

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-5-2

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. $16 \times 1 = 16$

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

(i) R-CO-NH₂ (ii) NaOH (iii) Br₂ (iv) CHCl₃

[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, RCONH₂, into a primary amine, RNH₂, with one carbon atom fewer.
- The reaction requires bromine in aqueous sodium hydroxide; the carbonyl carbon is removed as carbonate.

Step 1: Identify the substrate and reagents The primary amide (i) reacts with bromine (iii) in sodium hydroxide (ii). The balanced overall reaction is



Step 2: Compare the combinations Chloroform (iv) is not required; it is associated with the carbylamine test of primary amines. Thus (A) lacks bromine and includes chloroform, (B) omits the required alkali, and (D) also omits alkali while including chloroform. Only (C) contains the amide, alkali and bromine together.

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

Quick Tip to Solve: Pair Hoffmann degradation with an amide plus bromine and alkali; chloroform instead points to the carbylamine test.

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

[1 mark]

- (A) $\text{C}_6\text{H}_5\text{COCl}$
- (B) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$
- (C) $\text{C}_6\text{H}_5\text{CONHCH}_3$
- (D) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

Correct Answer: (B) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$

Solution:

Concept:

- Hinsberg's reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, used to distinguish primary, secondary and tertiary amines.
- Its characteristic reactive group is $-\text{SO}_2\text{Cl}$, a sulphonyl chloride group attached to a phenyl group.

Step 1: Recognise the functional group In the Hinsberg test, suitable amines react with benzenesulphonyl chloride to form sulphonamide derivatives. Therefore the formula must contain the phenyl group C_6H_5 bonded to SO_2Cl , as shown in option (B).

Step 2: Eliminate the other formulae Option (A), $\text{C}_6\text{H}_5\text{COCl}$, is benzoyl chloride and contains an acyl chloride group. Option (C), $\text{C}_6\text{H}_5\text{CONHCH}_3$, is an amide, while option (D), $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, is benzylamine. None has the required sulphonyl chloride group.

Step 3: Conclusion Hinsberg's reagent is $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. Hence, the correct option is (B).

Quick Tip to Solve: Look specifically for the sulphur-containing group $-\text{SO}_2\text{Cl}$; do not confuse it with benzoyl chloride's $-\text{COCl}$.

3. 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:

- Variable oxidation states arise when different numbers of electrons can participate in bonding or be removed with accessible energy changes.
- In actinoids, the energies of the $5f$, $6d$ and $7s$ orbitals are comparable, allowing electrons from these subshells to participate.

Step 1: Relate oxidation states to orbital energies The small energy differences between the $5f$, $6d$ and $7s$ orbitals make several electron arrangements accessible in actinoid compounds. Different numbers of these electrons can contribute to bonding, giving a wide range of oxidation states.

Step 2: Check the alternative explanations Radioactivity in (A) is a nuclear property and does not

Quick Tip to Solve: For variable oxidation states, compare the energies of the valence subshells rather than the nuclear mass or radioactivity.

explain the accessibility of bonding electrons. A large atomic number in (B) or a large atomic mass in (C), by itself, does not establish variable valency. The electronic energy explanation in (D) directly accounts for the observed behaviour.

Step 3: Conclusion Actinoids show many oxidation states because the $5f$, $6d$ and $7s$ orbitals have comparable energies. The correct option is (D).

Quick Tip to Solve: For variable oxidation states, compare the energies of the valence subshells rather than the nuclear mass or radioactivity.

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



[1 mark]

- (A) A = CH_3I , B = NaCl
(B) A = CH_3OH , B = NaCl
(C) A = CH_3CHO , B = NaCl
(D) A = C_2H_6 , B = CH_3I

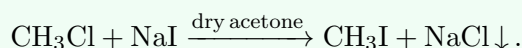
Correct Answer: (A) A = CH_3I , B = NaCl

Solution:

Concept:

- The Finkelstein reaction replaces chlorine or bromine in an alkyl halide with iodine using sodium iodide in dry acetone.
- Sodium chloride is insoluble in dry acetone; its precipitation favours the halogen-exchange reaction.

Step 1: Apply halogen exchange Iodide ion replaces chlorine in methyl chloride by nucleophilic substitution. The carbon skeleton remains unchanged:



The organic product is iodomethane, and the inorganic product is sodium chloride.

Step 2: Reject the other products Option (B) would require replacement by hydroxide rather than iodide. Option (C) would require a different transformation that forms an aldehyde and adds a carbon atom. Option (D) suggests carbon-chain coupling, which is not caused by sodium iodide in acetone. Option (A) alone represents the halogen exchange.

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

Quick Tip to Solve: Recognise NaI in dry acetone as Finkelstein conditions: replace the alkyl chlorine with iodine and precipitate NaCl.

5. The major product of carbylamine reaction is:

[1 mark]

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

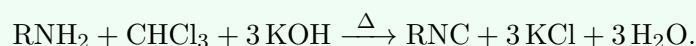
Correct Answer: (D) Isocyanide

Solution:

Concept:

- The carbylamine reaction is the reaction of a primary amine with chloroform and alcoholic potassium hydroxide on heating.
- The organic product is an isocyanide, $R-N\equiv C$, also called a carbylamine; nitrogen is bonded directly to the organic group.

Step 1: Write the reaction The balanced overall reaction is



Alcoholic alkali and heat convert the primary amine into the characteristically unpleasant-smelling carbylamine.

Step 2: Distinguish isocyanide from cyanide In an isocyanide the connectivity is $R-N\equiv C$, whereas an organic cyanide has $R-C\equiv N$. Thus the tempting option (C) describes a different connectivity. Neither a carboxylic acid in (A) nor an aldehyde in (B) is the characteristic organic product of this test.

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

Quick Tip to Solve: Remember that carbylamine means isocyanide: the starting amine's $R-N$ connection remains in $R-NC$.

6. 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

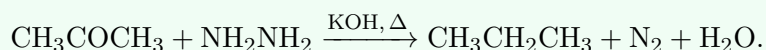
Solution:

Concept:

- Conversion of a ketone to the corresponding hydrocarbon replaces its carbonyl group, $C=O$, with a methylene group, CH_2 .
- Wolff-Kishner reduction uses hydrazine followed by heating with strong base in a high-boiling solvent such as ethylene glycol.

Quick Tip to Solve: When $C=O$ must become CH_2 , look for a carbonyl reduction such as Wolff-Kishner in the options.

Step 1: Match the required transformation The ketone first forms a hydrazone with hydrazine; heating with potassium hydroxide then removes nitrogen and gives the hydrocarbon. For example, propanone gives propane:



The carbon skeleton is retained while the carbonyl oxygen is replaced by two hydrogen atoms.

Step 2: Compare the named reactions Reimer-Tiemann reaction (A) introduces a formyl group into phenol. Aldol condensation (C) forms a carbon-carbon bond between suitable carbonyl compounds. Stephen reaction (D) converts nitriles into aldehydes after hydrolysis. Only Wolff-Kishner reduction carries out the required carbonyl-to-methylene conversion.

Step 3: Conclusion Wolff-Kishner reduction converts a ketone into a hydrocarbon. Hence, the correct option is (B).

Quick Tip to Solve: When C=O must become CH₂, look for a carbonyl reduction such as Wolff-Kishner in the options.

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

[1 mark]

- (A) Ammonia
- (B) Water
- (C) NO₂⁻
- (D) Oxalate ion

Correct Answer: (D) Oxalate ion

Solution:

Concept:

- Chelation occurs when a ligand binds the same metal ion through two or more donor atoms and forms a ring containing the metal.
- The oxalate ion, C₂O₄²⁻, is a bidentate ligand that can coordinate through two oxygen donor atoms.

Step 1: Identify a ligand that closes a ring Oxalate donates one lone pair from each of two oxygen atoms, one from each carboxylate group, to the same metal centre. The resulting metal-oxygen-carbon-carbon-oxygen linkage forms a five-membered chelate ring.

Step 2: Compare the other ligands Ammonia in (A) normally binds through its single nitrogen donor atom, and water in (B) through its oxygen atom. Nitrite in (C) is ambidentate: in the standard classification it can bind through nitrogen or oxygen, using one donor site at a time. Ambidentate behaviour alone does not give a chelate ring. Oxalate in (D) supplies two donor atoms simultaneously.

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

Quick Tip to Solve: Check for two donor atoms binding the same metal simultaneously; alternate donor sites in an ambidentate ligand are not enough.

8. 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, the half-life is $t_{1/2} = \ln 2/k$, where k is the rate constant.
- Since $\ln 2 \simeq 0.693$ is dimensionless, a half-life in seconds gives k in s^{-1} .

Step 1: Rearrange the half-life relation The reaction is explicitly first order, so its half-life is independent of initial concentration. Rearranging the relation gives

$$k = \frac{0.693}{t_{1/2}}.$$

Step 2: Substitute and compare the powers of ten Insert the given half-life without converting seconds:

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

Option (A) is 5000 s^{-1} , (C) is 0.000005 s^{-1} , and (D) is 0.005 s^{-1} ; none equals the calculated value.

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

Quick Tip to Solve: For a first-order half-life in seconds, divide 0.693 by the time and retain s^{-1} ; check the decimal before selecting an exponent.

9. 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 linear sequence of amino-acid residues joined by peptide bonds in a polypeptide chain.
- Secondary, tertiary and quaternary structures describe progressively different aspects of folding and association, rather than the residue sequence itself.

Quick Tip to Solve: Match sequence with primary structure; reserve folding and subunit arrangement for the higher structural levels.

Step 1: Identify what the question describes The key phrase is a specific sequence of amino acids. It asks which residue follows which along the polypeptide chain, not how that chain folds in space. Peptide bonds connect the residues in this definite order.

Step 2: Distinguish the other structural levels Secondary structure refers to local arrangements such as an α -helix or a β -pleated sheet, stabilised by hydrogen bonding. Tertiary structure is the overall three-dimensional folding of one chain. Quaternary structure describes the arrangement of multiple polypeptide subunits. Thus options (B), (C) and (D) refer to spatial organisation beyond the sequence.

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

Quick Tip to Solve: Match sequence with primary structure; reserve folding and subunit arrangement for the higher structural levels.

10. 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 carbohydrate unit that cannot be hydrolysed to simpler carbohydrates; a disaccharide gives two monosaccharide units on hydrolysis.
- A polysaccharide contains a large number of monosaccharide residues joined through glycosidic linkages.

Step 1: Classify the smaller carbohydrates Fructose, option (A), and glucose, option (C), are monosaccharides. Maltose, option (B), is a disaccharide: hydrolysis of one molecule yields two glucose molecules. None of these has the long chain required for a polysaccharide.

