

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

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

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

Section A (16 marks)

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each. $16 \times 1 = 16$

1. 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 is the oxidation state of the metal and is satisfied by negatively charged ions.
- Secondary valency is the coordination number: it is satisfied by neutral molecules or negative ions directly bonded to the metal.

Step 1: Identify the primary valency Primary valencies represent the charge balance associated with the metal oxidation state. They are ionisable in the usual Werner description, whereas secondary valencies represent coordination bonds and are non-ionisable.

Step 2: Check the alternatives Negative ions satisfy primary valencies, so option (C) gives the correct statement. Option (A) describes secondary valency; (B) identifies coordination number, also a secondary valency; and (D) states the non-ionisable property of secondary valency.

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

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

2. The oxidation number of Pt in $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ is:

[1 mark]

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

Correct Answer: (B) +4

Solution:

Concept:

- The sum of the metal oxidation state and ligand charges equals the overall charge of a complex ion.
- Ethylenediamine, en, is neutral; each chlorido ligand, Cl^- , contributes a charge of -1 .

Quick Tip to Solve: Count ligand charges, not donor atoms: neutral en contributes zero even though it occupies two coordination sites.

Step 1: Assign the ligand charges Let the oxidation number of platinum be x . The two ethylenediamine ligands contribute zero charge, even though each is bidentate. The two chlorido ligands contribute -2 in total. The complex ion has charge $+2$.

Step 2: Apply charge balance

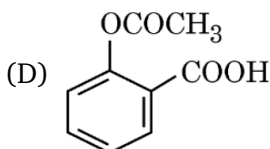
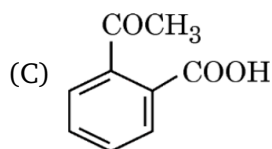
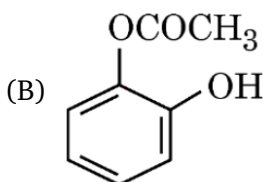
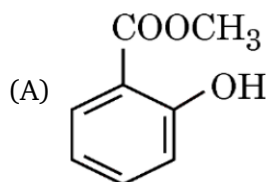
$$x + 2(0) + 2(-1) = +2 \Rightarrow x = +4.$$

Coordination number and oxidation number must not be confused: the six donor atoms do not imply an oxidation state of $+6$. Values $+3$ and $+2$ also fail the stated charge balance.

Step 3: Conclusion The oxidation number of Pt is $+4$. Hence, the correct option is (B).

Quick Tip to Solve: Count ligand charges, not donor atoms: neutral en contributes zero even though it occupies two coordination sites.

3. Which of the following product is formed when salicylic acid is treated with $(\text{CH}_3\text{CO})_2\text{O}$ in the presence of acid? [1 mark]



Correct Answer: (D)

Solution:

Concept:

- Acetic anhydride acetylates the phenolic $-\text{OH}$ group of salicylic acid in the presence of acid.
- Aspirin is acetylsalicylic acid: the ring retains its $-\text{COOH}$ group and has an adjacent $-\text{OCOCH}_3$ group.

Step 1: Identify the reacting group Salicylic acid contains a phenolic hydroxyl group ortho to a carboxyl group. Acetylation replaces the hydrogen of the phenolic hydroxyl group by COCH_3 , producing an ester linkage through oxygen. The carboxyl group remains intact.

Step 2: Match the printed structures Option (D) shows adjacent COOH and OCOCH_3 groups and therefore represents aspirin. Option (A) methylates the carboxyl group, (B) retains a phenolic OH and lacks the required carboxyl group, and (C) attaches COCH_3 directly to the ring rather than through oxygen.

Quick Tip to Solve: For aspirin, look for both COOH and OCOCH_3 on adjacent ring carbons; the oxygen before COCH_3 is essential.

Step 3: Conclusion The product is acetylsalicylic acid (aspirin), represented by option (D).

Quick Tip to Solve: For aspirin, look for both COOH and OCOCH₃ on adjacent ring carbons; the oxygen before COCH₃ is essential.

4. Which reagent is used to distinguish between primary, secondary and tertiary amines? [1 mark]

- (A) C₆H₅SO₂Cl
- (B) C₆H₅COCl
- (C) CHCl₃ + ethanolic KOH
- (D) NaOH + I₂

Correct Answer: (A) C₆H₅SO₂Cl

Solution:

Concept:

- The Hinsberg reagent is benzenesulphonyl chloride, C₆H₅SO₂Cl.
- Primary and secondary amines form sulphonamides with different solubilities in alkali; tertiary amines do not form such sulphonamides.

Step 1: Compare primary and secondary amines A primary amine forms a sulphonamide containing an N–H bond. This hydrogen is acidic, so the product dissolves in aqueous alkali. A secondary amine forms a sulphonamide without an N–H bond; it cannot form the corresponding salt and remains insoluble in alkali.

Step 2: Distinguish the tertiary amine and other tests A tertiary amine has no N–H bond and does not form a sulphonamide with the Hinsberg reagent; it dissolves in dilute acid as an ammonium salt. Benzoyl chloride is an acylating reagent, while chloroform with ethanolic KOH is the carbylamine test, which identifies only primary amines. Iodine with NaOH is the iodoform reagent.

Step 3: Conclusion Benzenesulphonyl chloride is used in the Hinsberg test. Hence, the correct option is (A).

Quick Tip to Solve: In the Hinsberg test, use alkali solubility of the sulphonamide to distinguish primary from secondary amines.

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

[1 mark]

- (A) H₂ gas is evolved at anode.
- (B) Na is produced at cathode.
- (C) O₂ gas is evolved at anode.
- (D) H₂ gas is evolved at cathode.

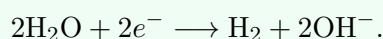
Correct Answer: Both (C) and (D) are correct: oxygen is evolved at the anode and hydrogen at the cathode.

Solution:

Concept:

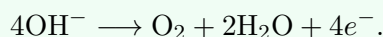
- At an inert cathode in aqueous NaCl, water is reduced more readily than Na⁺, releasing hydrogen.
- In a very dilute chloride solution, oxidation of water or hydroxide ions at the inert anode releases oxygen rather than chlorine.

Step 1: Identify the cathode reaction



Thus sodium metal is not deposited, ruling out option (B). Hydrogen is formed at the cathode, so the statement in option (D) is also chemically correct. Hydrogen evolution at the anode, as stated in (A), is incorrect.

Step 2: Identify the anode reaction For very dilute NaCl with platinum electrodes, oxygen evolution is represented by



This supports option (C). The word very dilute is essential: concentrated brine favours chlorine evolution at the anode. As printed, this question contains two true statements, C and D; C identifies the anode product associated with the dilution condition.

Step 3: Conclusion Both options (C) and (D) are correct for the printed conditions. Oxygen is evolved at the anode and hydrogen at the cathode, so the question does not have a unique correct option.

Quick Tip to Solve: For very dilute NaCl with inert electrodes, remember the product pair: hydrogen at the cathode and oxygen at the anode.

