanol and iodobenzene. Justify the statement. [1 mark]

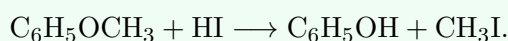
Solution:

Concept:

- In anisole, the aryl–oxygen bond has partial double-bond character through resonance and is difficult to cleave.
- After oxygen protonation, iodide attacks the methyl carbon by $\text{S}_{\text{N}}2$ substitution.

Step 1: Compare the two carbon–oxygen bonds The oxygen lone pair is conjugated with the benzene ring, strengthening the aryl–oxygen bond. Also, the aromatic carbon is sp^2 -hybridised and cannot undergo the usual $\text{S}_{\text{N}}2$ backside attack. Formation of a phenyl carbocation by $\text{S}_{\text{N}}1$ cleavage is also unfavourable.

Step 2: Explain the observed products HI first protonates the ether oxygen. Iodide then attacks the unhindered methyl carbon and breaks the methyl–oxygen bond. The oxygen stays attached to the phenyl group, yielding phenol:



Methanol and iodobenzene would require cleavage of the stronger aryl–oxygen bond, so they are not the products.

Step 3: Conclusion Anisole gives phenol and methyl iodide because cleavage occurs at the methyl–oxygen bond.

Quick Tip to Solve: In an aryl alkyl ether, keep oxygen attached to the aromatic ring when predicting cleavage by HI.

29(c). Why is C–O–C bond angle in ethers slightly greater than tetrahedral angle ? [1 mark]

Solution:

Concept:

- Ether oxygen has two bond pairs and two lone pairs, giving an approximately tetrahedral electron-pair arrangement.
- The two bulky alkyl groups repel one another and tend to move farther apart.

Step 1: Identify the reference geometry The oxygen atom of an ether is approximately sp^3 -hybridised. The ideal tetrahedral angle is 109.5° , which serves as the reference for the angle between the two carbon–oxygen bonds.

Step 2: Explain why the angle opens The alkyl groups attached to oxygen are bulkier than hydrogen atoms. Repulsion between these groups increases their separation, opening the C – O – C angle slightly beyond 109.5° (about 111.7° in dimethyl ether). Thus the actual bond angle reflects the repulsion between the alkyl groups in addition to the electron pairs around oxygen.

Quick Tip to Solve: When comparing ether bond angles with the tetrahedral angle, identify repulsion between the two alkyl groups.

Step 3: Conclusion The C – O – C angle is slightly greater than the tetrahedral angle because the two bulky alkyl groups repel each other.

Quick Tip to Solve: When comparing ether bond angles with the tetrahedral angle, identify repulsion between the two alkyl groups.

30(a). Case Study: Electrochemistry is the study of the relationship between chemical energy and electrical energy. Many spontaneously occurring chemical reactions liberate electrical energy. In electrolysis, electrical energy is converted directly into chemical energy. The product of an electrolytic reaction depends on the nature of the material being electrolysed and the type of electrode used. Oxidising and reducing species present in the electrolytic cell and their standard electrode potential too, affect the products of electrolysis. Electrolysis plays an important role in most people's daily lives, whether it is for the manufacturing of aluminium, electroplating of metals, or the synthesis of chemical compounds. Michael Faraday was the first scientist who proposed two laws to explain the quantitative aspects of electrolysis, popularly known as Faraday's laws of electrolysis. Faraday's laws of electrolysis provide a basis for mathematical analysis of the mass deposited at electrodes and the amount of charge passed through them. Faraday's laws are fundamental in various applications, including electroplating, metal extraction, battery technology and chemical synthesis. These laws also help in environmental monitoring and in various chemistry experiments.

Answer the following questions :

Predict the products of electrolysis in each of the following :

(i) An aqueous solution of CuCl_2 with platinum electrodes.

(ii) A concentrated solution of H_2SO_4 with platinum electrodes.

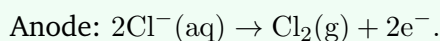
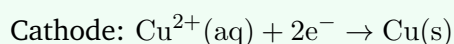
[2 marks]

Solution:

Concept:

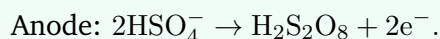
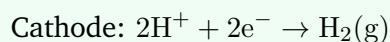
- At the cathode, reduction consumes electrons; at the anode, oxidation releases electrons. Platinum acts as an inert electrode.
- The products depend on the ions present and the concentration of the electrolyte. Concentrated sulphuric acid gives peroxodisulphuric acid at the platinum anode.