Step 2: Identify the polymeric carbohydrate Cellulose is a linear polymer containing many β -D-glucose residues linked by $\beta(1 \rightarrow 4)$ glycosidic bonds. Hydrolysis breaks these links and produces a large number of glucose molecules. Its repeated-unit structure fits the definition of a polysaccharide.

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

Quick Tip to Solve: Count the units released on hydrolysis: glucose and fructose are single units, maltose gives two, and cellulose gives many.

11. 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:

- Basicity depends on the availability of the nitrogen lone pair for accepting a proton and, in aqueous solution, the stabilisation of the conjugate acid by solvation.
- Resonance delocalisation reduces lone-pair availability, whereas the electron-releasing inductive effect of alkyl groups generally increases it.

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, making it less available than in NH_3 . In benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, a saturated CH_2 group separates nitrogen from the ring, so there is no direct resonance delocalisation of its lone pair. Benzylamine is therefore more basic than ammonia, although the phenyl group's electron-withdrawing inductive influence makes it weaker than ethylamine.

Step 2: Compare the ethyl-substituted amines The ethyl group increases electron density at nitrogen in $\text{C}_2\text{H}_5\text{NH}_2$. In aqueous solution, the combined inductive and solvation effects make diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$, more basic than ethylamine. Option (B) wrongly puts ammonia below aniline; (C) puts benzylamine below aniline; and (D) puts ethylamine below aniline. Each contradicts the lone-pair comparison.

Step 3: Conclusion The increasing order of basic strength is



Hence, the correct option is (A).

Quick Tip to Solve: First check whether nitrogen is directly bonded to the benzene ring: the intervening CH_2 in benzylamine prevents aniline-like lone-pair delocalisation.

12. 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 . It converts suitable alcohols into alkyl chlorides, whose insolubility produces turbidity.
- Under the usual test conditions, the rate of turbidity distinguishes ordinary primary, secondary and tertiary alcohols.

Step 1: Compare the Lucas-test observations At room temperature, a tertiary alcohol gives immediate turbidity, a secondary alcohol gives turbidity after a few minutes, and an ordinary primary alcohol gives no turbidity at room temperature. The characteristic difference in reaction rates provides the required classification.

Step 2: Check what the other tests identify Fehling's test and Tollens' test are commonly used to detect aldehydes through their reducing action; they do not classify alcohols into all three categories. Hinsberg's test distinguishes primary, secondary and tertiary amines, so it applies to a different functional group.

Step 3: Conclusion Primary, secondary and tertiary alcohols can be distinguished by the Lucas test. Hence, the correct option is (A).

Quick Tip to Solve: For alcohol classification, recall Lucas turbidity: tertiary immediately, secondary after a few minutes, primary no turbidity at room temperature.

13. 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.

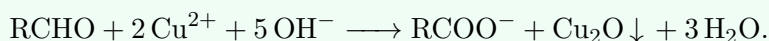
Solution:

Concept:

- Fehling's solution contains a blue alkaline copper(II) complex. A positive test gives a brick-red precipitate of copper(I) oxide, Cu_2O .
- An aliphatic aldehyde acts as the reducing agent: its aldehyde group is oxidised to a carboxylate group in the alkaline medium.

Step 1: Evaluate the assertion On warming with Fehling's solution, aliphatic aldehydes reduce copper(II) to copper(I), forming the characteristic brick-red precipitate. The assertion is true in the standard aldehyde test described in the question.

Step 2: Evaluate the reason The aldehyde is oxidised, not reduced. The net ionic equation may be written as



Copper is reduced from oxidation state +2 to +1, while the aldehyde becomes a carboxylate. The reason reverses the direction of the aldehyde's chemical change and is therefore false.

Step 3: Test the explanation link Since the reason is false, it cannot explain the true assertion. The positive test is explained by oxidation of the aldehyde together with reduction of the copper reagent. Options (A) and (B) wrongly accept the reason, and (D) wrongly rejects the assertion.

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

Quick Tip to Solve: Track both partners in Fehling's test: the aldehyde is oxidised, while blue copper(II) is reduced to brick-red Cu_2O .

14. 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 sign (–) denotes laevorotation.
- D and L specify relative configuration by comparison with glyceraldehyde; they do not by themselves determine the sign of optical rotation.

Step 1: Evaluate the assertion In the name D(+)-glucose, the (+) symbol explicitly indicates positive optical rotation. Thus this glucose is dextrorotatory, and the assertion is true.

Step 2: Evaluate the reason The reason correctly assigns two different meanings: (+) states the experimentally observed direction of optical rotation, whereas D identifies the relative configuration. For glucose in its standard Fischer projection, the hydroxyl group on the highest-numbered chiral carbon lies on the right, giving the D designation. The reason is therefore true.

Step 3: Check whether the reason explains the assertion The reason's explanation of the (+) sign directly establishes why D(+)-glucose is dextrorotatory. The D designation alone would not establish that rotation. Thus (B) incorrectly denies the explanatory link, while (C) and (D) wrongly reject one of the true statements.

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

Quick Tip to Solve: Read D and (+) separately: D gives configuration, while only the (+) sign tells you that rotation is to the right.

15. 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:

- Transition elements show variable oxidation states because their outer ns and inner $(n-1)d$ electrons have comparable energies.
- Manganese has electronic configuration $[\text{Ar}] 3d^5 4s^2$; its seven valence electrons account for the maximum oxidation state +7.

Step 1: Evaluate the assertion The assertion is true. Manganese attains +7, for example in MnO_4^- , since $x + 4(-2) = -1$ gives $x = +7$. This is the highest oxidation state reached in the first transition series.

Step 2: Evaluate the reason The reason is also true as a general characteristic of transition metals: different numbers of s and d electrons can participate in bonding, giving different oxidation states.

Step 3: Test the explanatory link Merely stating that oxidation states vary does not explain why manganese specifically reaches +7. That maximum follows from its $3d^5 4s^2$ configuration and seven valence electrons. Thus option (A) claims a link the reason does not supply, while (C) and (D) incorrectly make one statement false.

Step 4: Conclusion Both statements are true, but the reason is not the correct explanation of the assertion. Hence, the correct option is (B).

Quick Tip to Solve: For a highest oxidation state, count the available valence electrons; a general statement about variability does not explain its numerical value.

16. 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 becomes stronger when its conjugate base is more stable: loss of H^+ from a phenol gives the corresponding phenoxide ion.
- A para nitro group withdraws electron density by both the inductive and resonance effects, stabilising the phenoxide conjugate base.

Step 1: Evaluate the assertion The assertion is true: *p*-nitrophenol releases a proton more readily than phenol because its conjugate base is more stable than the unsubstituted phenoxide ion.

Step 2: Evaluate the reason The reason is true. The $-NO_2$ group attracts electron density. At the para position it also participates in resonance, allowing negative charge from the phenoxide system to be delocalised towards the nitro-group oxygen atoms.

Step 3: Relate stabilisation to acidity This additional dispersal of negative charge stabilises the product of proton loss and favours acid ionisation. Therefore the reason explains the greater acidity in the assertion. Option (B) incorrectly denies this causal link, and options (C) and (D) incorrectly classify a true statement as false.

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

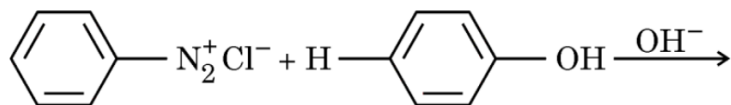
Quick Tip to Solve: Compare the conjugate bases: a para nitro group stabilises phenoxide through resonance as well as induction, so it increases acidity.

Section B (10 marks)

17. (a) Complete the following equation (shown below):

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

[2 marks]

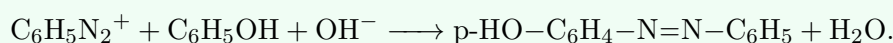


Solution:

Concept:

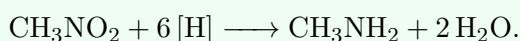
- A benzene diazonium salt couples with phenol in alkaline medium, predominantly at its free para position, forming an azo dye with the linkage $-\text{N}=\text{N}-$.
- Reduction converts a nitro compound into a primary amine. A primary amine gives an isocyanide on heating with chloroform and alcoholic potassium hydroxide (carbylamine reaction).

Step 1: Complete the azo coupling in part (a) The hydrogen para to the hydroxyl group is replaced by the phenylazo group. The organic product is *p*-hydroxyazobenzene, $p\text{-HO}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_5$, an orange azo dye. A balanced net ionic equation in the printed alkaline medium is



Chloride is a spectator ion. The para position is preferred because it is activated by the hydroxyl group and is less hindered than the ortho positions.

Step 2: Reduce nitromethane in part (b) Reduce nitromethane using tin and hydrochloric acid, then add alkali to liberate methylamine from its salt. The reduction is represented by



This gives the primary amine needed for the next reaction.

Step 3: Convert methylamine into the isocyanide Heat methylamine with chloroform and alcoholic potassium hydroxide:



The methyl group remains bonded to nitrogen in the product, so the compound formed is methyl isocyanide rather than methyl cyanide.

Step 4: Conclusion (a) The coupling product is *p*-hydroxyazobenzene, $p\text{-HO}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_5$. (b) The conversion proceeds as $\text{CH}_3\text{NO}_2 \longrightarrow \text{CH}_3\text{NH}_2 \longrightarrow \text{CH}_3\text{NC}$, using reduction followed by the carbylamine reaction.

Quick Tip to Solve: For an isocyanide, first prepare the primary amine and then use chloroform with alcoholic alkali; keep the product connectivity as $\text{R}-\text{NC}$.

18. (a) Name any two materials other than hydrogen that can be used as fuel in fuel cells.

(b) Define molar conductivity.

[2 marks]

Solution:

Concept:

- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy by a redox reaction.
- Molar conductivity, Λ_m , relates conductivity κ to molar concentration c : $\Lambda_m = \kappa/c$ when coherent SI units are used.

Step 1: Identify two alternative fuels in part (a) Methane, CH_4 , and methanol, CH_3OH , are two materials other than hydrogen that can be used as fuel in fuel cells. The fuel undergoes oxidation at the anode, while the oxidant undergoes reduction at the cathode; the separated electrode reactions supply electrons to the external circuit.

