

# CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-5-3

## Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

### General Instructions

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

## Section A (16 marks)

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

1. The major product of carbylamine reaction is:

[1 mark]

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

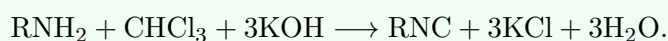
**Correct Answer:** (D) Isocyanide

### Solution:

#### Concept:

- The carbylamine reaction converts a primary amine into an isocyanide using chloroform and alcoholic potassium hydroxide.
- An isocyanide has the linkage  $R - N \equiv C$ , whereas a cyanide has  $R - C \equiv N$ .

**Step 1: Apply the reaction** A primary amine reacts on heating with chloroform and alcoholic alkali:



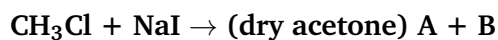
The organic product is an isocyanide, also called a carbylamine, and has a characteristic offensive odour.

**Step 2: Check all options** Carboxylic acid and aldehyde require different functional-group transformations and are not formed in this test. Cyanide has carbon attached to the organic group, whereas the carbylamine product has nitrogen attached to it. Thus options (A), (B) and (C) do not describe the product.

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

**Quick Tip to Solve:** In carbylamine, remember that the amine nitrogen remains attached to R: the product is RNC, not RCN.

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



[1 mark]

- (A) A = CH<sub>3</sub>I, B = NaCl  
(B) A = CH<sub>3</sub>OH, B = NaCl  
(C) A = CH<sub>3</sub>CHO, B = NaCl  
(D) A = C<sub>2</sub>H<sub>6</sub>, B = CH<sub>3</sub>I

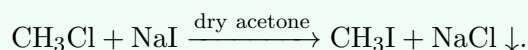
**Correct Answer:** (A) A = CH<sub>3</sub>I, B = NaCl

**Solution:**

**Concept:**

- Finkelstein reaction is halogen exchange of an alkyl chloride or bromide with sodium iodide in dry acetone.
- Iodide acts as a nucleophile; precipitation of sodium chloride or bromide in acetone favours product formation.

**Step 1: Identify the substitution products** Iodide replaces chlorine in chloromethane through nucleophilic substitution:



Hence the organic product A is iodomethane and B is sodium chloride. The carbon skeleton remains unchanged.

**Step 2: Check the alternatives** Option (A) gives precisely these products. There is no hydroxide reagent to produce methanol in (B), and no oxidation process to yield ethanal in (C). Formation of ethane in (D) would require coupling, such as reaction with sodium metal; sodium iodide in acetone instead exchanges halogens.

**Step 3: Conclusion** A = CH<sub>3</sub>I and B = NaCl. Hence, the correct option is (A).

**Quick Tip to Solve:** NaI in dry acetone signals Finkelstein exchange: replace Cl or Br by I and write the precipitated sodium salt.

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

[1 mark]

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

**Correct Answer:** (B) Wolff-Kishner reduction

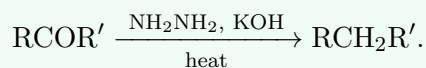
**Solution:**

**Concept:**

- Wolff-Kishner reduction replaces the carbonyl group  $>\text{C}=\text{O}$  of an aldehyde or ketone by  $>\text{CH}_2$ .
- The reagents are hydrazine followed by heating with strong base, usually KOH, in a high-boiling solvent.

**Quick Tip to Solve:** For carbonyl-to-methylene conversion, recognise hydrazine plus base as Wolff-Kishner reduction.

**Step 1: Recognise carbonyl deoxygenation** A ketone first forms a hydrazone with hydrazine. Heating under basic conditions removes nitrogen and yields the corresponding hydrocarbon:



This transformation is called Wolff-Kishner reduction.

**Step 2: Eliminate the other reactions** Reimer-Tiemann reaction introduces a formyl group into phenol. Aldol condensation joins suitable carbonyl compounds and produces an aldol or an unsaturated carbonyl product. Stephen reaction reduces a nitrile to an aldehyde after hydrolysis. None of (A), (C) or (D) performs the required ketone-to-hydrocarbon conversion.

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

**Quick Tip to Solve:** For carbonyl-to-methylene conversion, recognise hydrazine plus base as Wolff-Kishner reduction.

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

(i)  $\text{R-CO-NH}_2$  (ii)  $\text{NaOH}$  (iii)  $\text{Br}_2$  (iv)  $\text{CHCl}_3$

[1 mark]

(A) (i), (ii) and (iv)

(B) (i) and (iii)

(C) (i), (ii) and (iii)

(D) (i), (iii) and (iv)

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

**Solution:**

**Concept:**

- Hofmann bromamide degradation converts a primary amide  $\text{RCONH}_2$  into a primary amine  $\text{RNH}_2$ .
- Bromine and aqueous sodium hydroxide are required; the product has one fewer carbon atom than the amide.

**Step 1: Select the required chemicals** The primary amide is the substrate, and bromine in aqueous alkali brings about rearrangement and degradation:



Thus the required entries are (i), (ii) and (iii).

**Step 2: Check the combinations** Chloroform, entry (iv), is used in the carbylamine reaction and is not required here. Hence (A) and (D) introduce an unnecessary reagent. Option (B) omits sodium hydroxide, which is essential for the alkaline reaction medium. Only (C) contains the complete required combination.

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

**Quick Tip to Solve:** Hofmann degradation needs amide plus bromine plus alkali; chloroform instead points to the carbylamine test.

5. 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 reagent is benzenesulphonyl chloride, with formula  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ .
- Its reactions with amines, together with the alkali solubility of the products, distinguish primary, secondary and tertiary amines.

**Step 1: Identify the functional group** The reagent contains a phenyl group bonded to the sulphonyl chloride group,  $-\text{SO}_2\text{Cl}$ . Therefore its formula is  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ , which matches option (B). Primary and secondary amines react at this group to form sulphonamides.

**Step 2: Check the other formulas**  $\text{C}_6\text{H}_5\text{COCl}$  in (A) is benzoyl chloride, an acyl chloride.  $\text{C}_6\text{H}_5\text{CONHCH}_3$  in (C) is an amide, and  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  in (D) is benzylamine. These are different classes of compounds and none is the reagent used for the Hinsberg test.

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

**Quick Tip to Solve:** Look for the  $\text{SO}_2\text{Cl}$  group in Hinsberg reagent;  $\text{COCl}$  identifies benzoyl chloride instead.

6. 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:**

- Actinoids have valence electrons in 5f, 6d and 7s orbitals with comparable energies.
- Electrons from these orbitals can participate in bonding, giving actinoids several accessible oxidation states.

**Step 1: Relate orbital energy to oxidation states** The small energy differences among the 5f, 6d and 7s orbitals allow different numbers of their electrons to be involved in bond formation or removed. This explains why actinoids show a wide range of oxidation states, especially among the earlier members of the series.

**Quick Tip to Solve:** Explain oxidation-state variation using valence-orbital energies, rather than nuclear properties such as radioactivity.

**Step 2: Check the proposed causes** Radioactivity concerns instability of the nucleus, not the relative energies of valence orbitals, so (A) does not explain the chemical behaviour. Large atomic number and large atomic mass in (B) and (C) also do not directly establish multiple accessible valence states. Option (D) states the relevant electronic cause.

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

**Quick Tip to Solve:** Explain oxidation-state variation using valence-orbital energies, rather than nuclear properties such as radioactivity.

**7. 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 hydrochloric acid with anhydrous zinc chloride.
- Alcohols form insoluble alkyl chlorides at different rates, observed as turbidity; the reaction rate distinguishes their classes.

**Step 1: Use the Lucas test observations** At room temperature a tertiary alcohol gives immediate turbidity, a secondary alcohol gives turbidity after a few minutes, and a primary alcohol gives no turbidity under the usual room-temperature test conditions. The differing rates reflect the ease of substitution, so Lucas test distinguishes the three classes.

**Step 2: Eliminate tests for other functional groups** Fehling's and Tollens' tests chiefly detect aldehydes through their reducing behaviour; they do not classify ordinary primary, secondary and tertiary alcohols. Hinsberg test distinguishes classes of amines. Thus (B), (C) and (D) are unsuitable, whereas (A) directly tests alcohol substitution rates.

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

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

**8. Consider the following compounds:**

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

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

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

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

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

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

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

**Solution:**

**Concept:**

- Basic strength depends on the availability of the nitrogen lone pair for accepting a proton.
- Resonance decreases lone-pair availability in aniline; alkyl groups increase it through their electron-releasing inductive effect.

**Step 1: Compare aniline, ammonia and benzylamine** In aniline, the nitrogen lone pair is delocalised into the benzene ring, so aniline is weaker than ammonia. In benzylamine, the intervening  $\text{CH}_2$  group prevents this direct conjugation. Its lone pair remains available, making benzylamine stronger than ammonia.

**Step 2: Compare the ethylamines and check the options** Ethylamine has a stronger electron-releasing alkyl effect than benzylamine. Diethylamine has two ethyl groups and favourable solvation of its conjugate acid, so it is stronger than ethylamine in the usual aqueous comparison. Option (B) incorrectly places ammonia below aniline; (C) places aniline above ammonia and diethylamine below ammonia; (D) incorrectly makes ethylamine the weakest.

**Step 3: Conclusion** The increasing order is  $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ , followed by  $\text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$ . Hence, the correct option is (A).

**Quick Tip to Solve:** First place aniline last in basic strength because its lone pair participates in resonance; then compare the alkylamines.

**9. Identify the polysaccharide among the following:**

[1 mark]

(A) Fructose

(B) Maltose

(C) Glucose

(D) Cellulose

**Correct Answer:** (D) Cellulose

**Solution:**

**Concept:**

- A monosaccharide contains one sugar unit; a disaccharide contains two units joined by a glycosidic bond.

**Quick Tip to Solve:** Count the sugar units: glucose and fructose are single units, maltose has two, and cellulose has many.

- A polysaccharide contains a large number of monosaccharide units linked together.

**Step 1: Classify the smaller carbohydrates** Fructose and glucose are monosaccharides: they cannot be hydrolysed into simpler carbohydrates. Maltose is a disaccharide made from two glucose units. Thus options (A), (B) and (C) do not describe a polysaccharide.

**Step 2: Identify the polymeric carbohydrate** Cellulose is a long, unbranched polymer of  $\beta$ -D-glucose units connected by  $\beta(1 \rightarrow 4)$  glycosidic linkages. Its large number of repeating sugar units places it in the polysaccharide class; it is a structural component of plant cell walls.

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

**Quick Tip to Solve:** Count the sugar units: glucose and fructose are single units, maltose has two, and cellulose has many.

**10. 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:**

- Peptide bonds join amino acids in a polypeptide chain.
- The primary structure specifies the identity and linear sequence of amino acids in that chain.

