

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-3-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

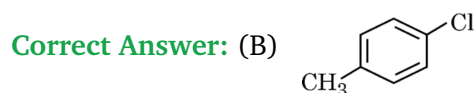
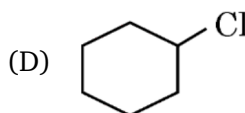
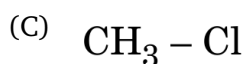
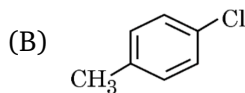
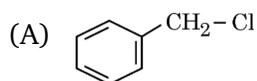
- (i) This question paper contains **33** questions. **All** questions are **compulsory**.
- (ii) This question paper is divided into **five** sections – **Section A, B, C, D and E**.
- (iii) **Section A** – questions number **1 to 16** are multiple choice type questions. Each question carries **1**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

Section A (16 marks)

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

1. Which of the following will be the least reactive towards nucleophilic substitution reaction?

[1 mark]



Solution:

Concept:

- Nucleophilic substitution depends on the carbon bonded to chlorine and the strength of the carbon-chlorine bond.
- In an aryl halide, the chlorine lone pair conjugates with the aromatic ring; the C-Cl bond acquires partial double-bond character.

Step 1: Identify the aryl halide In option (B), chlorine is attached directly to an aromatic ring: the compound is para-chlorotoluene. Its resonance-stabilised aryl C-Cl bond is shorter and stronger than the C-Cl bond of an alkyl halide. Ordinary nucleophilic substitution therefore occurs with great difficulty.

Step 2: Compare the other three options Option (A), benzyl chloride, has chlorine on a benzylic carbon rather than on the ring and reacts readily. Option (C), methyl chloride, has an unhindered carbon favourable for attack by a nucleophile. Option (D), chlorocyclohexane, is a secondary alkyl halide; although sterically hindered, it lacks the aryl bond strengthening present in (B).

Step 3: Conclusion Para-chlorotoluene is the least reactive towards nucleophilic substitution. Hence, the correct option is (B).

Quick Tip to Solve: Check whether Cl is bonded directly to the aromatic ring or to a side-chain carbon.

2. The intermediate formed during the slowest step involved in the dehydration of alcohol is: [1 mark]

- (A) protonated alcohol
- (B) carbanion
- (C) free radical
- (D) carbocation

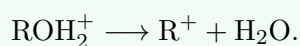
Correct Answer: (D) carbocation

Solution:

Concept:

- Acid-catalysed dehydration removes water from an alcohol to form an alkene.
- Protonation converts the poor leaving group OH into water; slow C–O bond cleavage gives a carbocation.

Step 1: Identify the slow step The oxygen of the alcohol first accepts a proton. The protonated alcohol then loses water in the rate-determining step. In the usual CBSE dehydration mechanism, heterolytic cleavage leaves the carbon electron deficient and produces a carbocation:



Step 2: Eliminate the alternatives The protonated alcohol in (A) is produced in the preceding fast protonation step. A carbanion in (B) would carry a negative charge, whereas water departure here produces a positive carbon centre. A free radical in (C) would require homolytic cleavage. Finally, loss of a proton from the carbocation yields the alkene and regenerates the acid catalyst.

Step 3: Conclusion The intermediate formed during the slowest step is a carbocation. Hence, the correct option is (D).

Quick Tip to Solve: In acid dehydration, follow protonation, slow water loss, then removal of a proton.

3. The oxidation number of Co in $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ is:

[1 mark]

- (A) +3
- (B) +2
- (C) +4
- (D) +6

Correct Answer: (A) +3

Solution:

Concept:

- The algebraic sum of oxidation numbers in a neutral compound is zero.
- Ethylenediamine, en, is a neutral bidentate ligand; each sulphate ion carries charge -2 .

Step 1: Write the charge balance Let the oxidation number of each cobalt atom be x . There are two $[\text{Co}(\text{en})_3]$ complex units and three sulphate ions. Since every en ligand is neutral, each complex has

Quick Tip to Solve: Count both complex units before balancing the three sulphate ions; en contributes zero charge.

charge x . Electrical neutrality requires

$$2x + 3(-2) = 0.$$

Step 2: Solve and compare the choices Thus $2x = 6$, giving $x = +3$. The charge +6 balances all three sulphate ions for the two complex units together; it is not the oxidation number of one cobalt atom. Values +2 and +4 would not balance the anion charge. The fact that en is bidentate changes the coordination number, not its neutral ligand charge.

Step 3: Conclusion The oxidation number of Co is +3. Hence, the correct option is (A).

Quick Tip to Solve: Count both complex units before balancing the three sulphate ions; en contributes zero charge.

4. According to Werner's theory, the primary valencies of the central metal atom:

[1 mark]

- (A) are satisfied by neutral molecules or negative ions.
- (B) are equal to its coordination number.
- (C) are satisfied by negative ions.
- (D) are non-ionisable.

Correct Answer: (C) are satisfied by negative ions.

Solution:

Concept:

- Werner's primary valency equals the oxidation state of the central metal and is ionisable.
- Secondary valency equals the coordination number and is satisfied by neutral molecules or negative ions.

Step 1: Apply the definition of primary valency Primary valencies represent the charge-balancing requirements of the central metal. They are satisfied by negative ions, which may occur outside the coordination sphere as counterions. For example, in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, cobalt has primary valency three, satisfied by three chloride ions.

Step 2: Distinguish secondary valency Option (A) describes the kinds of species that can satisfy secondary valency. Option (B) also describes secondary valency because coordination number counts donor atoms attached to the metal. Option (D) is incorrect for primary valencies, which are ionisable; non-ionisable bonding requirements belong to secondary valency. Thus only (C) states the required property.

Step 3: Conclusion Primary valencies are satisfied by negative ions. Hence, the correct option is (C).

Quick Tip to Solve: Associate primary valency with oxidation state and negative ions; secondary with coordination number.

5. Which of the following reagent is used to distinguish between $(\text{C}_2\text{H}_5)_2\text{NH}$ and $(\text{C}_2\text{H}_5)_3\text{N}$? [1 mark]

- (A) $\text{CHCl}_3 + \text{KOH}$
- (B) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$
- (C) Conc. $\text{HCl} + \text{ZnCl}_2$
- (D) $\text{NaOH} + \text{I}_2$

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

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$.
- A secondary amine has an N–H bond and forms a sulphonamide; a tertiary amine has no N–H bond.

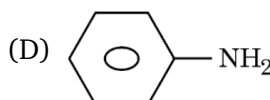
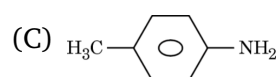
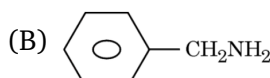
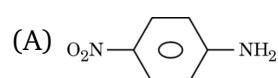
Step 1: Apply the Hinsberg test Diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$, is secondary and reacts with benzenesulphonyl chloride to form N,N-diethylbenzenesulphonamide. The product has no N–H hydrogen and is insoluble in alkali. Triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$, is tertiary and does not form a sulphonamide under the test conditions; it dissolves in dilute acid by forming an ammonium salt.

Step 2: Check the other reagents Chloroform and KOH in (A) give the carbylamine test only with primary amines, so neither given amine responds positively. Concentrated HCl with ZnCl_2 in (C) is Lucas reagent for alcohols. NaOH and iodine in (D) are used in the iodoform test, rather than the standard distinction between these secondary and tertiary amines.

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

Quick Tip to Solve: For secondary versus tertiary amines, check the N–H bond and choose the Hinsberg test.

6. Among the following, which is the strongest base? [1 mark]



Correct Answer: (B)

Solution:

Concept:

- A base accepts a proton through the lone pair on nitrogen; greater lone-pair availability generally increases basic strength.
- In aniline derivatives, the nitrogen lone pair is delocalised into the aromatic ring by resonance.

Step 1: Locate the nitrogen relative to the ring Option (B) is benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$. Its nitrogen is separated from the aromatic ring by a saturated CH_2 group. Consequently its lone pair cannot

Quick Tip to Solve: A CH_2 spacer between the aromatic ring and NH_2 prevents direct lone-pair delocalisation.

conjugate directly with the ring and is readily available to accept a proton.

Step 2: Compare the aniline derivatives Option (D), aniline, has its amino group attached directly to the ring, so resonance lowers lone-pair availability. The para-methyl group in (C), para-toluidine, donates electron density and makes it more basic than aniline, but the lone pair still participates in aromatic conjugation. The para-nitro group in (A) strongly withdraws electron density and makes para-nitroaniline still less basic. Benzylamine therefore exceeds all three in basic strength.

Step 3: Conclusion Benzylamine is the strongest base. Hence, the correct option is (B).

Quick Tip to Solve: A CH₂ spacer between the aromatic ring and NH₂ prevents direct lone-pair delocalisation.

7. In aqueous solution, Cr₂O₇²⁻ ion converts to which of the following in alkaline medium? [1 mark]

(A) Cr³⁺

(B) CrO₄²⁻

(C) CrO

(D) CrO₃

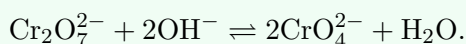
Correct Answer: (B) CrO₄²⁻

Solution:

Concept:

- Chromate and dichromate ions interconvert through an acid–base equilibrium.
- Chromium remains in oxidation state +6 in both ions; the conversion requires no reducing agent.

Step 1: Write the alkaline conversion Adding hydroxide ions converts orange dichromate into yellow chromate. The balanced ionic equation is



Both sides contain two chromium atoms, nine oxygen atoms and two hydrogen atoms, with net charge –4.

Step 2: Compare the alternatives Chromate, CrO₄²⁻, is therefore the ion favoured in alkaline solution. The Cr³⁺ ion in (A) and CrO in (C) contain chromium in lower oxidation states and would require reduction. CrO₃ in (D) is not the chromate ion produced by the stated aqueous alkaline conversion. Acidifying reverses the equilibrium toward dichromate.

Step 3: Conclusion Dichromate converts into CrO₄²⁻ in alkaline medium. Hence, the correct option is (B).

Quick Tip to Solve: Remember alkaline solution favours yellow chromate; acidic solution favours orange dichromate.

8. The boiling point of an azeotropic mixture of water and ethanol is less than that of pure water and ethanol. The mixture shows: [1 mark]

- (A) positive deviation from Raoult's Law.
- (B) negative deviation from Raoult's Law.
- (C) no deviation from Raoult's Law.
- (D) that the solution is an ideal solution.

Correct Answer: (A) positive deviation from Raoult's Law.

Solution:

Concept:

- Raoult's law for an ideal solution is $p_i = x_i p_i^\circ$, where x_i is the liquid mole fraction and p_i° is the pure-component vapour pressure.
- Positive deviation raises the total vapour pressure above the ideal value; boiling occurs when this pressure equals the external pressure.

Step 1: Connect boiling point with vapour pressure The stated mixture boils below both pure liquids. At a given temperature its vapour pressure is therefore unusually high, and it reaches the external pressure at a lower temperature. This is the behaviour of a minimum-boiling azeotrope.

Step 2: Check the alternatives Positive deviation is associated with weaker effective attractions between unlike molecules and greater escaping tendency. Negative deviation instead produces a maximum-boiling azeotrope. No deviation means ideal behaviour; an ideal mixture does not produce the stated minimum-boiling azeotrope. Thus the other three descriptions do not match.