6. The correct order of decreasing basic strength in aqueous solution of the following is: [1 mark]

- (A) $(\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH}$
(B) $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_3\text{N}$
(C) $\text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N}$
(D) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2$

Correct Answer: (D) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2$

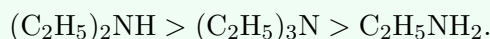
Solution:

Concept:

- Aqueous basicity depends on the electron-donating effect of alkyl groups, solvation of the conjugate acid and steric effects.
- For ethylamines in water, the combined effects give secondary > tertiary > primary basic strength.

Step 1: Balance electron donation and solvation Ethyl groups increase electron density on nitrogen by their positive inductive effect, helping the amine accept a proton. However, the resulting ammonium ion must also be stabilised by water. Increasing substitution changes solvation and steric accessibility, so basicity cannot be predicted by electron donation alone.

Step 2: Apply the aqueous ethylamine order Diethylamine has the most favourable combination of electron donation and solvation. For ethyl substituents, triethylamine is more basic than ethylamine in water, giving



Option (A) places the tertiary amine above the secondary; (B) reverses the last two; and (C) incorrectly places the primary first.

Step 3: Conclusion The decreasing basic strength is diethylamine > triethylamine > ethylamine. Hence, the correct option is (D).

Quick Tip to Solve: Do not transfer the aqueous methylamine order to ethylamines: for ethyl groups, remember secondary, tertiary, primary.

7. 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 moles of solute per kilogram of solvent: $m = n_{\text{solute}}/m_{\text{solvent}}(\text{kg})$.
- The solute mole fraction is $x_{\text{solute}} = n_{\text{solute}}/(n_{\text{solute}} + n_{\text{solvent}})$.

Quick Tip to Solve: For aqueous molality questions, use 1 kg water: its mole count is 1000/18, and add solute moles in the denominator.

Step 1: Choose a solvent basis Take 1.000 kg of water. A 2.0 molal solution then contains 2.0 mol of solute. Using the molar mass of water, 18 g mol^{-1} , the solvent amount is

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

Step 2: Calculate the solute mole fraction

$$x_{\text{solute}} = \frac{2.0}{2.0 + 55.56} = 0.03475 \simeq 0.0347.$$

Both solute and solvent enter the denominator. The value 1.87 cannot be a mole fraction because it exceeds one, while 0.347 and 0.00347 differ by factors of ten from the calculated ratio.

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

Quick Tip to Solve: For aqueous molality questions, use 1 kg water: its mole count is $1000/18$, and add solute moles in the denominator.

8. Which of the following transition metals shows +1 and +2 oxidation states?

[1 mark]

- (A) Mn
- (B) Zn
- (C) Cu
- (D) Sc

Correct Answer: (C) Cu

Solution:

Concept:

- An oxidation state describes the formal electron loss or gain of an atom in a compound.
- Copper has the electronic configuration $[\text{Ar}] 3d^{10}4s^1$; removal of one or two electrons gives Cu^+ or Cu^{2+} .

Step 1: Examine copper Removing the single $4s$ electron from copper gives Cu^+ , with configuration $3d^{10}$. Removing one more electron from the $3d$ subshell gives Cu^{2+} , with configuration $3d^9$. Copper therefore commonly exhibits both +1 and +2 states, for example in Cu_2O and CuO .

Step 2: Eliminate the other metals Manganese commonly shows +2 and several higher oxidation states; the characteristic pair sought here is not manganese. Zinc predominantly forms Zn^{2+} , with a filled $3d^{10}$ subshell. Scandium predominantly forms Sc^{3+} , losing its two $4s$ electrons and one $3d$ electron. Neither zinc nor scandium commonly shows the stated pair.

Step 3: Conclusion Copper shows +1 and +2 oxidation states. Hence, the correct option is (C).

Quick Tip to Solve: Remember the copper pair: Cu_2O contains Cu^+ , whereas CuO contains Cu^{2+} .

9. On hydrolysis, which of the following carbohydrates gives only β -glucose?

[1 mark]

- (A) Starch
- (B) Sucrose
- (C) Maltose
- (D) Cellulose

Correct Answer: (D) Cellulose

Solution:

Concept:

- Hydrolysis cleaves glycosidic bonds and releases the monosaccharide units of a carbohydrate.
- Cellulose is a linear polymer of β -D-glucose units joined through $\beta(1 \rightarrow 4)$ glycosidic linkages.

Step 1: Identify the units in cellulose The repeating monosaccharide units in cellulose are all β -D-glucose. Cleavage of the glycosidic bonds by complete hydrolysis therefore gives glucose derived from these β -glucose units. This is the carbohydrate identified by the wording of the question.

Step 2: Compare the remaining carbohydrates Starch is made of α -D-glucose units, and maltose consists of two α -D-glucose units linked through an $\alpha(1 \rightarrow 4)$ bond. They are therefore not polymers or dimers of β -glucose. Sucrose yields two different monosaccharides, glucose and fructose, on hydrolysis, so it cannot give only glucose.

Step 3: Conclusion Cellulose gives only β -glucose on hydrolysis in the standard classification of these carbohydrates. Hence, the correct option is (D).

Quick Tip to Solve: Associate cellulose with β -glucose and starch with α -glucose; sucrose gives glucose plus fructose.

10. Consider the following compounds:

Chlorobenzene (I), 2,4,6-trinitrochlorobenzene (II),

2,4-dinitrochlorobenzene (III), 4-nitrochlorobenzene (IV)

The correct order of increasing ease of nucleophilic substitution reactions of these compounds is:

[1 mark]

- (A) $I < IV < III < II$
- (B) $I < III < IV < II$
- (C) $II < III < IV < I$
- (D) $IV < III < II < I$

Correct Answer: (A) $I < IV < III < II$

Solution:

Concept:

- Electron-withdrawing nitro groups at the ortho and para positions activate an aryl halide towards nucleophilic aromatic substitution.
- These groups stabilise the negatively charged intermediate formed when a nucleophile attacks the

Quick Tip to Solve: Count only activating nitro groups at ortho or para positions relative to chlorine: more such groups make substitution easier.

carbon bearing chlorine.

Step 1: Count the activating nitro groups Chlorobenzene (I) has no nitro group. Compound IV has one para nitro group. Compound III has two nitro groups, one ortho and one para to chlorine. Compound II has three nitro groups, at both ortho positions and the para position.

Step 2: Compare intermediate stabilisation As the number of these electron-withdrawing groups increases, negative charge in the addition intermediate is better stabilised by resonance and the inductive effect. Substitution consequently becomes easier in the sequence of zero, one, two and three nitro groups. Option B incorrectly places the dinitro compound below the mononitro compound; option C reverses the activation trend by placing the trinitro compound first and unactivated chlorobenzene last; option D incorrectly makes unactivated chlorobenzene the easiest to substitute.

Step 3: Conclusion The increasing order is $I < IV < III < II$. Hence, the correct option is (A).

Quick Tip to Solve: Count only activating nitro groups at ortho or para positions relative to chlorine: more such groups make substitution easier.

11. The half-life periods of decomposition of NH_3 for different initial pressures are given below:

p (torr)	704	75	34.5
$t_{1/2}$ (min)	80	80	80

The order of the reaction is:

[1 mark]

- (A) zero order
- (B) first order
- (C) 0.5
- (D) second order

Correct Answer: (B) first order

Solution:

Concept:

- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant.
- For a gas at fixed temperature, its concentration is proportional to its partial pressure, so pressure dependence can be used to test concentration dependence.