**Step 1: Identify what the question specifies** The statement describes amino acids connected in a particular sequence. This gives the order of residues along the chain, conventionally read from its amino-terminal end to its carboxyl-terminal end. It defines the primary structure.

**Step 2: Distinguish the other levels** Secondary structure refers to local folding, such as an  $\alpha$ -helix or a  $\beta$ -pleated sheet. Tertiary structure is the overall three-dimensional folding of one polypeptide. Quaternary structure describes the arrangement of multiple polypeptide subunits. None of these terms means the linear amino-acid sequence.

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

**Quick Tip to Solve:** Associate sequence with primary, local coils or sheets with secondary, and overall folding with tertiary structure.

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

[1 mark]

- (A)  $0.5 \times 10^4 \text{ s}^{-1}$
- (B)  $5.0 \times 10^{-4} \text{ s}^{-1}$
- (C)  $0.5 \times 10^{-5} \text{ s}^{-1}$
- (D)  $0.5 \times 10^{-2} \text{ s}^{-1}$

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

**Solution:**

**Concept:**

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

**Step 1:** Substitute the given half-life Rearranging the half-life relation gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386 \text{ s}}.$$

Since  $1386 = 2 \times 693$ , the quotient can be simplified without a logarithm calculation.

**Step 2:** Simplify and compare all choices

$$k = \frac{693 \times 10^{-3}}{2 \times 693} \text{ s}^{-1} = 0.5 \times 10^{-3} \text{ s}^{-1} = 5.0 \times 10^{-4} \text{ s}^{-1}.$$

Option (A), with positive exponent 4, is far too large; option (C) is one hundredth of this value, while option (D) is ten times this value. Only (B) agrees with the half-life relation.

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

**Quick Tip to Solve:** Use  $1386 = 2$  times 693: the half-life quotient is immediately 0.5 times 10 to the power -3.

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

[1 mark]

- (A) Ammonia
- (B) Water
- (C)  $\text{NO}_2^-$
- (D) Oxalate ion

**Correct Answer:** (D) Oxalate ion

**Solution:**

**Concept:**

- Chelation occurs when one ligand binds the same metal ion through two or more donor atoms, forming a ring.
- A bidentate ligand has two donor sites; merely having alternative donor atoms does not make a ligand bidentate.

**Quick Tip to Solve:** Distinguish bidentate from ambidentate: oxalate uses two donors together, whereas nitrite ordinarily uses one alternative donor.

**Step 1: Examine the non-chelating choices** Ammonia coordinates through its nitrogen atom, and water through its oxygen atom; both are monodentate. Nitrite,  $\text{NO}_2^-$ , is an ambidentate ligand: in the usual CBSE classification it binds through nitrogen or oxygen, using one donor site at a time. Hence these choices do not produce the required chelate ring.

**Step 2: Identify the bidentate ligand** Oxalate,  $\text{C}_2\text{O}_4^{2-}$ , coordinates to the same metal through two oxygen donor atoms, one from each carboxylate group. The two coordinate bonds close a ring containing the metal and ligand atoms, so oxalate forms a chelate complex.

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

**Quick Tip to Solve:** Distinguish bidentate from ambidentate: oxalate uses two donors together, whereas nitrite ordinarily uses one alternative donor.

### 13. Assertion (A): p-nitrophenol is more acidic than phenol.

**Reason (R): Nitro group is an electron-withdrawing group, it stabilises phenoxide ion by dispersal of negative charge.** [1 mark]

- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).  
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).  
(C) Assertion (A) is true, but Reason (R) is false.  
(D) Assertion (A) is false, but Reason (R) is true.

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

#### Solution:

##### Concept:

- An acid is stronger when the conjugate base formed by proton loss is more stable.
- The para nitro group withdraws electron density through inductive and resonance effects.

**Step 1: Judge the Assertion** On losing  $\text{H}^+$ , phenol forms phenoxide and p-nitrophenol forms p-nitrophenoxide. The latter conjugate base is more stabilised, so p-nitrophenol releases a proton more readily than phenol. Thus Assertion (A) is true.

**Step 2: Judge the Reason** The  $-\text{NO}_2$  group is electron-withdrawing. At the para position it participates in resonance with the phenoxide system and allows the negative charge to be dispersed further; its inductive effect also supports stabilisation. Thus Reason (R) is true.

**Step 3: Test the explanatory connection** The extra stabilisation of p-nitrophenoxide is exactly why p-nitrophenol has greater acidity. Therefore R directly explains A. Option (B) incorrectly denies this link, while (C) and (D) incorrectly classify one of the statements as false.

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

**Quick Tip to Solve:** For substituted phenols, compare conjugate-base stability: a para electron-withdrawing nitro group increases acidity.

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

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

[1 mark]

- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
- (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
- (C) Assertion (A) is true, but Reason (R) is false.
- (D) Assertion (A) is false, but Reason (R) is true.

**Correct Answer:** (C) Assertion (A) is true, but Reason (R) is false.

**Solution:**

**Concept:**

- Fehling's reagent is an alkaline solution containing complexed copper(II) ions.
- A positive test produces a brick-red precipitate of  $\text{Cu}_2\text{O}$ : copper(II) is reduced while the aldehyde is oxidised.

**Step 1: Judge the Assertion** Aliphatic aldehydes give a positive Fehling's test on warming with the reagent. The characteristic brick-red copper(I) oxide precipitate is formed. Therefore Assertion (A) is true in the standard aldehyde classification used here.

**Step 2: Judge the Reason** The aldehyde is not reduced by Fehling's reagent. Its  $-\text{CHO}$  group is oxidised to the corresponding carboxylate ion in the alkaline medium. The aldehyde acts as the reducing agent, converting  $\text{Cu}^{2+}$  into copper(I) oxide. Thus Reason (R) is false.

**Step 3: Select the matching code** The test is a redox reaction, but the roles must be assigned correctly: aldehyde undergoes oxidation and copper undergoes reduction. Hence neither a true-reason option nor the false-assertion option applies. The code for true A and false R is (C).

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

**Quick Tip to Solve:** In Fehling's test remember the roles: the aldehyde reduces copper ions and is itself oxidised to carboxylate.

**15. 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:**

- Optical rotation is specified by the signs (+) and (–): positive rotation is clockwise and is called dextrorotation.
- The symbols D and L specify relative configuration, compared with glyceraldehyde; they do not by themselves specify the sign of optical rotation.

**Step 1: Judge the assertion** D(+)-glucose rotates plane-polarised light clockwise. Therefore the assertion that this glucose is dextrorotatory is true.

**Step 2: Judge the reason** The (+) in its name explicitly represents dextrorotation. D specifies its configuration relative to D-glyceraldehyde. Both statements in the reason are true.

**Step 3: Connect the reason with the assertion** The positive sign directly identifies the direction of optical rotation stated in the assertion. Thus the reason correctly explains the assertion; D alone would not establish dextrorotation. Options (C) and (D) wrongly make one statement false, while (B) wrongly denies the explanatory link.

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

**Quick Tip to Solve:** Read the (+) for rotation and D for configuration; do not infer rotation from D alone.

**16. 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 both their outer  $ns$  and nearby  $(n-1)d$  electrons may participate in bonding.
- Manganese has electronic configuration  $[\text{Ar}] 3d^5 4s^2$ , providing seven electrons that can participate in its highest oxidation state.

**Step 1: Judge the assertion** Manganese reaches oxidation state +7, for example in  $\text{KMnO}_4$ . With K equal to +1 and four O atoms contributing  $-8$ , charge neutrality gives Mn equal to +7. This is the highest oxidation state in the first transition series, so A is true.

**Step 2: Judge the reason** Transition metals generally show multiple oxidation states because the energies of the outer  $s$  and  $d$  orbitals are close. Thus R is true.

**Step 3: Test the explanation** Variable oxidation states is a general property; it does not explain why Mn specifically reaches +7. That requires its  $3d^5 4s^2$  configuration and participation of all seven valence electrons. Thus R is not the correct explanation of A. Option (A) overstates the link, while (C) and (D) incorrectly reject a true statement.

**Step 4: Conclusion** Both A and R are true, but R does not correctly explain A. Hence, the correct option is (B).

**Quick Tip to Solve:** To explain a highest oxidation state, count the particular element's  $s$  and  $d$  electrons; a general statement about variability is insufficient.

**Section B (10 marks)**

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

**(b) What are essential amino acids?**

[2 marks]

**Solution:**

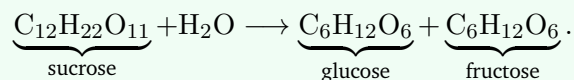
**Concept:**

- Hydrolysis cleaves a disaccharide's glycosidic linkage using water and releases its constituent monosaccharides.

**Quick Tip to Solve:** For sucrose remember glucose plus fructose; define essential using dietary need, not biological importance.

- Essential amino acids are required for protein synthesis but cannot be synthesised by the human body in sufficient amounts; they must be supplied by food.

**Step 1: Identify the hydrolysis products in part (a)** Sucrose contains one glucose unit and one fructose unit. On hydrolysis with dilute acid or the enzyme invertase, it yields equimolar D(+)-glucose and D(–)-fructose:



Both products have the same molecular formula, but they have different structures.

**Step 2: Define essential amino acids in part (b)** Essential amino acids are amino acids that the body cannot synthesise in adequate quantities and therefore must obtain through the diet. Valine, leucine and lysine are examples. Their essential character concerns dietary supply; it does not mean that other amino acids are unimportant.

**Step 3: Conclusion** (a) Hydrolysis gives D(+)-glucose and D(–)-fructose. (b) Essential amino acids must be obtained from food because the body cannot synthesise adequate amounts.

**Quick Tip to Solve:** For sucrose remember glucose plus fructose; define essential using dietary need, not biological importance.

**18. (a) Name the cell used in hearing aids and watches.**

**(b) Define conductivity. Why is direct current (DC) not used for the measurement of resistance of an ionic solution ?** [2 marks]

**Solution:**

**Concept:**

- A mercury cell is a compact primary cell with a nearly constant potential during its working life, useful in low-current devices.
- Conductivity  $\kappa$  is the reciprocal of resistivity  $\rho$ :  $\kappa = 1/\rho = l/(RA)$ , where  $R$  is resistance,  $l$  is electrode separation and  $A$  is electrode area.

**Step 1: Name the cell in part (a)** The cell used in hearing aids and watches in the standard electrochemistry context is the mercury cell. It gives a nearly constant voltage, approximately 1.35 V, because its overall reaction does not change the concentration of ions in the electrolyte significantly.