Step 2: Define molar conductivity in part (b) Molar conductivity is the conductance of the volume of solution containing one mole of an electrolyte, placed between two parallel electrodes separated by unit distance, with sufficient electrode area to accommodate that entire volume. Equivalently, it is conductivity multiplied by the volume containing one mole of electrolyte:

$$\Lambda_m = \kappa V = \frac{\kappa}{c}.$$

Here $V = 1/c$ is the volume per mole. With κ in S m^{-1} and c in mol m^{-3} , its SI unit is $\text{S m}^2 \text{mol}^{-1}$. If conductivity is in S cm^{-1} and concentration C in mol L^{-1} , the practical expression is $\Lambda_m = 1000\kappa/C$, in $\text{S cm}^2 \text{mol}^{-1}$.

Step 3: Conclusion (a) Methane and methanol are suitable examples. (b) Molar conductivity measures conductance for the volume containing one mole of electrolyte and is given by $\Lambda_m = \kappa/c$ in SI units.

Quick Tip to Solve: Keep conductivity and concentration units consistent: the factor 1000 is needed when using centimetres for conductivity and litres for concentration.

19(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:

- Elevation of boiling point is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the solvent's ebullioscopic constant and m the molality.
- The van't Hoff factor compares the observed colligative effect with the value for the same analytical amount of undissociated, unassociated solute: $i = \Delta T_b/(K_b m)$.

Step 1: Calculate the observed elevation The normal boiling point of pure water is 100.00°C , while

Quick Tip to Solve: First subtract the pure solvent's boiling point, then divide by $K_b m$; using 100.18 instead of 0.18 would give a spurious factor.

the stated solution boils at 100.18 °C. Therefore,

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

A temperature difference has the same numerical value in kelvin and degrees Celsius; the absolute boiling temperature must not be substituted for the elevation.

Step 2: Substitute the given molality and constant Using $m = 1.00 \text{ mol kg}^{-1}$ and $K_b = 0.512 \text{ K kg mol}^{-1}$,

$$i = \frac{\Delta T_b}{K_b m} = \frac{0.18}{0.512 \times 1.00} = 0.3515625.$$

The units in the denominator reduce to kelvin and cancel those of the numerator, so i is dimensionless. This calculation uses the measured elevation stated in the question; no assumed dissociation factor is inserted in place of it.

Step 3: Conclusion The van't Hoff factor implied by the given boiling-point data is $i \approx 0.35$ (unrounded value 0.3515625).

Quick Tip to Solve: First subtract the pure solvent's boiling point, then divide by $K_b m$; using 100.18 instead of 0.18 would give a spurious factor.

OR

19(b). State Henry's law. Calculate the mole fraction of CO₂ in water at 298 K under 760 mm Hg.

(Given: K_H for CO₂ in H₂O at 298 K = $1.25 \times 10^6 \text{ mm Hg}$)

[2 marks]

Solution:

Concept:

- Henry's law states that, at a constant temperature, the partial pressure of a gas above a solution is directly proportional to its mole fraction in that solution.
- The relation is $p = K_H x$, where p is the gas pressure, K_H is Henry's law constant and x is the dimensionless mole fraction of the dissolved gas.

Step 1: Express the mole fraction using Henry's law For dissolved CO₂ at 298 K, use the given gas pressure $p = 760 \text{ mm Hg}$. Rearranging Henry's law gives

$$x_{\text{CO}_2} = \frac{p}{K_H}.$$

The pressure and Henry's law constant must be expressed in the same pressure unit. Both are already in millimetres of mercury, so no conversion is required.

Step 2: Substitute the pressure and the constant Substitute $K_H = 1.25 \times 10^6 \text{ mm Hg}$:

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

The pressure units cancel. The small mole fraction is consistent with a dilute solution of the gas in

Quick Tip to Solve: With p and K_H both in mm Hg, divide directly; converting only one of them to atmospheres gives an incorrect mole fraction.

water.

Step 3: Conclusion Henry's law is $p = K_H x$ at constant temperature. The mole fraction of CO_2 in water is 6.08×10^{-4} .

Quick Tip to Solve: With p and K_H both in mm Hg, divide directly; converting only one of them to atmospheres gives an incorrect mole fraction.

20. (a) Write the hydrolysis products of lactose.

(b) What are non-essential amino acids ?

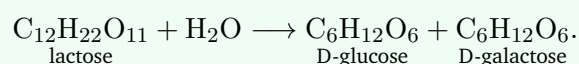
[2 marks]

Solution:

Concept:

- A disaccharide is hydrolysed by cleavage of its glycosidic linkage, producing its constituent monosaccharides. Lactose contains one glucose unit and one galactose unit.
- Amino acids are classified as essential or non-essential according to whether the human body can synthesise enough of them to meet its requirements.

Step 1: Identify the products of lactose hydrolysis (a) Hydrolysis breaks the glycosidic bond in lactose by addition of water, releasing one molecule each of D-glucose and D-galactose per molecule of lactose. The reaction can be represented as



The two products have the same molecular formula but different stereochemical configurations.

Step 2: Define non-essential amino acids (b) Non-essential amino acids are amino acids that the human body can synthesise in adequate amounts; hence, they need not be supplied as such in the diet. Examples include alanine and glycine. The term describes their dietary requirement, and does not mean that these amino acids are unnecessary for protein synthesis or normal body functions.

Step 3: Conclusion (a) Lactose yields D-glucose and D-galactose on hydrolysis. (b) Non-essential amino acids are those that can be synthesised by the body in sufficient amounts.

Quick Tip to Solve: Remember lactose as glucose plus galactose; define non-essential amino acids by the body's ability to synthesise them, rather than by their importance.

21. (a) Name two water-soluble vitamins.

(b) How will you prove the absence of free -CHO group in the cyclic structure of glucose molecule ?

[2 marks]

Solution:

Concept:

- Water-soluble vitamins include the B-group vitamins and vitamin C. Vitamins are classified by their solubility in water or fat.
- A free aldehyde carbonyl reacts with hydroxylamine, NH_2OH , to form an oxime. In the cyclic hemiacetal form of glucose, the aldehyde group is involved in ring formation.

Step 1: Name two water-soluble vitamins (a) Vitamin B_1 (thiamine) and vitamin C (ascorbic acid) are two water-soluble vitamins. Vitamin B_1 is a specific member of the water-soluble B-complex group, whereas vitamins A, D, E and K are fat-soluble.

Step 2: Use the hydroxylamine test on glucose pentaacetate (b) Glucose pentaacetate does not react with hydroxylamine to form an oxime. If a free $-\text{CHO}$ group were present in this derivative, its carbonyl group would undergo the usual oxime-forming reaction. The absence of this reaction shows that glucose pentaacetate has no free aldehyde group and supports the cyclic structure of glucose. In cyclic glucose, the hydroxyl group at C-5 adds to the C-1 aldehyde group to form a hemiacetal. Acetylation fixes the cyclic structure by acetylating the anomeric hydroxyl group as well. This evidence must be distinguished from free glucose in solution, which can open to its aldehydic form and react with hydroxylamine.

Step 3: Conclusion (a) Vitamins B_1 and C are water-soluble. (b) The failure of glucose pentaacetate to form an oxime with hydroxylamine demonstrates the absence of a free $-\text{CHO}$ group in that cyclic derivative and supports cyclic glucose.

Quick Tip to Solve: Cite glucose pentaacetate for the negative hydroxylamine test; free glucose can open its ring and therefore does form an oxime.

Section C (21 marks)

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

$\text{Al(s)} \mid \text{Al}^{3+}(\text{aq}) (0.1 \text{ M}) \parallel \text{Ni}^{2+}(\text{aq}) (0.01 \text{ M}) \mid \text{Ni(s)}$

(Given : $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$, $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$, $[\log 10 = 1]$)

[3 marks]

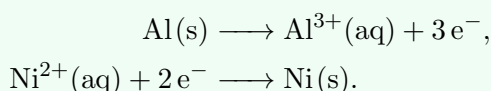
Solution:

Concept:

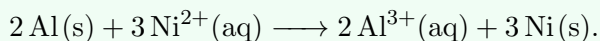
- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, with both electrode potentials taken as reduction potentials.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, where n is the number of electrons transferred in the balanced cell reaction and Q is its reaction quotient. Pure solids have unit activity.

Quick Tip to Solve: Balance the Al/Ni reaction first: six electrons are transferred, and the quotient is aluminium-ion concentration squared over nickel-ion concentration cubed.

Step 1: Balance the electrode reactions Aluminium is oxidised at the anode and nickel ions are reduced at the cathode. The half-reactions are



Multiply the oxidation half-reaction by 2 and the reduction half-reaction by 3 to cancel six electrons:



Hence the electron-transfer number for this balanced reaction is $n = 6$.

Step 2: Calculate the standard potential and reaction quotient Using the stated reduction potentials,

$$E_{\text{cell}}^{\circ} = -0.25 - (-1.66) = 1.41 \text{ V}.$$

Electrode potentials are not multiplied by the half-reaction coefficients. Taking the ion activities as their molar concentrations relative to the standard concentration,

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

The solid metals are omitted from the quotient, and the powers follow the balanced reaction coefficients.

Step 3: Apply the Nernst correction Since $\log Q = \log 10^4 = 4$, substitution at 298 K gives

$$\begin{aligned}E_{\text{cell}} &= 1.41 - \frac{0.0591}{6} \times 4 \\ &= 1.41 - 0.0394 = 1.3706 \text{ V}.\end{aligned}$$

Since $Q > 1$, the correction lowers the emf below its standard value, consistent with the sign in the Nernst equation.

Step 4: Conclusion The emf of the cell at 298 K is $E_{\text{cell}} \approx 1.37 \text{ V}$.

Quick Tip to Solve: Balance the Al/Ni reaction first: six electrons are transferred, and the quotient is aluminium-ion concentration squared over nickel-ion concentration cubed.

23. How do you convert the following ?

(a) Toluene to Benzaldehyde

(b) Benzoyl chloride to Acetophenone

(c) Bromobenzene to Benzoic acid

[3 marks]

Solution:

Concept:

- Selective oxidation of the methyl side chain of toluene gives benzaldehyde; vigorous oxidation would instead form benzoic acid.
- Dialkylcadmium reagents convert acid chlorides into ketones. A Grignard reagent reacts with carbon dioxide to introduce one additional carbon as a carboxyl group after acidification.

Step 1: (a) Carry out the Etard reaction Treat toluene with chromyl chloride, CrO_2Cl_2 , in carbon disulphide, CS_2 . The Etard complex formed is then hydrolysed to benzaldehyde:



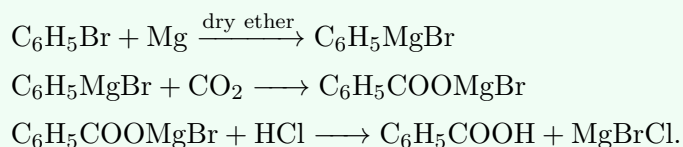
This controlled side-chain oxidation stops at the aldehyde stage. Hot alkaline permanganate is unsuitable because it oxidises the side chain further to the carboxylate.