Step 1: Compare the measured half-lives The initial pressures are 704, 75 and 34.5 torr, but the half-life remains 80 min in all three experiments. Thus the half-life is independent of the initial amount or concentration of NH_3 .

Step 2: Test the candidate orders First-order kinetics has exactly this property. For zero-order kinetics, $t_{1/2} = [A]_0/(2k)$, so the half-life increases with initial concentration. For second order, $t_{1/2} = 1/(k[A]_0)$, so it decreases with initial concentration. For order 0.5, the half-life is proportional to $[A]_0^{1/2}$, which is also concentration dependent. These three alternatives disagree with the constant half-life.

Step 3: Conclusion The reaction is first order. Hence, the correct option is (B).

Quick Tip to Solve: A half-life unchanged across different initial gas pressures is the diagnostic pattern for a first-order reaction.

12. 1 mole of liquid A and 2 moles of liquid B make a solution having a total vapour pressure 40 torr. The vapour pressure of pure A and pure B are 30 torr and 45 torr respectively. The above solution:

[1 mark]

- (A) is an ideal solution.
- (B) shows negative deviation from Raoult's Law.
- (C) shows positive deviation from Raoult's Law.
- (D) is a maximum boiling azeotrope.

Correct Answer: (A) is an ideal solution.

Solution:

Concept:

- For an ideal binary solution, Raoult's law gives $P = x_A P_A^\circ + x_B P_B^\circ$. Here x_i is the liquid mole fraction and P_i° is the pure-liquid vapour pressure.
- Positive or negative deviation means the measured total pressure is respectively greater or less than the Raoult-law prediction.

Step 1: Calculate the liquid mole fractions The total amount of liquid is $1 + 2 = 3$ mol. Therefore $x_A = 1/3$ and $x_B = 2/3$; their sum is one, as required for a binary solution.

Step 2: Compare predicted and observed pressures Using the given pure-component vapour pressures,

$$P_{\text{ideal}} = \frac{1}{3}(30) + \frac{2}{3}(45) = 10 + 30 = 40 \text{ torr.}$$

The measured pressure is also 40 torr, so it agrees with ideal-solution behaviour. It is neither below nor above the prediction, rejecting negative and positive deviation. A maximum-boiling azeotrope is associated with negative deviation and cannot be inferred from these data.

Step 3: Conclusion The solution obeys Raoult's law for the given composition and is classified as ideal. Hence, the correct option is (A).

Quick Tip to Solve: First calculate the mole fractions, then compare the measured pressure with their weighted sum of pure vapour pressures.

13. Assertion (A): Ethers have lower boiling points than the boiling points of alcohols.

Reason (R): This is due to the presence of hydrogen bonding in alcohols.

[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:

- Boiling requires enough energy to overcome intermolecular attractions; stronger attractions generally raise the boiling point.
- Alcohol molecules contain an O–H group and can form intermolecular hydrogen bonds with one another. Ethers have no such hydrogen-bond donor.

Step 1: Evaluate the assertion For comparable molar masses, ethers have lower boiling points than alcohols. Ether molecules possess dipole-dipole and dispersion attractions but cannot form the extensive self-associated hydrogen-bond network of alcohols. The assertion is true in the intended comparison of the two homologous classes.

Step 2: Evaluate the reason Alcohols have hydrogen attached directly to electronegative oxygen. This hydrogen can interact with a lone pair on the oxygen of another alcohol molecule, producing intermolecular hydrogen bonding. The reason is therefore true.

Step 3: Check the explanatory connection The additional hydrogen bonding makes alcohol molecules more strongly associated and requires more energy to separate them into vapour. This directly explains why comparable alcohols boil at higher temperatures than ethers. Thus the reason does explain the assertion; options B, C and D give an incorrect explanatory relationship or truth value.

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

Quick Tip to Solve: Check for an O–H bond: alcohols can hydrogen-bond to each other, whereas ethers lack a hydrogen-bond donor.

14. Assertion (A): Transition metals show their highest oxidation state with oxygen.

Reason (R): The ability of oxygen to form multiple bonds to metals.

[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:

- High oxidation states of transition metals are stabilised by strong bonds to electronegative elements such as oxygen.
- Oxygen can form multiple bonds with transition metals, helping stabilise very high formal positive oxidation states.

Step 1: Evaluate the assertion Transition metals exhibit their highest oxidation states in their oxides and oxoanions. For example, manganese is in the +7 state in MnO_4^- , and chromium is in the +6 state in CrO_4^{2-} . Thus the assertion expresses the standard trend and is true.

Step 2: Evaluate the reason Oxygen can form multiple metal-oxygen bonds in high-valent compounds. Such strong bonding helps stabilise the metal when its formal oxidation state is high. The stated ability of oxygen is therefore true.

Step 3: Relate the reason to the trend The formation of strong multiple bonds provides the stabilisation needed for very high oxidation states. This is why oxygen is particularly effective in supporting these states, so the reason explains the assertion. Option B wrongly denies this explanation, while options C and D wrongly treat one of the two statements as false.

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

Quick Tip to Solve: For very high transition-metal oxidation states, look for oxides or oxoanions and the stabilising metal-oxygen multiple bonds.

15. Assertion (A): Monobromination of aniline can be conveniently done by protecting the amino group by acetylation.

Reason (R): Acetylation increases the activation effect of the amino group.

[1 mark]

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

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

Solution:

Concept:

- Aniline has a strongly activating amino group, $-\text{NH}_2$, whose nitrogen lone pair is donated into the benzene ring.
- Acetylation converts $-\text{NH}_2$ to $-\text{NHCOCH}_3$; sharing the lone pair with the carbonyl reduces its availability for ring activation.

Step 1: Judge the assertion The assertion is true. Direct bromination of aniline with bromine water readily gives 2,4,6-tribromoaniline because its ring is strongly activated. Protecting the amino group by acetylation produces acetanilide, whose controlled bromination gives mainly the para monobromo derivative. Hydrolysis then removes the acetyl group to give para-bromoaniline.

Step 2: Judge the reason The reason is false. Acetylation decreases, rather than increases, the activating effect of the amino group. In acetanilide, the nitrogen lone pair is involved in resonance with the carbonyl group and is less available to activate the aromatic ring.

Step 3: Connect the statements The reduced activation after acetylation explains why monobromination becomes convenient. Thus neither option (A) nor (B), both of which require a true reason, applies. Option (D) is also excluded because the assertion is true.

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

Quick Tip to Solve: Remember that acetyl protection reduces amino-group activation and prevents extensive ring bromination.

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

Reason (R): For a complex reaction, molecularity has no meaning.

[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:

- For an experimental rate law $r = k[A]^m[B]^n$, the reaction order is $m + n$, and is defined for elementary and complex reactions.
- Molecularity counts the reacting species in a single elementary step; an overall multistep reaction has no single molecularity.

Step 1: Judge the assertion The assertion is true. Reaction order is obtained from the experimentally determined dependence of rate on reactant concentrations. Such a rate law can be determined both for a single elementary reaction and for an overall complex reaction.