**Step 2: Define conductivity in part (b)** Conductivity is the conductance of a conductor of unit length and unit cross-sectional area, or equivalently the reciprocal of resistivity. Since  $R = \rho l/A$ , we obtain

$$\kappa = \frac{1}{\rho} = \frac{l}{RA}.$$

Its SI unit is  $\text{S m}^{-1}$ .

**Step 3: Explain the avoidance of direct current** DC causes electrolysis and electrode polarisation. Ions are discharged or accumulate near the electrodes, changing the composition of the solution and creating an opposing potential. The measured resistance then does not represent the unaltered ionic

**Quick Tip to Solve:** Use AC for ionic resistance measurements to suppress electrode polarisation; remember conductivity as reciprocal resistivity.

solution. Alternating current is used to minimise these effects.

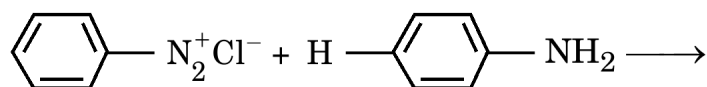
**Step 4: Conclusion** (a) Mercury cell. (b)  $\kappa = 1/\rho$ ; DC is avoided because electrolysis and polarisation change the solution and distort the resistance measurement.

**Quick Tip to Solve:** Use AC for ionic resistance measurements to suppress electrode polarisation; remember conductivity as reciprocal resistivity.

19. (a) Complete the equation :

(b) How will you convert chlorobenzene to p-chloroaniline ?

[2 marks]

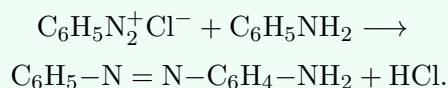


**Solution:**

**Concept:**

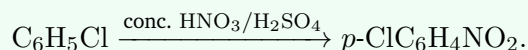
- Aromatic diazonium salts undergo azo coupling with activated aromatic rings, forming the  $-\text{N}=\text{N}-$  linkage.
- The  $-\text{NH}_2$  group activates the ring and directs coupling mainly to its para position. Chlorine is deactivating but ortho/para directing in electrophilic substitution.

**Step 1: Complete the coupling equation in part (a)** Benzenediazonium chloride couples with aniline, chiefly at the para position relative to  $-\text{NH}_2$ , in a mildly acidic medium. The hydrogen shown on the aniline ring is replaced by the azo group. The balanced equation is

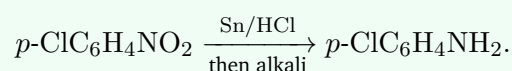


The  $-\text{NH}_2$  group is para to the azo linkage in the principal product, p-aminoazobenzene.

**Step 2: Nitrate chlorobenzene in part (b)** Treat chlorobenzene with concentrated  $\text{HNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$ . Chlorine directs nitration to the ortho and para positions. Separate the para isomer from the mixture:



**Step 3: Reduce the para nitro group** Reduce the isolated p-nitrochlorobenzene with  $\text{Sn}/\text{HCl}$ , then add alkali to liberate the free amine from its ammonium salt. The nitro group becomes  $-\text{NH}_2$ , while the aryl chlorine remains attached:



**Step 4: Conclusion** (a) The main organic product is p-aminoazobenzene, with  $\text{HCl}$  as coproduct. (b) Nitrate chlorobenzene, isolate the para nitro isomer, then reduce with  $\text{Sn}/\text{HCl}$  and liberate p-chloroaniline with alkali.

**Quick Tip to Solve:** Keep chlorine on the ring: introduce a para nitro group first, isolate that isomer, then reduce only the nitro group.

**20(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 K kg mol<sup>-1</sup>)

[2 marks]

**Solution:**

**Concept:**

- Elevation of boiling point is a colligative property:  $\Delta T_b = iK_b m$ , where  $i$  is the dimensionless van't Hoff factor,  $K_b$  is the molal elevation constant and  $m$  is molality.
- The elevation  $\Delta T_b$  is the solution boiling point minus that of pure water; a temperature difference has the same numerical value in kelvin and degrees Celsius.

**Step 1: Find the boiling-point elevation** Pure water boils at 100.00 °C. The given solution boils at 100.18 °C, hence

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

Use this increase, rather than the entire boiling temperature, in the colligative-property equation.

**Step 2: Substitute the given molality** Rearranging  $\Delta T_b = iK_b m$  gives

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

The units cancel. The factor is calculated directly from the measured elevation and the supplied data; no assumed degree of dissociation is needed.

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

**Quick Tip to Solve:** Subtract 100.00 from 100.18 first, then divide the elevation by 0.512 times the molality.

OR

**20(b).** State Henry's law. Calculate the mole fraction of CO<sub>2</sub> in water at 298 K under 760 mm Hg.

(Given:  $K_H$  for CO<sub>2</sub> in H<sub>2</sub>O at 298 K =  $1.25 \times 10^6$  mm Hg)

[2 marks]

**Solution:**

**Concept:**

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

**Step 1: State and apply Henry's law** For carbon dioxide dissolved in water at 298 K, write  $p_{\text{CO}_2} = K_H x_{\text{CO}_2}$ . At this fixed temperature, doubling the gas pressure would double its dissolved mole fraction. The pressure given in the question is 760 mm Hg.

**Step 2: Calculate the dissolved mole fraction** Rearrange the law and use the same pressure unit in

**Quick Tip to Solve:** Since both pressure values are in mm Hg, divide 760 directly by 1.25 times ten to the sixth.

numerator and denominator:

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

The pressure units cancel, as required for a mole fraction. This small value indicates that the dissolved carbon dioxide forms a small fraction of the total moles in the aqueous solution.

**Step 3: Conclusion** Henry's law is  $p = K_H x$  at constant temperature; the required mole fraction is

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

**Quick Tip to Solve:** Since both pressure values are in mm Hg, divide 760 directly by 1.25 times ten to the sixth.

**21. (a) Name the disease caused by the deficiency of Vitamin A.**

**(b) How will you confirm the presence of carbonyl group as an aldehydic group in glucose ?** [2 marks]

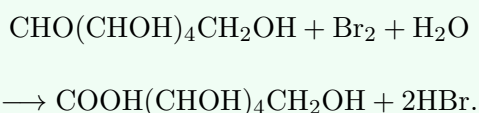
**Solution:**

**Concept:**

- Vitamin A is necessary for normal vision, particularly vision in dim light; its deficiency causes night blindness.
- A mild oxidising agent converts an aldehyde group  $-\text{CHO}$  into a carboxylic acid group  $-\text{COOH}$ . Bromine water provides this test for glucose.

**Step 1: (a) Identify the deficiency disease** The disease is night blindness, also called nyctalopia. A person with this deficiency has difficulty seeing in dim light or at night because vitamin A is needed for the normal visual cycle. Thus the specific deficiency disease asked for is night blindness.

**Step 2: (b) Oxidise glucose with bromine water** Treat glucose with bromine water, a mild oxidising agent. Glucose is oxidised to gluconic acid, a six-carbon monocarboxylic acid:



Only the terminal aldehydic carbonyl group is oxidised to a carboxyl group under these mild conditions, while the carbon chain remains intact. This formation of gluconic acid confirms that the carbonyl group of glucose is aldehydic.

**Step 3: Conclusion** (a) Vitamin A deficiency causes night blindness. (b) Oxidation of glucose by bromine water to gluconic acid confirms its aldehydic group.

**Quick Tip to Solve:** Use mild bromine-water oxidation to gluconic acid to distinguish glucose's aldehydic carbonyl group.

### Section C (21 marks)

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



(Given :  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ ,  $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$ ,  $[\log 10 = 1]$ )

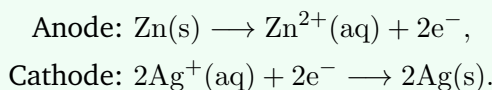
[3 marks]

#### Solution:

##### Concept:

- The standard cell potential is  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ , using both tabulated values 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 electrons transferred and  $Q$  is the reaction quotient; pure solids have unit activity.

**Step 1: Write the electrode and overall reactions** Zinc is oxidised at the left electrode and silver ions are reduced at the right electrode:



Therefore the overall reaction is  $\text{Zn(s)} + 2\text{Ag}^{+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$ , and  $n = 2$ .

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

$$E^{\circ}_{\text{cell}} = 0.80 - (-0.76) = 1.56 \text{ V}.$$

For the balanced overall reaction,

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

The exponent on the silver-ion concentration follows its coefficient in the balanced reaction. The solid zinc and silver do not appear in  $Q$ .

**Step 3: Apply the Nernst correction** Since  $\log 10 = 1$ , we have  $\log(10^3) = 3$ . Thus

$$\begin{aligned}E_{\text{cell}} &= 1.56 - \frac{0.0591}{2} \log(10^3) \\ &= 1.56 - 0.08865 \\ &= 1.47135 \text{ V}.\end{aligned}$$

The quotient exceeds unity, so the correction lowers the emf below its standard value, consistent with the calculated sign.

**Step 4: Conclusion** The emf of the given cell at 298 K is  $E_{\text{cell}} \approx 1.47 \text{ V}$ .

**Quick Tip to Solve:** Balance the silver half-reaction first: it fixes  $n = 2$  and the square on the silver-ion concentration in  $Q$ .

23. (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:**

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law. For rate =  $k[A]^m[B]^n$ , the overall order is  $m + n$ .
- At fixed temperature,  $k$  is constant. If one reactant is in large excess, its concentration is approximately constant during the reaction and can be included in an effective rate constant.

**Step 1: Define the order of reaction** Order is determined from the rate law, rather than simply from the balanced reaction equation. Here the given law is  $r = k[A][B]^2$ . Its individual orders are one with respect to A and two with respect to B; the true overall order under ordinary conditions is therefore  $1 + 2 = 3$ .

**Step 2: Compare the rates on doubling B** Keep the concentration of A and the temperature unchanged. If initially  $r = k[A][B]^2$ , after doubling B the rate is

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

Thus  $r'/r = 4$ ; the exponent of B, rather than its stoichiometric coefficient, controls the concentration effect.

**Step 3: Absorb excess A into the rate constant** When A is present in large excess, its consumption produces a negligible fractional change in  $[A]$ . Write  $k' = k[A]$ , with  $k'$  effectively constant. The measured rate law becomes

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

Only the changing concentration of B appears explicitly, so the observed overall order is two. This is a pseudo-second-order reaction; the underlying complete rate law still has order three.

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

**Quick Tip to Solve:** For a concentration multiplier, raise it to that reactant's exponent; for an excess reactant, absorb its nearly constant concentration into  $k'$ .

24. The rate of a particular reaction quadruples when the temperature increases from 300 K to 320 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  $E_a$  is the activation energy,  $A$  the pre-exponential factor,  $R$  the gas constant and  $T$  the absolute temperature.
- For the same reaction at unchanged reactant concentrations, the rate ratio equals the rate-constant ratio. Taking common logarithms gives  $\log(k_2/k_1) = \frac{E_a}{2.303R}(1/T_1 - 1/T_2)$ .