Step 1: Electrolyse aqueous copper(II) chloride Copper(II) ions are preferentially reduced and copper metal is deposited at the cathode. Chloride ions are oxidised to chlorine gas at the anode. The electrode reactions are



The platinum electrodes do not supply copper ions or themselves dissolve.

Step 2: Electrolyse concentrated sulphuric acid Hydrogen ions are reduced to hydrogen gas at the cathode. In the concentrated acid, oxidation of bisulphate at the platinum anode produces peroxodisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$.



Quick Tip to Solve: Underline "concentrated" before identifying the sulphuric acid anode product.

Concentration matters here: the anode product for this concentrated electrolyte should not be replaced by the oxygen usually discussed for dilute aqueous sulphuric acid.

Step 3: Conclusion (i) Cathode: copper; anode: chlorine. (ii) Cathode: hydrogen; anode: peroxodisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$.

Quick Tip to Solve: Underline "concentrated" before identifying the sulphuric acid anode product.

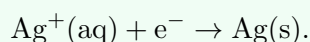
30(b). How much charge in faraday is required for the reduction of 1 mol of Ag^+ to Ag ? [1 mark]

Solution:

Concept:

- One faraday, F , is the charge carried by one mole of electrons: $F \approx 96485 \text{ C mol}^{-1}$.
- The charge requirement is $Q = nzF$, where n is the amount of metal deposited and z is the number of electrons required per ion.

Step 1: Write the reduction half-reaction Silver is present as Ag^+ , so each ion requires exactly one electron to become a neutral silver atom:



The electron coefficient is one, not two; the charge on the ion determines this coefficient.

Step 2: Count the electrons required Reducing 1 mol of Ag^+ therefore consumes 1 mol of electrons. Substitution gives

$$Q = 1 \times 1 \times F = F.$$

This corresponds to approximately 96485 C.

Step 3: Conclusion The required charge is 1 faraday.

Quick Tip to Solve: For one mole of ions, the numerical charge in faradays equals the electron coefficient.

OR

30(b). State Faraday's second law of electrolysis. [1 mark]

Solution:

Concept:

- The equivalent mass of a substance is $E = M/z$, where M is its molar mass and z is the electron transfer number.
- For electrolysis, $m = (M/zF)Q$, where m is the deposited mass and Q is the charge passed.

Step 1: State the second law When the same quantity of electricity is passed through different electrolytes, the masses of substances deposited or liberated at their electrodes are proportional to their chemical equivalent masses. The requirement of equal charge is essential; comparing arbitrary currents or arbitrary electrolysis times is insufficient.

Quick Tip to Solve: Always include both "same quantity of electricity" and "equivalent masses" in the law.

Step 2: Express the proportionality If m_1, m_2 are the masses and E_1, E_2 their equivalent masses, then

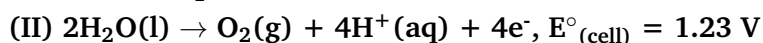
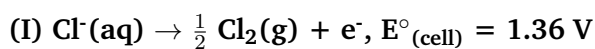
$$\frac{m_1}{m_2} = \frac{E_1}{E_2} = \frac{M_1/z_1}{M_2/z_2}.$$

This follows because the common factor Q/F cancels. The masses are proportional to molar masses only if both substances have the same electron transfer number.

Step 3: Conclusion For equal charge passed through different electrolytes, $m_1/m_2 = E_1/E_2$: deposited masses are proportional to equivalent masses.

Quick Tip to Solve: Always include both "same quantity of electricity" and "equivalent masses" in the law.

30(c). The following reactions occur at the anode during the electrolysis of aqueous sodium chloride solution :



Which reaction is feasible at the anode and why ?

[1 mark]

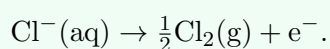
Solution:

Concept:

- At the anode, oxidation may liberate chlorine from chloride ions or oxygen from water.
- Actual discharge depends on the applied potential needed, including overpotential; standard electrode potentials alone do not determine the observed product.

Step 1: Compare the listed potentials The printed values are 1.36 V for the chlorine process and 1.23 V for the oxygen process. Considering only these values would suggest oxidation of water at a lower potential. However, this comparison neglects the kinetic barrier to oxygen evolution.

Step 2: Include oxygen overpotential Oxygen evolution at the anode requires a substantial additional potential, called oxygen overpotential. Consequently, the effective potential required to liberate oxygen becomes higher than that for chlorine evolution in aqueous sodium chloride electrolysis. Chloride ions are therefore preferentially discharged:



Step 3: Conclusion Reaction (I) is feasible preferentially at the anode, because oxygen evolution has a high overpotential; chlorine is liberated.