Step 2: (b) React benzoyl chloride with dimethylcadmium Use dimethylcadmium in dry ether. Its methyl groups replace chloride at the acyl carbon, giving the ketone acetophenone:



The organocadmium reagent is less reactive than a Grignard reagent and allows the conversion to stop at the ketone; direct use of excess methylmagnesium halide would lead to further addition.

Step 3: (c) Form and carboxylate the Grignard reagent React bromobenzene with magnesium in dry ether to obtain phenylmagnesium bromide. Add dry carbon dioxide and then hydrolyse the magnesium carboxylate with dilute acid:



Moisture is excluded until the final work-up because water destroys the Grignard reagent.

Step 4: Conclusion The required routes are (a) Etard oxidation followed by hydrolysis, (b) reaction with dimethylcadmium, and (c) Grignard formation followed by carbon dioxide and acidification, giving benzaldehyde, acetophenone and benzoic acid respectively.

Quick Tip to Solve: Check the carbon skeleton first: part (a) retains the side-chain carbon, part (b) adds methyl, and part (c) adds the carboxyl carbon from carbon dioxide.

24. The rate of a particular reaction quadruples when the temperature increases from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.

(Given : $\log 4 = 0.60$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

[3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy and R the gas constant.
- For unchanged reactant concentrations, the ratio of reaction rates equals the ratio of rate constants. The two-temperature equation assumes that E_a and A are effectively constant over the interval.

Step 1: Identify the rate-constant ratio The temperature rises from $T_1 = 293 \text{ K}$ to $T_2 = 313 \text{ K}$, and the rate becomes four times its initial value. Thus, comparing rates at the same reactant concentrations,

$$\frac{k_2}{k_1} = 4, \quad \log_{10} \frac{k_2}{k_1} = 0.60.$$

We use the Kelvin temperatures directly; their difference is 20 K.

Step 2: Apply the two-temperature Arrhenius equation Taking common logarithms of the Arrhenius equation at both temperatures and subtracting eliminates $\log_{10} A$:

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Since $T_2 > T_1$, the reciprocal-temperature difference is positive, consistent with the increase in rate. Rearranging,

$$E_a = 2.303R \log_{10} \frac{k_2}{k_1} \frac{T_1 T_2}{T_2 - T_1}.$$

Step 3: Substitute and convert the energy units Using $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and the supplied logarithm,

$$\begin{aligned} E_a &= \frac{2.303(8.314)(0.60)(293)(313)}{313 - 293} \\ &= 52678.96 \text{ J mol}^{-1} \\ &\simeq 52.7 \text{ kJ mol}^{-1}. \end{aligned}$$

The temperature factor has units of kelvin, which cancel the inverse-kelvin unit in R .

Step 4: Conclusion The activation energy of the reaction is $E_a \simeq 52.7 \text{ kJ mol}^{-1}$, using the given value $\log 4 = 0.60$.

Quick Tip to Solve: With common logarithms keep the factor 2.303, and write the reciprocal difference as $(T_2 - T_1)/(T_1 T_2)$ to avoid a sign error.

25(a). Write the IUPAC name of the given complex : $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$

[1 mark]

Solution:

Concept:

- Name coordinated ligands alphabetically, ignoring multiplicative prefixes; state the metal oxidation number in Roman numerals.
- Ammine and aqua are neutral ligands, whereas chlorido has charge -1 . Counter-ions balance the charge of the coordination entity.

Step 1: Determine the cobalt oxidation state The two outer Cl^- ions show that $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ has charge $+2$. If cobalt has oxidation state x , then $x + 4(0) + 0 - 1 = +2$, giving $x = +3$.

Step 2: Arrange the ligand names The ligand names are ammine, aqua and chlorido, in that alphabetical order. Four ammine ligands give tetraammine. Since the complex ion is cationic, retain the metal name cobalt and place chloride, the counter-ion name, after the complex name.

Step 3: Conclusion The IUPAC name is **tetraammineaquachloridocobalt(III) chloride**.

Quick Tip to Solve: Count outer chlorides first to obtain the complex charge; ignore the prefix tetra when alphabetising ammine, aqua and chlorido.

25(b). Define polydentate ligand. Give an example.

[1 mark]

Solution:

Concept:

- A ligand donates a lone pair from a donor atom to a central metal atom or ion to form a coordinate bond.
- Denticity is the number of donor atoms of one ligand that simultaneously bind to the same central metal ion.

Step 1: Define a polydentate ligand A polydentate ligand can attach to a single central metal ion through several donor atoms belonging to the same ligand. Thus, one ligand occupies multiple coordination sites rather than binding through only one atom.

Step 2: Identify the donor atoms in an example The ethylenediaminetetraacetate ion, EDTA^{4-} , is an example. It can bind through two nitrogen donor atoms and four oxygen donor atoms, one from each carboxylate group, so it acts as a hexadentate ligand.

Step 3: Conclusion A polydentate ligand binds to a metal ion through several donor atoms; EDTA^{4-} , with six donor atoms, is a standard example.

Quick Tip to Solve: For EDTA, count two nitrogen donors plus four carboxylate oxygen donors to remember its denticity of six.

25(c). Mention the type of isomerism exhibited by the given complex : $[\text{Co}(\text{en})_3]\text{Cl}_3$

[1 mark]

Solution:

Concept:

- Optical isomers are non-superimposable mirror images, called enantiomers, which rotate plane-polarised light in opposite directions.
- Ethane-1,2-diamine, en, is a bidentate ligand: its two nitrogen donor atoms occupy two coordination positions.

Step 1: Identify the coordination geometry In $[\text{Co}(\text{en})_3]\text{Cl}_3$, the coordination entity is $[\text{Co}(\text{en})_3]^{3+}$. Three bidentate ligands provide six donor atoms around cobalt, giving an octahedral complex with three chelate rings. The chloride ions lie outside the coordination sphere.

Step 2: Check the mirror-image arrangements The three chelate rings can wind around the metal in two opposite senses. These arrangements are mirror images that cannot be superimposed, conventionally labelled Δ and Λ . The tris-chelate ion therefore has a pair of optical isomers; three identical bidentate ligands do not give a separate cis-trans pair here.

Step 3: Conclusion $[\text{Co}(\text{en})_3]\text{Cl}_3$ exhibits **optical isomerism**.

Quick Tip to Solve: Recognise an octahedral complex with three identical bidentate en ligands as the standard tris-chelate example of optical isomerism.

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

[1 mark]

Solution:

Concept:

- Excess silver nitrate precipitates ionisable chloride ions outside the coordination sphere as AgCl .
- Chromium(III) has coordination number six in these hydrated complexes; coordinated chloride and water together occupy six positions.

Step 1: Count chloride ions outside the sphere One mole of AgCl per mole of compound shows that only one of the three chloride ions is outside the coordination sphere. The other two chloride ions are coordinated to chromium.

Step 2: Account for all six water molecules Two coordinated chloride ions leave four positions for water ligands. Of the six water molecules in the formula, four are coordinated and the remaining two are water of crystallisation. The complex ion has charge $+3 - 2 = +1$, balanced by one external chloride ion.

Step 3: Conclusion The structural formula is $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$.

Quick Tip to Solve: First count external chloride from AgCl ; then fill chromium's six coordination positions with the remaining chloride and water.

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

Solution:

Concept:

- The sum of the metal oxidation state and the charges of all ligands equals the charge on the complex ion.
- Cyanide is a strong-field ligand. In an octahedral iron(III) complex it produces a low-spin arrangement by pairing the d electrons.

Step 1: Determine the iron oxidation state Each CN^- ligand has charge -1 . If the oxidation state of iron is x , then $x + 6(-1) = -3$, giving $x = +3$. Neutral iron is $[\text{Ar}]3d^64s^2$, so Fe^{3+} is $[\text{Ar}]3d^5$.

Step 2: Determine the hybridisation With strong-field cyanide ligands, the five d electrons occupy the three lower-energy orbitals as $t_{2g}^5e_g^0$. Two 3d orbitals are vacant. In valence-bond terms, these two 3d orbitals, one 4s orbital and three 4p orbitals form six d^2sp^3 hybrid orbitals for an inner-orbital octahedral complex.

Step 3: Conclusion The oxidation state of iron is $+3$ and its hybridisation is d^2sp^3 .

Quick Tip to Solve: Remove the 4s electrons first when forming $\text{Fe}(\text{III})$, then use cyanide's strong-field character to identify inner-orbital hybridisation.

26(c). Why is $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ coloured ? [Atomic number : Ti = 22] [1 mark]

Solution:

Concept:

- In an octahedral ligand field, the five d orbitals split into lower-energy t_{2g} and higher-energy e_g orbitals.
- Absorption of visible light can promote an electron between these levels; the observed colour is complementary to the absorbed light.

Step 1: Find the d-electron configuration Water is a neutral ligand, so titanium has oxidation state $+3$. Titanium has atomic number 22 and ground-state configuration $[\text{Ar}]3d^24s^2$. Removing three electrons gives Ti^{3+} the configuration $[\text{Ar}]3d^1$.

Step 2: Explain the electronic transition The six water ligands produce octahedral splitting. The single d electron initially occupies a lower t_{2g} orbital. It absorbs visible light of energy equal to the splitting and is promoted to a higher e_g orbital. This d-d transition selectively removes part of the visible light passing through the solution.

Step 3: Conclusion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured because its $3d^1$ ion undergoes a d-d transition by absorbing visible light.

Quick Tip to Solve: Establish the metal ion's d-electron count before explaining colour through octahedral splitting and visible-light absorption.

27. (a) Define order of a reaction.

(b) The rate for the following reaction is given by: $A + B \rightarrow C$, 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:

- For an experimentally determined rate law $r = k[A]^m[B]^n$, the order with respect to A is m , the order with respect to B is n , and the overall order is $m + n$.
- When one reactant is present in large excess, its concentration remains practically constant during the reaction and can be incorporated into an observed rate constant.

Step 1: (a) Define the order of a reaction The order of a reaction is the sum of the powers to which the reactant concentrations are raised in the experimentally determined rate law. It is determined from kinetics and need not equal the sum of the stoichiometric coefficients in the balanced reaction. For the given law $r = k[A][B]^2$, the orders with respect to A and B are one and two, respectively.