**Step 1: Identify the temperature and rate ratios** The temperatures are already in kelvin:  $T_1 = 300 \text{ K}$  and  $T_2 = 320 \text{ K}$ . Since the rate quadruples,  $k_2/k_1 = 4$ , so use the supplied common logarithm  $\log 4 = 0.60$ . The larger rate constant at the higher temperature is consistent with a positive activation energy.

**Step 2: Rearrange the two-temperature equation** Assuming the activation energy and pre-exponential factor remain constant over this temperature range, subtract the logarithmic Arrhenius equations:

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

Hence

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

Using  $T_2 - T_1$  in the denominator makes the sign positive.

**Step 3: Substitute and convert the energy unit** Insert the given values in SI units:

$$\begin{aligned} E_a &= 2.303(8.314)(0.60) \frac{300 \times 320}{320 - 300} \\ &= 55143.6 \text{ J mol}^{-1} \\ &= 55.14 \text{ kJ mol}^{-1}. \end{aligned}$$

The kelvin factor from the temperature quotient cancels the inverse kelvin in  $R$ . Use the supplied rounded logarithm instead of a more precise value so that the numerical answer follows the question data.

**Step 4: Conclusion** The activation energy is  $E_a \approx 55.1 \text{ kJ mol}^{-1}$  (approximately  $5.51 \times 10^4 \text{ J mol}^{-1}$ ).

**Quick Tip to Solve:** Use  $\log 4 = 0.60$  with the factor 2.303; do not mix a common logarithm with the natural-log form of Arrhenius.

25(a). Write the IUPAC name of the given complex :  $K_2[Zn(OH)_4]$

[1 mark]

**Solution:**

**Concept:**

- Name the cation before the complex anion. The ligand  $OH^-$  has the IUPAC ligand name hydroxido.
- An anionic coordination entity uses the metal ending -ate, and the metal oxidation state is written as a Roman numeral.

**Step 1: Find the oxidation state of zinc** Two potassium ions give a total charge of +2, so the coordination entity  $[Zn(OH)_4]^{2-}$  has charge -2. If zinc has oxidation state  $x$ , then  $x + 4(-1) = -2$ , giving  $x = +2$ .

**Step 2: Assemble the name in ionic order** The four hydroxido ligands give tetrahydroxido. Since the coordination entity is an anion, zinc is named zincate; append (II) for its oxidation state. The potassium counterion is named first without adding a numerical prefix.

**Step 3: Conclusion** The IUPAC name is potassium tetrahydroxidozincate(II).

**Quick Tip to Solve:** For  $K_2[Zn(OH)_4]$ , first infer the complex charge -2, then use hydroxido and the anionic metal name zincate.

25(b). Differentiate between a double salt and a complex.

[1 mark]

**Solution:**

**Concept:**

- A double salt is a crystalline combination of salts which dissociates into all its constituent simple ions in water.
- A coordination compound retains its complex ion in solution; ligands bound within that ion do not ordinarily appear as free constituent ions.

**Step 1: Describe the dissociation of a double salt** A double salt loses its combined identity on dissolving. For example, Mohr's salt gives  $Fe^{2+}$ ,  $NH_4^+$  and  $SO_4^{2-}$  ions in aqueous solution. These constituent ions display their usual ionic properties and tests.

**Step 2: Contrast the behaviour of a complex** A complex salt dissociates into counterions and a stable coordination ion. For example,  $K_4[Fe(CN)_6]$  gives  $K^+$  and  $[Fe(CN)_6]^{4-}$ . It does not simply release free  $Fe^{2+}$  and  $CN^-$  ions in the way a double salt releases its constituent ions.

**Step 3: Conclusion** A double salt dissociates completely into simple constituent ions in water, whereas a complex retains its coordination entity as a complex ion.

**Quick Tip to Solve:** Distinguish them by the species present in aqueous solution: simple constituent ions for a double salt, retained complex ions for a complex.

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

[1 mark]

**Solution:**

**Concept:**

- Platinum(II) complexes with coordination number four normally have square-planar geometry.
- Geometrical isomerism arises when ligands can occupy different relative positions around the same metal without changing composition or connectivity.

**Step 1: Identify the coordination geometry** In  $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$ , ammonia and water are neutral and each chlorido ligand has charge  $-1$ . Platinum therefore has oxidation state  $+2$ , with four donor atoms arranged in a square plane.

**Step 2: Compare the two chlorido positions** The two chlorido ligands may occupy adjacent positions, giving the cis form with a  $90^\circ$  angle between them, or opposite positions, giving the trans form with a  $180^\circ$  angle. Ammonia and water occupy the remaining positions in each arrangement. These are distinct geometrical arrangements of the same complex.

**Step 3: Conclusion** The complex exhibits geometrical (cis-trans) isomerism.

**Quick Tip to Solve:** In this square-planar complex, compare the two identical chlorido ligands: adjacent means cis, and opposite means trans.

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

[1 mark]

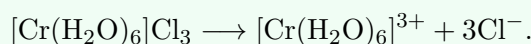
**Solution:**

**Concept:**

- Only ionisable chloride ions outside the coordination sphere precipitate with  $\text{Ag}^+$  as  $\text{AgCl}$ .
- Water is a neutral ligand; chromium(III) normally has coordination number six.

**Step 1: Locate the chloride ions** Three moles of  $\text{AgCl}$  per mole of compound mean that all three chloride ions are outside the coordination sphere. No chloride ligand is bonded to chromium.

**Step 2: Place the water ligands** The six water molecules occupy the six coordination positions around  $\text{Cr}^{3+}$ . The resulting complex cation has charge  $+3$ , balanced by three chloride counterions. Its dissociation is



Each chloride gives one precipitate unit:  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl(s)}$ .

**Step 3: Conclusion** The structural formula is  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ : hexaaquachromium(III) chloride.

**Quick Tip to Solve:** Count the moles of  $\text{AgCl}$  first: three imply that all three chlorides lie outside the square brackets.

**26(b).** Write the oxidation state and hybridisation of the central metal in the given complex :  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ . [Atomic number : Cr = 24] [1 mark]

**Solution:**

**Concept:**

- Ammonia,  $\text{NH}_3$ , is a neutral ligand, so the complex charge equals the metal oxidation state.
- For octahedral inner-orbital complexes, two vacant  $3d$ , one  $4s$  and three  $4p$  orbitals form  $d^2sp^3$  hybrids.

**Step 1: Find the oxidation state** Let the chromium oxidation state be  $x$ . Since each of the six ammonia ligands has zero charge,  $x + 6(0) = +3$ , giving  $x = +3$ .

**Step 2: Determine the orbitals available** Chromium has atomic number 24 and ground-state configuration  $[\text{Ar}]3d^54s^1$ . Removing the  $4s$  electron and two  $3d$  electrons gives  $\text{Cr}^{3+} : [\text{Ar}]3d^3$ . Three electrons occupy three different  $3d$  orbitals, leaving two vacant  $3d$  orbitals. These combine with  $4s$  and three  $4p$  orbitals to accommodate six ligand pairs in an octahedral arrangement; pairing of the three metal electrons is unnecessary.

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

**Quick Tip to Solve:** For  $\text{Cr(III)}$ , write the  $d^3$  configuration: two empty  $3d$  orbitals directly allow inner-orbital octahedral hybrids.

**26(c).** Why is  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  colourless ? [1 mark]

**Solution:**

**Concept:**

- Visible colour in many transition-metal complexes comes from  $d-d$  transitions between crystal-field-split orbitals.
- Water is neutral, so scandium in  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is  $\text{Sc}^{3+}$ .

**Step 1: Find the metal-ion configuration** Scandium has configuration  $[\text{Ar}]3d^14s^2$ . Loss of two  $4s$  electrons and one  $3d$  electron gives  $\text{Sc}^{3+} : [\text{Ar}]3d^0$ . Thus its five  $d$  orbitals contain no electrons.

**Step 2: Explain the absence of colour** Although the water ligands split the metal  $d$  orbitals into different energy levels, a  $d-d$  transition requires an electron in a lower level that can absorb light and be promoted. The  $d^0$  ion has no such electron, so it cannot absorb visible light through these transitions.

**Step 3: Conclusion**  $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$  is colourless because  $\text{Sc}^{3+}$  is  $d^0$ , and hence no  $d-d$  transition is possible.

**Quick Tip to Solve:** Remove all three valence electrons from Sc before judging colour; use the ion configuration, not that of neutral Sc.

27. How do you convert the following ?

(a) Benzene to m-Nitroacetophenone

(b) Bromobenzene to 1-Phenylethanol

(c) But-3-en-2-one to Prop-2-en-1-oic acid

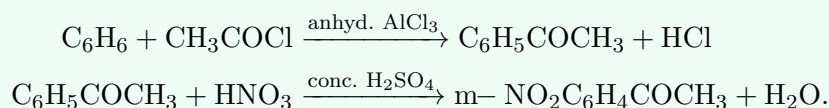
[3 marks]

**Solution:**

**Concept:**

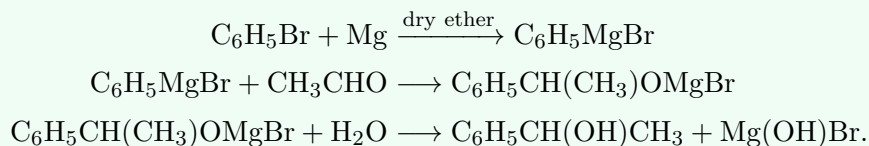
- The acetyl group is meta directing; install it by Friedel–Crafts acylation before nitration.
- A Grignard reagent adds to an aldehyde; acid hydrolysis of the magnesium alkoxide gives an alcohol.
- A methyl ketone undergoes the haloform reaction, forming a carboxylate with one fewer carbon atom.

**Step 1: (a) Acylate benzene, then nitrate** First treat benzene with acetyl chloride and anhydrous  $\text{AlCl}_3$  to obtain acetophenone. Then nitrate with concentrated nitric and sulphuric acids.



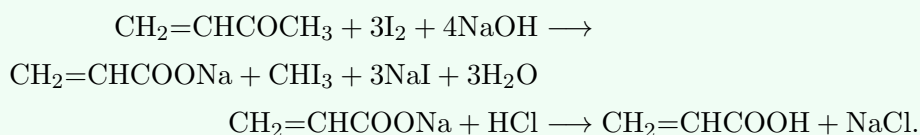
The electron-withdrawing acetyl group directs the incoming nitro group predominantly to the meta position. Nitrating first would produce nitrobenzene, which does not undergo normal Friedel–Crafts acylation.