Quick Tip to Solve: In aqueous NaCl electrolysis, check oxygen overpotential before comparing the printed potentials.

Section E (15 marks)

31(a)(i). Calculate the freezing point of a solution when 10.5 g of MgBr_2 was dissolved in 250 g of water, assuming MgBr_2 undergoes complete dissociation.

(Given : Molar mass of $\text{MgBr}_2 = 184 \text{ g mol}^{-1}$, K_f for water = $1.86 \text{ K kg mol}^{-1}$)

[3 marks]

Solution:

Concept:

- Freezing point depression is $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f is the solvent freezing point depression constant, and m is molality.
- Molality is the number of moles of solute formula units per kilogram of solvent. Complete dissociation determines the number of particles from each formula unit.

Step 1: Determine the van't Hoff factor Magnesium bromide dissociates completely as



One formula unit yields three ions, so $i = 3$. The factor counts solute particles, not the algebraic sum of their charges.

Step 2: Calculate the molality The given solute mass is 10.5 g, its molar mass is 184 g mol^{-1} , and the water mass is $250 \text{ g} = 0.250 \text{ kg}$. Thus

$$n = \frac{10.5}{184} = 0.05707 \text{ mol},$$
$$m = \frac{0.05707}{0.250} = 0.22826 \text{ mol kg}^{-1}.$$

The denominator is the mass of water, not the total mass of solution.

Step 3: Find the freezing point Using $K_f = 1.86 \text{ K kg mol}^{-1}$,

$$\Delta T_f = 3 \times 1.86 \times 0.22826 = 1.2737 \text{ K}.$$

Pure water freezes at 0°C . Depression means that the solution freezes below this temperature, hence

$$T_f = 0 - 1.2737 = -1.2737^\circ\text{C}.$$

The temperature interval in kelvin has the same numerical value as the interval in degrees Celsius.

Step 4: Conclusion The freezing point of the solution is -1.27°C (approximately 271.88 K).

Quick Tip to Solve: Count all three ions from MgBr_2 , then use solvent mass in kilograms and subtract the depression.

31(a)(ii). Write two differences between ideal and non-ideal solutions.

[2 marks]

Solution:

Concept:

- An ideal solution obeys Raoult's law: $p_i = x_i p_i^0$, where x_i is the mole fraction and p_i^0 is the vapour pressure of pure component i .
- Non-ideal behaviour results when unlike-molecule interactions differ appreciably from like-molecule interactions.

Step 1: Compare vapour-pressure behaviour An ideal solution obeys Raoult's law over the entire range of composition: each partial vapour pressure is proportional to that component's mole fraction. A non-ideal solution does not obey this law throughout the composition range; its vapour pressure shows positive or negative deviation.

Step 2: Compare changes on mixing For an ideal solution, $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$: mixing produces neither heat absorption/evolution nor a volume change. For a non-ideal solution, these quantities are generally non-zero, because forming unlike-molecule contacts changes the intermolecular attractions and packing.

Step 3: Conclusion The two differences are: ideal solutions obey Raoult's law at all compositions and have zero enthalpy and volume changes on mixing; non-ideal solutions deviate from the law and generally have non-zero mixing changes.

Quick Tip to Solve: Pair one difference about vapour pressure with one about the changes on mixing.

OR

31(b)(i). A solution is prepared by dissolving 0.025 g of potassium sulphate in 2 L of water at 27°C. Assuming potassium sulphate is completely dissociated, determine its osmotic pressure.

(Given : $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$, Molar mass of $\text{K}_2\text{SO}_4 = 174 \text{ g mol}^{-1}$)

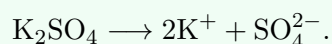
[3 marks]

Solution:

Concept:

- Osmotic pressure of a dilute solution is $\pi = iCRT = i(n/V)RT$, where i counts the particles formed per formula unit, C is molarity and T is absolute temperature.
- Complete dissociation of potassium sulphate produces three ions per formula unit, so its van't Hoff factor is $i = 3$.

Step 1: Count the solute particles Potassium sulphate dissociates according to



Thus one mole of dissolved salt yields three moles of ions. Complete dissociation therefore gives $i = 2 + 1 = 3$; using $i = 1$ would underestimate the pressure by a factor of three.

Quick Tip to Solve: First count all ions from one formula unit, then use kelvin and litres with the supplied gas constant.