Step 3: Conclusion The mixture shows positive deviation from Raoult's law. Hence, the correct option is (A).

Quick Tip to Solve: A boiling point below both pure components identifies a minimum-boiling azeotrope and positive deviation.

9. The mole fraction of a solute in 2.0 molal aqueous solution is: [1 mark]

- (A) 1.87
- (B) 0.347
- (C) 0.0347
- (D) 0.00347

Correct Answer: (C) 0.0347

Solution:

Concept:

- Molality is $m = n_s/M_w$, where n_s is solute amount in moles and M_w is solvent mass in kilograms.
- The solute mole fraction is $x_s = n_s/(n_s + n_w)$, with n_w the moles of water.

Step 1: Choose the solvent basis Take 1.000 kg of water. A 2.0 mol kg^{-1} solution then contains 2.0 mol

Quick Tip to Solve: For aqueous molality, take 1 kg of water and use 55.56 mol of solvent in the mole-fraction denominator.

of solute. Using the molar mass of water, 18 g mol^{-1} , gives

$$n_w = \frac{1000}{18} = 55.56 \text{ mol.}$$

Step 2: Calculate the mole fraction The denominator includes both solute and solvent moles:

$$x_s = \frac{2.0}{2.0 + 55.56} = 0.03475 \approx 0.0347.$$

A mole fraction cannot exceed unity, ruling out 1.87. The values 0.347 and 0.00347 differ by factors of ten from the calculated fraction.

Step 3: Conclusion The solute mole fraction is 0.0347. Hence, the correct option is (C).

Quick Tip to Solve: For aqueous molality, take 1 kg of water and use 55.56 mol of solvent in the mole-fraction denominator.

10. On electrolysis of very dilute aqueous solution of NaCl using platinum electrodes:

[1 mark]

- (A) H_2 gas is evolved at anode.
- (B) Na is produced at cathode.
- (C) O_2 gas is evolved at anode.
- (D) H_2 gas is evolved at cathode.

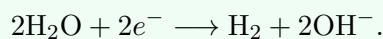
Correct Answer: Both (C) oxygen at the anode and (D) hydrogen at the cathode are correct for the printed conditions; no unique single answer exists.

Solution:

Concept:

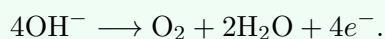
- With inert platinum electrodes, aqueous species compete for discharge: reduction occurs at the cathode and oxidation at the anode.
- In very dilute aqueous sodium chloride, water is discharged in preference to sodium ions at the cathode and chloride ions at the anode.

Step 1: Identify the cathodic product Water is reduced more readily than Na^+ in aqueous solution:



Thus hydrogen is released at the cathode, whereas sodium metal is not deposited. Hydrogen evolution at the anode would require reduction at an oxidation electrode and is incorrect.

Step 2: Identify the anodic product and check the choices At the very low chloride concentration specified, water or hydroxide is oxidised to oxygen. One balanced form is



Thus oxygen evolution at the anode is correct. The printed statement about hydrogen at the cathode

Quick Tip to Solve: For very dilute NaCl with inert electrodes, check both electrodes: water gives hydrogen at the cathode and oxygen at the anode.

is also true: both electrode products arise together during electrolysis.

Step 3: Conclusion Option (C), oxygen gas at the anode, is correct. Option (D), hydrogen gas at the cathode, is also correct for the printed conditions; the printed choices do not provide a unique single answer.

Quick Tip to Solve: For very dilute NaCl with inert electrodes, check both electrodes: water gives hydrogen at the cathode and oxygen at the anode.

11. For a reaction $3A \rightarrow 2B$, the rate of reaction $+\frac{d[B]}{dt}$ is equal to:

[1 mark]

- (A) $-\frac{3}{2} \frac{d[A]}{dt}$
(B) $-\frac{2}{3} \frac{d[A]}{dt}$
(C) $-\frac{1}{3} \frac{d[A]}{dt}$
(D) $+2 \frac{d[A]}{dt}$

Correct Answer: (B) $-\frac{2}{3} \frac{d[A]}{dt}$

Solution:

Concept:

- For $3A \rightarrow 2B$, the normalised reaction rate is $r = -\frac{1}{3} \frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$.
- Reactant disappearance has a negative concentration derivative; product formation has a positive derivative.

Step 1: Apply the stoichiometric relation Every three moles of A consumed form two moles of B. At constant volume, the corresponding concentration changes obey

$$-\frac{d[A]}{dt} : \frac{d[B]}{dt} = 3 : 2.$$

The same time interval applies to both changes, so their rate magnitudes have this ratio.

Step 2: Isolate the requested derivative Multiplying the normalised-rate relation by two gives

$$\frac{d[B]}{dt} = -\frac{2}{3} \frac{d[A]}{dt}.$$

The coefficient 3/2 reverses the required ratio, while 1/3 is the normalised rate expressed through A, not the appearance rate of B. A positive multiple of the negative derivative of A would incorrectly predict disappearance of B.

Step 3: Conclusion $+\frac{d[B]}{dt} = -\frac{2}{3} \frac{d[A]}{dt}$. Hence, the correct option is (B).

Quick Tip to Solve: Distinguish the appearance rate of B from the normalised reaction rate; multiply by the product coefficient 2.

12. On hydrolysis, which of the following carbohydrates gives only glucose?

[1 mark]

- (A) Sucrose
- (B) Galactose
- (C) Lactose
- (D) Maltose

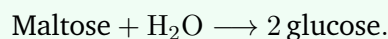
Correct Answer: (D) Maltose

Solution:

Concept:

- Hydrolysis of a disaccharide cleaves its glycosidic linkage by addition of water, producing its constituent monosaccharides.
- Maltose contains two glucose units joined by a glycosidic linkage.

Step 1: Examine maltose hydrolysis Both monosaccharide residues in maltose are glucose. Cleaving the linkage therefore gives two molecules of glucose:



No second kind of monosaccharide is produced.

Step 2: Compare the other carbohydrates Sucrose yields glucose and fructose on hydrolysis, while lactose yields glucose and galactose. They therefore do not give only glucose. Galactose itself is a monosaccharide and cannot be hydrolysed into glucose by breaking a disaccharide linkage. This eliminates the remaining alternatives on the basis of their constituent sugar units.

Step 3: Conclusion Maltose gives only glucose on hydrolysis. Hence, the correct option is (D).

Quick Tip to Solve: Remember the disaccharide pairs: maltose is glucose plus glucose, lactose adds galactose, and sucrose adds fructose.

13. Assertion (A): Separation of Zr and Hf is difficult.

Reason (R): Because Zr and Hf lie in the same group of the periodic table.

[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:

- Lanthanoid contraction is the progressive decrease in atomic and ionic radii across the lanthanoids, caused by poor shielding by 4f electrons.
- The contraction makes the radii of Zr and Hf nearly equal, giving very similar chemical properties.

Step 1: Judge the assertion Separation of zirconium and hafnium is difficult because their nearly identical sizes and similar chemistry cause them to behave alike in separation processes. Thus the assertion is true.

Step 2: Judge the reason Zr and Hf both belong to Group 4 of the periodic table and exhibit similar valence-electron arrangements. The reason is therefore a true statement of their group membership.

Step 3: Test the explanatory link Membership of the same group alone does not account for their exceptional similarity in size and the consequent difficulty of separation. The specific explanation is lanthanoid contraction before Hf, which offsets the expected increase in radius down the group. The reason omits this essential cause and is not the correct explanation of the assertion.

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

Quick Tip to Solve: For the unusual Zr-Hf similarity, look for lanthanoid contraction as the explanation, beyond their common group.

14. Assertion (A): Phenol is less acidic than 4-methylphenol.

Reason (R): The presence of an electron releasing group in phenol makes it less acidic. [1 mark]

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

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

Solution:

Concept:

- Phenol acidity depends on the stability of the phenoxide ion formed by loss of H^+ .
- An electron-releasing methyl group increases electron density and destabilises the negatively charged conjugate base relative to phenoxide.

Step 1: Judge the assertion In 4-methylphenol, the methyl group releases electron density into the aromatic system. This makes its conjugate base less stable relative to phenoxide. Consequently 4-methylphenol is less acidic than phenol, so the assertion states the order in reverse and is false.

Step 2: Judge the reason An electron-releasing substituent reduces the acidity of a substituted phenol by making formation of its negative conjugate base less favourable. The reason correctly describes this substituent effect and is true.

Step 3: Apply the assertion-reason code The reason supports the opposite of the printed assertion: phenol is more acidic than 4-methylphenol. Since the assertion is false and the reason is true, the code for two true statements cannot apply; neither can the code stating that the reason is false.

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

Quick Tip to Solve: Compare conjugate bases: an electron-releasing methyl group weakens phenol acidity, so phenol is more acidic than p-cresol.

15. Assertion (A): Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

Reason (R): Gabriel phthalimide synthesis is used for the preparation of primary aliphatic amines.

[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:

- Gabriel synthesis uses the phthalimide anion as a nucleophile, followed by hydrolysis to give a primary amine.
- Aryl halides resist the nucleophilic substitution required in this synthesis.

Step 1: Judge the assertion The assertion is true. An aromatic primary amine such as aniline cannot be prepared by Gabriel phthalimide synthesis. In an aryl halide, the carbon bonded to halogen is an sp^2 carbon and the carbon-halogen bond has partial double-bond character. The required substitution by the phthalimide anion therefore does not proceed.

Step 2: Judge the reason The reason is also true: Gabriel phthalimide synthesis is a standard method for preparing primary aliphatic amines from suitable alkyl halides. Hydrolysis of the alkylated phthalimide releases the primary amine.

Step 3: Check the explanatory connection The reason states the useful scope of the reaction but does not give the cause of its failure with aryl halides. That cause is the resistance of aryl halides to the necessary nucleophilic substitution. Thus the reason is not the correct explanation; (A) incorrectly claims an explanation, while (C) and (D) incorrectly deny 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: For Gabriel synthesis, distinguish a statement of its scope from the aryl-halide substitution barrier.

16. Assertion (A): Order of reaction is applicable to elementary as well as complex reactions.

Reason (R): Order of a reaction is an experimental quantity.

[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:

- For $r = k[A]^m[B]^n$, the overall order is $m + n$, determined from the experimental rate law.
- Molecularity describes one elementary step, whereas order describes the measured rate dependence.

Step 1: Judge the assertion The assertion is true. A rate law and its order can be determined for an elementary reaction as well as for a complex reaction proceeding through several elementary steps. Order is not restricted to a single collision event.

Step 2: Judge the reason The reason is true. Order is an experimental quantity: the exponents of reactant concentrations are found by observing how the rate changes when concentrations change. They are not generally obtained by adding the coefficients in the overall balanced equation.

Step 3: Connect reason to assertion Because order is defined through an experimentally determined rate law, it can be assigned irrespective of whether the mechanism has one step or several steps. The reason therefore correctly explains the assertion. Option (B) misses this connection, while (C) and (D) incorrectly treat 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: Apply order to the measured rate law; reserve molecularity for an individual elementary step.

Section B (10 marks)

17. For the compound having molecular formula C_4H_9Br , write:

(a) the isomer which is most reactive towards S_N1 displacement.