**Step 2: (b) Prepare a Grignard reagent and add ethanal** Use magnesium in dry ether to convert bromobenzene into phenylmagnesium bromide. Add ethanal in dry ether, then hydrolyse with dilute acid.



The last step is acid-assisted hydrolysis. The secondary alcohol obtained is 1-phenylethanol; dry conditions before hydrolysis prevent destruction of the Grignard reagent.

**Step 3: (c) Apply the iodoform reaction and acidify** But-3-en-2-one,  $\text{CH}_2=\text{CHCOCH}_3$ , contains a methyl-ketone group. Treat it with iodine and aqueous sodium hydroxide, then acidify the sodium prop-2-enoate formed.



The methyl carbon leaves as iodoform; the carbonyl carbon becomes the carboxyl carbon, giving prop-2-en-1-oic acid.

**Step 4: Conclusion** (a) Acylation followed by nitration; (b) Grignard formation, ethanal addition and hydrolysis; (c)  $\text{I}_2/\text{NaOH}$  followed by acidification give the three required products.

**Quick Tip to Solve:** For the three routes remember: install the meta director first, add a phenyl Grignard to ethanal, and remove the methyl-ketone carbon by haloform cleavage.

**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  $\text{CH}_3\text{CHO}$  more reactive than acetone towards reaction with  $\text{HCN}$ ?

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

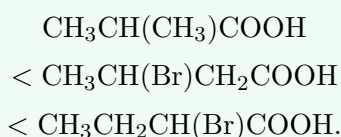
[3 marks]

**Solution:**

**Concept:**

- Electron-withdrawing groups stabilise a carboxylate ion and increase acidity; the inductive effect weakens with distance.
- Nucleophilic addition depends on carbonyl-carbon electrophilicity and steric accessibility.
- A carbonyl compound condenses with hydrazine to form a hydrazone and water.

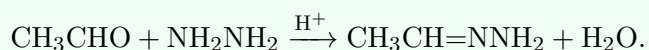
**Step 1: (i) Compare inductive effects** An alkyl group has a  $+I$  effect, which destabilises the carboxylate ion and lowers acidity. Bromine has a  $-I$  effect that stabilises the conjugate base. This effect is stronger when bromine is on the carbon adjacent to  $\text{COOH}$  than when it is one carbon farther away. Therefore the increasing order is



The last acid has bromine at the alpha position; the middle one has bromine at the beta position.

**Step 2: (ii) Compare ethanal and acetone** In  $\text{HCN}$  addition,  $\text{CN}^-$  attacks the electrophilic carbonyl carbon. Ethanal has one electron-donating methyl group whereas acetone has two. The two  $+I$  groups in acetone decrease the positive character of the carbonyl carbon more strongly. Ethanal also has a hydrogen in place of one methyl group, so it presents less steric hindrance to attack. Both factors make  $\text{CH}_3\text{CHO}$  more reactive than acetone.

**Step 3: (iii) Form the hydrazone** Ethanal reacts with hydrazine under acid catalysis to replace the carbonyl oxygen by  $=\text{N-NH}_2$ , eliminating one molecule of water.



The product is ethanal hydrazone; one nitrogen forms the double bond to carbon while the terminal nitrogen remains  $\text{NH}_2$ .

**Step 4: Conclusion** (i) Branched alkyl acid  $<$  beta-bromo acid  $<$  alpha-bromo acid. (ii) Ethanal has greater electrophilicity and less steric hindrance. (iii) The product is  $\text{CH}_3\text{CH}=\text{NNH}_2$ , together with water.

**Quick Tip to Solve:** Locate bromine relative to  $\text{COOH}$ , count alkyl groups on the carbonyl, and replace  $\text{C}=\text{O}$  by  $\text{C}=\text{N-NH}_2$  for the hydrazone.

**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]

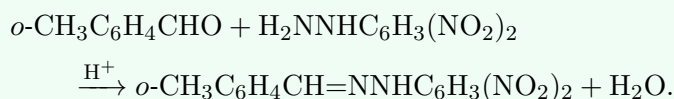
**Solution:**

**Concept:**

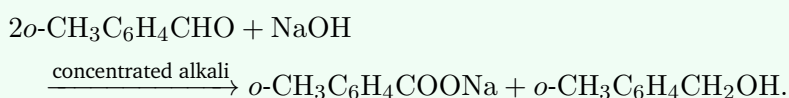
- 2,4-DNP forms a hydrazone with a carbonyl compound; reduction of Tollens' reagent identifies an aldehyde group,  $-CHO$ .
- An aldehyde without an  $\alpha$ -hydrogen undergoes the Cannizzaro reaction in concentrated alkali: one molecule is oxidised and another is reduced.
- Vigorous oxidation converts oxidisable aromatic side chains into  $-COOH$  groups; the positions of the side chains are retained.

**Step 1: Identify the structure from the tests** The 2,4-DNP test establishes a carbonyl group and the Tollens test establishes an aldehyde. The formula  $C_8H_8O$  fits a methyl-substituted benzaldehyde,  $CH_3C_6H_4CHO$ . The carbon adjacent to the aldehyde carbon is an aromatic ring carbon with no hydrogen available for enolate formation, explaining the Cannizzaro reaction. On oxidation, both the methyl and aldehyde groups become carboxyl groups. Since the product is benzene-1,2-dicarboxylic acid, the groups must be adjacent. Thus the structure is  $o\text{-CH}_3C_6H_4CHO$ , called 2-methylbenzaldehyde or o-tolualdehyde.

**Step 2: Write the 2,4-DNP reaction** The aldehyde condenses with 2,4-dinitrophenylhydrazine in acidic medium, eliminating water and forming the corresponding 2,4-dinitrophenylhydrazone. In the following equation, the nitro groups on the hydrazine phenyl ring occupy positions 2 and 4:



**Step 3: Write the Cannizzaro reaction** With concentrated aqueous sodium hydroxide, two molecules disproportionate to give sodium 2-methylbenzoate and 2-methylbenzyl alcohol:



The aldehyde carbon of one molecule is oxidised to a carboxylate; that of the other is reduced to a primary alcohol. The ring methyl group remains unchanged in this reaction.

**Step 4: Conclusion** The compound is  $o\text{-CH}_3C_6H_4CHO$ , 2-methylbenzaldehyde. It forms its 2,4-DNP hydrazone and gives sodium 2-methylbenzoate plus 2-methylbenzyl alcohol in the Cannizzaro reaction.

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

### Section D (8 marks)

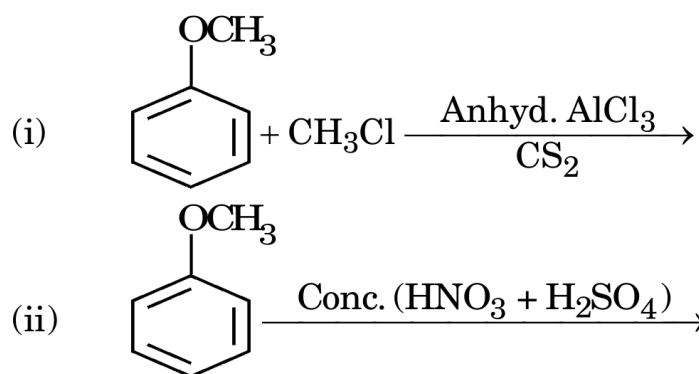
The following questions are Case-based questions. Read the case carefully and answer the questions that follow.

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

Answer the following questions:

Complete the following equations:

[2 marks]

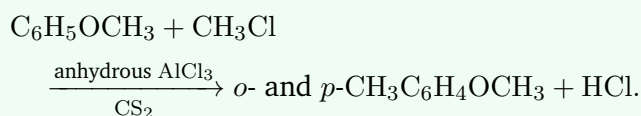


#### Solution:

##### Concept:

- The methoxy group  $-OCH_3$  donates electron density to the benzene ring by resonance and directs electrophilic substitution to ortho and para positions.
- Friedel-Crafts alkylation introduces an alkyl group; nitration introduces  $-NO_2$ . Steric crowding usually favours the para product.

**Step 1: (i) Friedel-Crafts methylation** Anhydrous  $AlCl_3$  activates methyl chloride. Anisole reacts in  $CS_2$  to form a mixture of 2-methylanisole and 4-methylanisole, with the para isomer as the major product:

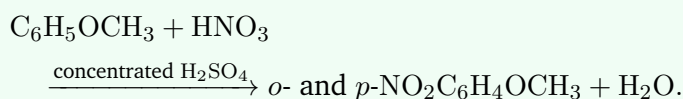


Here ortho and para specify the position of the newly introduced methyl group relative to the methoxy

**Quick Tip to Solve:** Keep the methoxy group fixed and place the incoming methyl or nitro group at positions 2 and 4 on the ring.

group. Meta substitution is disfavoured because the methoxy group preferentially stabilises the ortho and para intermediates.

**Step 2: (ii) Nitration** The mixture of concentrated nitric and sulphuric acids generates the nitronium ion,  $\text{NO}_2^+$ . Anisole gives 2-nitroanisole and 4-nitroanisole, with the para isomer as the major product:



The methoxy group stays attached to the ring in both reactions; an aromatic hydrogen is replaced by the incoming electrophile.

**Step 3: Conclusion** (i) 2-Methylanisole and 4-methylanisole; (ii) 2-nitroanisole and 4-nitroanisole. The para product predominates in each mixture.

**Quick Tip to Solve:** Keep the methoxy group fixed and place the incoming methyl or nitro group at positions 2 and 4 on the ring.

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

[1 mark]

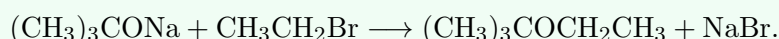
**Solution:**

**Concept:**

- Williamson synthesis proceeds by  $S_N2$  displacement on an alkyl halide by an alkoxide ion.
- Use a primary alkyl halide for substitution; a tertiary halide preferentially undergoes elimination with a strong alkoxide base.

**Step 1: Choose the primary halide** For tert-butyl ethyl ether,  $(\text{CH}_3)_3\text{COCH}_2\text{CH}_3$ , use ethyl bromide (bromoethane),  $\text{CH}_3\text{CH}_2\text{Br}$ , as the alkyl halide. Its primary carbon permits the alkoxide ion to attack by the  $S_N2$  mechanism.

**Step 2: Choose the matching alkoxide** The alkoxide must supply the tert-butoxy group, so use sodium tert-butoxide,  $(\text{CH}_3)_3\text{CONa}$ :



The opposite choice, a tert-butyl halide with sodium ethoxide, favours elimination to 2-methylpropene because a tertiary carbon blocks the required backside attack.

**Step 3: Conclusion** Use ethyl bromide and sodium tert-butoxide.

**Quick Tip to Solve:** Put the less hindered ethyl group on the halide side and the tertiary group on the alkoxide side.