Step 2: (b)(i) Compare rates on doubling B Keep the temperature and concentration of A unchanged. The original rate is $r = k[A][B]^2$. Replacing $[B]$ by $2[B]$ gives

$$r' = k[A](2[B])^2 = 4k[A][B]^2, \quad \frac{r'}{r} = 4.$$

The exponent of B is two, so its concentration change enters as the square of the multiplying factor.

Step 3: (b)(ii) Apply the large-excess condition When A is in large excess, its fractional consumption is negligible, so $[A] \approx [A]_0$ throughout the measurement. Defining $k_{\text{obs}} = k[A]_0$ gives

$$r = k_{\text{obs}}[B]^2.$$

The observed rate now depends only on the second power of B. The original full rate law remains third order; the excess-A experiment exhibits pseudo-second-order kinetics.

Step 4: Conclusion (a) Order is the sum of concentration exponents in the rate law. (b)(i) Doubling B makes the rate four times its original value. (b)(ii) With A in large excess, the observed overall order is $\boxed{2}$, a pseudo-second-order reaction.

Quick Tip to Solve: Square any multiplying factor applied to B; when A is in excess, absorb only its nearly constant concentration into the rate constant.

- 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:



[3 marks]

Solution:

Concept:

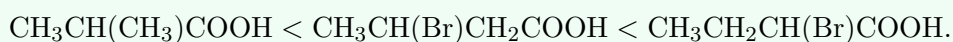
- A carboxylic acid is stronger when its conjugate carboxylate ion is more stable. Electron-withdrawing groups stabilise this ion by the negative inductive effect, which decreases rapidly with distance.
- Nucleophilic addition to a carbonyl group is favoured by greater positive character on the carbonyl carbon and lower steric hindrance around it.
- Aldehydes and ketones condense with hydrazine, NH_2NH_2 , to form hydrazones with elimination of water.

Step 1: (i) Compare the inductive effects The methyl groups in $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$ donate electron density through the positive inductive effect and destabilise the carboxylate ion. Bromine withdraws electron density and stabilises the conjugate base. In $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, bromine is at the beta carbon, whereas in $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ it is at the alpha carbon. Its withdrawing effect is stronger at the nearer alpha position. Thus, acidity increases from the alkyl-substituted acid to the beta-bromo acid and then to the alpha-bromo acid.

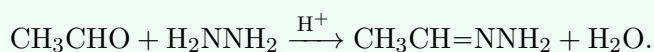
Step 2: (ii) Explain the reactivity towards HCN Cyanide ion attacks the electrophilic carbonyl carbon. Acetaldehyde, CH_3CHO , has one methyl group and one hydrogen, while acetone has two methyl groups. The additional methyl group in acetone donates electron density by its positive inductive effect, reducing the positive character of the carbonyl carbon. It also increases steric hindrance to cyanide attack. Both the electronic and steric factors favour acetaldehyde.

Step 3: (iii) Identify the condensation product Hydrazine adds through nitrogen to the aldehyde carbonyl group. Acid-catalysed condensation then eliminates one molecule of water and replaces $\text{C}=\text{O}$ by $\text{C}=\text{N}-\text{NH}_2$. The methyl group and hydrogen originally attached to the carbonyl carbon are retained in the hydrazone.

Step 4: Conclusion (i) The increasing acidic-strength order is



(ii) Acetaldehyde is more reactive because its carbonyl carbon is more electrophilic and less sterically hindered. (iii) The completed equation is



The organic product is acetaldehyde hydrazone.

Quick Tip to Solve: Locate Br relative to COOH before ranking acidity; with hydrazine, replace the carbonyl oxygen by $\text{N}-\text{NH}_2$ and release water.

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]

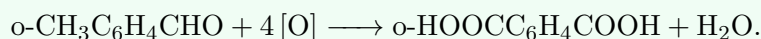
Solution:

Concept:

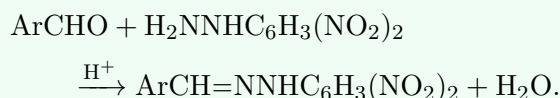
- Formation of a 2,4-dinitrophenylhydrazone indicates a carbonyl group; reduction of Tollens' reagent identifies the compound as an aldehyde.
- An aldehyde without an alpha hydrogen undergoes Cannizzaro disproportionation in concentrated alkali: one aldehyde molecule is oxidised and another is reduced.
- Vigorous oxidation converts oxidisable aromatic side chains into $-COOH$ groups while preserving their positions on the benzene ring.

Step 1: Use the tests to identify the functional group The 2,4-DNP test establishes the presence of $C=O$, and the Tollens' test requires an aldehyde group, $-CHO$. The formula C_8H_8O is consistent with a methyl-substituted benzaldehyde. Here the carbon directly attached to the aldehyde carbon is an aromatic ring carbon and carries no alpha hydrogen, so Cannizzaro reaction is possible.

Step 2: Locate the substituents on the ring Oxidation produces benzene-1,2-dicarboxylic acid, so the methyl and aldehyde groups must occupy adjacent ring positions. Both side chains become carboxyl groups:

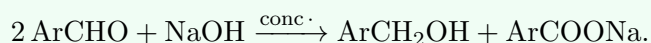


Step 3: Write the 2,4-DNP reaction Write Ar for the 2-methylphenyl group $o-CH_3C_6H_4^-$. In an acidic medium, the aldehyde condenses with 2,4-dinitrophenylhydrazine, eliminating water:



The nitro groups are at positions 2 and 4 of the hydrazine reagent's ring. The product is the corresponding 2,4-dinitrophenylhydrazone precipitate.

Step 4: Write the Cannizzaro reaction With concentrated sodium hydroxide, two molecules of the aldehyde give one molecule each of the alcohol and the carboxylate salt:



The products are 2-methylbenzyl alcohol and sodium 2-methylbenzoate.

Step 5: Conclusion The compound is 2-methylbenzaldehyde (*o*-tolualdehyde), $o-CH_3C_6H_4CHO$. Its 2,4-DNP and Cannizzaro reactions are given above.

Quick Tip to Solve: Use Tollens' reagent to choose the aldehyde, then use the 1,2-dicarboxylic acid oxidation product to fix the ortho positions.

Section D (8 marks)

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

29. 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:

[4 marks]

Predict the products of electrolysis in each of the following:

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

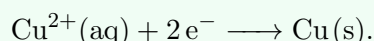
[1 mark]

Solution:

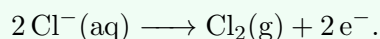
Concept:

- Reduction occurs at the cathode and oxidation at the anode. Platinum provides an inert conducting surface and does not supply metal ions.
- In aqueous copper chloride, copper ions are preferentially reduced, while chloride ions are oxidised at the anode.

Step 1: Write the cathode reaction Copper ions accept two electrons each to give copper metal. Copper is deposited on the platinum cathode:



Step 2: Write the anode reaction Chloride ions lose electrons at the inert platinum anode and combine to form chlorine gas:



The electrons released at the anode equal the electrons consumed at the cathode, giving the net decomposition of copper chloride into copper and chlorine.

Step 3: Conclusion Aqueous CuCl_2 with platinum electrodes gives copper metal at the cathode and chlorine gas at the anode.

Quick Tip to Solve: First assign reduction to the cathode: Cu^{2+} gains electrons, while Cl^{-} loses electrons at the anode.

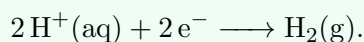
29(a)(ii). A concentrated solution of H_2SO_4 with platinum electrodes.

[1 mark]

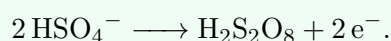
Solution:**Concept:**

- Platinum is inert: hydrogen ions are reduced at the cathode, while oxidation occurs at the anode.
- Concentration affects the anode product. Concentrated sulphuric acid gives peroxodisulphuric acid through oxidation of hydrogen sulphate ions.

Step 1: Write the cathode reaction Hydrogen ions from the acid accept electrons to form hydrogen gas at the platinum cathode:



Step 2: Write the anode reaction for concentrated acid Hydrogen sulphate ions undergo oxidation at the platinum anode, forming peroxodisulphuric acid:



The equation conserves hydrogen, sulphur, oxygen and charge. The word concentrated is essential: dilute sulphuric acid ordinarily gives oxygen through water oxidation instead.

Step 3: Conclusion Concentrated H_2SO_4 with platinum electrodes gives hydrogen gas at the cathode and peroxodisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, at the anode.

Quick Tip to Solve: Circle concentrated before selecting the anode product: it favours peroxodisulphuric acid, whereas dilute acid gives oxygen.

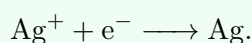
29(b)(i). How much charge in faraday is required for the reduction of 1 mol of Ag^+ to Ag ?

[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 needed is $Q = nzF$, where n is the amount of substance in moles and z is the number of electrons accepted by each ion.

Step 1: Balance the silver reduction half-reaction A silver ion has charge +1, so each ion must accept one electron to become a neutral silver atom:



Thus one mole of silver ions requires one mole of electrons, and $z = 1$.

Step 2: Calculate the required charge For $n = 1 \text{ mol}$, substitute into Faraday's relation:

$$Q = (1 \text{ mol})(1)(96485 \text{ C mol}^{-1}) = 96485 \text{ C}.$$

This is precisely the charge of one mole of electrons, so its value in the requested unit is one faraday.

Quick Tip to Solve: For one mole of metal ions, read the electron coefficient in the reduction half-reaction directly as the number of faradays required.

Step 3: Conclusion The charge required to reduce 1 mol of Ag^+ to Ag is 1 faraday, approximately $9.65 \times 10^4 \text{ C}$.

Quick Tip to Solve: For one mole of metal ions, read the electron coefficient in the reduction half-reaction directly as the number of faradays required.

OR

29(b)(ii). State Faraday's second law of electrolysis.

[1 mark]

Solution:

Concept:

- Faraday's second law compares the masses deposited or liberated from different electrolytes by the same electric charge.
- The chemical equivalent mass is $E = M/z$, where M is the molar mass and z is the number of electrons exchanged per formula unit in the electrode reaction.

Step 1: State the equal-charge condition 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 equality of charge passed is the essential condition for this comparison.

Step 2: Express the law mathematically If m_1 and m_2 are the masses produced and E_1 and E_2 their respective equivalent masses, then

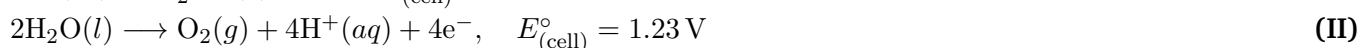
$$\frac{m_1}{m_2} = \frac{E_1}{E_2} = \frac{M_1/z_1}{M_2/z_2} \quad \text{for equal charge.}$$

Thus the relevant proportionality is with equivalent mass; molar mass alone is insufficient when the electron numbers differ.