(b) the isomer which, on reacting with Na metal in the presence of dry ether, gives 2,5-Dimethylhexane.

[2 marks]

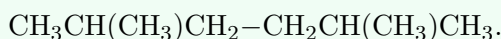
Solution:

Concept:

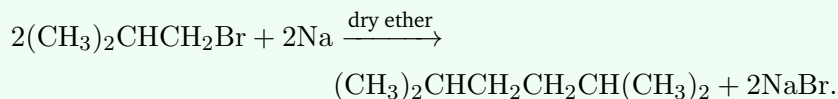
- An S_N1 reaction proceeds through a carbocation; tertiary carbocations are more stable than secondary and primary carbocations.
- Wurtz coupling joins two alkyl groups: $2RBr + 2Na \longrightarrow R-R + 2NaBr$, in dry ether.

Step 1: (a) Select the fastest S_N1 isomer The printed molecular formula is C_4H_9Br . Its isomers include 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. The last is a tertiary bromide, $(CH_3)_3CBr$. Ionisation gives the tertiary tert-butyl carbocation, stabilised by the electron-releasing methyl groups and hyperconjugation. It therefore undergoes S_N1 displacement most readily.

Step 2: (b) Identify the two groups joined by Wurtz coupling Write the product as



Cleaving the central bond gives two identical 2-methylpropyl groups. Their bromide is 1-bromo-2-methylpropane (isobutyl bromide), $(CH_3)_2CHCH_2Br$. The reaction is



Coupling occurs at the carbon originally bonded to bromine, producing the required eight-carbon skeleton.

Step 3: Conclusion (a) 2-Bromo-2-methylpropane, $(CH_3)_3CBr$. (b) 1-Bromo-2-methylpropane, $(CH_3)_2CHCH_2Br$.

Quick Tip to Solve: For symmetrical Wurtz products, cut the central carbon-carbon bond and attach Br to each cut end.

18. For a reaction $A + B \rightarrow \text{Products}$, the rate law is:

$$\text{Rate} = k[A][B]^{3/2}$$

Write the overall order of the reaction. Can this reaction be an elementary reaction? Give reason in support of your answer. [2 marks]

Solution:

Concept:

- The overall order is the sum of the concentration exponents in the experimental rate law.
- For an elementary reaction, rate-law powers correspond to the numbers of reacting particles and are whole numbers.

Step 1: Find the overall order The given rate law is $r = k[A][B]^{3/2}$. The order with respect to A is 1 and the order with respect to B is $3/2$. Therefore

$$n = 1 + \frac{3}{2} = \frac{5}{2} = 2.5.$$

The exponents, rather than the coefficients in the displayed overall equation, determine the order. In particular, the coefficient 1 for B does not make its experimentally given partial order equal to 1.

Step 2: Test whether the reaction can be elementary An elementary reaction is a single molecular event. For the elementary step $A + B \rightarrow \text{products}$, one particle of A and one particle of B would participate, giving a rate law $r = k[A][B]$ and order 2. The given fractional power $[B]^{3/2}$ cannot represent the number of B particles in one elementary event. Consequently, the reaction is not elementary; its observed rate law reflects a mechanism involving more than one step.

Step 3: Conclusion The overall order is $5/2$. The reaction cannot be elementary because its rate law contains the fractional exponent $3/2$.

Quick Tip to Solve: Add the given rate-law powers first; a fractional power rules out a single elementary collision.

19. Explain why, on addition of 1 mol of KCl to 1 litre of water, the boiling point of water increases, while the addition of 1 mol of methyl alcohol to 1 litre of water decreases the boiling point. [2 marks]

Solution:

Concept:

- A liquid boils when its total vapour pressure equals the external atmospheric pressure.
- A nonvolatile solute lowers the solvent vapour pressure; a sufficiently volatile second liquid contributes its own vapour pressure.

Step 1: Explain the effect of KCl KCl is a nonvolatile electrolyte. On dissolving, it forms K^+ and Cl^- ions and reduces the mole fraction and escaping tendency of water. At the original boiling temperature, the vapour pressure of water over the solution is therefore lower than atmospheric pressure. More heating is needed to reach atmospheric pressure, so the boiling point increases. For a dilute solution the relation is $\Delta T_b = iK_b m > 0$, where i accounts for ion formation, K_b is the ebullioscopic constant

Quick Tip to Solve: Before using a colligative boiling-point formula, check whether the added substance is nonvolatile.

and m is molality.

Step 2: Explain the effect of methyl alcohol Methyl alcohol (methanol) is a volatile liquid with a lower boiling point and greater volatility than water. Unlike KCl, it contributes appreciably to the vapour above the solution. Its addition raises the total vapour pressure compared with water at the relevant temperature. The mixture thus reaches atmospheric pressure at a lower temperature, and its boiling point decreases. The nonvolatile-solute boiling-point elevation formula cannot be applied to methanol as though it made no contribution to the vapour.

Step 3: Conclusion KCl lowers water vapour pressure and raises the boiling point; volatile methanol raises the total vapour pressure and lowers the boiling point.

Quick Tip to Solve: Before using a colligative boiling-point formula, check whether the added substance is nonvolatile.

20(a). Write IUPAC names of the following compounds:

(i) $[\text{PtCl}_2(\text{en})_2]\text{SO}_4$

(ii) $(\text{NH}_4)_2[\text{CoF}_4]$

[2 marks]

Solution:

Concept:

- Ligands are named alphabetically before the central metal. Chloride and fluoride ligands are named chlorido and fluoro; *en*, ethane-1,2-diamine, is neutral.
- The sum of the metal oxidation state and ligand charges equals the complex charge. An anionic cobalt complex uses the metal name cobaltate.

Step 1: (i) Name the platinum compound The sulphate ion is SO_4^{2-} , so the complex cation has charge +2. If platinum has oxidation state x , then

$$x + 2(-1) + 2(0) = +2 \Rightarrow x = +4.$$

Two chlorido ligands precede two ethane-1,2-diamine ligands alphabetically. The latter name already contains a numerical prefix, so use bis with parentheses. The name is **dichloridobis(ethane-1,2-diamine)platinum(IV) sulphate**.

Step 2: (ii) Name the cobalt compound Two ammonium cations contribute a total charge of +2, giving $[\text{CoF}_4]^{2-}$. Thus

$$x + 4(-1) = -2 \Rightarrow x = +2.$$

There are four fluoro ligands and the complex is anionic. Its name is **ammonium tetrafluoridocobaltate(II)**. The oxidation number in parentheses refers to cobalt, not to the charge of the entire complex.

Step 3: Conclusion (i) Dichloridobis(ethane-1,2-diamine)platinum(IV) sulphate.

(ii) Ammonium tetrafluoridocobaltate(II).

Quick Tip to Solve: Find the charge of the coordination entity from the counter-ion before calculating the metal oxidation state.

20(b). Define the following terms with a suitable example in each case:

(i) Ambidentate ligand

(ii) Double salt

[2 marks]

Solution:

Concept:

- A ligand donates an electron pair to a central metal through a donor atom. Ambidentate ligands have two alternative donor atoms, but attach through only one at a time.
- A double salt is a crystalline combination of simple salts in a fixed proportion; in aqueous solution it dissociates completely into the constituent simple ions.

Step 1: (i) Ambidentate ligand with an example An **ambidentate ligand** can coordinate to a metal through either of two different donor atoms, using one donor atom in a given coordination bond. For example, NO_2^- may bind through nitrogen (nitro) or through oxygen (nitrito). These are alternative bonding modes of the same ligand. It is not a bidentate ligand: a bidentate ligand binds through two donor atoms simultaneously.

Step 2: (ii) Double salt with an example A **double salt** is formed by crystallisation of two or more simple salts in a definite stoichiometric ratio and loses its separate identity on dissolution in water, yielding the simple constituent ions. For example, Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, dissociates in water to give Fe^{2+} , NH_4^+ and SO_4^{2-} ions. Unlike a coordination salt, it does not retain a complex ion as its characteristic species.

Step 3: Conclusion An ambidentate ligand has alternative donor atoms, for example NO_2^- . A double salt dissociates into simple ions in water, for example Mohr's salt.

Quick Tip to Solve: Remember that ambidentate means either donor atom; bidentate means two donor atoms bind together.

21. How do you explain the following?

(a) Presence of a straight chain in glucose.

(b) Presence of five -OH groups in glucose which are attached to different carbon atoms.

[2 marks]

Solution:

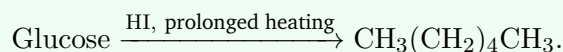
Concept:

- Reactions of glucose reveal its carbon skeleton and the number of hydroxyl groups. A product with six carbons in one unbranched chain is evidence for a straight-chain skeleton.
- Acetylation replaces the hydrogen of each alcoholic hydroxyl group by an acetyl group. A stable pentaacetate indicates five separate hydroxyl groups.

Step 1: (a) Evidence for a straight carbon chain On prolonged heating with hydrogen iodide, glucose

Quick Tip to Solve: Link each observation to its inference: n-hexane tests the carbon skeleton, whereas pentaacetate counts hydroxyl groups.

is converted into *n*-hexane:



This reduction removes the oxygen-containing groups while retaining the carbon skeleton. Since *n*-hexane has six carbon atoms joined in a single unbranched chain, its formation establishes the straight chain of six carbon atoms in glucose.

Step 2: (b) Evidence for five hydroxyl groups Glucose reacts with acetic anhydride to form glucose pentaacetate. Each hydroxyl group undergoes acetylation, $-\text{OH} \rightarrow -\text{OCOCH}_3$; therefore, five acetyl groups show that glucose contains five hydroxyl groups. The pentaacetate is stable, supporting attachment of these hydroxyl groups to different carbon atoms, as in the accepted glucose structure. Thus the reaction provides both the count of hydroxyl groups and evidence for their distribution on separate carbon atoms.

Step 3: Conclusion Formation of *n*-hexane on prolonged heating with HI supports a straight six-carbon chain; formation of stable glucose pentaacetate supports five hydroxyl groups on different carbon atoms.

Quick Tip to Solve: Link each observation to its inference: *n*-hexane tests the carbon skeleton, whereas pentaacetate counts hydroxyl groups.

Section C (21 marks)

22. The half-life period of a radioactive element is 1.5×10^{10} years. Calculate the time in which the activity of the element is reduced to 75% of its original value.

[Given: $\log 2 = 0.30$, $\log 3 = 0.48$, $\log 4 = 0.60$]

[3 marks]

Solution:

Concept:

- Radioactive decay follows first-order kinetics: $N = N_0 e^{-kt}$, where N is the number of undecayed nuclei and k is the decay constant.
- Activity $A = kN$ is proportional to the number of undecayed nuclei. Therefore $A/A_0 = N/N_0$ and $kt = 2.303 \log(A_0/A)$.
- The half-life obeys $kt_{1/2} = 2.303 \log 2$. Dividing the time equation by this relation avoids rounding the decay constant.

Step 1: Identify the remaining activity The half-life is $t_{1/2} = 1.5 \times 10^{10}$ years. The final activity is 75 percent of the original activity, so

$$A = 0.75A_0, \quad \frac{A_0}{A} = \frac{1}{0.75} = \frac{4}{3}.$$

This is the remaining fraction: only 25 percent has decayed. Using $A/A_0 = 0.25$ would answer a different question.