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

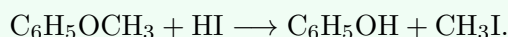
**Solution:**

**Concept:**

- Acid first protonates the ether oxygen, making cleavage of an alkyl–oxygen bond easier.
- The aryl–oxygen bond has partial double-bond character from resonance; the aryl carbon is  $sp^2$ -hybridised and resists  $S_N2$  attack.

**Step 1: Identify the bond that breaks** In anisole, the oxygen lone pair is conjugated with the benzene ring, giving the aryl–oxygen bond partial double-bond character. This bond is stronger than the methyl–oxygen bond. Neither ordinary backside substitution at the aryl carbon nor formation of an unstable phenyl carbocation is favoured.

**Step 2: Explain formation of the products** After protonation of oxygen by HI, iodide attacks the unhindered methyl carbon by the  $S_N2$  mechanism. The methyl–oxygen bond breaks, releasing phenol:



Thus oxygen remains attached to the aromatic ring. Formation of methanol and iodobenzene would require breaking the resistant aryl–oxygen bond, so that product pair is not obtained.

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

**Quick Tip to Solve:** For an aryl alkyl ether, retain oxygen on the aryl group and attach iodide to the alkyl group.

**29(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.
- The ideal tetrahedral angle is  $109.5^\circ$ ; repulsion between bulky alkyl groups modifies the actual bond angle.

**Step 1: Consider the arrangement at oxygen** The two carbon–oxygen bonds and two lone pairs around ether oxygen suggest a roughly tetrahedral electron-pair arrangement. The angle asked for is the angle between the two carbon–oxygen bonds,  $\angle \text{C} - \text{O} - \text{C}$ , rather than an angle involving a lone pair.

**Step 2: Account for the enlarged bond angle** The two alkyl groups attached to oxygen are bulkier than hydrogen atoms. Repulsion between these groups pushes the carbon–oxygen bonds farther apart, widening the  $\text{C} - \text{O} - \text{C}$  angle slightly beyond  $109.5^\circ$ . The observed enlargement is therefore attributed to the repulsion between the attached alkyl groups; merely counting lone pairs does not

**Quick Tip to Solve:** When explaining the enlarged ether angle, explicitly mention repulsion between the two bulky alkyl groups.

explain this comparison.

**Step 3: Conclusion** The C – O – C angle is slightly greater than the tetrahedral angle because the bulky alkyl groups repel each other and push the bonds apart.

**Quick Tip to Solve:** When explaining the enlarged ether angle, explicitly mention repulsion between the two bulky alkyl groups.

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

Answer the following questions:

Predict the products of electrolysis in each of the following:

(i) An aqueous solution of  $\text{CuCl}_2$  with platinum electrodes.

(ii) A concentrated solution of  $\text{H}_2\text{SO}_4$  with platinum electrodes.

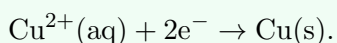
[2 marks]

**Solution:**

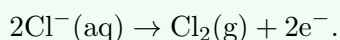
**Concept:**

- At the cathode reduction occurs; at the anode oxidation occurs. Platinum is an inert electrode and does not supply metal ions.
- Products depend on concentration and competing electrode reactions; concentrated sulphuric acid can give peroxodisulphuric acid at the anode.

**Step 1: (i) Aqueous copper(II) chloride** Copper ions are reduced preferentially at the cathode, depositing copper metal:



At the platinum anode, chloride ions are oxidised to chlorine gas:

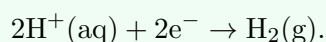


Thus the copper deposit is on the negative electrode and chlorine is liberated at the positive electrode.

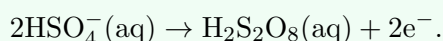
**Step 2: (ii) Concentrated sulphuric acid** Hydrogen ions gain electrons at the cathode, liberating

**Quick Tip to Solve:** Check whether sulphuric acid is concentrated before assigning the anode product; concentrated acid gives peroxodisulphuric acid.

hydrogen gas:



At the anode, sulphate species undergo oxidation to the peroxodisulphate species. In acid form the reaction is



The anode product is peroxodisulphuric acid, also called persulphuric acid. The specified concentrated acid must be distinguished from dilute sulphuric acid, for which water oxidation gives oxygen.

**Step 3: Conclusion** (i) Cathode:  $\text{Cu}$ ; anode:  $\text{Cl}_2$ . (ii) Cathode:  $\text{H}_2$ ; anode:  $\text{H}_2\text{S}_2\text{O}_8$ .

**Quick Tip to Solve:** Check whether sulphuric acid is concentrated before assigning the anode product; concentrated acid gives peroxodisulphuric acid.

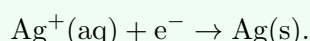
**30(b). How much charge in faraday is required for the reduction of 1 mol of  $\text{Ag}^+$  to  $\text{Ag}$ ?** [1 mark]

**Solution:**

**Concept:**

- One faraday,  $F$ , is the charge carried by one mole of electrons:  $F \approx 96485 \text{ C mol}^{-1}$ .
- The charge required is  $Q = n_e F$ , where  $n_e$  is the amount of electrons in moles.

**Step 1: Write the reduction half-reaction**



The silver ion has charge  $+1$ , so each ion requires exactly one electron to become a neutral silver atom.

**Step 2: Count the moles of electrons** The stoichiometric ratio of silver ions to electrons is  $1 : 1$ . Therefore, reducing 1 mol of  $\text{Ag}^+$  requires 1 mol of electrons and  $Q = 1 \times F$ . The molar mass of silver is unnecessary because the quantity is already given in moles.

**Step 3: Conclusion** The required charge is 1 faraday, approximately  $9.65 \times 10^4 \text{ C}$ .

**Quick Tip to Solve:** For one mole of metal ions, the number of faradays equals the number of electrons in the reduction half-reaction.

OR

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

**Solution:**

**Concept:**

- The chemical equivalent mass is  $E = M/z$ , where  $M$  is molar mass and  $z$  is the number of electrons transferred per ion.

**Quick Tip to Solve:** Include the equal-charge condition and equivalent masses when stating the second law; both are essential.

- Faraday's second law compares different substances electrolysed by the same quantity of charge.

**Step 1: State the law** When the same quantity of electricity passes through different electrolytes, the masses of substances deposited or liberated at their respective electrodes are proportional to their chemical equivalent masses.

**Step 2: Express the proportionality** For two substances receiving the same charge,

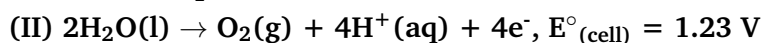
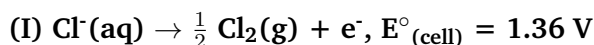
$$\frac{m_1}{m_2} = \frac{E_1}{E_2} = \frac{M_1/z_1}{M_2/z_2}.$$

Here  $m_1, m_2$  are the masses deposited or liberated. Thus the comparison uses equivalent masses, rather than molar masses alone when the electron requirements differ.

**Step 3: Conclusion** For equal quantities of electricity,  $m \propto E$ : deposited or liberated masses are proportional to chemical equivalent masses.

**Quick Tip to Solve:** Include the equal-charge condition and equivalent masses when stating the second law; both are essential.

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



Which reaction is feasible at the anode and why?

[1 mark]

**Solution:**

**Concept:**

- At the anode, oxidation occurs. Chloride oxidation and water oxidation compete in aqueous sodium chloride.
- The actual discharge also depends on overpotential, the extra potential needed to drive an electrode reaction at an appreciable rate.

**Step 1: Compare the stated potentials** The printed values are 1.36 V for the chlorine process and 1.23 V for the oxygen process. On the basis of these values alone, water oxidation would appear easier. This comparison does not account for the kinetic barrier to oxygen evolution.

**Step 2: Include oxygen overpotential** Oxygen evolution has a substantial overpotential at the anode. Consequently, the effective potential required to evolve oxygen is higher than the simple standard-potential comparison suggests. Chloride ions are therefore oxidised preferentially, and chlorine gas is liberated by reaction (I).

**Step 3: Conclusion** Reaction (I) is feasible:  $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + \text{e}^-$ , because oxygen evolution has a high overpotential.

**Quick Tip to Solve:** When chloride and water compete at the anode, account for oxygen overpotential before predicting the discharged species.

## Section E (15 marks)

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

[1 mark]

**Solution:**

**Concept:**

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

**Step 1: Identify the available electrons** The outer  $ns$  electrons can be removed first, but the nearby  $(n - 1)d$  electrons can also be lost or used in bonding. The energy separation does not prevent successive participation of additional electrons.

**Step 2: Relate participation to oxidation state** Different numbers of  $ns$  and  $(n - 1)d$  electrons participate in different compounds. This gives more than one oxidation state for the same metal; for example, iron commonly forms  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

**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 to participate in bonding.

**Quick Tip to Solve:** Mention both subshells and their similar energies, then link them to different numbers of electrons used in bonding.

31(a)(i)(II). Out of  $\text{Mn}^{2+}$  and  $\text{Ti}^{2+}$  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 spin-only magnetic moment.
- The spin-only moment is  $\mu = \sqrt{n(n + 2)} \mu_B$ , where  $n$  is the number of unpaired electrons.

**Step 1: Write the ionic configurations** For titanium,  $Z = 22$ : Ti :  $[\text{Ar}]3d^24s^2$ , so  $\text{Ti}^{2+}$  :  $[\text{Ar}]3d^2$ . For manganese,  $Z = 25$ : Mn :  $[\text{Ar}]3d^54s^2$ , so  $\text{Mn}^{2+}$  :  $[\text{Ar}]3d^5$ . The two  $4s$  electrons are removed in forming each divalent ion.

**Step 2: Compare the unpaired electrons** By Hund's rule,  $3d^2$  has two unpaired electrons, whereas  $3d^5$  has five. The corresponding spin-only moments are  $\sqrt{8} \mu_B$  and  $\sqrt{35} \mu_B$ , respectively, so the manganese ion has the greater magnetic moment.

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

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

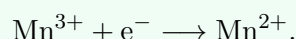
**31(a)(i)(III).** Which ion is the strongest oxidising agent in the options given below :  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Mn}^{3+}$ .  
Give reason. [Atomic No. : Cr = 24, V = 23, Mn = 25] [1 mark]

**Solution:**

**Concept:**

- An oxidising agent accepts electrons and is itself reduced. A particularly stable reduced state favours electron acceptance.
- The configurations of the ions are  $\text{Cr}^{3+} : 3d^3$ ,  $\text{V}^{3+} : 3d^2$  and  $\text{Mn}^{3+} : 3d^4$ .