Step 2: Judge the reason The reason is true. A complex reaction proceeds through several elementary steps. Each step may have its own molecularity, but the overall complex reaction cannot be assigned one molecularity by counting species in its overall balanced equation.

Step 3: Test the explanatory connection The assertion follows from the experimental definition of order. The reason states a limitation of molecularity, a different concept; it does not explain why order can be measured for both types of reaction. Options (C) and (D) are excluded because both statements are true, while option (A) incorrectly treats the reason as the explanation.

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

Quick Tip to Solve: For assertion-reason items, test the explanation separately after deciding the truth of each statement.

Section B (10 marks)

17. 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 concentration exponents in the rate law, not the sum of coefficients in the balanced equation.
- An elementary reaction occurs in a single step, so its rate-law exponents correspond to the whole-number counts of reactant species participating in that step.

Step 1: Calculate the overall order The given rate law is

$$r = k[A][B]^{3/2}.$$

The partial order with respect to A is 1, while that with respect to B is $3/2$. Adding these experimentally specified powers gives

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

The coefficients of $A + B \rightarrow \text{Products}$ do not replace the exponents in this calculation.

Step 2: Decide whether the reaction is elementary It cannot be an elementary reaction. For an elementary step $A + B \rightarrow \text{Products}$, one particle each of A and B participates, so its rate law would have the form $r = k[A][B]$, with overall order two. The given fractional exponent $3/2$ cannot represent a fractional number of reacting particles in a single elementary event. It indicates that the observed overall rate arises from a multistep mechanism rather than the written equation being a single elementary step.

Step 3: Conclusion The overall order is $\boxed{5/2}$. The reaction is not elementary because its rate law contains a fractional order in B .

Quick Tip to Solve: Add rate-law powers to obtain order; a fractional power rules out a single elementary reaction step.

18. 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]

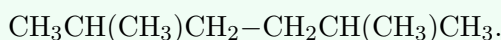
Solution:

Concept:

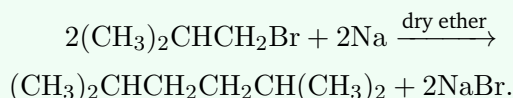
- In an S_N1 reaction, slow carbon-halogen bond ionisation forms a carbocation; greater carbocation stability increases the rate.
- The Wurtz reaction couples two alkyl groups: $2RBr + 2Na \rightarrow R-R + 2NaBr$, in dry ether.

Step 1: Identify the fastest isomer for part (a) The most reactive isomer is 2-bromo-2-methylpropane, $(CH_3)_3CBr$, also called tert-butyl bromide. Its carbon-bromine bond can ionise to give the tertiary carbocation $(CH_3)_3C^+$. Alkyl groups stabilise this ion through the positive inductive effect and hyperconjugation. A tertiary carbocation is more stable than the secondary or primary ions formed from the other C_4H_9Br isomers, so this isomer undergoes S_N1 displacement most readily.

Step 2: Trace the Wurtz coupling for part (b) Write the desired product as



Cutting its central carbon-carbon bond gives two identical 2-methylpropyl groups, $(CH_3)_2CHCH_2-$. Therefore the starting bromide is 1-bromo-2-methylpropane, $(CH_3)_2CHCH_2Br$, also called isobutyl bromide. Its reaction is



The longest product chain has six carbons, with methyl substituents at positions 2 and 5.

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 a symmetrical Wurtz product, split the central bond and attach bromine to each exposed carbon.

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

(i) $[PtCl_2(en)_2]SO_4$

(ii) $(NH_4)_2[CoF_4]$

[2 marks]

Solution:

Concept:

- Name the cation before the anion. Within a coordination entity, ligand names precede the metal name and are placed in alphabetical order.
- Use oxidation states from charge balance: chlorido and fluorido each carry charge -1 , while ethane-1,2-diamine (en) is neutral. An anionic cobalt complex uses the name cobaltate.

Quick Tip to Solve: First obtain the complex charge from its counter-ion, then calculate the metal oxidation state before naming it.

Step 1: Name the platinum compound In $[\text{PtCl}_2(\text{en})_2]\text{SO}_4$, sulfate has charge -2 , so the complex cation has charge $+2$. If platinum has oxidation state x ,

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

The two chloride ligands are named dichlorido. The two neutral en ligands are named bis(ethane-1,2-diamine), using bis because the ligand name itself is complex. Chlorido precedes ethane-1,2-diamine alphabetically. Since the coordination entity is cationic, the metal retains the name platinum. The compound is dichloridobis(ethane-1,2-diamine)platinum(IV) sulfate.

Step 2: Name the cobalt compound In $(\text{NH}_4)_2[\text{CoF}_4]$, the two ammonium cations contribute charge $+2$, so the complex anion has charge -2 . With cobalt oxidation state y ,

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

The four fluoride ligands are named tetrafluorido. The anionic coordination entity requires cobaltate rather than cobalt, followed by the oxidation state (II). Naming the ammonium cation first gives ammonium tetrafluoridocobaltate(II).

Step 3: Conclusion (i) Dichloridobis(ethane-1,2-diamine)platinum(IV) sulfate. (ii) Ammonium tetrafluoridocobaltate(II).

Quick Tip to Solve: First obtain the complex charge from its counter-ion, then calculate the metal oxidation state before naming it.

OR

19(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 from a donor atom to a central metal ion; ambidentate ligands have two alternative donor atoms.
- A double salt is a crystalline combination of two simple salts in a definite proportion which dissociates completely into its constituent ions in water.

Step 1: (i) Ambidentate ligand An ambidentate ligand can coordinate to a metal through either of two different donor atoms, but uses only one of these atoms at a time. For example, the nitrite ion, NO_2^- , coordinates through nitrogen as a nitro ligand or through oxygen as a nitrito ligand. Thus, having two possible attachment sites does not make it a bidentate ligand: a bidentate ligand binds through two donor atoms simultaneously.

Step 2: (ii) Double salt A double salt is formed when two simple salts crystallise together in a fixed stoichiometric ratio. On dissolving in water, it loses its identity and gives all the ions of the constituent

Quick Tip to Solve: For ambidentate ligands say "either donor atom, one at a time"; for double salts mention complete dissociation in water.

salts. An example is Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which gives Fe^{2+} , NH_4^+ and SO_4^{2-} ions in aqueous solution. These ions show their individual characteristic tests.

Step 3: Conclusion Nitrite, NO_2^- , is an ambidentate ligand; Mohr's salt is a double salt.

Quick Tip to Solve: For ambidentate ligands say "either donor atom, one at a time"; for double salts mention complete dissociation in water.

20. How do you explain the following?

(a) Presence of an aldehyde group in glucose.

(b) Presence of a primary alcoholic group in glucose.

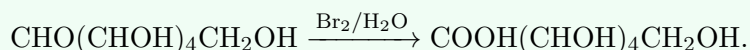
[2 marks]

Solution:

Concept:

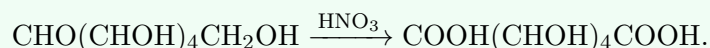
- Mild oxidation of an aldehyde changes $-\text{CHO}$ to $-\text{COOH}$, whereas a primary alcoholic group is oxidised to a carboxyl group by a strong oxidising agent.
- Evidence for glucose's functional groups comes from the products obtained using oxidising agents of different strengths.