Step 2: Calculate the molar concentration The amount of potassium sulphate is

$$n = \frac{0.025 \text{ g}}{174 \text{ g mol}^{-1}} = 1.4368 \times 10^{-4} \text{ mol.}$$

For this very dilute solution, the solution volume is taken as the given water volume, $V = 2 \text{ L}$. Hence

$$C = \frac{1.4368 \times 10^{-4}}{2} = 7.1839 \times 10^{-5} \text{ mol L}^{-1}.$$

This is the concentration of salt formula units; the total ionic concentration is three times this value.

Step 3: Apply the osmotic-pressure equation Convert the temperature to kelvin: $T = 27 + 273 = 300 \text{ K}$. Substituting values in units compatible with the given gas constant,

$$\begin{aligned}\pi &= 3 \times (7.1839 \times 10^{-5}) \times 0.082 \times 300 \\ &= 5.3017 \times 10^{-3} \text{ atm.}\end{aligned}$$

The litre, mole and kelvin factors cancel, leaving atmospheric pressure units.

Step 4: Conclusion The osmotic pressure of the solution is $\pi = 5.30 \times 10^{-3} \text{ atm}$.

Quick Tip to Solve: First count all ions from one formula unit, then use kelvin and litres with the supplied gas constant.

31(b)(ii). What type of azeotrope will be formed by a solution of acetone and chloroform ? Give reason. [2 marks]

Solution:

Concept:

- Negative deviation from Raoult's law occurs when unlike-molecule attractions are stronger than the attractions in the pure liquids.
- A maximum-boiling azeotrope is a constant-boiling mixture with lower vapour pressure and a higher boiling temperature than either pure component.

Step 1: Identify the intermolecular attraction In an acetone–chloroform mixture, the hydrogen atom of chloroform interacts with the oxygen atom of acetone through hydrogen bonding. The three electronegative chlorine atoms make the chloroform hydrogen sufficiently electron deficient for this interaction. The acetone–chloroform attractions are stronger than the corresponding attractions in the separate liquids.

Step 2: Relate attraction to boiling behaviour The stronger unlike-molecule attraction reduces the escaping tendency of molecules from the liquid. Therefore the total vapour pressure is below that predicted by Raoult's law: the solution shows negative deviation. A higher temperature is required for its vapour pressure to reach atmospheric pressure. At the azeotropic composition, the liquid and vapour compositions are equal, giving constant boiling at a maximum boiling temperature.

Step 3: Conclusion Acetone and chloroform form a maximum-boiling azeotrope, due to hydrogen

Quick Tip to Solve: Stronger attraction lowers vapour pressure and raises the boiling point: negative deviation means maximum boiling.

bonding between unlike molecules and consequent negative deviation from Raoult's law.

Quick Tip to Solve: Stronger attraction lowers vapour pressure and raises the boiling point: negative deviation means maximum boiling.

32(a)(i)(I). Why do transition metals show variable oxidation states ?

[1 mark]

Solution:

Concept:

- Transition-metal valence electrons occupy the ns and $(n - 1)d$ subshells.
- The energies of these two subshells are sufficiently close for electrons from both to participate in bonding.

Step 1: Identify the available valence electrons The outer ns electrons can be removed or used in bonding. Because the $(n - 1)d$ electrons have comparable energies, some of these electrons can also participate; their participation is not restricted to a fixed number.

Step 2: Connect this with oxidation states Different chemical environments can involve different numbers of ns and $(n - 1)d$ electrons. This gives the same metal more than one oxidation state. For example, iron forms Fe^{2+} by losing two outer electrons and Fe^{3+} by losing an additional d electron.

Step 3: Conclusion Transition metals show variable oxidation states because their ns and $(n - 1)d$ electrons have similar energies and different numbers of these electrons can take part in bonding.

Quick Tip to Solve: Mention both subshells and their similar energies; an incomplete d subshell alone is not the full reason.

32(a)(i)(II). Out of Mn^{2+} and Ti^{2+} which will be more paramagnetic and why ? [Atomic No. : $\text{Ti} = 22$, $\text{Mn} = 25$]

[1 mark]

Solution:

Concept:

- Paramagnetism arises from unpaired electrons; more unpaired electrons give a larger magnetic moment.
- The spin-only moment is $\mu = \sqrt{n(n + 2)} \mu_B$, where n is the number of unpaired electrons.

Step 1: Write the ionic configurations Neutral manganese is $[\text{Ar}]3d^54s^2$, so removal of the two $4s$ electrons gives $\text{Mn}^{2+} : [\text{Ar}]3d^5$, with five unpaired electrons. Neutral titanium is $[\text{Ar}]3d^24s^2$, so $\text{Ti}^{2+} : [\text{Ar}]3d^2$, with two unpaired electrons.