**Step 1: Examine reduction of manganese(III)** On accepting one electron,  $\text{Mn}^{3+}$  becomes  $\text{Mn}^{2+}$ :



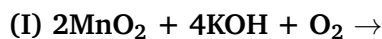
The product has the particularly stable half-filled  $3d^5$  configuration. This makes reduction of manganese(III) favourable.

**Step 2: Compare the other two ions** Reduction of  $\text{Cr}^{3+}$  gives  $\text{Cr}^{2+}$ , changing  $3d^3$  to  $3d^4$ , while reduction of  $\text{V}^{3+}$  gives  $\text{V}^{2+}$ , changing  $3d^2$  to  $3d^3$ . Neither reduction produces the half-filled  $3d^5$  state obtained for manganese. Chromium(III) is itself relatively stable, so it resists reduction compared with manganese(III).

**Step 3: Conclusion**  $\text{Mn}^{3+}$  is the strongest oxidising agent among the given ions because it readily gains an electron to form stable, half-filled  $3d^5$   $\text{Mn}^{2+}$ .

**Quick Tip to Solve:** For these ions, write the configuration after electron gain; manganese(III) alone reaches the stable half-filled d subshell.

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



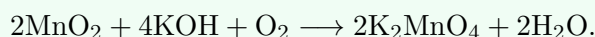
[2 marks]

**Solution:**

**Concept:**

- In alkaline medium, oxidation of  $\text{MnO}_2$  by oxygen produces potassium manganate,  $\text{K}_2\text{MnO}_4$ , with manganese in oxidation state +6.
- In acidic medium, permanganate is reduced from Mn(VII) to Mn(II); oxalate is oxidised to carbon dioxide. A balanced ionic equation conserves atoms and total charge.

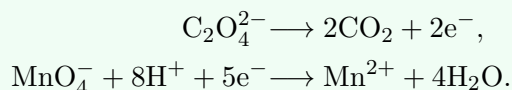
**Step 1: Complete the alkaline oxidation equation** The products are potassium manganate and water:



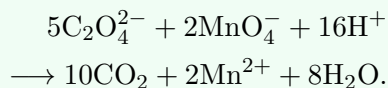
Both sides contain two Mn atoms, four K atoms, four H atoms and ten O atoms. Each manganese changes from +4 to +6, releasing two electrons; oxygen accepts the total four electrons.

**Quick Tip to Solve:** Match the permanganate half-reaction to the medium: acidic solution gives manganese(II), while alkaline oxidation of manganese dioxide gives manganate.

**Step 2: Balance the acidic permanganate reaction** The half-reactions are



Multiply the first by five and the second by two, then cancel ten electrons. The resulting equation is



The total charge on each side is +4, and carbon, manganese, hydrogen and oxygen are conserved.

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

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

**Quick Tip to Solve:** Match the permanganate half-reaction to the medium: acidic solution gives manganese(II), while alkaline oxidation of manganese dioxide gives manganate.

OR

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

**(ii) Why do transition metals form coloured compounds?**

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

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

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

[5 marks]

**Solution:**

**Concept:**

- Electronic configuration and ligand-field splitting explain stability and colour.
- Electrode potentials reflect atomisation, ionisation and hydration energies; oxidising agents accept electrons.

**Step 1: (i) Define lanthanoid contraction** Lanthanoid contraction is the gradual decrease in atomic and ionic radii, as atomic number increases across the lanthanoid series. The added electrons enter the 4f subshell, whose electrons shield the increasing nuclear charge poorly. Effective nuclear attraction therefore increases.

**Step 2: (ii) Explain coloured compounds** Ligands split the d orbitals into groups of different energies. In a partially filled d subshell, visible-light absorption promotes an electron from a lower to a higher level. Such d-d transitions remove selected wavelengths, so the remaining light gives the complementary colour. Ions with  $d^0$  or  $d^{10}$  configurations cannot undergo these transitions.

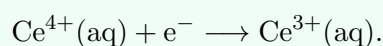
**Step 3: (iii) Explain the anomalous electrode potentials**  $\text{Mn}^{2+}$  has a stable half-filled  $3d^5$  configuration and  $\text{Zn}^{2+}$  has a stable completely filled  $3d^{10}$  configuration. Their stability favours the divalent aqueous ions. Their reduction to the metals is consequently less favourable than expected, so their  $E^\circ_{\text{M}^{2+}/\text{M}}$  values are more negative than expected.

**Quick Tip to Solve:** For copper, explicitly include hydration rather than choosing copper(I) solely from its filled d subshell; for cerium, identify the electron-accepting reduction.

**Step 4: (iv) State the most stable oxidation state of copper** In aqueous solution, copper is most stable in oxidation state +2. Although  $\text{Cu}^+$  has a filled  $3d^{10}$  configuration, the much more favourable hydration enthalpy of  $\text{Cu}^{2+}$  compensates for the energy needed for the second ionisation. Thus  $\text{Cu}^{2+}$  is stabilised in water, and  $\text{Cu}^+$  tends to disproportionate:



**Step 5: (v) Explain the oxidising action of cerium(IV)** In aqueous solution  $\text{Ce}^{4+}$  readily accepts an electron and is reduced to the more stable  $\text{Ce}^{3+}$  state, which is characteristic of the lanthanoids:



Its strongly positive reduction potential makes this electron gain favourable; the electron donor is oxidised.

**Step 6: Conclusion** The answers are: (i) progressive decrease in lanthanoid radii; (ii) visible-light absorption in  $d-d$  transitions; (iii) stable  $d^5$  and  $d^{10}$  divalent ions; (iv) +2, stabilised by hydration; (v) favourable reduction to  $\text{Ce}^{3+}$ .

**Quick Tip to Solve:** For copper, explicitly include hydration rather than choosing copper(I) solely from its filled d subshell; for cerium, identify the electron-accepting reduction.

**32(a)(i)(I). Which of the following is more reactive towards  $\text{S}_{\text{N}}1$  reaction : 2-Bromo-2-methylbutane or 1-Bromopentane** [1 mark]

**Solution:**

**Concept:**

- The rate-determining step of an  $\text{S}_{\text{N}}1$  reaction is ionisation of the carbon–halogen bond to form a carbocation.
- Carbocation stability generally follows tertiary > secondary > primary because alkyl groups stabilise positive charge by the +I effect and hyperconjugation.

**Step 1: Compare the intermediates** Loss of  $\text{Br}^-$  from 2-bromo-2-methylbutane produces  $(\text{CH}_3)_2\text{C}^+\text{CH}_2\text{CH}_3$ , a tertiary carbocation. Loss of bromide from 1-bromopentane produces  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$ , a primary carbocation.

**Step 2: Relate stability to ionisation** Formation of the tertiary carbocation is energetically easier than formation of the primary carbocation. Since both substrates contain the same leaving group, bromide, this difference in carbocation stability makes the tertiary bromide undergo the rate-determining ionisation much faster.

**Step 3: Conclusion** 2-Bromo-2-methylbutane is more reactive towards the  $\text{S}_{\text{N}}1$  reaction.

**Quick Tip to Solve:** For an  $\text{S}_{\text{N}}1$  comparison with the same leaving group, classify the carbon that bears the halogen first.

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

[1 mark]

**Solution:**

**Concept:**

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

**Step 1: Locate the carbon bonded to chlorine** In  $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{C}(\text{Cl}) = \text{CH}_2$ , chlorine is attached to the carbon written as  $\text{C}(\text{Cl})$ . This carbon is one of the two carbons of the  $\text{C} = \text{C}$  double bond, so it is  $sp^2$ -hybridised.

**Step 2: Apply the classification** The chlorine is therefore attached directly to an unsaturated carbon. It is not attached to the neighbouring saturated  $\text{CH}$  group, which would make the compound allylic. The presence of alkyl branches elsewhere does not change the classification of the carbon-chlorine bond.

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

**Quick Tip to Solve:** Trace the bond from the halogen to its carbon; classify that carbon, not a neighbouring carbon.

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

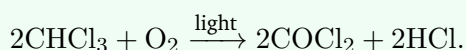
[1 mark]

**Solution:**

**Concept:**

- Chloroform,  $\text{CHCl}_3$ , undergoes oxidation in air in the presence of light.
- The oxidation product carbonyl chloride,  $\text{COCl}_2$ , commonly called phosgene, is highly poisonous.

**Step 1: Identify the harmful reaction** Light promotes the slow oxidation of chloroform by atmospheric oxygen. The balanced reaction is



Thus storage exposed to light can lead to formation of poisonous phosgene.

**Step 2: Explain the bottle colour** A dark-coloured bottle reduces the amount of light reaching the chloroform and therefore suppresses this light-promoted oxidation. The reason for the dark colour is protection against phosgene formation, rather than a change in chloroform composition caused by the colour itself.

**Step 3: Conclusion** Chloroform is stored in dark-coloured bottles to prevent its light-promoted oxidation to highly poisonous phosgene,  $\text{COCl}_2$ .

**Quick Tip to Solve:** Connect dark storage with light-promoted oxidation, and name phosgene as the poisonous product.

32(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 stereoisomers that rotate plane-polarised light equally in opposite directions under identical conditions.

**Step 1: (I) Define ambident nucleophiles** Ambident nucleophiles are nucleophiles having two alternative reactive sites through which they can donate an electron pair and attack an electrophile. For example,  $\text{CN}^-$  can attack through carbon or nitrogen: carbon attack gives a nitrile,  $\text{R} - \text{C} \equiv \text{N}$ , whereas nitrogen attack gives an isocyanide,  $\text{R} - \text{N} \equiv \text{C}$ . Similarly,  $\text{NO}_2^-$  can react through nitrogen or oxygen. The term refers to alternative attacking atoms, not simultaneous formation of two bonds in a single substitution.

**Step 2: (II) Define a racemic mixture** A racemic mixture is an equimolar mixture of the two enantiomers of a chiral compound, namely its dextrorotatory and laevorotatory forms. Each enantiomer rotates plane-polarised light by the same magnitude in the opposite direction, so their effects cancel in the mixture. Consequently the racemic mixture is optically inactive by external compensation, even though its individual enantiomers are optically active.

**Step 3: Conclusion** Ambident nucleophiles possess two alternative nucleophilic sites; a racemic mixture contains equal amounts of the two enantiomers and has zero net optical rotation.

**Quick Tip to Solve:** Remember ambident as two possible attacking atoms and racemic as a 1:1 enantiomer mixture with cancelling rotations.