Step 3: Conclusion Faraday's second law states that equal quantities of electricity passed through different electrolytes deposit or liberate masses proportional to their chemical equivalent masses.

Quick Tip to Solve: Remember second law as same charge, different electrolytes; compare M/z values rather than molar masses alone.

29(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]

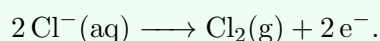
Solution:

Concept:

- Chloride oxidation and water oxidation compete at the anode in aqueous sodium chloride electrolysis.
- The actual potential needed for gas evolution includes overpotential, an additional potential caused by slow electrode kinetics; standard potentials alone do not decide the observed product.

Step 1: Compare the standard-potential prediction From the quoted values, 1.23 V for oxygen evolution is lower than 1.36 V for chlorine evolution. Comparing these values alone would suggest that water oxidation, reaction (II), is easier.

Step 2: Account for oxygen overpotential Oxygen evolution has a high overpotential. Consequently, the actual potential needed to evolve oxygen is higher than the standard-potential comparison suggests, and chloride ions are preferentially oxidised under the usual aqueous sodium chloride electrolysis conditions:



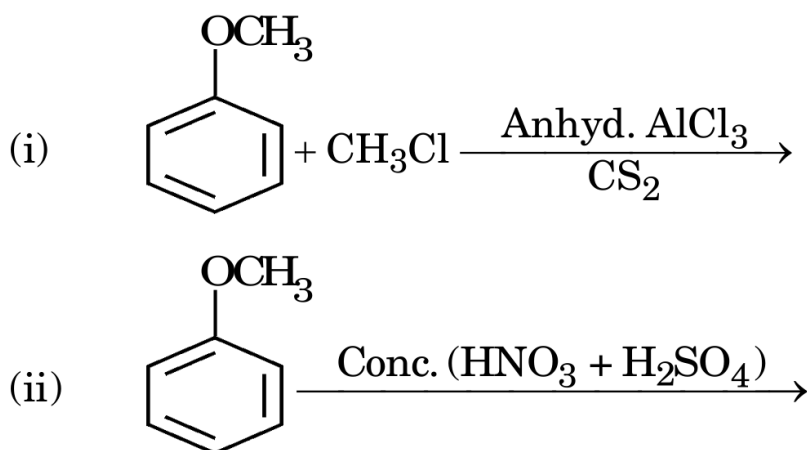
This is twice reaction (I) as printed and describes chlorine evolution at the anode.

Step 3: Conclusion Reaction (I) is feasible at the anode: chlorine is evolved because the high oxygen-evolution overpotential suppresses the competing water oxidation reaction.

Quick Tip to Solve: For aqueous sodium chloride, include oxygen overpotential before choosing the anode gas; the smaller quoted standard value alone is misleading.

30. 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. [4 marks]

30(a). Complete the following equations: [2 marks]

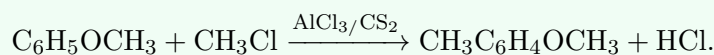


Solution:

Concept:

- The methoxy group, $-OCH_3$, donates an oxygen lone pair into the benzene ring by resonance, increasing electron density at the ortho and para positions.
- Anisole therefore undergoes electrophilic aromatic substitution to give ortho and para products; the para product generally predominates because it has less steric crowding.

Step 1: (i) Friedel–Crafts methylation Anhydrous $AlCl_3$ activates chloromethane, and a methyl group replaces a ring hydrogen ortho or para to the methoxy group. In CS_2 , the organic products are 2-methylanisole and 4-methylanisole (major):

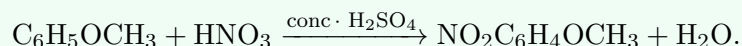


The product formula represents either the ortho or the para isomer, not two molecules from one anisole molecule.

Step 2: (ii) Nitration Concentrated nitric and sulphuric acids generate the nitronium ion, NO_2^+ . This electrophile substitutes at the same activated ring positions, producing 2-nitroanisole and

Quick Tip to Solve: Keep $-OCH_3$ at carbon 1, then put the incoming $-CH_3$ or $-NO_2$ at carbon 2 and carbon 4; label the para product major.

4-nitroanisole (major):



Again, the formula represents either positional isomer. The methoxy group remains attached to the ring.

Step 3: Conclusion (i) *o*-Methylanisole and *p*-methylanisole (major); (ii) *o*-nitroanisole and *p*-nitroanisole (major).

Quick Tip to Solve: Keep $-\text{OCH}_3$ at carbon 1, then put the incoming $-\text{CH}_3$ or $-\text{NO}_2$ at carbon 2 and carbon 4; label the para product major.

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

[1 mark]

Solution:

Concept:

- Williamson ether synthesis uses an alkoxide ion and an alkyl halide in an $\text{S}_{\text{N}}2$ substitution.
- Choose the less hindered, primary group as the alkyl halide; a tertiary alkyl halide favours elimination with a strong alkoxide base.

Step 1: Choose the two reagents The required ether is $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_2\text{CH}_3$. Use bromoethane (ethyl bromide), $\text{CH}_3\text{CH}_2\text{Br}$, and sodium tert-butoxide, $(\text{CH}_3)_3\text{CONa}$. The ethyl carbon bearing bromine is primary and accessible to nucleophilic attack.

Step 2: Apply Williamson substitution The tert-butoxide ion attacks the ethyl carbon and displaces bromide:



Reversing the choice to tert-butyl bromide and sodium ethoxide would favour elimination of the tertiary halide to 2-methylpropene, so it is unsuitable for the intended ether synthesis.

Step 3: Conclusion Use bromoethane and sodium tert-butoxide.

Quick Tip to Solve: Split the ether at oxygen: put the tert-butyl group on the alkoxide and the primary ethyl group on the halide.

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

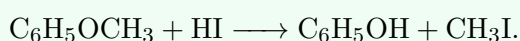
Solution:

Concept:

- In anisole, resonance gives the aryl–oxygen bond partial double-bond character, making it shorter and stronger than the methyl–oxygen bond.
- After protonation of ether oxygen, iodide cleaves the bond to the unhindered methyl carbon by $\text{S}_{\text{N}}2$ attack.

Step 1: Identify the bond that can be cleaved Hydrogen iodide protonates the oxygen atom of $\text{C}_6\text{H}_5\text{-O-CH}_3$. Iodide attacks the methyl carbon and breaks the $\text{CH}_3\text{-O}$ bond. The aryl carbon is sp^2 -hybridised and does not undergo the ordinary $\text{S}_{\text{N}}2$ displacement; the resonance-strengthened aryl–oxygen bond is retained.

Step 2: Identify the products The oxygen stays with the phenyl group, giving phenol, while the methyl group combines with iodide:



Methanol and iodobenzene would require cleavage of the aryl–oxygen bond, which is not the favourable pathway.

Step 3: Conclusion Anisole gives phenol and methyl iodide because the methyl–oxygen bond is cleaved and the stronger aryl–oxygen bond remains intact.

Quick Tip to Solve: In an aryl–alkyl ether treated with HI, keep oxygen attached to the aryl group and attach iodide to the alkyl group.

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

Solution:

Concept:

- Ether oxygen is approximately sp^3 -hybridised, with two bond pairs and two lone pairs; its electron-pair arrangement is approximately tetrahedral.
- The observed bond angle depends on repulsions among electron pairs and on repulsion between the groups attached to oxygen.

Step 1: Identify the reference angle An ideal tetrahedral arrangement has a bond angle of about 109.5° . In an ether, R-O-R' , two of the four electron-pair directions on oxygen contain the bonds to carbon groups, and the other two contain lone pairs.

Step 2: Explain the increase Repulsion between the two relatively bulky alkyl groups pushes them farther apart. This opens the C–O–C angle slightly beyond the ideal tetrahedral value. The enlargement is therefore explained by the mutual repulsion of the attached alkyl groups, rather than

Quick Tip to Solve: For the ether angle, mention repulsion between the two alkyl groups and compare the angle with 109.5° .

by assigning a different hybridisation to oxygen.

Step 3: Conclusion The C–O–C bond angle in ethers is slightly greater than 109.5° because of repulsion between the two bulky alkyl groups.

Quick Tip to Solve: For the ether angle, mention repulsion between the two alkyl groups and compare the angle with 109.5° .

Section E (15 marks)

31(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 substitution begins with slow heterolytic cleavage of the carbon–halogen bond to produce a carbocation.
- The more stable the intermediate carbocation, the easier its formation; alkyl carbocation stability follows tertiary greater than secondary greater than primary.

Step 1: Identify the intermediates Loss of bromide from 2-bromo-2-methylbutane gives $(CH_3)_2C^+CH_2CH_3$, a tertiary carbocation. Loss of bromide from 1-bromopentane would give $CH_3CH_2CH_2CH_2CH_2^+$, a primary carbocation.

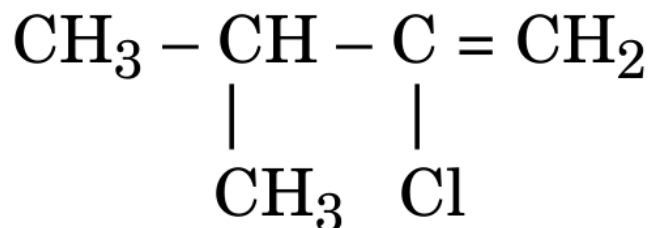
Step 2: Compare carbocation stability Three alkyl groups stabilise the tertiary carbocation through their electron-releasing inductive effect and hyperconjugation. The primary carbocation has much less stabilisation. Since carbocation formation is the rate-determining step and both leaving groups are bromide, the tertiary substrate reacts faster.

Step 3: Conclusion 2-Bromo-2-methylbutane is more reactive towards an S_N1 reaction than 1-bromopentane.

Quick Tip to Solve: For an S_N1 comparison with the same leaving group, remove that group mentally and rank the resulting carbocations.

31(a)(i)(II). What type of halide is present in the following compound :

[1 mark]



Solution:

Concept:

- A vinylic halide contains a halogen bonded directly to an sp^2 -hybridised carbon of a carbon-carbon double bond.
- An allylic halide instead has its halogen attached to an sp^3 -hybridised carbon adjacent to a double bond.

Step 1: Locate the carbon bonded to chlorine In $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{C}(\text{Cl}) = \text{CH}_2$, the chlorine is bonded to the third carbon in the displayed chain. This carbon is itself one of the two carbons forming the double bond.