Step 2: Compare the magnetic moments By Hund's rule, the five d orbitals are singly occupied before pairing. Thus the spin-only moments are $\sqrt{35} \mu_B$ for Mn^{2+} and $\sqrt{8} \mu_B$ for Ti^{2+} . The ion with five unpaired electrons has the stronger paramagnetism.

Step 3: Conclusion Mn^{2+} is more paramagnetic because it has five unpaired electrons, whereas Ti^{2+} has only two.

Quick Tip to Solve: Remove the $4s$ electrons first when forming these ions, then count the unpaired $3d$ electrons.

32(a)(i)(III). Which ion is the strongest oxidising agent in the options given below : Cr^{3+} , V^{3+} , Mn^{3+} .
Give reason. [Atomic No. : Cr = 24, V = 23, Mn = 25] [1 mark]

Solution:

Concept:

- An oxidising agent accepts electrons and is itself reduced. Compare the stability gained when each M^{3+} ion becomes M^{2+} .
- A half-filled $3d^5$ subshell is particularly stable; chromium, vanadium and manganese have atomic numbers 24, 23 and 25 respectively.

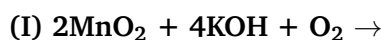
Step 1: Write the relevant electronic configurations The configurations are $\text{Cr}^{3+} : 3d^3$, $\text{V}^{3+} : 3d^2$ and $\text{Mn}^{3+} : 3d^4$. On accepting an electron, these give $\text{Cr}^{2+} : 3d^4$, $\text{V}^{2+} : 3d^3$ and $\text{Mn}^{2+} : 3d^5$, respectively.

Step 2: Compare the tendency to accept an electron Reduction of Mn^{3+} gives the especially stable half-filled $3d^5$ configuration of Mn^{2+} . Thus $\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$ is strongly favoured. Neither of the other two reductions produces a half-filled subshell; Cr^{3+} itself also has a stable $3d^3$ configuration.

Step 3: Conclusion Mn^{3+} is the strongest oxidising agent because it readily accepts an electron to form stable, half-filled $3d^5$ Mn^{2+} .

Quick Tip to Solve: Compare the configuration after electron gain: manganese(III) reaches the half-filled d subshell on reduction.

32(a)(ii). Complete and balance the following equations :



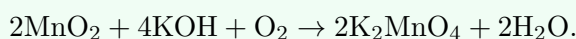
[2 marks]

Solution:

Concept:

- Oxidation of manganese dioxide in hot alkali with oxygen produces green potassium manganate, K_2MnO_4 .
- In acidic solution, permanganate is reduced to Mn^{2+} , while oxalate is oxidised to carbon dioxide. A balanced ionic equation conserves both atoms and total charge.

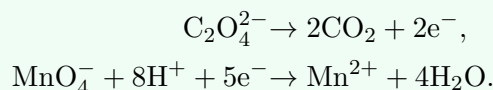
Step 1: Complete reaction (I): formation of potassium manganate Manganese changes from oxidation state +4 in MnO_2 to +6 in manganate. The two manganese atoms lose four electrons in total, which oxygen accepts. Balancing potassium, hydrogen and oxygen gives



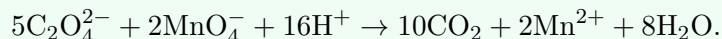
There are two Mn atoms, four K atoms, four H atoms and ten O atoms on each side.

Quick Tip to Solve: Remember the five-oxalate to two-permanganate ratio in acid; check charge as well as every atom after balancing.

Step 2: Complete reaction (II): oxidation of oxalate The half-reactions in acidic medium are



Multiply the first by five and the second by two, then cancel ten electrons. This gives



The net charge is +4 on both sides; carbon, manganese, oxygen and hydrogen are also balanced.

Step 3: Conclusion (I) The products are $2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$.

(II) The products are $10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$. The given reactant coefficients remain unchanged.

Quick Tip to Solve: Remember the five-oxalate to two-permanganate ratio in acid; check charge as well as every atom after balancing.

OR

32(b). (i) What is meant by lanthanoid contraction ?

(ii) Why do transition metals form coloured compounds ?

(iii) Why are $E^\circ_{\text{M}^{2+}/\text{M}}$ values for Mn and Zn more negative than expected ?

(iv) Which is the most stable oxidation state of Cu and why ?

(v) Why is Ce^{4+} in aqueous solution a good oxidising agent ?