Step 2: Relate the required time to the half-life For the required decay, $kt = 2.303 \log(4/3)$. For one

Quick Tip to Solve: For a first-order decay, use the ratio of time to half-life equals the logarithm of initial/final divided by $\log 2$; interpret the stated percentage as the remaining fraction.

half-life, $kt_{1/2} = 2.303 \log 2$. Dividing eliminates both k and 2.303:

$$\frac{t}{t_{1/2}} = \frac{\log(4/3)}{\log 2} = \frac{\log 4 - \log 3}{\log 2}.$$

This relation is valid for activity because the decay constant of the element remains fixed.

Step 3: Substitute the supplied logarithms and check the scale Using exactly the logarithms supplied in the question,

$$\begin{aligned} t &= 1.5 \times 10^{10} \times \frac{0.60 - 0.48}{0.30} \text{ years} \\ &= 1.5 \times 10^{10} \times 0.40 \text{ years} \\ &= 6.0 \times 10^9 \text{ years.} \end{aligned}$$

The remaining activity, 75 percent, exceeds 50 percent; hence the required time must be less than one half-life. The obtained value is $0.40t_{1/2}$, consistent with that check.

Step 4: Conclusion The required time, using the given logarithms, is 6.0×10^9 years.

Quick Tip to Solve: For a first-order decay, use the ratio of time to half-life equals the logarithm of initial/final divided by $\log 2$; interpret the stated percentage as the remaining fraction.

23. State Kohlrausch's law of independent migration of ions. With the help of a curve, explain why it is not easy to determine Λ_m^0 for weak electrolytes by extrapolating the concentration - molar conductivity curve, as it is for strong electrolytes. [3 marks]

Solution:

Concept:

- At infinite dilution, ions migrate independently: each ion makes a definite contribution to the limiting molar conductivity, independent of the other ion present.
- Kohlrausch's law is $\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$, where ν_+ and ν_- are the stoichiometric numbers of cations and anions and λ_i^0 is the limiting ionic molar conductivity.

Step 1: State the law At infinite dilution, each ion makes a definite contribution to the molar conductivity regardless of the nature of the other ion. The total is the sum of these contributions, multiplied by the respective stoichiometric coefficients. Thus for calcium chloride, $\Lambda_m^0 = \lambda_{\text{Ca}^{2+}}^0 + 2\lambda_{\text{Cl}^-}^0$.

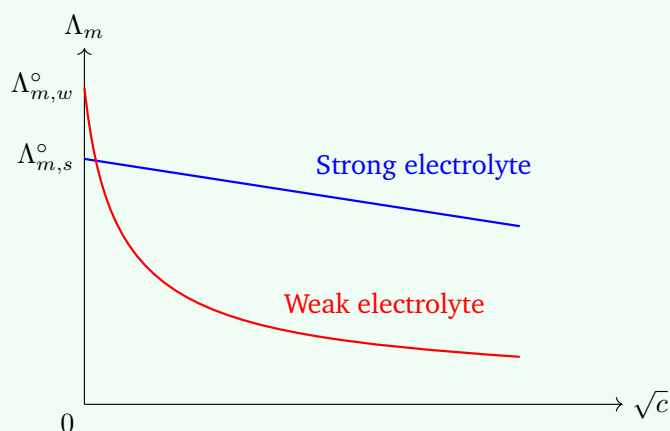
Step 2: Explain the strong-electrolyte curve Strong electrolytes are nearly completely ionised. At low concentrations, $\Lambda_m = \Lambda_m^0 - A\sqrt{c}$, where c is concentration and A is a positive constant. The plot of Λ_m against $\sqrt{c}$ is approximately straight, so extending it to $\sqrt{c} = 0$ gives Λ_m^0 as the intercept.

Step 3: Explain the weak-electrolyte curve A weak electrolyte becomes increasingly ionised on dilution. Its molar conductivity therefore increases sharply near zero concentration, giving a strongly curved plot. Measurements at finite concentrations do not provide a straight line that can be reliably extrapolated to the limiting intercept. The schematic curves show the difference. Instead, calculate

Quick Tip to Solve: Plot against $\sqrt{c}$, not simply c , when explaining the straight-line extrapolation for a strong electrolyte.

the limiting value using Kohlrausch's law and strong-electrolyte data, for example

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{CH}_3\text{COONa}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NaCl}).$$



Schematic variation of molar conductivity with square root of concentration

Step 4: Conclusion Each ion contributes independently at infinite dilution. A strong electrolyte permits a nearly linear extrapolation of Λ_m versus $\sqrt{c}$; the sharp nonlinear rise for a weak electrolyte makes this determination unreliable.

Quick Tip to Solve: Plot against $\sqrt{c}$, not simply c , when explaining the straight-line extrapolation for a strong electrolyte.

24. An antifreeze solution is prepared by dissolving 31 g of ethylene glycol (Molar mass = 62 g mol⁻¹) in 600 g of water. Calculate the freezing point of the solution. (K_f for water = 1.86 K kg mol⁻¹) [3 marks]

Solution:

Concept:

- For a dilute solution of a nonvolatile solute, freezing-point depression is $\Delta T_f = iK_fm$, with m the moles of solute per kilogram of solvent.
- Ethylene glycol is a molecular nonelectrolyte, so $i = 1$. Pure water freezes at 0 °C, and the solution freezing point is lower by ΔT_f .

Step 1: Calculate the amount of ethylene glycol The given solute mass is 31 g and its molar mass is 62 g mol⁻¹. Hence

$$n = \frac{31 \text{ g}}{62 \text{ g mol}^{-1}} = 0.500 \text{ mol}.$$

Ethylene glycol does not dissociate into ions in water; each dissolved molecule contributes one solute particle.

Step 2: Calculate molality using the solvent mass The mass of water is 600 g = 0.600 kg. Molality

Quick Tip to Solve: Convert the 600 g of water to 0.600 kg before finding molality, then subtract the depression from the freezing point of pure water.

uses the mass of solvent, not the total mass of solution. Therefore

$$m = \frac{0.500 \text{ mol}}{0.600 \text{ kg}} = 0.8333 \text{ mol kg}^{-1}.$$

No solution-volume conversion or density is needed because the data already provide the solvent mass.

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

$$\begin{aligned}\Delta T_f &= 1 \times 1.86 \times 0.8333 \\ &= 1.55 \text{ K}.\end{aligned}$$

A temperature difference of 1.55 K equals a difference of 1.55 °C. Thus

$$T_f(\text{solution}) = 0 - 1.55 = -1.55 \text{ °C}.$$

Equivalently, the freezing temperature is $273.15 - 1.55 = 271.60 \text{ K}$. The negative Celsius value is consistent with an antifreeze lowering the freezing point of water.

Step 4: Conclusion The freezing-point depression is 1.55 K, so the solution freezes at -1.55 °C (271.60 K).

Quick Tip to Solve: Convert the 600 g of water to 0.600 kg before finding molality, then subtract the depression from the freezing point of pure water.

25(a). Answer the following questions about the complexes $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$:

- (i) Write the hybridization involved in each case.
- (ii) Which of them is the inner orbital complex and which one is the outer orbital complex?
- (iii) Compare their magnetic behaviour.

[Atomic number: Ni = 28]

[3 marks]

Solution:

Concept:

- For both complexes, four ligands each carry charge -1 , giving nickel oxidation state $+2$: $x - 4 = -2$. Thus Ni^{2+} has the $3d^8$ configuration.
- A weak-field ligand such as Cl^- does not force electron pairing; the strong-field ligand CN^- allows pairing and formation of a square-planar dsp^2 complex.
- Unpaired electrons cause paramagnetism, whereas a complex in which all electrons are paired is diamagnetic.

Step 1: Establish the metal-ion electronic configuration Nickel has atomic number 28 and ground-state configuration $[\text{Ar}]3d^84s^2$. Removal of the two $4s$ electrons gives $\text{Ni}^{2+} : [\text{Ar}]3d^8$. Both complexes have coordination number four, but ligand strength determines the orbital arrangement and geometry.

Step 2: (i) Identify the hybridisation in each complex In $[\text{NiCl}_4]^{2-}$, the weak-field chloride ligands

Quick Tip to Solve: First obtain the common d^8 configuration; then use weak-field chloride versus strong-field cyanide to decide pairing, hybridisation and magnetism.

leave the $3d^8$ electrons with two unpaired electrons. The metal uses one $4s$ and three $4p$ orbitals, giving sp^3 hybridisation and tetrahedral geometry. In $[\text{Ni}(\text{CN})_4]^{2-}$, strong-field cyanide ligands cause pairing in the $3d$ orbitals, leaving one $3d$ orbital vacant. This orbital, one $4s$, and two $4p$ orbitals give dsp^2 hybridisation and square-planar geometry.

Step 3: (ii) Classify the orbital use $[\text{Ni}(\text{CN})_4]^{2-}$ is an inner-orbital complex because its dsp^2 hybrids use an inner $3d$ orbital. $[\text{NiCl}_4]^{2-}$ is classified as the outer-orbital complex in the requested comparison: its sp^3 hybrids use the outer $4s$ and $4p$ orbitals; no $3d$ orbital participates in its hybridisation.

Step 4: (iii) Compare magnetic behaviour $[\text{NiCl}_4]^{2-}$ has two unpaired $3d$ electrons and is paramagnetic. Its spin-only magnetic moment is $\mu = \sqrt{n(n+2)} = \sqrt{8} \approx 2.83$ Bohr magnetons for $n = 2$. In $[\text{Ni}(\text{CN})_4]^{2-}$, all the $3d$ electrons are paired, so it is diamagnetic with zero spin-only magnetic moment. Thus the two complexes have different magnetic behaviour despite having the same metal oxidation state.

Step 5: Conclusion $[\text{NiCl}_4]^{2-}$: sp^3 , outer-orbital, tetrahedral and paramagnetic (two unpaired electrons). $[\text{Ni}(\text{CN})_4]^{2-}$: dsp^2 , inner-orbital, square planar and diamagnetic.

Quick Tip to Solve: First obtain the common d^8 configuration; then use weak-field chloride versus strong-field cyanide to decide pairing, hybridisation and magnetism.

OR

25(b). (i) Name two coordination compounds which are important in biological systems.

(ii) What is meant by chelate effect? Give an example.

(iii) Why are low spin tetrahedral complexes rarely formed?

[3 marks]

Solution:

Concept:

- A coordination compound contains a central metal ion bonded to donor atoms of ligands; many essential biological molecules contain such metal centres.
- A chelating ligand binds through two or more donor atoms and forms ring structures with a metal ion, increasing complex stability.
- In a tetrahedral field, the crystal-field splitting energy Δ_t is generally smaller than the electron-pairing energy P .

Step 1: (i) Identify biological coordination compounds Haemoglobin and chlorophyll are two important examples. Haemoglobin contains an iron centre coordinated within a porphyrin system and transports oxygen in blood. Chlorophyll contains a magnesium centre coordinated in a ring system and participates in the absorption of light for photosynthesis. Thus, metal coordination supports both oxygen transport and light harvesting in living systems.