Step 1: (a) Evidence for the aldehyde group Glucose is oxidised by bromine water, a mild oxidising agent, to gluconic acid, a monocarboxylic acid. This shows that its carbonyl group is an aldehyde group, because bromine water oxidises $-\text{CHO}$ to $-\text{COOH}$:



The terminal alcoholic group remains unchanged in this mild oxidation.

Step 2: (b) Evidence for the primary alcoholic group On oxidation with nitric acid, glucose gives saccharic acid, a dicarboxylic acid. Nitric acid oxidises both the aldehyde end and the other terminal group:



Formation of the second carboxyl group establishes the presence of a terminal primary alcoholic group, $-\text{CH}_2\text{OH}$. Gluconic acid also gives saccharic acid on oxidation with nitric acid, confirming this identification.

Step 3: Conclusion Bromine-water oxidation to gluconic acid proves the aldehyde group; nitric-acid oxidation to saccharic acid proves the primary alcoholic group.

Quick Tip to Solve: Remember mild bromine water gives one carboxyl group, while nitric acid gives two carboxyl groups.

21. 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 vapour pressure becomes equal to the external atmospheric pressure.
- A non-volatile solute lowers solvent vapour pressure, whereas a volatile component contributes its own partial vapour pressure to the solution.

Step 1: Addition of potassium chloride KCl is a non-volatile electrolyte. Dissolved KCl lowers the vapour pressure of water; its dissociation into K^+ and Cl^- increases the number of solute particles and hence the colligative effect. At the boiling point of pure water, the solution's vapour pressure is therefore below atmospheric pressure. The solution must be heated to a higher temperature to attain atmospheric pressure, so its boiling point rises. For a dilute solution, $\Delta T_b = iK_b m > 0$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality.

Step 2: Addition of methyl alcohol Methyl alcohol (methanol) is volatile and has a lower boiling point than water. Unlike KCl, it contributes vapour above the solution. Its relatively high vapour pressure increases the total vapour pressure of the water-methanol mixture, so atmospheric pressure is attained at a temperature below the boiling point of pure water. Thus the boiling point decreases. The boiling-point-elevation formula for a non-volatile solute cannot be applied to methanol merely because the same amount, 1 mol, is added.

Step 3: Conclusion KCl lowers water's vapour pressure and raises its boiling point; volatile methanol increases the mixture's total vapour pressure and lowers its boiling point.

Quick Tip to Solve: First classify the added substance as volatile or non-volatile before applying a colligative-property formula.

Section C (21 marks)

22. 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° for weak electrolytes by extrapolating the concentration-molar conductivity curve, as it is for strong electrolytes. [3 marks]

Solution:

Concept:

- Molar conductivity Λ_m is the conductivity associated with one mole of electrolyte; its limiting value Λ_m° is obtained at infinite dilution, $c \rightarrow 0$.
- At infinite dilution, the contribution of each ion to molar conductivity is independent of the nature of the other ion.

Step 1: State Kohlrausch's law Kohlrausch's law of independent migration of ions states that at infinite dilution each ion contributes a definite amount to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present. Hence the limiting molar conductivity is the sum of

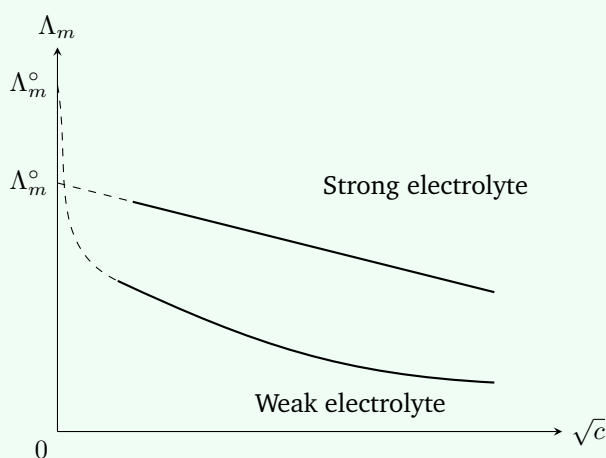
Quick Tip to Solve: Use a square-root concentration axis: the strong-electrolyte line has an accessible intercept, while the weak-electrolyte curve does not.

the individual ionic contributions:

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ,$$

where ν_+ and ν_- are the numbers of cations and anions per formula unit, and λ_+° and λ_-° are their limiting ionic molar conductivities.

Step 2: Compare the conductivity curves Plot Λ_m against $\sqrt{c}$, with concentration increasing towards the right. For a strong electrolyte, dissociation is practically complete. In the dilute region it obeys $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$, where A is a constant for the given electrolyte, solvent and temperature. The approximately straight line can therefore be extrapolated to $\sqrt{c} = 0$; its vertical intercept gives Λ_m° . A weak electrolyte is only partially ionised. On dilution its degree of ionisation increases greatly, so Λ_m rises sharply and the plot is strongly curved near zero concentration. There is no reliable straight-line trend to extrapolate from the measurable range to the limiting intercept. The schematic curve below shows this contrast; its scales are qualitative.



Schematic molar-conductivity plots against square-root concentration

Step 3: Conclusion Strong electrolytes permit a linear extrapolation of Λ_m against $\sqrt{c}$ to infinite dilution. Weak electrolytes show pronounced curvature due to increasing ionisation, so their Λ_m° is obtained using Kohlrausch's law.

Quick Tip to Solve: Use a square-root concentration axis: the strong-electrolyte line has an accessible intercept, while the weak-electrolyte curve does not.

23. 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:

- A dissolved non-volatile solute lowers the freezing point of a solvent. The depression is $\Delta T_f = T_f^0 - T_f$, where T_f^0 and T_f are the freezing points of the pure solvent and solution, respectively.
- For a dilute solution, $\Delta T_f = iK_fm$, where K_f is the molal freezing-point depression constant, m is

Quick Tip to Solve: For this non-electrolyte, use $i = 1$, convert only the 600 g of water to kilograms, and subtract the calculated depression from 0 °C.

the molality and i is the van't Hoff factor. Ethylene glycol is a non-electrolyte, so $i = 1$.

- Molality is the number of moles of solute per kilogram of solvent. The mass in its denominator is the mass of water, not the total mass of the solution.

Step 1: Calculate the moles of ethylene glycol Divide the given solute mass by its molar mass:

$$n = \frac{31 \text{ g}}{62 \text{ g mol}^{-1}} = 0.50 \text{ mol.}$$

Ethylene glycol remains as molecules in water; it does not produce additional ions on dissolution.

Step 2: Calculate the molality Convert the solvent mass into kilograms before using the molal constant:

$$m_{\text{water}} = \frac{600}{1000} = 0.600 \text{ kg}, \quad m = \frac{0.50}{0.600} = 0.8333 \text{ mol kg}^{-1}.$$

The added solute mass is not included in the denominator because molality is defined using solvent mass.