[5 marks]

Solution:

Concept:

- Poor $4f$ shielding increases effective nuclear attraction across the lanthanoids. Ligand-field splitting permits visible-light $d-d$ transitions in suitable transition-metal ions.
- Ionic stability and hydration affect redox potentials. Half-filled d^5 and filled d^{10} configurations are particularly stable.

Step 1: (i) Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in the atomic and ionic radii of lanthanoids with increasing atomic number from lanthanum to lutetium. Added electrons enter the $4f$ subshell, whose poor shielding allows the increasing nuclear charge to pull the electron cloud inward.

Step 2: (ii) Explain the colour of transition-metal compounds Many transition-metal ions have partially filled d subshells. The surrounding ligands split the d orbitals into levels of different energy. An electron absorbs visible light of suitable energy and undergoes a $d-d$ transition from a lower to a higher level. The remaining transmitted or reflected light gives the compound its observed colour. Ions with d^0 and d^{10} configurations cannot show these transitions.

Step 3: (iii) Explain the unusually negative potentials of Mn and Zn Mn^{2+} has the especially stable half-filled configuration $3d^5$, while Zn^{2+} has the stable filled configuration $3d^{10}$. This extra stability favours the ions relative to the metallic state. Reduction to the metals is therefore comparatively

Quick Tip to Solve: Use electronic configuration for Mn and Zn, but include hydration when comparing aqueous Cu(I) with Cu(II).

unfavourable, giving unusually negative $E_{M^{2+}/M}^{\circ}$ values.

Step 4: (iv) Identify the most stable oxidation state of Cu In aqueous solution, copper's most stable oxidation state is +2. Although Cu^{+} has a filled $3d^{10}$ configuration, Cu^{2+} has a much more negative hydration enthalpy. The energy released on hydration compensates for the additional energy needed to remove the second electron. Thus aqueous Cu(I) tends to disproportionate into Cu(II) and copper metal.

Step 5: (v) Explain the oxidising action of aqueous Ce(IV) The +3 oxidation state is the usual stable state of lanthanoids in aqueous solution. Ce(IV) readily accepts an electron: $Ce^{4+} + e^{-} \rightarrow Ce^{3+}$. Its high positive reduction potential reflects this favourable conversion. By accepting an electron, Ce(IV) oxidises the other reacting species.

Step 6: Conclusion Thus poor shielding causes contraction, and visible-light absorption causes colour. Stable Mn(II) and Zn(II) explain their potentials; hydration favours Cu(II), while Ce(IV) readily reduces to Ce(III).

Quick Tip to Solve: Use electronic configuration for Mn and Zn, but include hydration when comparing aqueous Cu(I) with Cu(II).

33(a)(i)(I). Which of the following is more reactive towards S_N1 reaction : 2-Bromo-2-methylbutane or 1-Bromopentane [1 mark]

Solution:

Concept:

- An S_N1 reaction proceeds through a carbocation; the slow step is ionisation of the carbon-halogen bond.
- Carbocation stability generally follows $3^{\circ} > 2^{\circ} > 1^{\circ}$, owing to the electron-releasing effect and hyperconjugation of alkyl groups.

Step 1: Identify the carbon bonded to bromine In 2-bromo-2-methylbutane, the carbon bearing Br is attached to three carbon groups, so it is tertiary. In 1-bromopentane, this carbon is attached to only one carbon group, so it is primary.

Step 2: Compare the intermediates Loss of Br^{-} from the first compound gives a relatively stable tertiary carbocation. The second would have to form a much less stable primary carbocation. Formation of the more stable intermediate is easier, making the ionisation step faster.

Step 3: Conclusion 2-Bromo-2-methylbutane is more reactive towards S_N1 reaction.

Quick Tip to Solve: Count the carbon groups on the carbon bearing Br: tertiary halides favour the carbocation pathway.

33(a)(i)(II). What type of halide is present in the following compound : $\text{CH}_3\text{-CH}(\text{CH}_3)\text{-C}(\text{Cl})=\text{CH}_2$

[1 mark]

Solution:

Concept:

- Halides are classified by the hybridisation and environment of the carbon directly bonded to the halogen.
- A vinylic halide has its halogen directly bonded to an sp^2 -hybridised carbon of a carbon-carbon double bond.

Step 1: Locate the chlorine-bearing carbon The given compound is $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{C}(\text{Cl}) = \text{CH}_2$. Chlorine is attached to the carbon that is itself one end of the $\text{C} = \text{C}$ bond, rather than to the neighbouring saturated carbon.