Step 2: (ii) Explain the chelate effect with an example The chelate effect is the enhanced stability of a complex containing a multidentate ligand compared with a comparable complex containing monodentate ligands. For example, ethane-1,2-diamine (en) coordinates through both nitrogen atoms; $[\text{Ni}(\text{en})_3]^{2+}$ contains three bidentate ligands forming chelate rings and is more stable than the

Quick Tip to Solve: Compare Δ_t with pairing energy: small splitting favours separate occupation before pairing.

corresponding ammine complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Ring formation and the favourable entropy change on replacing several monodentate ligands contribute to the stability.

Step 3: (iii) Compare splitting and pairing energies In tetrahedral complexes, the four ligands do not approach directly along the coordinate axes, so the splitting of the metal d orbitals is small. For comparable metal and ligand conditions, $\Delta_t \approx \frac{4}{9}\Delta_o$, where Δ_o is octahedral splitting. Usually $\Delta_t < P$, so occupying the higher-energy orbitals separately costs less energy than pairing electrons in the lower-energy orbitals. High-spin arrangements are therefore favoured, and low-spin tetrahedral complexes are rarely formed.

Step 4: Conclusion Haemoglobin and chlorophyll are biological complexes; chelation enhances complex stability; and the small tetrahedral splitting normally favours high spin.

Quick Tip to Solve: Compare Δ_t with pairing energy: small splitting favours separate occupation before pairing.

26. Give reasons for the following:

- (a) Although chlorine is an electron-withdrawing group, yet it is ortho-, para-directing in electrophilic aromatic substitution reactions.
- (b) Aryl halides cannot be prepared by reacting phenol with concentrated halogen acids or phosphorus halides.
- (c) Chloroform is stored in closed dark coloured bottles. [3 marks]

Solution:

Concept:

- Inductive withdrawal changes overall ring reactivity, while resonance donation determines the preferred positions for electrophilic substitution.
- Resonance gives the phenolic C – O bond partial double-bond character, making its cleavage difficult.
- Chloroform undergoes oxidation in air and light to highly poisonous phosgene.

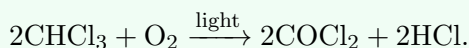
Step 1: (a) Explain chlorine directing effects Chlorine withdraws electron density through its strong negative inductive effect ($-I$), so chlorobenzene is less reactive than benzene towards electrophilic substitution. However, a lone pair on chlorine can overlap with the aromatic system and donate electron density by resonance ($+R$). This resonance donation increases electron density especially at the ortho and para positions and stabilises the corresponding arenium-ion intermediates. Therefore, despite overall deactivation by induction, substitution is preferentially ortho and para.

Step 2: (b) Explain why phenol does not give aryl halides In phenol, an oxygen lone pair is delocalised into the benzene ring. Consequently the bond between oxygen and the aromatic carbon has partial double-bond character and is stronger than the corresponding bond in an alcohol. The carbon bonded to oxygen is also sp^2 -hybridised. This bond is not readily cleaved by concentrated halogen acids or phosphorus halides, so the usual conversion of alcohols into alkyl halides cannot be applied to phenol to prepare aryl halides.

Step 3: (c) Explain storage of chloroform In the presence of air and light, chloroform is slowly

Quick Tip to Solve: For substituent questions, separate the effect on overall reactivity from the effect on the position of substitution.

oxidised to poisonous phosgene (carbonyl chloride):



A closed bottle limits contact with atmospheric oxygen, while dark-coloured glass reduces exposure to light. Both precautions suppress this oxidation and minimise phosgene formation during storage.

Step 4: Conclusion Chlorine directs ortho and para by resonance; the strengthened phenolic carbon-oxygen bond resists replacement; closed dark bottles inhibit phosgene formation.

Quick Tip to Solve: For substituent questions, separate the effect on overall reactivity from the effect on the position of substitution.

27. How will you obtain the following from benzenediazonium chloride? Give chemical equations involved:

(a) Chlorobenzene

(b) Benzene

(c) Benzonitrile

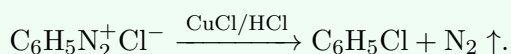
[3 marks]

Solution:

Concept:

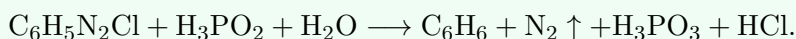
- The diazonium group in $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ can be replaced by several groups with liberation of nitrogen gas.
- Sandmeyer reactions use cuprous salts to replace the diazonium group by chloride or cyanide.
- Hypophosphorous acid reduces the diazonium group to hydrogen, producing benzene.

Step 1: (a) Prepare chlorobenzene Treat benzenediazonium chloride with cuprous chloride in hydrochloric acid. This is the Sandmeyer reaction; the diazonium group is replaced by chlorine and nitrogen gas escapes:



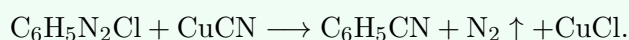
Cuprous chloride supplies the required copper(I) reagent, and the product is chlorobenzene. The aromatic carbon skeleton is retained in this replacement.

Step 2: (b) Prepare benzene Treat benzenediazonium chloride with hypophosphorous acid (H_3PO_2) in the presence of water. Reduction replaces the diazonium group with hydrogen. The balanced equation is



Hypophosphorous acid is oxidised to phosphorous acid while the aromatic product is benzene; nitrogen evolution accompanies the removal of the diazonium group.

Step 3: (c) Prepare benzonitrile Treat benzenediazonium chloride with cuprous cyanide. In this Sandmeyer reaction, cyanide replaces the diazonium group:



Quick Tip to Solve: Remember the replacements as CuCl gives Cl, H_3PO_2 gives H, and CuCN gives CN; each conversion liberates nitrogen.

The product is benzonitrile, in which the nitrile carbon is directly bonded to the phenyl group. This conversion introduces one additional carbon into the organic molecule compared with the starting diazonium salt.

Step 4: Conclusion Use cuprous chloride in hydrochloric acid for chlorobenzene, hypophosphorous acid and water for benzene, and cuprous cyanide for benzonitrile.

Quick Tip to Solve: Remember the replacements as CuCl gives Cl , H_3PO_2 gives H , and CuCN gives CN ; each conversion liberates nitrogen.

28. An organic compound (A) with molecular formula $\text{C}_3\text{H}_5\text{N}$ on reaction with $\text{C}_6\text{H}_5\text{MgBr}$ followed by hydrolysis, gives a compound (B). Compound (B) forms an orange-red precipitate with 2,4-DNP reagent and does not give iodoform test. It neither reduces Tollens' or Fehling's reagent nor does it decolourise bromine water. On drastic oxidation with chromic acid it gives a carboxylic acid (C) having molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Identify the compounds (A), (B) and (C). Write the reactions of compound (A) with $\text{C}_6\text{H}_5\text{MgBr}$ followed by hydrolysis to give compound (B). [3 marks]

Solution:

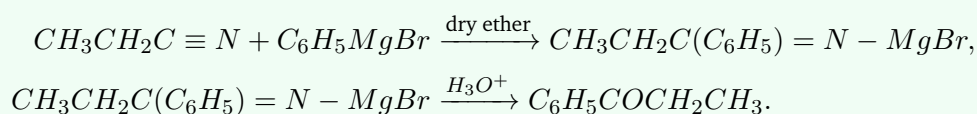
Concept:

- A nitrile $R - C \equiv N$ reacts with a Grignard reagent to give an imine magnesium salt, which yields a ketone on acidic hydrolysis.
- 2,4-DNP detects a carbonyl group. Ordinary ketones do not reduce Tollens' or Fehling's reagent; a negative iodoform test excludes a methyl ketone.
- Drastic oxidation of an alkyl phenyl ketone can produce benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, with molecular formula $\text{C}_7\text{H}_6\text{O}_2$.

Step 1: Identify the functional group and carbon skeleton The orange-red precipitate with 2,4-DNP establishes that (B) contains a carbonyl group. Its failure to reduce Tollens' and Fehling's reagents indicates a ketone rather than an aldehyde. The negative iodoform test shows that its carbonyl group is not attached to a methyl group. A nitrile with formula $\text{C}_3\text{H}_5\text{N}$ that gives a ketone with phenylmagnesium bromide is propanenitrile, $\text{CH}_3\text{CH}_2\text{C} \equiv \text{N}$. The phenyl group from the Grignard reagent becomes bonded to its nitrile carbon.

Step 2: Check the identities against the chemical tests The resulting ketone is propiophenone (1-phenylpropan-1-one), $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$. It contains the $> \text{C} = \text{O}$ group needed for the 2,4-DNP test, but lacks the $\text{CH}_3\text{CO}-$ group needed for the iodoform test. It has no non-aromatic carbon-carbon double bond to decolourise bromine water. Under drastic oxidation, the aromatic carbonyl-containing fragment gives benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, matching the specified formula $\text{C}_7\text{H}_6\text{O}_2$.

Step 3: Write Grignard addition followed by hydrolysis The nucleophilic phenyl group adds to the nitrile carbon, forming the magnesium salt of an imine. Acidic hydrolysis converts this intermediate to the ketone:



Quick Tip to Solve: For nitrile plus Grignard questions, retain the nitrile carbon as the ketone carbonyl carbon and attach the Grignard alkyl or aryl group to it.

The first stage must be carried out in dry ether because water destroys a Grignard reagent.

Step 4: Conclusion (A) is propanenitrile, CH_3CH_2CN ; (B) is propiophenone, $C_6H_5COCH_2CH_3$; and (C) is benzoic acid, C_6H_5COOH .

Quick Tip to Solve: For nitrile plus Grignard questions, retain the nitrile carbon as the ketone carbonyl carbon and attach the Grignard alkyl or aryl group to it.

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 (Biomolecules): Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms. All proteins are polymers of α -amino acids. Proteins can be classified into two types on the basis of their molecular shape - Fibrous and Globular proteins. Vitamins are accessory food factors required in the diet. They are classified as fat-soluble and water-soluble. Deficiency of vitamins leads to many diseases. Nucleic acids are the polymers of nucleotides which in turn consist of a base, a pentose sugar and phosphate moiety. There are two types of nucleic acids - DNA and RNA. Nucleic acids are responsible for the transfer of characters from parents to offsprings.

(a) Write the name of basic building units of proteins and nucleic acids. How can you differentiate between Fibrous and Globular proteins on the basis of their structures? [2 marks]

Solution:

Concept:

- Proteins are polymers of α -amino acids joined by peptide bonds.
- Nucleic acids are polymers of nucleotides joined through phosphodiester linkages.
- Fibrous and globular describe the overall shape and folding of protein chains.

Step 1: Name the basic building units The basic building units of proteins are α -amino acids. Their amino and carboxyl groups form peptide bonds during polymerisation. The basic building units of nucleic acids are nucleotides. Each nucleotide contains a nitrogenous base, a pentose sugar and a phosphate group; a base with sugar alone is a nucleoside and is not the complete repeating unit.

Step 2: Compare the structures of the proteins In fibrous proteins, polypeptide chains run largely parallel and are held together by hydrogen bonds and other interactions, producing long, thread-like or fibre-like structures. Keratin is an example. In globular proteins, polypeptide chains coil and fold into compact, approximately spherical structures; insulin is an example. Thus, the required structural distinction is elongated fibres versus compact folded globules.