Step 3: Find the depression and the freezing point Substitute the molality and the given constant:

$$\Delta T_f = 1 \times 1.86 \times 0.8333 = 1.55 \text{ K.}$$

Pure water freezes at 0°C . A temperature difference of 1.55 K equals a difference of 1.55°C , so subtract this depression from the freezing point of pure water.

Step 4: Conclusion The freezing point of the antifreeze solution is

$$T_f = 0 - 1.55 = \boxed{-1.55^\circ\text{C}}$$

(equivalently, 271.60 K). The negative sign expresses the lowering below the freezing point of pure water.

Quick Tip to Solve: For this non-electrolyte, use $i = 1$, convert only the 600 g of water to kilograms, and subtract the calculated depression from 0°C .

24(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: $\text{Ni} = 28$]

[3 marks]

Solution:

Concept:

- The oxidation state of nickel is $+2$ in both $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$, since each ligand carries charge -1 . With atomic number 28 , Ni is $[\text{Ar}]3d^84s^2$, while Ni^{2+} is $[\text{Ar}]3d^8$.
- In valence bond theory, weak-field ligands do not force pairing of the metal's unpaired electrons; strong-field ligands can pair them, making an inner d orbital available for bonding.

Quick Tip to Solve: Both complexes contain Ni^{2+} , so begin with $3d^8$; then use weak-field chloride versus strong-field cyanide to decide pairing, geometry and magnetism together.

- A complex with unpaired electrons is paramagnetic; a complex with all electrons paired is diamagnetic. For n unpaired electrons, the spin-only magnetic moment is $\mu = \sqrt{n(n+2)}$ BM.

Step 1: Identify the hybridisation in each complex (i) The chloride ion, Cl^- , is a weak-field ligand. In $[\text{NiCl}_4]^{2-}$, the $3d^8$ electrons retain two unpaired electrons, so no empty inner $3d$ orbital is made available. One $4s$ and three $4p$ orbitals undergo sp^3 hybridisation, giving a tetrahedral complex. Cyanide, CN^- , is a strong-field ligand. In $[\text{Ni}(\text{CN})_4]^{2-}$, it causes pairing of the $3d$ electrons, leaving one $3d$ orbital empty. This orbital mixes with one $4s$ and two $4p$ orbitals to give dsp^2 hybridisation and square-planar geometry.

Step 2: Classify the orbital character (ii) $[\text{Ni}(\text{CN})_4]^{2-}$ is the inner orbital complex because its dsp^2 set uses an inner $3d$ orbital. $[\text{NiCl}_4]^{2-}$ is classified as the outer orbital complex in this comparison: its sp^3 hybrid orbitals use the outer $4s$ and $4p$ orbitals. No d orbital enters this tetrahedral hybridisation.

Step 3: Compare the magnetic behaviour (iii) $[\text{NiCl}_4]^{2-}$ has two unpaired electrons and is paramagnetic. Its spin-only moment is $\sqrt{2(2+2)} = \sqrt{8} \approx 2.83$ BM. In $[\text{Ni}(\text{CN})_4]^{2-}$, all eight $3d$ electrons are paired, so it is diamagnetic and has zero spin-only magnetic moment.

Step 4: Conclusion $[\text{NiCl}_4]^{2-}$: sp^3 , tetrahedral, outer orbital and paramagnetic (two unpaired electrons). $[\text{Ni}(\text{CN})_4]^{2-}$: dsp^2 , square planar, inner orbital and diamagnetic (no unpaired electrons).

Quick Tip to Solve: Both complexes contain Ni^{2+} , so begin with $3d^8$; then use weak-field chloride versus strong-field cyanide to decide pairing, geometry and magnetism together.

OR

24(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:

- Coordination compounds contain a central metal atom or ion bonded to ligands through donated electron pairs. Several metal complexes perform essential functions in living systems.
- A multidentate ligand binds a metal through two or more donor atoms and forms one or more chelate rings. Such complexes generally have greater stability than comparable complexes containing monodentate ligands: this is the chelate effect.
- The electron arrangement depends on the competition between crystal-field splitting energy and pairing energy P . Low-spin arrangements require pairing to be energetically preferable to occupying higher-energy orbitals.

Step 1: Name two biological coordination compounds (i) Haemoglobin is an iron-containing coordination compound. The iron centre in its haem groups binds oxygen reversibly, enabling oxygen transport in blood. Chlorophyll is a magnesium-containing coordination compound; its coordinated magnesium lies within the pigment's ring system, which participates in absorbing light for photosynthesis. Thus haemoglobin and chlorophyll are two important examples.

Quick Tip to Solve: Link the three answers to the key features: Fe in haemoglobin, Mg in chlorophyll, ring formation by en, and $\Delta_t < P$ for the rarity of low-spin tetrahedral complexes.

Step 2: Explain the chelate effect with an example (ii) The chelate effect is the enhanced stability of a complex formed by a multidentate ligand compared with a corresponding complex formed by similar monodentate ligands. For example, ethane-1,2-diamine (en), $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, donates lone pairs from both nitrogen atoms to the same metal ion and forms a five-membered chelate ring. The complex $[\text{Ni}(\text{en})_3]^{2+}$ is more stable than the analogous ammonia complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Multiple points of attachment and the favourable entropy of chelate formation help explain this enhanced stability.

Step 3: Explain why low-spin tetrahedral complexes are rare (iii) Tetrahedral crystal-field splitting, Δ_t , is small; for the same metal and comparable ligands it is approximately $\frac{4}{9}\Delta_o$, where Δ_o is the octahedral splitting. Usually $\Delta_t < P$, so placing an electron in a higher tetrahedral orbital requires less energy than pairing it in a lower one. Electrons therefore tend to occupy orbitals singly before pairing, producing high-spin arrangements. Low-spin tetrahedral complexes would require unusually large splitting relative to the pairing energy and are consequently rarely formed.

Step 4: Conclusion (i) Haemoglobin and chlorophyll are biological coordination compounds. (ii) Chelation increases stability; $[\text{Ni}(\text{en})_3]^{2+}$ is an example. (iii) The generally small Δ_t compared with pairing energy favours high-spin tetrahedral complexes.

Quick Tip to Solve: Link the three answers to the key features: Fe in haemoglobin, Mg in chlorophyll, ring formation by en, and $\Delta_t < P$ for the rarity of low-spin tetrahedral complexes.

25. How will you obtain the following from aniline? Write the chemical equations involved:

(a) Sulphanilic acid

(b) 2,4,6-Tribromoaniline

(c) Acetanilide

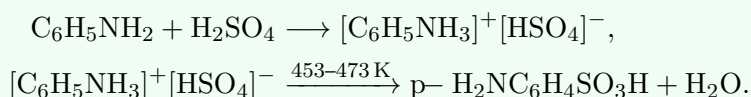
[3 marks]

Solution:

Concept:

- Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, undergoes electrophilic substitution on its benzene ring and acylation at its amino nitrogen.
- The $-\text{NH}_2$ group strongly activates the ring and directs bromination to the ortho and para positions. Acylation replaces an N-H hydrogen with an acetyl group, $\text{CH}_3\text{CO}-$.