Step 2: Assign the halide class The chlorine-bearing carbon is sp^2 -hybridised and belongs to the alkene unit. This is the defining arrangement of a vinylic halide. An allylic halide would instead have chlorine on an sp^3 carbon adjacent to the double bond.

Step 3: Conclusion The compound is a vinylic halide (vinyl chloride derivative).

Quick Tip to Solve: Look at the carbon directly attached to Cl: on the double bond means vinylic; beside it means allylic.

33(a)(i)(III). Why is chloroform stored in dark coloured bottles ?

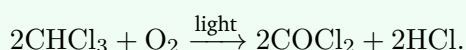
[1 mark]

Solution:

Concept:

- Chloroform, CHCl_3 , undergoes slow oxidation by atmospheric oxygen in the presence of light.
- This oxidation produces phosgene, COCl_2 , which is highly poisonous.

Step 1: Identify the harmful reaction In air and sunlight, chloroform is oxidised according to the balanced equation



The carbonyl chloride formed is called phosgene.

Step 2: Explain the storage precaution Dark-coloured bottles reduce the light reaching chloroform and thus suppress this photochemical oxidation. Keeping the bottle tightly stoppered also limits exposure to atmospheric oxygen, helping prevent the formation of the poisonous product.

Step 3: Conclusion Chloroform is stored in dark-coloured bottles to prevent light-assisted oxidation to poisonous phosgene.

Quick Tip to Solve: Remember the link: chloroform plus oxygen and light gives poisonous phosgene, so exclude light during storage.

33(a)(ii). Define the following terms :

(I) Ambident Nucleophiles (II) Racemic mixture

[2 marks]

Solution:

Concept:

- A nucleophile donates an electron pair to an electrophile; an ambident nucleophile has two alternative reactive donor atoms.
- Enantiomers rotate plane-polarised light equally in magnitude and oppositely in direction under identical conditions.

Step 1: Define ambident nucleophiles Ambident nucleophiles are nucleophiles that can attack through either of two different atoms or nucleophilic centres. For example, CN^- can bond through carbon or nitrogen, giving a cyanide or an isocyanide respectively. Similarly, NO_2^- can attack through nitrogen or oxygen. Each reaction uses one of the alternative sites.

Step 2: Define a racemic mixture A racemic mixture contains equal amounts (a 1:1 molar ratio) of the two enantiomers of an optically active compound. It is optically inactive because the clockwise rotation produced by one enantiomer is exactly cancelled by the equal anticlockwise rotation produced by the other. This cancellation is called external compensation; it does not mean that the individual molecules are achiral.

Step 3: Conclusion (I) Ambident nucleophiles have two alternative attacking atoms. (II) A racemic mixture is an equimolar mixture of two enantiomers with zero net optical rotation.

Quick Tip to Solve: For ambident nucleophiles name the two attacking atoms; for a racemate state both the 1:1 ratio and cancellation of rotation.

OR

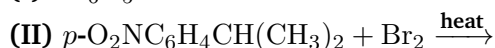
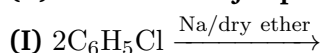
33(b). (i) Answer the following :

(I) Which isomer of $\text{C}_4\text{H}_9\text{Br}$ is most reactive towards $\text{S}_{\text{N}}1$ reaction ?

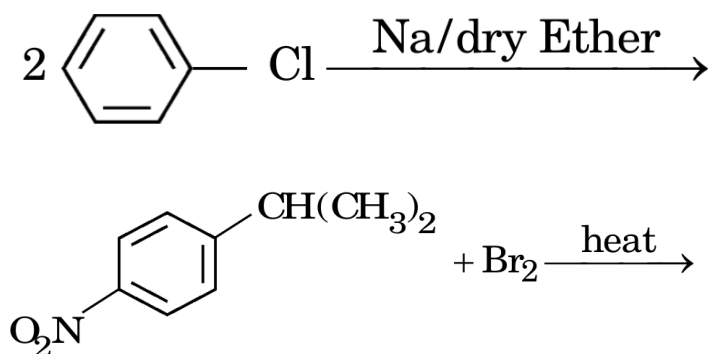
(II) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.

(III) Although chlorine shows strong -I effect, yet it is ortho/para-directing in electrophilic aromatic substitution reactions. Why ?