Step 3: Conclusion Proteins are built from α -amino acids and nucleic acids from nucleotides. Fibrous proteins have elongated, parallel-chain structures; globular proteins have compact, coiled and folded structures.

Quick Tip to Solve: Keep nucleotide distinct from nucleoside: the nucleotide additionally contains phosphate.

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

[1 mark]

Solution:

Concept:

- A DNA nucleotide consists of a nitrogenous base, 2-deoxy-D-ribose and a phosphate group.
- Complete hydrolysis separates these three components by breaking its glycosidic and phosphate ester bonds.

Step 1: Identify the base and sugar The question specifies thymine as the nitrogenous base. Because the nucleotide belongs to DNA, its pentose sugar is 2-deoxy-D-ribose, rather than the ribose present in RNA. Hydrolysis releases these components from their covalent linkages.

Step 2: Identify the phosphate component A nucleotide also contains a phosphate moiety attached to the sugar. Complete hydrolysis therefore yields phosphoric acid along with thymine and 2-deoxy-D-ribose. Stopping at a nucleoside would omit cleavage of the base-sugar bond.

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

Quick Tip to Solve: List all three nucleotide components: base, the correct DNA sugar, and phosphoric acid.

OR

29(b). Write one structural difference between DNA and RNA.

[1 mark]

Solution:

Concept:

- DNA contains 2-deoxy-D-ribose whereas RNA contains D-ribose.
- The sugars differ in the group attached to the 2' carbon of the pentose ring.

Step 1: State the sugar in DNA The sugar component of DNA is 2-deoxy-D-ribose. At its 2' carbon, the substituent is hydrogen: the hydroxyl group present in ribose has been replaced by hydrogen. This is the meaning of the term deoxy.

Step 2: Compare it with the sugar in RNA RNA contains D-ribose, which has a hydroxyl group at the 2' carbon. The presence of $-OH$ in RNA and $-H$ at this position in DNA provides one precise structural difference between these nucleic acids.

Step 3: Conclusion DNA has 2-deoxy-D-ribose (2'-H), whereas RNA has D-ribose (2'-OH).

Quick Tip to Solve: Use the sugar distinction for one structural difference: DNA is deoxy, so it lacks the ribose 2'-OH.

29(c). Give one example each of a fat-soluble vitamin and a water-soluble vitamin.

[1 mark]

Solution:

Concept:

- Vitamins are classified by their solubility in fats or in water.
- Vitamins A, D, E and K are fat-soluble; B-group vitamins and vitamin C are water-soluble.

Step 1: Choose a fat-soluble vitamin Vitamin A is a valid example of a fat-soluble vitamin. It belongs to the group A, D, E and K, whose members are associated with fats and can be stored in the body. Only one example is required here.

Step 2: Choose a water-soluble vitamin Vitamin C (ascorbic acid) is a valid example of a water-soluble vitamin. It belongs to the water-soluble class together with the B-group vitamins. These examples must be assigned to the correct classes rather than simply listed without their classification.

Step 3: Conclusion Fat-soluble vitamin: vitamin A. Water-soluble vitamin: vitamin C.

Quick Tip to Solve: Remember ADEK for fat-soluble vitamins; choose vitamin C as an unambiguous water-soluble example.

30(a). Case study (Alcohols, Phenols and Ethers): Alcohols have higher boiling points than other compounds, namely hydrocarbons, ethers and haloalkanes of comparable molecular masses. On oxidation, primary alcohols yield aldehydes with mild oxidizing agents and carboxylic acids with strong oxidizing agents. Secondary alcohols yield ketones on oxidation while tertiary alcohols are resistant to oxidation. Ethers may be prepared by dehydration of alcohols and Williamson synthesis. The C-O bond in ethers can be cleaved by hydrogen halides. The presence of -OH group in phenols activates the aromatic ring towards electrophilic substitution and directs the incoming group to ortho and para positions due to resonance effect. In presence of NaOH, phenol generates phenoxide ion which is even more reactive than phenol. Thus, in alkaline medium, phenol undergoes Kolbe's reaction.

(a) Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to aldehyde

(ii) Oxidation of a primary alcohol to carboxylic acid

[2 marks]

Solution:

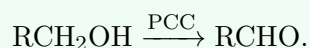
Concept:

- Primary alcohols have the form RCH_2OH , where R is an alkyl group; oxidation first gives an aldehyde RCHO .
- A mild oxidant allows isolation of the aldehyde, whereas a strong oxidant in aqueous medium oxidises it further to RCOOH .

Step 1: (i) Reagent for aldehyde formation Use pyridinium chlorochromate (PCC), commonly in anhydrous dichloromethane. PCC is a mild oxidising agent, so the primary alcohol is converted to the

Quick Tip to Solve: Match aldehyde to a mild oxidant such as PCC, and carboxylic acid to a strong aqueous oxidant under reflux.

aldehyde without further oxidation to the acid under these conditions:



Choosing a mild reagent and avoiding aqueous strongly oxidising conditions is what allows the aldehyde to be obtained.

Step 2: (ii) Reagent for carboxylic acid formation Use acidified potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, with heating under reflux. It oxidises the primary alcohol through the aldehyde stage to the carboxylic acid:



Acidified potassium permanganate is also a suitable strong oxidising reagent. Reflux retains the material in the reaction mixture so oxidation can proceed to completion.

Step 3: Conclusion (i) PCC. (ii) Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (or acidified KMnO_4).

Quick Tip to Solve: Match aldehyde to a mild oxidant such as PCC, and carboxylic acid to a strong aqueous oxidant under reflux.

30(b). Write the reaction involved in Kolbe's reaction.

[1 mark]

Solution:

Concept:

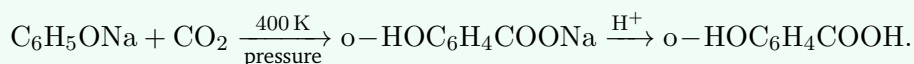
- Sodium phenoxide undergoes carboxylation with CO_2 under pressure at about 400 K.
- Acidification of sodium salicylate produces salicylic acid, with OH and COOH at adjacent ring positions.

Step 1: Form the phenoxide salt Phenol reacts with sodium hydroxide to form sodium phenoxide:



The phenoxide ion activates the aromatic ring towards the incoming electrophile.

Step 2: Carboxylate and acidify In Kolbe's reaction, carbon dioxide reacts with sodium phenoxide under pressure. The ortho product is sodium salicylate; acidification gives salicylic acid:



Step 3: Conclusion Kolbe's reaction converts sodium phenoxide into sodium salicylate with CO_2 ; acidification yields salicylic acid (2-hydroxybenzoic acid).

Quick Tip to Solve: Remember the sequence: sodium phenoxide, carbon dioxide under pressure, then acidification to salicylic acid.

30(c). Why are tertiary alcohols resistant to oxidation?

[1 mark]

Solution:

Concept:

- Usual alcohol oxidation to a carbonyl group removes the hydrogen of the OH group and a hydrogen on the carbon carrying OH.
- A tertiary alcohol has the structure R_3COH ; the carbon bonded to OH bears no hydrogen.

Step 1: Examine the carbon bearing the hydroxyl group In a tertiary alcohol, the hydroxyl-bearing carbon is attached to three other carbon atoms. All its remaining valences are occupied, so there is no hydrogen directly attached to that carbon.

Step 2: Explain the resistance to oxidation The normal oxidation pathway to a carbonyl compound therefore cannot occur by removal of hydrogen alone. Oxidation would require cleavage of a carbon-carbon bond, which is difficult under ordinary oxidising conditions. Under very vigorous conditions, however, such cleavage can occur.

Step 3: Conclusion Tertiary alcohols resist ordinary oxidation because the carbon bearing OH has no hydrogen; their oxidation requires carbon-carbon bond cleavage.

Quick Tip to Solve: Inspect the carbon carrying OH: absence of a hydrogen there explains resistance to ordinary alcohol oxidation.

OR

30(c). Write the products of the following reaction:



[1 mark]

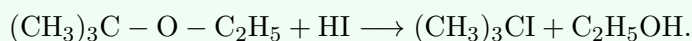
Solution:

Concept:

- HI protonates the ether oxygen, making cleavage of the carbon-oxygen bond easier.
- For an ether containing a tertiary alkyl group, cleavage favours formation of the stable tertiary carbocation, followed by reaction with iodide.

Step 1: Identify the favoured bond cleavage The ether is tert-butyl ethyl ether, $(CH_3)_3C - O - C_2H_5$. After protonation of oxygen by HI, cleavage occurs at the tertiary carbon-oxygen bond because a tertiary carbocation is relatively stable. The other fragment becomes ethanol.

Step 2: Form the products Iodide attacks the tert-butyl carbocation to give tert-butyl iodide. Thus the reaction as written is



The tertiary fragment gives the iodide and the ethyl fragment retains the oxygen as an alcohol.

Step 3: Conclusion The products are tert-butyl iodide (2-iodo-2-methylpropane), $(CH_3)_3CI$, and ethanol, C_2H_5OH .

Quick Tip to Solve: When one ether group is tertiary, cleave on that side: the tertiary group gives iodide and the other gives alcohol.

Section E (15 marks)

31(a). (i) Describe giving reason which one of the following pairs has the property indicated:

(I) Fe or Cu - higher melting point

(II) Ti^{3+} or Sc^{3+} - coloured in aqueous solution

(III) Cr or Zn - higher third ionisation enthalpy

(ii) Write the ionic equations for the oxidizing action of MnO_4^- in acidic medium with:

(I) Fe^{2+} ion

(II) I^- ion

[5 marks]

Solution:

Concept:

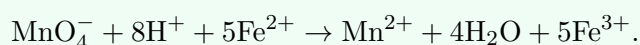
- Strong metallic bonding involving outer s and d electrons generally produces a high melting point.
- A partially filled d subshell permits visible-light absorption through $d-d$ transitions; a d^0 ion has no such transitions.
- Third ionisation removes an electron from M^{2+} . Breaking a stable filled d subshell requires especially high energy.
- Acidic permanganate accepts five electrons: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$.

Step 1: (a)(i)(I) Higher melting point Iron has the higher melting point. Its configuration is $[\text{Ar}]3d^64s^2$, whereas copper is $[\text{Ar}]3d^{10}4s^1$. Iron has more unpaired d electrons available for strong metallic bonding. Copper has a filled $3d$ subshell and weaker metallic bonding in this comparison. More energy is therefore needed to overcome the bonding in iron on melting.

Step 2: (a)(i)(II) Colour in aqueous solution Ti^{3+} is coloured because its configuration is $[\text{Ar}]3d^1$. Water ligands split the d -orbital energies, allowing its electron to absorb visible light and move to a higher-energy d orbital. Sc^{3+} has configuration $[\text{Ar}]3d^0$, so it has no d electron for this transition and is colourless.

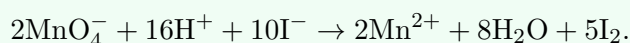
Step 3: (a)(i)(III) Higher third ionisation enthalpy Zinc has the higher third ionisation enthalpy. Before this ionisation, Cr^{2+} is $[\text{Ar}]3d^4$ and Zn^{2+} is $[\text{Ar}]3d^{10}$. Removing an electron from zinc's stable, completely filled $3d^{10}$ subshell requires much more energy than removing one from Cr^{2+} . The configuration of the doubly charged ion, rather than the neutral atom, determines this comparison.