Step 1: (a) Preparation of sulphanilic acid Treat aniline with concentrated sulphuric acid to form anilinium hydrogensulphate. Heating this salt at 453–473 K gives sulphanilic acid, the para sulphonic acid derivative:

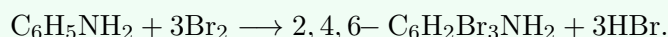


Sulphanilic acid exists predominantly as the zwitterion $\text{p- H}_3\text{N}^+\text{C}_6\text{H}_4\text{SO}_3^-$.

Step 2: (b) Preparation of 2,4,6-tribromoaniline Add bromine water to aniline at room temperature. Its strongly activated ring undergoes substitution at both ortho positions and the para position,

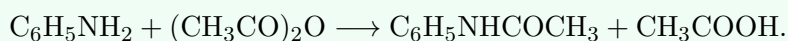
Quick Tip to Solve: For aniline conversions, distinguish ring substitution from N-acylation: bromine water gives all three ortho/para substitutions, whereas acetic anhydride acetylates nitrogen.

producing a white precipitate:



No Lewis-acid catalyst is required for this bromination.

Step 3: (c) Preparation of acetanilide React aniline with acetic anhydride. Acetylation occurs at nitrogen, giving acetanilide and acetic acid:



The product contains an amide linkage, $-\text{NHCO}-$; the acetyl group is attached to nitrogen, not directly to the benzene ring.

Step 4: Conclusion The required products are $p\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$ by sulphonation and heating, $2,4,6\text{-C}_6\text{H}_2\text{Br}_3\text{NH}_2$ using bromine water, and $\text{C}_6\text{H}_5\text{NHCOCH}_3$ using acetic anhydride.

Quick Tip to Solve: For aniline conversions, distinguish ring substitution from N-acylation: bromine water gives all three ortho/para substitutions, whereas acetic anhydride acetylates nitrogen.

26. 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]

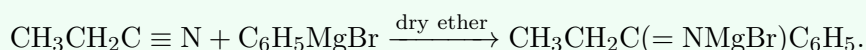
Solution:

Concept:

- A nitrile $\text{R}-\text{C}\equiv\text{N}$ reacts with one equivalent of a Grignard reagent to form an imine magnesium salt; subsequent acidic hydrolysis produces a ketone.
- 2,4-DNP identifies an aldehyde or ketone. A negative iodoform test excludes a methyl ketone, RCOCH_3 , while negative Tollens' and Fehling' tests support a ketone.

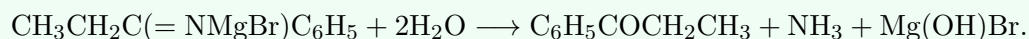
Step 1: Identify the carbonyl compound The orange-red precipitate with 2,4-DNP shows that B has a carbonyl group. Its failure to reduce Tollens' and Fehling's reagents indicates a ketone rather than an ordinary aldehyde. The negative iodoform test shows that the group next to the carbonyl is not methyl. Failure to decolourise bromine water is consistent with absence of an alkene group.

Step 2: Identify A and write the Grignard reaction The three-carbon nitrile with formula $\text{C}_3\text{H}_5\text{N}$ is propanenitrile, $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$. Phenylmagnesium bromide adds its phenyl group to the nitrile carbon in dry ether:



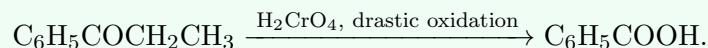
Quick Tip to Solve: In a nitrile-Grignard conversion, retain the nitrile carbon as the ketone carbonyl carbon and attach the Grignard carbon group directly to it.

Acidic hydrolysis of this imine salt gives propiophenone:



Thus B is 1-phenylpropan-1-one. The acid work-up protonates the ammonia formed; the equation above expresses the hydrolysis stoichiometry.

Step 3: Identify C and check consistency Drastic oxidation with chromic acid cleaves the side chain of the aromatic ketone and yields benzoic acid as the stated aromatic carboxylic acid:



Benzoic acid has formula $\text{C}_7\text{H}_6\text{O}_2$, agreeing with C. Propiophenone has an ethyl group beside its carbonyl, so it lacks the $-\text{COCH}_3$ unit necessary for the iodoform reaction.

Step 4: Conclusion $\text{A} = \text{CH}_3\text{CH}_2\text{CN}$ (propanenitrile), $\text{B} = \text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$ (propiophenone) and $\text{C} = \text{C}_6\text{H}_5\text{COOH}$ (benzoic acid).

Quick Tip to Solve: In a nitrile-Grignard conversion, retain the nitrile carbon as the ketone carbonyl carbon and attach the Grignard carbon group directly to it.

27. 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: $a_t = a_0 e^{-kt}$, where a_0 and a_t are the initial activity and the activity after time t , and k is the decay constant.
- The half-life satisfies $kt_{1/2} = \ln 2 = 2.303 \log 2$. Hence $t/t_{1/2} = \log(a_0/a_t)/\log 2$, with all logarithms taken to the same base.

Step 1: Interpret the remaining activity The activity is reduced to 75% of the original value, so the remaining fraction is $a_t/a_0 = 75/100 = 3/4$. Since activity is proportional to the number of undecayed nuclei, this is also the remaining fraction of radioactive nuclei. Therefore the ratio to use in the first-order expression is

$$\frac{a_0}{a_t} = \frac{4}{3}.$$

Only 25% has decayed at this time.

Step 2: Eliminate the decay constant using the half-life Apply the integrated first-order rate equation to the target activity and to one half-life:

$$kt = 2.303 \log \left(\frac{4}{3} \right),$$
$$kt_{1/2} = 2.303 \log 2.$$

Quick Tip to Solve: Reduced to 75 percent means 3/4 remains. Use the half-life ratio $t/t_{1/2} = \log(4/3)/\log 2$ to cancel the decay constant before substitution.

Dividing these equations eliminates both k and the common factor 2.303:

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

This ratio avoids unnecessary rounding of the decay constant.

Step 3: Substitute the supplied logarithms Using the given values $\log 4 = 0.60$, $\log 3 = 0.48$ and $\log 2 = 0.30$,

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

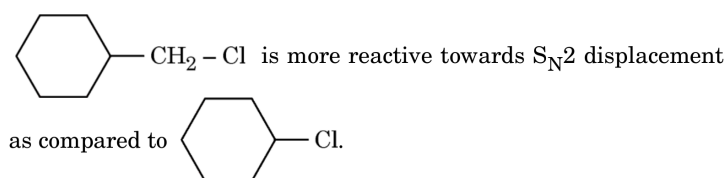
The time is less than one half-life, as expected: 75% remains before the activity falls to 50%.

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

Quick Tip to Solve: Reduced to 75 percent means $3/4$ remains. Use the half-life ratio $t/t_{1/2} = \log(4/3)/\log 2$ to cancel the decay constant before substitution.