(ii) Write the major product in the following reactions :



[5 marks]

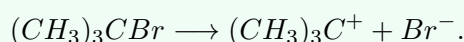


Solution:

Concept:

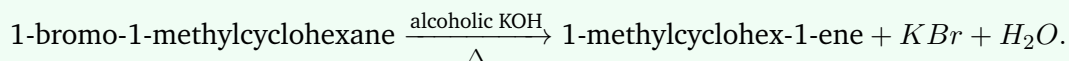
- An S_N1 reaction proceeds by slow ionisation to a carbocation. Greater carbocation stability gives faster reaction: tertiary > secondary > primary.
- Dehydrohalogenation removes a halogen and a hydrogen from adjacent carbon atoms. According to Saytzeff's rule, the more substituted alkene is the major product.
- Chlorine withdraws electrons inductively but donates a lone pair by resonance. Its inductive effect deactivates the ring, whereas resonance controls the ortho/para orientation.
- Sodium in dry ether couples aryl halides by the Fittig reaction. Bromine under heat substitutes a benzylic hydrogen through a free-radical mechanism.

Step 1: (i)(I) Select the fastest isomer for S_N1 The most reactive isomer is **2-bromo-2-methylpropane**, also called tert-butyl bromide, $(CH_3)_3CBr$. Its ionisation forms a tertiary carbocation:



Three methyl groups stabilise this carbocation through their electron-releasing inductive effect and hyperconjugation. The other isomers, 1-bromobutane and 1-bromo-2-methylpropane, would form primary carbocations, while 2-bromobutane forms a secondary carbocation. Thus none ionises as readily as tert-butyl bromide under comparable conditions.

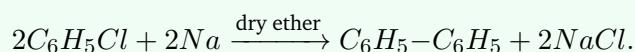
Step 2: (i)(II) Predict the elimination product With alcoholic alkali and heating, bromine is removed from carbon 1 and a beta-hydrogen is removed from an adjacent ring carbon (carbon 2 or the equivalent carbon 6). The new double bond lies between carbon 1 and that adjacent carbon. The major product is **1-methylcyclohex-1-ene**.



Removing a hydrogen from the methyl substituent could instead give methylenecyclohexane. Its exocyclic double bond is less substituted, so the more substituted endocyclic alkene is favoured according to Saytzeff's rule.

Step 3: (i)(III) Explain chlorine's directing effect Chlorine's strong $-I$ effect withdraws electron density from the benzene ring, making chlorobenzene less reactive than benzene towards electrophilic substitution. However, a chlorine lone pair overlaps with the ring's pi system and donates electron density by resonance ($+R$ effect), particularly to the ortho and para positions. During electrophilic attack at an ortho or para position, the intermediate sigma complex has an additional resonance contributor involving donation from chlorine. This additional stabilisation is unavailable for the corresponding meta intermediate. Chlorine therefore directs substitution to ortho and para positions even though its overall effect is deactivating.

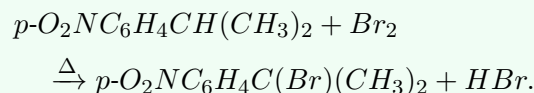
Step 4: (ii)(I) Couple the aryl halide The printed substrate is chlorobenzene. Two phenyl groups couple in the presence of sodium and dry ether, forming **biphenyl** (diphenyl):



Quick Tip to Solve: First identify the reagent: Na/dry ether couples aryl groups, while Br₂/heat replaces a benzylic hydrogen. For S_N1 , rank carbocation stability before choosing the isomer.

A carbon-carbon bond forms between the two ring carbons that originally carried chlorine. Since both coupling partners are aryl halides, this is the Fittig reaction.

Step 5: (ii)(II) Replace the benzylic hydrogen The substrate has a nitro group para to an isopropyl group. With Br_2 and heat, free-radical substitution occurs at the benzylic carbon of $-CH(CH_3)_2$, replacing its hydrogen with bromine:



The intermediate benzylic radical is stabilised by resonance with the aromatic ring and by the two methyl groups. The major product is **2-bromo-2-(4-nitrophenyl)propane**; the nitro group remains in its original para position. The heat condition identifies side-chain bromination, rather than electrophilic bromination of the aromatic ring.

Step 6: Conclusion (i)(I) 2-Bromo-2-methylpropane; (II) 1-methylcyclohex-1-ene; (III) chlorine's lone-pair resonance donation stabilises ortho/para intermediates despite its deactivating $-I$ effect. (ii)(I) Biphenyl, $C_6H_5-C_6H_5$; (II) $p-O_2NC_6H_4C(Br)(CH_3)_2$.

Quick Tip to Solve: First identify the reagent: Na/dry ether couples aryl groups, while Br_2 /heat replaces a benzylic hydrogen. For SN_1 , rank carbocation stability before choosing the isomer.