Step 2: Apply the definition of the halide class The carbon bearing chlorine is sp^2 -hybridised and belongs directly to the alkene unit. The halogen is not attached to the neighbouring saturated carbon, so the compound is not an allylic halide. The alkyl branches elsewhere in the molecule do not change this classification.

Step 3: Conclusion The compound is a **vinylic halide**, specifically a vinylic chloride.

Quick Tip to Solve: Trace the bond from chlorine to its carbon: attachment directly to a double-bond carbon identifies a vinylic halide.

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

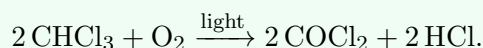
[1 mark]

Solution:

Concept:

- Chloroform, CHCl_3 , slowly undergoes oxidation by atmospheric oxygen in the presence of light.
- Its oxidation product, carbonyl chloride or phosgene, COCl_2 , is highly poisonous.

Step 1: Identify the harmful photochemical change Air and light together promote oxidation of chloroform to phosgene:



Thus prolonged exposure to light can make the stored liquid hazardous.

Step 2: Relate bottle colour to protection Dark coloured glass reduces the light reaching chloroform and hence inhibits this light-promoted oxidation. The bottle is also kept tightly closed to limit contact with air.

Quick Tip to Solve: Link dark glass to exclusion of light, then name the toxic product phosgene; evaporation is not the reason for the bottle colour.

Step 3: Conclusion Chloroform is stored in dark coloured bottles to suppress its oxidation by air in light to highly poisonous phosgene, COCl_2 .

Quick Tip to Solve: Link dark glass to exclusion of light, then name the toxic product phosgene; evaporation is not the reason for the bottle colour.

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

(I) Ambident Nucleophiles (II) Racemic mixture

[2 marks]

Solution:

Concept:

- A nucleophile donates an electron pair to an electron-deficient centre to form a covalent bond.
- Enantiomers are non-superimposable mirror-image forms; their specific optical rotations have equal magnitudes and opposite signs under identical conditions.

Step 1: Define an ambident nucleophile (I) An ambident nucleophile is a nucleophile having two alternative nucleophilic sites through either of which it can attack an electrophile. For example, the cyanide ion, CN^- , may bond through carbon to give an alkyl cyanide, $\text{R}-\text{C}\equiv\text{N}$, or through nitrogen to give an alkyl isocyanide, $\text{R}-\text{N}\equiv\text{C}$. Here R represents an alkyl group. The term refers to alternative attacking atoms, not to simultaneous bond formation through both atoms.

Step 2: Define a racemic mixture (II) A racemic mixture contains equal amounts of the two enantiomers of an optically active compound. The dextrorotatory (+) form and the laevorotatory (–) form rotate plane-polarised light equally in opposite directions. Their rotations cancel, so the mixture has zero net optical rotation. This is external compensation; each enantiomer remains individually optically active.

Step 3: Conclusion An ambident nucleophile can attack through either of two sites. A racemic mixture is an equimolar mixture of two enantiomers and is optically inactive by external compensation.

Quick Tip to Solve: For ambident nucleophiles name both attacking atoms; for a racemate specify equal enantiomer amounts and cancellation of optical rotation.

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

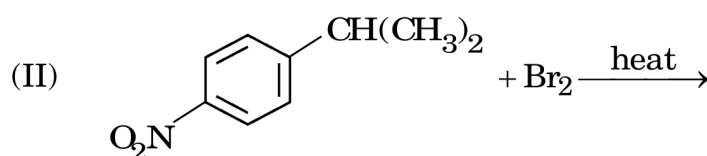
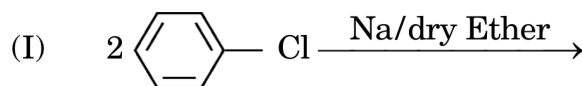
(I) Which isomer of C_4H_9Br is most reactive towards S_N1 reaction?

(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.
- In dehydrohalogenation, removal of a β -hydrogen and halide produces an alkene. The more substituted alkene is generally the major product by Saytzeff's rule.
- Chlorine withdraws electrons inductively but donates a lone pair by resonance; overall reactivity and directing influence are distinct effects.
- Sodium in dry ether couples aryl halides (Fittig reaction). Bromine with heat causes free-radical substitution at a favourable benzylic position.

Step 1: Select the fastest isomer for ionisation (i)(I) The most reactive isomer is 2-bromo-2-methylpropane, or tert-butyl bromide, $(CH_3)_3CBr$. Cleavage of its carbon-bromine bond forms the tertiary tert-butyl carbocation. Alkyl groups stabilise this ion by the electron-releasing inductive effect and hyperconjugation. The other C_4H_9Br isomers form secondary or primary carbocations, so their ionisation is less favourable under comparable S_N1 conditions.

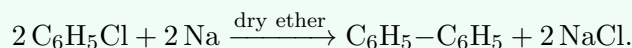
Step 2: Apply Saytzeff's rule to the cyclic halide (i)(II) The carbon bearing bromine is C-1. Removal of bromine from C-1 and a hydrogen from either adjacent ring carbon, C-2 or C-6, gives the same endocyclic double bond. The major product is **1-methylcyclohex-1-ene**. This double bond is trisubstituted and more stable than the disubstituted exocyclic double bond of methylenecyclohexane, which would result from removing a hydrogen from the methyl substituent.

Step 3: Separate deactivation from orientation (i)(III) Chlorine's strong $-I$ effect lowers the overall electron density of the ring and makes chlorobenzene less reactive than benzene towards electrophilic substitution. Nevertheless, a chlorine lone pair can overlap with the ring's π system and donate by resonance ($+R$). This donation enhances electron density at the ortho and para positions and provides additional resonance stabilisation of the carbocation intermediate for attack at those positions. The corresponding stabilisation is absent for meta attack. Hence chlorine deactivates the ring but directs

Quick Tip to Solve: Read the reaction conditions first: sodium/dry ether signals aryl coupling, while bromine/heat signals benzylic substitution. Count benzylic hydrogens before placing bromine.

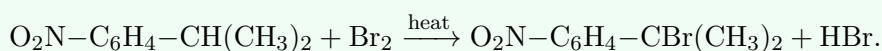
incoming electrophiles mainly to ortho and para positions.

Step 4: Couple the two phenyl groups (ii)(I) Sodium in dry ether replaces the carbon–chlorine bonds of two chlorobenzene molecules by a bond between their phenyl groups:



The major organic product is **biphenyl**. This is the Fittig reaction because both coupling partners are aryl halides.

Step 5: Substitute the benzylic hydrogen (ii)(II) The starting molecule has an isopropyl group para to the nitro group. Heating with Br_2 favours a radical side-chain reaction. The single hydrogen on the carbon attached directly to the ring is replaced by bromine because abstraction there gives a particularly stable tertiary benzylic radical. With the nitro and side-chain groups remaining para to one another, the reaction is



The product is **2-bromo-2-(4-nitrophenyl)propane**; neither the ring nitro group nor either methyl group is replaced.

Step 6: Conclusion (i) The answers are: (I) tert-butyl bromide, (II) 1-methylcyclohex-1-ene, and (III) resonance donation causes ortho/para direction despite inductive deactivation. (ii) The major products are (I) biphenyl and (II) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CBr}(\text{CH}_3)_2$, with the nitro group para to the brominated side chain.

Quick Tip to Solve: Read the reaction conditions first: sodium/dry ether signals aryl coupling, while bromine/heat signals benzylic substitution. Count benzylic hydrogens before placing bromine.

32(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 = $1.86 \text{ K kg mol}^{-1}$)

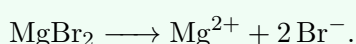
[3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f is the solvent's molal depression constant, and m is the molality of the solute before dissociation.
- Molality is the number of moles of solute per kilogram of solvent. Complete dissociation increases the number of dissolved particles and therefore increases the depression in freezing point.

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



Each formula unit produces one magnesium ion and two bromide ions. There are therefore three dissolved particles per formula unit, giving $i = 3$. The ionic charges do not change this particle count.

Quick Tip to Solve: For completely dissociated MgBr_2 , count three ions and use 250 g = 0.250 kg of water; subtract the resulting depression from zero.

Step 2: Calculate the molality Convert the given mass of solute into moles and the mass of water into kilograms:

$$n = \frac{10.5}{184} = 0.05707 \text{ mol}, \quad m_{\text{water}} = 0.250 \text{ kg}.$$

Thus the molality calculated from the undissociated formula units is

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

Use the solvent mass in this denominator; adding the solute mass would give an incorrect molality.

Step 3: Find the depression in freezing point Substitute the particle factor, the given constant and the molality:

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

Pure water freezes at 0°C . Since dissolution lowers its freezing point, subtract this temperature interval from that of pure water. A temperature difference has the same numerical value in kelvin and degrees Celsius.

Step 4: Conclusion The solution's freezing point is $T_f = 0 - 1.2737 \simeq -1.27^\circ\text{C}$.

Quick Tip to Solve: For completely dissociated MgBr_2 , count three ions and use $250 \text{ g} = 0.250 \text{ kg}$ of water; subtract the resulting depression from zero.

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

[2 marks]

Solution:

Concept:

- For an ideal solution, Raoult's law holds throughout the entire composition range: $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$, where x is liquid mole fraction and p° is the pure component's vapour pressure.
- Mixing behaviour depends on the relative strengths of unlike and like intermolecular attractions. Ideal mixing has zero enthalpy change, while non-ideal mixing may release or absorb heat.

Step 1: Compare obedience to Raoult's law First difference: An ideal solution obeys Raoult's law at every composition. Thus each component's partial vapour pressure is proportional to its mole fraction. A non-ideal solution does not obey this relation throughout the composition range: its vapour pressure shows positive or negative deviation from the ideal prediction.

Step 2: Compare the enthalpy of mixing Second difference: For an ideal solution, $\Delta H_{\text{mix}} = 0$; no heat is absorbed or evolved on mixing because unlike and like interactions are comparable. For a non-ideal solution, generally $\Delta H_{\text{mix}} \neq 0$: weaker unlike attractions produce endothermic mixing, whereas stronger unlike attractions produce exothermic mixing.

Step 3: Conclusion Ideal solutions obey Raoult's law over the full composition range and have $\Delta H_{\text{mix}} = 0$. Non-ideal solutions deviate from Raoult's law and generally have nonzero enthalpy of mixing.

Quick Tip to Solve: Write each difference as a paired comparison: first Raoult's law, then the value of ΔH_{mix} .