OR

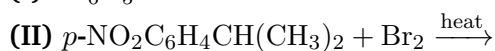
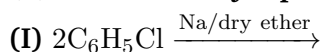
32(b). (i) Answer the following:

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

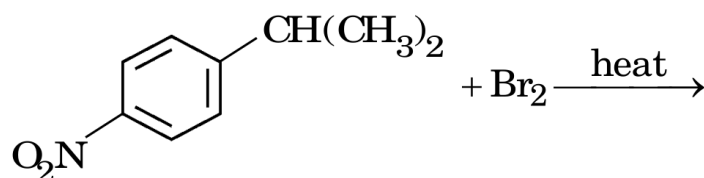
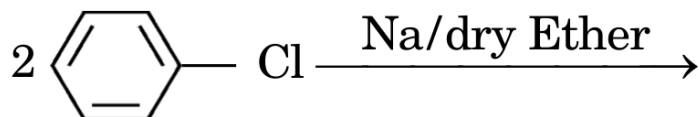
(II) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.

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

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



[5 marks]



### Solution:

#### Concept:

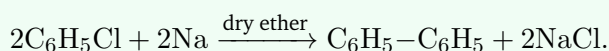
- An  $S_N1$  reaction forms a carbocation in its rate-determining step; a more stable carbocation is formed more readily.
- Dehydrohalogenation removes a halogen and a hydrogen from adjacent carbon atoms. The more substituted alkene is generally the major product (Saytzeff rule).
- Chlorine withdraws electron density inductively but donates a lone pair by resonance; these effects control reactivity and orientation respectively.
- Sodium in dry ether couples aryl halides (Fittig reaction). Bromine with heat substitutes a benzylic hydrogen by a free-radical mechanism.

**Step 1: (i)(I) Compare the carbocations formed by the isomers** The isomers are 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. Ionisation of the last compound,  $(CH_3)_3CBr$ , produces the tertiary tert-butyl carbocation. The others initially produce primary or secondary carbocations. The tertiary ion is stabilised by the electron-releasing inductive effect and hyperconjugation of three alkyl groups. Its formation therefore has the lowest barrier, so 2-bromo-2-methylpropane is most reactive towards  $S_N1$ .

**Step 2: (i)(II) Select the major elimination product** In 1-bromo-1-methylcyclohexane the carbon bearing bromine is carbon 1. Removing a hydrogen from neighbouring ring carbon 2 (or equivalent carbon 6) forms an endocyclic double bond. This gives 1-methylcyclohex-1-ene, a trisubstituted alkene. Removing a hydrogen from the methyl group would instead give methylenecyclohexane, a less substituted exocyclic alkene. Hence the endocyclic product, 1-methylcyclohex-1-ene, predominates according to Saytzeff's rule.

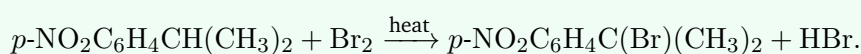
**Step 3: (i)(III) Explain chlorine's directing effect** Chlorine's strong  $-I$  effect lowers the overall electron density of the benzene ring and therefore deactivates it towards electrophilic substitution. However, its lone pair overlaps with the ring's  $\pi$  system and is donated by resonance. This donation increases electron density at the ortho and para positions and gives additional resonance stabilisation to the intermediates formed by attack there. Meta attack lacks this additional stabilisation. Thus chlorobenzene reacts more slowly than benzene but directs incoming electrophiles mainly to ortho and para positions.

**Step 4: (ii)(I) Couple the two phenyl groups** The printed substrate is chlorobenzene. Sodium in dry ether joins two phenyl groups at the positions originally bearing chlorine:



The organic product is biphenyl. This is the Fittig coupling of two aryl halide molecules.

**Step 5: (ii)(II) Replace the benzylic hydrogen** Heating bromine favours free-radical side-chain bromination. In the printed para-nitroisopropylbenzene, the carbon directly attached to the ring bears one hydrogen and two methyl groups. Loss of this benzylic hydrogen generates a resonance-stabilised tertiary benzylic radical. Bromine replaces that hydrogen:



**Quick Tip to Solve:** For bromine with heat, first locate the benzylic hydrogen; for sodium in dry ether, join the two carbons originally bonded to halogen.

Bromination at a methyl carbon gives a less stable primary radical, while the stated conditions favour side-chain rather than electrophilic ring bromination.

**Step 6: Conclusion** (i) (I) 2-bromo-2-methylpropane; (II) 1-methylcyclohex-1-ene; (III) chlorine's resonance donation favours ortho/para substitution despite inductive deactivation. (ii) (I) Biphenyl,  $C_6H_5-C_6H_5$ ; (II)  $p\text{-NO}_2C_6H_4C(Br)(CH_3)_2$ .

**Quick Tip to Solve:** For bromine with heat, first locate the benzylic hydrogen; for sodium in dry ether, join the two carbons originally bonded to halogen.

**33(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  $MgBr_2 = 184 \text{ g mol}^{-1}$ ,  $K_f$  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 freezing-point depression constant and  $m$  is molality.
- Molality is moles of solute formula units per kilogram of solvent. Complete dissociation increases the effective number of dissolved particles.
- The solution's freezing temperature is  $T_f = T_f^\circ - \Delta T_f$ ; pure water freezes at  $0^\circ\text{C}$ .

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



Each formula unit produces three independent ions, so  $i = 3$ . The charges do not determine the particle count; one magnesium ion and two bromide ions constitute three dissolved particles.

**Step 2: Calculate the molality from the given masses** Using the supplied molar mass,

$$n = \frac{10.5 \text{ g}}{184 \text{ g mol}^{-1}} = 0.05707 \text{ mol}.$$

The mass of water is 250 g = 0.250 kg, so

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

Use the mass of the solvent alone in this denominator, rather than the combined mass of water and salt.

**Step 3: Calculate the depression and the freezing temperature** Substitute the van't Hoff factor and molality into the colligative-property expression:

$$\Delta T_f = 3(1.86 \text{ K kg mol}^{-1})(0.22826 \text{ mol kg}^{-1}) = 1.2737 \text{ K}.$$

A temperature difference of one kelvin equals a difference of one Celsius degree. Dissolved particles

**Quick Tip to Solve:** Count all ions to obtain  $i = 3$ , convert 250 g of solvent to 0.250 kg, and subtract the positive depression from zero Celsius.

lower the freezing point; consequently subtract this positive depression from pure water's freezing point:

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

**Step 4: Conclusion** The freezing point of the solution is approximately  $-1.27^\circ\text{C}$  (about 271.88 K).

**Quick Tip to Solve:** Count all ions to obtain  $i = 3$ , convert 250 g of solvent to 0.250 kg, and subtract the positive depression from zero Celsius.

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

[2 marks]

**Solution:**

**Concept:**

- An ideal solution obeys Raoult's law over the entire composition range:  $p_A = x_A p_A^\circ$  and  $p_B = x_B p_B^\circ$ , where  $x$  denotes mole fraction and  $p^\circ$  the vapour pressure of the pure component.
- Mixing behaviour depends on the relative strengths of unlike and like intermolecular attractions. Ideal mixing has  $\Delta H_{\text{mix}} = 0$ ; non-ideal mixing generally has a nonzero enthalpy change.

**Step 1: Compare their vapour-pressure behaviour** An ideal solution obeys Raoult's law at all compositions. Its component partial pressures are proportional to their mole fractions, so the total vapour pressure is  $p = x_A p_A^\circ + x_B p_B^\circ$ . A non-ideal solution does not obey this relation throughout the composition range: its observed vapour pressure shows positive or negative deviation from Raoult's law.

**Step 2: Compare the enthalpy change on mixing** For an ideal solution, the attractions between unlike molecules are effectively comparable to those between like molecules, so mixing neither absorbs nor releases heat:  $\Delta H_{\text{mix}} = 0$ . For a non-ideal solution, unlike interactions differ from like interactions; mixing is generally endothermic for positive deviation and exothermic for negative deviation, giving  $\Delta H_{\text{mix}} \neq 0$ .

**Step 3: Conclusion** The two differences are: ideal solutions obey Raoult's law at every composition and have zero enthalpy of mixing; non-ideal solutions deviate from Raoult's law and have a nonzero enthalpy of mixing.

**Quick Tip to Solve:** State each difference as a paired comparison: Raoult's law first, then the enthalpy of mixing.

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

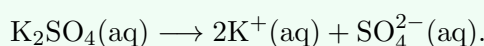
[3 marks]

**Solution:**

**Concept:**

- The osmotic pressure of a dilute solution is  $\pi = iCRT = i(n/V)RT$ , where  $i$  is the van't Hoff factor,  $C$  is the molar concentration of the solute before dissociation,  $R$  is the gas constant and  $T$  is the absolute temperature.
- Complete dissociation increases the number of independently moving solute particles. The van't Hoff factor equals the number of ions formed per formula unit when dissociation is complete.

**Step 1: Determine the van't Hoff factor** Potassium sulphate dissociates as



Each formula unit gives two potassium ions and one sulphate ion, hence three solute particles in total. Under the stated complete-dissociation condition,  $i = 3$ . Using  $i = 1$  would ignore the increase in particle number and underestimate the osmotic pressure by a factor of three.

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

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

For this dilute solution, take the solution volume as the given 2 L. Thus

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

Convert the temperature to kelvin:  $T = 27 + 273 = 300 \text{ K}$ .

**Step 3: Substitute in the osmotic-pressure equation** With  $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ,

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

The litre, mole and kelvin units cancel, leaving pressure in atmospheres, consistent with the supplied value of  $R$ .

**Step 4: Conclusion** The osmotic pressure is  $\pi \approx 5.30 \times 10^{-3} \text{ atm}$ , accounting for complete dissociation of potassium sulphate.

**Quick Tip to Solve:** Count all ions before substituting: one potassium sulphate formula unit produces three particles, so use  $i = 3$ .

**33(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 constant-boiling mixture whose vapour and liquid have the same composition at a particular pressure; it cannot be separated into pure components by fractional distillation.
- Solutions showing sufficiently strong negative deviation from Raoult's law form maximum-boiling azeotropes. Stronger unlike intermolecular attractions lower vapour pressure and raise the boiling point.

**Step 1: Identify the interaction between acetone and chloroform** The oxygen atom of the carbonyl group in acetone accepts a hydrogen bond from the hydrogen of chloroform. The three electron-withdrawing chlorine atoms make this hydrogen sufficiently electron deficient to interact with the carbonyl oxygen. These acetone–chloroform attractions are stronger than the corresponding attractions between like molecules in the pure liquids.

**Step 2: Connect this interaction to boiling behaviour** Stronger unlike attractions reduce the tendency of molecules to escape into the vapour phase. The solution therefore has a lower vapour pressure than predicted by Raoult's law and shows negative deviation. Since boiling occurs when vapour pressure equals the external pressure, the solution needs a higher temperature to boil. At the azeotropic composition, this gives a maximum in the boiling-point curve.

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

**Quick Tip to Solve:** Link stronger unlike attractions to lower vapour pressure, then to a higher boiling point and a maximum-boiling azeotrope.