Step 4: (a)(ii)(I) Oxidation of iron(II) Each iron(II) ion loses one electron: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$. Multiply this half-reaction by five and add the permanganate reduction:



Both sides have total charge +17, and the atoms balance. Iron is oxidised from +2 to +3, while manganese is reduced from +7 to +2.

Step 5: (a)(ii)(II) Oxidation of iodide Iodide forms iodine by $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$. Multiply this half-reaction by five and the permanganate reduction by two to exchange ten electrons. Adding and cancelling electrons gives:



Quick Tip to Solve: Write the configuration of the doubly charged ion for third ionisation; use five electrons per permanganate ion in acidic redox equations.

The total charge is +4 on each side; oxygen and hydrogen are balanced using water and hydrogen ions because the medium is acidic.

Step 6: Conclusion The choices in (i) are Fe , Ti^{3+} , Zn , respectively. In (ii), acidic permanganate oxidises Fe^{2+} to Fe^{3+} and I^- to I_2 , according to the balanced ionic equations above.

Quick Tip to Solve: Write the configuration of the doubly charged ion for third ionisation; use five electrons per permanganate ion in acidic redox equations.

OR

31(b). (i) A black-brown coloured solid (A) when fused with KOH in the presence of air, produces a dark green coloured compound (B) which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound (C). Identify (A), (B) and (C). Write the reactions involved.

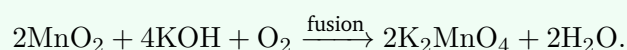
(ii) What happens when an acidic solution of the green compound (B) is allowed to stand for some time? Also write the equation involved. What is this type of reaction called? [5 marks]

Solution:

Concept:

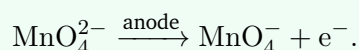
- Manganese dioxide contains manganese in oxidation state +4; alkaline fusion with an oxidant converts it to green manganate containing manganese in state +6.
- Electrolytic oxidation removes one electron from each manganate ion to form purple permanganate, in which manganese is in state +7.
- Disproportionation occurs when the same species is simultaneously oxidised and reduced. In acid, manganate gives permanganate and manganese dioxide.

Step 1: (b)(i) Identify the black-brown starting solid The black-brown solid A is manganese dioxide, MnO_2 . When it is fused with potassium hydroxide in the presence of air, oxygen acts as the oxidant. Manganese changes from oxidation state +4 in the dioxide to +6 in the manganate. The dark green compound B is potassium manganate, K_2MnO_4 . The balanced preparation equation is

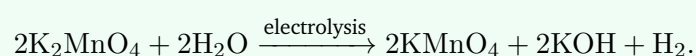


Oxygen from air and the alkaline medium are both required for this conversion.

Step 2: (b)(i) Identify the electrolytic oxidation product The dark purple compound C is potassium permanganate, KMnO_4 . At the anode, manganate loses one electron and manganese changes from +6 to +7:



At the cathode, water is reduced: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. Combining these electrode reactions and including potassium ions gives the overall equation



Thus the green manganate is converted into purple permanganate by electrolytic oxidation in alkaline

Quick Tip to Solve: Track manganese through the colours: brown dioxide is +4, green manganate is +6, and purple permanganate is +7; acid splits +6 into +7 and +4.

medium.

Step 3: (b)(ii) Behaviour of acidified manganate on standing An acidic solution of the green manganate is unstable. On standing, it forms purple permanganate ions and a brown precipitate of manganese dioxide. The balanced ionic equation is



This is a disproportionation reaction: two manganese atoms are oxidised from +6 to +7, each losing one electron, while one manganese atom is reduced from +6 to +4, accepting two electrons. The two lost electrons exactly match the two gained electrons. The left and right charges are both -2 , and all atoms balance. This explains both the purple colour developing in solution and the brown solid separating out.

Step 4: Conclusion $A = \text{MnO}_2$, $B = \text{K}_2\text{MnO}_4$, $C = \text{KMnO}_4$. Acidified manganate disproportionates into purple permanganate and brown manganese dioxide, as shown by the balanced ionic equation above.

Quick Tip to Solve: Track manganese through the colours: brown dioxide is +4, green manganate is +6, and purple permanganate is +7; acid splits +6 into +7 and +4.

32(a). (i) Write the product(s) when:

(I) One mol of ethanal is treated with 1 mol of CH_3OH in the presence of dry HCl gas.

(II) Benzaldehyde is treated with conc. NaOH .

(III) Ethanoic acid is heated in the presence of P_2O_5 .

(ii) Write a simple chemical test to distinguish between Ethanal and Propanal.

(iii) Write the name of the reagent to transform Allyl alcohol to Propenal.

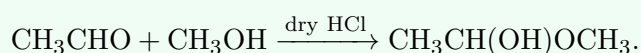
[5 marks]

Solution:

Concept:

- An aldehyde adds one molecule of alcohol under acid catalysis to form a hemiacetal, with an $-\text{OH}$ and an $-\text{OR}$ group on the same carbon.
- Aldehydes without an α -hydrogen undergo the Cannizzaro reaction in concentrated alkali. One molecule is reduced to an alcohol and another is oxidised to a carboxylate salt.
- P_2O_5 is a dehydrating agent. Ethanal gives the iodoform test, and a mild oxidant converts a primary alcohol into an aldehyde.

Step 1: (a)(i)(I) Methanol addition to ethanal The addition of one mol of methanol to one mol of ethanal gives the hemiacetal, 1-methoxyethan-1-ol:



Acid catalysis facilitates nucleophilic attack by methanol on the carbonyl carbon. The carbonyl oxygen becomes the hydroxyl group and methanol contributes the methoxy group. An acetal requires two

Quick Tip to Solve: Count alcohol molecules for hemiacetal versus acetal, check for an α -hydrogen before Cannizzaro, and use the iodoform test to distinguish these two aldehydes.

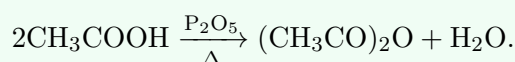
molecules of alcohol per aldehyde molecule; the stated one-to-one addition gives the hemiacetal.

Step 2: (a)(i)(II) Cannizzaro reaction Benzaldehyde has no α -hydrogen. Concentrated sodium hydroxide therefore causes disproportionation:



The products are benzyl alcohol and sodium benzoate. One molecule of benzaldehyde is reduced to the alcohol, while another is oxidised. Because the medium is alkaline, the oxidation product is the carboxylate salt. Benzoic acid is obtained only if this salt is subsequently acidified.

Step 3: (a)(i)(III) Dehydration of ethanoic acid Heating ethanoic acid with phosphorus pentoxide forms ethanoic anhydride (acetic anhydride):



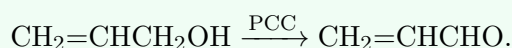
Two acid molecules condense with loss of one water molecule. The dehydrating agent removes the water formed and promotes formation of the anhydride; the equation shows the net condensation of the acid molecules.

Step 4: (a)(ii) Iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3 , whereas propanal gives no such precipitate:



Ethanal is the aldehyde that gives the iodoform test. Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, lacks the required CH_3CHO unit. Tollens' reagent is not a distinguishing test here, since both aldehydes reduce it and produce a silver mirror.

Step 5: (a)(iii) Selective oxidation of allyl alcohol Use pyridinium chlorochromate (PCC), typically in an anhydrous solvent such as dichloromethane:



PCC converts the primary alcohol group to an aldehyde while retaining the carbon-carbon double bond. The product is propenal (acrolein). Strong aqueous oxidants are unsuitable for this selective conversion because the aldehyde can undergo further oxidation to the acid.

Step 6: Conclusion (i) The products are (I) $\text{CH}_3\text{CH}(\text{OH})\text{OCH}_3$, (II) benzyl alcohol and sodium benzoate, and (III) ethanoic anhydride. (ii) Ethanal gives a yellow iodoform precipitate with I_2/NaOH , whereas propanal does not. (iii) Use PCC (pyridinium chlorochromate).

Quick Tip to Solve: Count alcohol molecules for hemiacetal versus acetal, check for an alpha-hydrogen before Cannizzaro, and use the iodoform test to distinguish these two aldehydes.

32(b). (i) Draw the structure of the semicarbazone of acetone.

(ii) Why are α -hydrogen atoms of aldehydes and ketones acidic in nature?

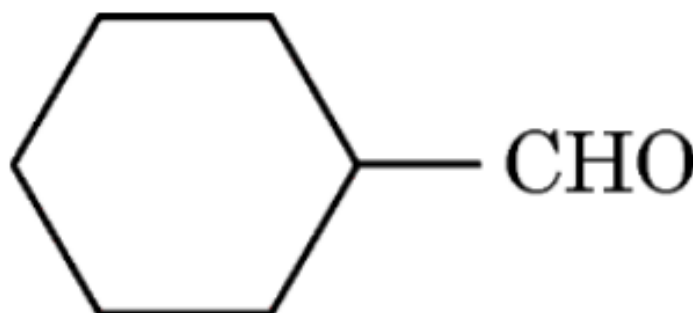
(iii) Arrange the following compounds in increasing order of their reactivity towards HCN:

CH_3COCH_3 , CH_3CHO , $(\text{CH}_3)_3\text{C-CO-CH}_3$

(iv) Write the reaction involved in Etard reaction.

(v) Write the product when reacts with Zn(Hg)/conc. HCl .

[5 marks]

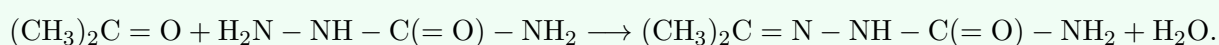


Solution:

Concept:

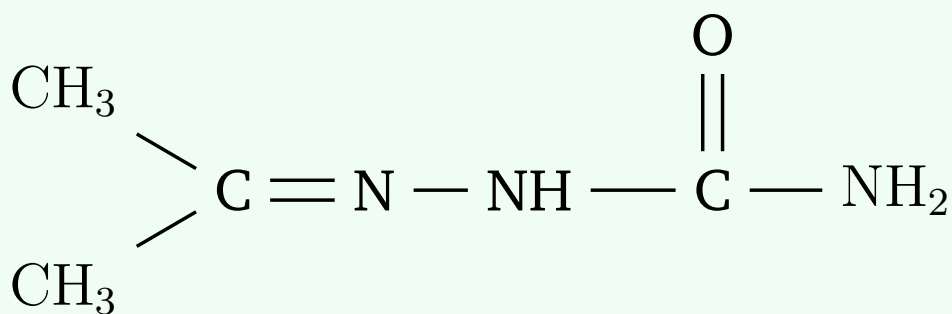
- A carbonyl compound condenses with semicarbazide, $\text{H}_2\text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$, through its terminal amino group to give a semicarbazone, with elimination of water.
- An α -hydrogen is attached to the carbon adjacent to a carbonyl group. Its removal produces an enolate ion whose negative charge is delocalised between carbon and oxygen.
- Addition of CN^- to a carbonyl carbon is favoured by greater electrophilicity and smaller steric hindrance. Alkyl groups reduce electrophilicity through their electron-releasing effect.
- Etard oxidation converts the methyl group of toluene into an aldehyde using chromyl chloride. Clemmensen reduction, using Zn(Hg)/conc. HCl , converts $-\text{CHO}$ into $-\text{CH}_3$.