32(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 $\text{K}_2\text{SO}_4 = 174 \text{ g mol}^{-1}$)

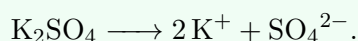
[3 marks]

Solution:

Concept:

- The osmotic pressure of a dilute electrolyte solution is $\pi = iCRT = i(n/V)RT$, where i is the van't Hoff factor, C is formula-unit molarity, n is moles of solute, V is solution volume, and T is absolute temperature.
- Complete dissociation makes the van't Hoff factor equal to the total number of ions produced per formula unit. Temperature must be in kelvin and the volume units must match the gas constant.

Step 1: Count the particles produced by dissociation Potassium sulphate dissociates as



One formula unit gives two potassium ions and one sulphate ion. Hence complete dissociation gives $i = 3$. The sulphate ion remains one particle; its constituent atoms are not counted separately.

Step 2: Calculate the concentration and absolute temperature The amount of potassium sulphate dissolved is

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

For this very dilute solution, take its volume as the stated water volume, $V = 2 \text{ L}$. Therefore

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

and the temperature is $T = 27 + 273 = 300 \text{ K}$. Litres are appropriate because the given R contains litre-atmosphere units.

Step 3: Substitute into the osmotic-pressure equation Using the formula-unit concentration and accounting for dissociation once through i ,

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

The concentration, gas constant and temperature units cancel to leave atmospheres. The small concentration explains why the pressure is much less than one atmosphere.

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

Quick Tip to Solve: For K_2SO_4 , use $i = 3$, convert 27 °C to 300 K, and keep the volume in litres with this value of R .

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

Solution:

Concept:

- An azeotrope is a mixture that boils at constant temperature with the same composition in the liquid and vapour phases. A sufficiently large negative deviation from Raoult's law gives a maximum-boiling azeotrope.
- Stronger attractions between unlike molecules reduce their escaping tendency and lower the mixture's vapour pressure below the ideal value.

Step 1: Identify the intermolecular attraction Acetone, CH_3COCH_3 , has an electron-rich carbonyl oxygen. The hydrogen of chloroform, CHCl_3 , is sufficiently positively polarised by the three chlorine atoms to form a hydrogen bond with that oxygen. On mixing, these acetone–chloroform attractions are stronger than the corresponding interactions between like molecules in the pure liquids.

Step 2: Relate vapour pressure to boiling behaviour The stronger unlike attractions hold molecules in the liquid and reduce their tendency to enter the vapour phase. The mixture therefore shows negative deviation from Raoult's law. A higher temperature is needed for its vapour pressure to reach the external pressure; at the azeotropic composition the boiling temperature is a maximum, above those of the pure components.

Step 3: Conclusion Acetone and chloroform form a **maximum-boiling azeotrope** because hydrogen bonding between unlike molecules causes negative deviation from Raoult's law.

Quick Tip to Solve: Link the reasoning in order: hydrogen bonding between acetone and chloroform, lower vapour pressure, then higher boiling point and a maximum-boiling azeotrope.

33(a)(i)(I). Why do transition metals show variable oxidation states ? [1 mark]

Solution:

Concept:

- Oxidation state depends on the number of electrons that an atom loses or uses in bonding.
- In transition metals, the outer ns and inner $(n - 1)d$ orbitals have comparable energies.

Step 1: Identify the available electrons The valence configuration generally contains electrons in both the ns and $(n - 1)d$ subshells. The energy difference between these subshells is small enough that electrons from both can participate in bond formation.

Step 2: Relate participation to oxidation state The ns electrons are usually lost first, but different numbers of $(n - 1)d$ electrons can also be involved. Thus the same metal can use different total numbers of electrons in different compounds; for example, iron forms Fe^{2+} and Fe^{3+} .

Step 3: Conclusion Transition metals show variable oxidation states because their ns and $(n - 1)d$ orbitals have similar energies, allowing different numbers of electrons from these subshells to participate in bonding.

Quick Tip to Solve: Link variable oxidation states to the small energy gap between the ns and $(n - 1)d$ orbitals, rather than merely stating that d orbitals are present.

33(a)(i)(II). Out of Mn^{2+} and Ti^{2+} which will be more paramagnetic and why ? [Atomic No. : Ti = 22, Mn = 25] [1 mark]

Solution:

Concept:

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

Step 1: Write the configurations of the ions Neutral manganese has configuration $[\text{Ar}]3d^5 4s^2$, whereas titanium has $[\text{Ar}]3d^2 4s^2$. Formation of each divalent ion removes the two $4s$ electrons first. Hence Mn^{2+} is $[\text{Ar}]3d^5$, and Ti^{2+} is $[\text{Ar}]3d^2$.

Step 2: Count the unpaired electrons By Hund's rule, the five d orbitals fill singly before pairing. Thus Mn^{2+} has five unpaired electrons, giving $\mu = \sqrt{35} \approx 5.92 \text{ BM}$, while Ti^{2+} has two, giving $\mu = \sqrt{8} \approx 2.83 \text{ BM}$.

Step 3: Conclusion Mn^{2+} is more paramagnetic because it has five unpaired d electrons, compared with two in Ti^{2+} .

Quick Tip to Solve: Remove the $4s$ electrons before counting unpaired $3d$ electrons in transition-metal cations.

33(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. A favourable reduction makes the species a stronger oxidising agent.
- A half-filled $3d^5$ subshell has additional stability, which can favour its formation during reduction.

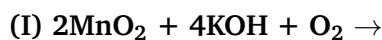
Step 1: Compare the d-electron configurations The given trivalent ions have configurations $\text{Cr}^{3+} : 3d^3$, $\text{V}^{3+} : 3d^2$ and $\text{Mn}^{3+} : 3d^4$. On accepting one electron, they form divalent ions with $3d^4$, $3d^3$ and $3d^5$ configurations, respectively.

Step 2: Identify the especially stable reduction product The reduction $\text{Mn}^{3+} + e^- \longrightarrow \text{Mn}^{2+}$ produces the especially stable half-filled $3d^5$ configuration. This gives Mn^{3+} a strong tendency to accept an electron. Neither Cr^{3+} nor V^{3+} gains a half-filled d subshell on this reduction; Cr^{3+} also has a stable $3d^3$ configuration.

Step 3: Conclusion Mn^{3+} is the strongest oxidising agent among the three ions because its reduction gives Mn^{2+} , with the particularly stable half-filled $3d^5$ configuration.

Quick Tip to Solve: Compare the configurations after electron gain: a strong oxidising ion is reduced to a particularly stable product.

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



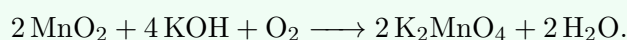
[2 marks]

Solution:

Concept:

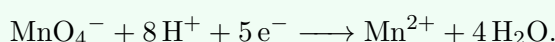
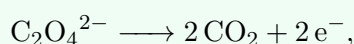
- On fusion with potassium hydroxide in oxygen, manganese dioxide is oxidised to potassium manganate, containing manganese in the +6 oxidation state.
- In acidic solution, permanganate is reduced to Mn^{2+} , while oxalate is oxidised to CO_2 . A balanced ionic equation conserves both atoms and total charge.

Step 1: Complete the alkaline oxidation in part (I) Manganese changes from +4 in MnO_2 to +6 in K_2MnO_4 . Oxygen acts as the oxidising agent. With the coefficients supplied, the two manganese atoms produce two units of potassium manganate, and the four hydrogen atoms produce two water molecules:

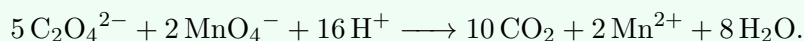


The equation contains two Mn, four K, four H and ten O atoms on each side.

Step 2: Balance the acidic redox reaction in part (II) The oxidation and reduction half-reactions are



Multiply the first by five and the second by two to cancel ten electrons. Addition gives



Both sides contain ten carbon, two manganese, twenty-eight oxygen and sixteen hydrogen atoms. The net charge on each side is +4, confirming the ionic balance.

Step 3: Conclusion The required products are (I) $2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$ and (II) $10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$, with the balanced equations shown above.

Quick Tip to Solve: In alkaline fusion, manganese dioxide forms manganate; in acidic oxalate oxidation, permanganate forms Mn^{2+} . Check charge as well as atoms.

- 33(b). (i) What is meant by lanthanoid contraction?
 (ii) Why do transition metals form coloured compounds?
 (iii) Why are $E^\circ_{M^{2+}/M}$ 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 shielding increases effective nuclear attraction and contracts atomic or ionic radii.
- Ligands split d -orbital energies; visible-light absorption can produce $d-d$ transitions.
- Aqueous oxidation-state stability depends on electronic configuration, ionisation and hydration. A positive reduction potential favours reduction.

Step 1: (i) Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic radii and the radii of trivalent lanthanoid ions with increasing atomic number across the lanthanoid series. Added $4f$ electrons shield the increasing nuclear charge poorly. The resulting increase in effective nuclear attraction pulls the electron cloud inward.

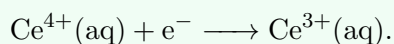
Step 2: (ii) Explain the origin of colour Surrounding ligands split the five d orbitals into groups of different energies. In a suitably partially filled d subshell, an electron absorbs visible light, $\Delta E = h\nu$, and moves to a higher-energy d orbital. The compound shows the complementary colour of the absorbed light. Ions with d^0 or d^{10} configurations cannot undergo this type of transition.

Step 3: (iii) Identify the stable divalent configurations The potential refers to $M^{2+}(aq) + 2e^- \longrightarrow M(s)$. The half-filled $[Ar]3d^5$ configuration of Mn^{2+} and completely filled $[Ar]3d^{10}$ configuration of Zn^{2+} give these ions extra stability. Their reduction to the metals is therefore less favourable than the general trend suggests, making their $E^\circ_{M^{2+}/M}$ values more negative than expected.

Step 4: (iv) Explain the stability of copper(II) Copper's most stable common aqueous oxidation state is +2. The much more negative hydration enthalpy of Cu^{2+} compensates for the high second ionisation enthalpy, despite the filled $3d^{10}$ configuration of Cu^+ . Consequently, aqueous copper(I) disproportionates:



Step 5: (v) Explain the oxidising action of cerium(IV) In water, Ce^{4+} readily accepts an electron to form the more stable aqueous ion Ce^{3+} :



This couple has a highly positive standard reduction potential. Thus Ce^{4+} is readily reduced and oxidises other substances; its $4f^0$ configuration alone does not decide aqueous stability.

Step 6: Conclusion Poor $4f$ shielding explains contraction; $d-d$ transitions explain colour. Stable divalent configurations explain the negative potential anomalies. Hydration favours Cu^{2+} , while ready reduction to Ce^{3+} makes Ce^{4+} oxidising.

Quick Tip to Solve: Use ionic configurations for manganese and zinc, but also consider hydration when comparing aqueous copper and cerium oxidation states.