Step 1: (i) Form the semicarbazone of acetone The oxygen of acetone's carbonyl group is replaced by the $=\text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$ group. The two methyl groups remain bonded to the same carbon:



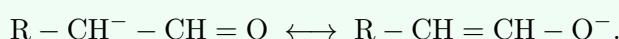
The terminal $-\text{NH}_2$ next to $-\text{NH}-$ performs the condensation; the amino group attached directly to the amide carbonyl is not the reacting group. The structure is drawn below.

Quick Tip to Solve: In Clemmensen reduction, replace the printed $-\text{CHO}$ group by $-\text{CH}_3$ without deleting its carbon or changing the ring.



Structure of acetone semicarbazone

Step 2: (ii) Explain the acidity of alpha-hydrogen atoms Removal of an α -hydrogen as H^+ leaves an enolate ion. For an aldehyde, its two principal resonance forms can be written as

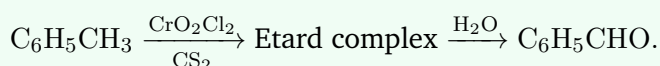


Thus the conjugate base is stabilised by delocalisation of negative charge, including a form with charge on electronegative oxygen. The electron-withdrawing carbonyl group also facilitates removal of the adjacent hydrogen. This explains why these hydrogens are acidic compared with ordinary alkane hydrogens.

Step 3: (iii) Compare reactivity towards HCN Cyanide attacks the electrophilic carbonyl carbon. In ethanal, only one alkyl group donates electron density and the other substituent is a small hydrogen atom. Acetone has two methyl groups, so it is less electrophilic and more hindered. The ketone containing a bulky tert-butyl group has still greater hindrance around the carbonyl carbon. Therefore increasing reactivity is

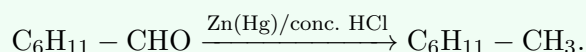


Step 4: (iv) Write the Etard reaction Toluene is treated with chromyl chloride in a non-aqueous solvent such as carbon disulphide. The resulting Etard complex is hydrolysed to benzaldehyde:



This is controlled oxidation of the benzylic methyl group to the aldehyde stage.

Step 5: (v) Apply Clemmensen reduction to the given aldehyde The printed structure is a cyclohexane ring bearing a $-\text{CHO}$ substituent. Zinc amalgam and concentrated hydrochloric acid reduce this aldehyde group to $-\text{CH}_3$, retaining its carbon atom and leaving the saturated ring intact:



The product is methylcyclohexane; it has seven carbon atoms, just as the starting aldehyde does.

Step 6: Conclusion (i) Acetone semicarbazone is $(\text{CH}_3)_2\text{C} = \text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$. (ii) Alpha-hydrogens are acidic because their removal gives a resonance-stabilised enolate. (iii)

Quick Tip to Solve: In Clemmensen reduction, replace the printed $-\text{CHO}$ group by $-\text{CH}_3$ without deleting its carbon or changing the ring.

$(\text{CH}_3)_3\text{C} - \text{CO} - \text{CH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO}$. (iv) Etard oxidation converts toluene into benzaldehyde. (v) The given aldehyde gives methylcyclohexane.

Quick Tip to Solve: In Clemmensen reduction, replace the printed $-\text{CHO}$ group by $-\text{CH}_3$ without deleting its carbon or changing the ring.

33(a). (i) Calculate the electrode potential of a half-cell for zinc electrode dipping in 0.01 M ZnSO_4 solution at 25°C .

Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$; $[\log 10 = 1]$

(ii) Write anode, cathode and overall reaction involved in dry cell.

(iii) Equilibrium constant (K_c) is related to E°_{cell} , but not to E_{cell} . Why?

[5 marks]

Solution:

Concept:

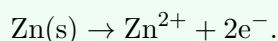
- For the reduction $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$, the Nernst equation at 298 K is $E = E^\circ - (0.0591/2) \log Q$, where $Q = 1/[\text{Zn}^{2+}]$; the activity of pure solid zinc is unity.
- In a dry cell, zinc is oxidised at the anode and manganese dioxide is reduced at the cathode. Ammonium ions participate in the cathode reaction.
- Standard cell potential is related to equilibrium by $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K_c$. Actual cell potential also depends on the reaction quotient Q .

Step 1: (i) Apply the Nernst equation to the zinc half-cell Zinc sulphate provides $[\text{Zn}^{2+}] = 0.01 \text{ mol L}^{-1}$. The half-cell potential is conventionally the reduction potential. With two electrons transferred,

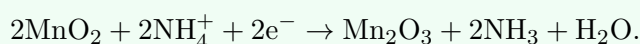
$$\begin{aligned} E_{\text{Zn}^{2+}/\text{Zn}} &= -0.76 - \frac{0.0591}{2} \log \frac{1}{0.01} \\ &= -0.76 - 0.02955 \log 100 \\ &= -0.76 - 0.02955(2) \\ &= -0.8191 \text{ V.} \end{aligned}$$

Since $\log 100 = 2 \log 10 = 2$, dilution makes the reduction potential more negative than its standard value. This is consistent with the lower availability of zinc ions for reduction.

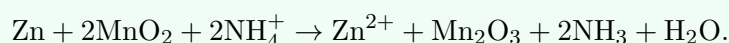
Step 2: (ii) Write the reactions in the dry cell The zinc container acts as the anode and undergoes oxidation:



At the cathode, manganese dioxide surrounding the carbon rod is reduced:



Adding the two equations cancels the electrons and gives the overall reaction:



Quick Tip to Solve: For a metal-ion reduction, use $Q = 1/[\text{metal ion}]$; check that dilution lowers the reduction potential before accepting its sign.

The carbon rod serves as the current collector; it is not consumed in the reaction. Ammonia formed at the cathode can complex with zinc ions, giving $[\text{Zn}(\text{NH}_3)_2]^{2+}$; this does not change the electron balance of the displayed cell reaction.

Step 3: (iii) Distinguish standard potential from actual potential At a fixed temperature, K_c is a property of the reaction and does not depend on the initial concentrations. Combining the two expressions for standard Gibbs energy gives

$$\ln K_c = \frac{nFE_{\text{cell}}^{\circ}}{RT}.$$

In contrast, $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (RT/nF) \ln Q$ changes with reactant and product concentrations. At equilibrium, $Q = K_c$ and the actual cell potential is zero, whereas the standard potential retains the information about the equilibrium constant. Hence the direct equilibrium relation uses the standard cell potential.

Step 4: Conclusion (i) The zinc electrode reduction potential is $-0.8191 \text{ V} \approx -0.82 \text{ V}$. (ii) The dry-cell reactions are the zinc oxidation and manganese dioxide reduction equations above, with their sum giving the overall reaction. (iii) K_c is related to E_{cell}° through standard Gibbs energy; actual E_{cell} also depends on concentrations and is zero at equilibrium.

Quick Tip to Solve: For a metal-ion reduction, use $Q = 1/[\text{metal ion}]$; check that dilution lowers the reduction potential before accepting its sign.

OR

33(b). (i) The conductivity of 0.001 M solution of acetic acid is $3.905 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation (α).

Given: $\lambda_{\text{CH}_3\text{COO}^-}^{\circ} = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda_{\text{H}^+}^{\circ} = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$.

(ii) Give reasons for the following:

(I) Why does a mercury cell deliver a constant voltage for its entire life?

(II) Why is it necessary to use salt bridge in a galvanic cell?

[5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} . Its unit is $\text{S cm}^2 \text{ mol}^{-1}$.
- Kohlrausch's law gives $\Lambda_m^{\circ} = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{CH}_3\text{COO}^-}^{\circ}$. For a weak electrolyte, its degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^{\circ}$.
- Cell voltage depends on the activities appearing in its reaction quotient. A salt bridge provides

Quick Tip to Solve: Add the limiting ionic conductivities first, then divide the measured molar conductivity by that sum; the ratio gives the dissociated fraction directly.

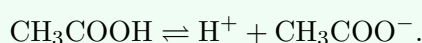
ionic conduction and maintains electrical neutrality in the two half-cells.

Step 1: (i) Calculate the molar conductivity The solution has $\kappa = 3.905 \times 10^{-5} \text{ S cm}^{-1}$ and $c = 0.001 \text{ mol L}^{-1}$. The factor 1000 converts the litre-based concentration to the cubic-centimetre volume convention needed for the conductivity units:

$$\begin{aligned}\Lambda_m &= \frac{1000\kappa}{c} \\ &= \frac{1000(3.905 \times 10^{-5})}{0.001} \\ &= 39.05 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

Acetic acid is weakly dissociated at this concentration, so its measured molar conductivity is substantially smaller than the value at infinite dilution.

Step 2: (i) Use the limiting ionic conductivities to obtain dissociation Acetic acid dissociates into hydrogen and acetate ions:

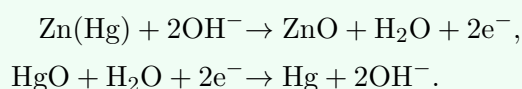


The limiting molar conductivity is the sum of the limiting ionic contributions:

$$\begin{aligned}\Lambda_m^\circ &= 349.6 + 40.9 \\ &= 390.5 \text{ S cm}^2 \text{ mol}^{-1}, \\ \alpha &= \frac{39.05}{390.5} = 0.100.\end{aligned}$$

Thus the fraction of acid molecules dissociated is 0.100, corresponding to 10.0%. The ratio is dimensionless because numerator and denominator have the same conductivity units.

Step 3: (ii)(I) Explain the constant voltage of a mercury cell The anode is zinc amalgam and the cathode contains mercury(II) oxide. In the alkaline electrolyte the half-reactions are



The overall reaction is $\text{Zn(Hg)} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$. No ions from the electrolyte appear in this net reaction; the hydroxide ions and water cancel. Consequently, electrolyte concentration does not change as a result of the net reaction, and the activities governing the cell reaction remain effectively constant during normal operation. The cell therefore supplies an approximately constant voltage, about 1.35 V, over its useful life.

Step 4: (ii)(II) Explain the functions of the salt bridge Oxidation in the anode compartment tends to create an excess of positive charge, while reduction in the cathode compartment tends to remove cations or produce negative charge. Without ion migration, this charge separation would rapidly op-

Quick Tip to Solve: Add the limiting ionic conductivities first, then divide the measured molar conductivity by that sum; the ratio gives the dissociated fraction directly.

pose further electron flow. The salt bridge allows its anions to migrate toward the anode compartment and its cations toward the cathode compartment, maintaining electrical neutrality and completing the internal circuit. Electrons travel through the external wire; ions carry charge through the bridge. It also limits direct mixing of the two solutions and minimises the liquid-junction potential.

Step 5: Conclusion (i) $\Lambda_m = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$ and $\alpha = 0.100 = 10.0\%$. (ii)(I) A mercury cell gives a constant voltage because the net reaction does not change electrolyte-ion concentration. (ii)(II) A salt bridge completes the ionic circuit and maintains electrical neutrality, while limiting mixing and liquid-junction potential.

Quick Tip to Solve: Add the limiting ionic conductivities first, then divide the measured molar conductivity by that sum; the ratio gives the dissociated fraction directly.