28. Give reasons for the following:

- (a) Haloalkanes react with KCN to form alkyl cyanides, while with AgCN, they form isocyanides.
(b) $\text{C}_6\text{H}_{11}\text{CH}_2\text{Cl}$ is more reactive towards $\text{S}_{\text{N}}2$ displacement as compared to $\text{C}_6\text{H}_{11}\text{Cl}$, as shown in the structures below.
(c) Grignard reagents should be prepared under anhydrous conditions. [3 marks]

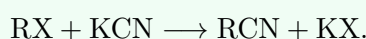


Solution:

Concept:

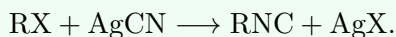
- An ambident cyanide group can attach through carbon, giving $\text{R}-\text{C} \equiv \text{N}$, or through nitrogen, giving $\text{R}-\text{N} \equiv \text{C}$.
- In $\text{S}_{\text{N}}2$, back-side nucleophilic attack displaces the leaving group in one step; steric crowding slows the reaction.
- Grignard reagents, RMgX , have strongly basic carbon centres that react with acidic hydrogen, including that in water.

Step 1: Explain the different products with KCN and AgCN KCN is predominantly ionic and supplies free CN^- ions. Attack through carbon gives the alkyl cyanide:



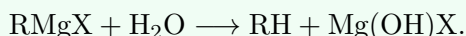
Quick Tip to Solve: First locate the carbon directly bonded to chlorine: the external CH_2 carbon is primary, while the ring carbon is secondary.

In covalent AgCN, carbon is bonded to silver. Attack through the available nitrogen end gives an isocyanide:



Step 2: Compare the two printed saturated-ring chlorides The first compound, cyclohexylmethyl chloride, $C_6H_{11}CH_2Cl$, has a primary chlorine-bearing carbon outside the ring. In cyclohexyl chloride, $C_6H_{11}Cl$, this carbon is secondary and lies in the ring. The primary carbon allows less hindered back-side attack by the nucleophile. Ring carbons hinder this approach in the secondary compound, so the first compound undergoes S_N2 substitution faster.

Step 3: Explain why moisture must be excluded Water protonates the carbon centre and destroys the Grignard reagent:



Dry ether, dry apparatus and exclusion of moisture are necessary during preparation; otherwise water consumes the reagent as it forms.

Step 4: Conclusion KCN gives alkyl cyanides; AgCN gives isocyanides. Primary cyclohexylmethyl chloride is less hindered for S_N2 than secondary cyclohexyl chloride. Water decomposes Grignard reagents.

Quick Tip to Solve: First locate the carbon directly bonded to chlorine: the external CH_2 carbon is primary, while the ring carbon is secondary.

Section D (8 marks)

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

29(a). 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:

- A polymer is formed by linking repeating monomer units. Proteins and nucleic acids have different monomers and different bonds joining those units.
- Fibrous and globular proteins are distinguished by the overall arrangement of their polypeptide

Quick Tip to Solve: Name the full nucleotide unit including phosphate, then compare long parallel fibres with compact folded globules.

chains, rather than by a different basic building unit.

Step 1: Name the basic building units Proteins are polymers of α -amino acids, whose general structure is $\text{H}_2\text{N}-\text{CH}(\text{R})-\text{COOH}$. Amino acids are joined by peptide bonds, $-\text{CO}-\text{NH}-$. Nucleic acids are polymers of nucleotides, each comprising a nitrogenous base, a pentose sugar and a phosphate group. Successive nucleotides are linked through phosphodiester bonds. A nucleotide, rather than a nitrogenous base alone or a nucleoside without phosphate, is therefore the complete basic unit of a nucleic acid.

Step 2: Distinguish their molecular structures In fibrous proteins, polypeptide chains extend in long thread-like arrangements and lie approximately parallel; hydrogen bonds and, where present, disulphide bonds stabilise the structure. In globular proteins, polypeptide chains fold and coil into compact, approximately spherical shapes. Keratin is an example of a fibrous protein, while insulin is a globular protein. The essential structural distinction is an elongated fibre compared with a compact folded molecule.

Step 3: Conclusion The building units are α -amino acids for proteins and nucleotides for nucleic acids. Fibrous proteins have extended, thread-like chains; globular proteins have compact, folded, approximately spherical structures.

Quick Tip to Solve: Name the full nucleotide unit including phosphate, then compare long parallel fibres with compact folded globules.

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-deoxyribose sugar and a phosphate group.
- Complete hydrolysis breaks the bonds joining these three components; the identity of the specified base is retained.

Step 1: Identify the components of this nucleotide The question specifies a nucleotide from DNA containing thymine. Hence its nitrogenous base is thymine, its pentose is 2-deoxy-D-ribose, and its third component is phosphate. DNA contains deoxyribose rather than the ribose found in RNA.

Step 2: List the complete hydrolysis products Complete hydrolysis separates the base from the sugar and releases the phosphate component. The products are therefore thymine, 2-deoxy-D-ribose and phosphoric acid. Naming only the base and sugar would describe the components of a nucleoside and would omit the nucleotide's phosphate.

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

Quick Tip to Solve: For complete nucleotide hydrolysis, list all three components: base, pentose sugar and phosphoric acid.

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

[1 mark]

Solution:

Concept:

- DNA and RNA both contain nucleotide chains, but their pentose sugars differ at the 2' carbon.
- Deoxyribose has one fewer oxygen atom than ribose; this is a direct structural distinction between the two nucleic acids.

Step 1: Identify the sugar in DNA DNA contains 2-deoxy-D-ribose. At the 2' carbon of this sugar, the substituent corresponding to the hydroxyl group of ribose is hydrogen. The term deoxy indicates this absence of an oxygen atom.

Step 2: Compare it with the sugar in RNA RNA contains D-ribose, whose 2' carbon bears an –OH group. Thus the sugar component of RNA has an oxygen-containing hydroxyl group at a position where DNA has hydrogen. This comparison gives one structural difference, without needing to add a second distinction.

Step 3: Conclusion DNA contains 2-deoxyribose, with –H at the 2' carbon; RNA contains ribose, with –OH at that carbon.

Quick Tip to Solve: Compare the sugar at the 2-prime carbon: DNA has H where RNA has 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: fat-soluble vitamins dissolve in fats, while water-soluble vitamins dissolve in water.
- Vitamins A, D, E and K are fat-soluble; the B-group vitamins and vitamin C are water-soluble.

Step 1: Choose a fat-soluble example Vitamin A is a fat-soluble vitamin and is a correct example for the first category. Vitamins D, E or K would also satisfy that part, but one example is sufficient. The classification refers to solubility, not to the amount required in the diet.

Step 2: Choose a water-soluble example Vitamin C, also called ascorbic acid, is a water-soluble vitamin and is a correct example for the second category. A B-group vitamin would also belong to this category. Pairing vitamin A with vitamin C therefore supplies one example from each of the two requested classes.

Step 3: Conclusion Fat-soluble vitamin: vitamin A. Water-soluble vitamin: vitamin C (ascorbic acid).

Quick Tip to Solve: Remember A, D, E and K as fat-soluble; choose vitamin C for a clear water-soluble example.

30(a). 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

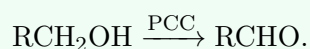
[2 marks]

Solution:

Concept:

- Primary alcohols have the group RCH_2OH . Their oxidation first produces an aldehyde, RCHO ; further oxidation gives a carboxylic acid, RCOOH .
- A mild, selective oxidising reagent stops at the aldehyde stage, whereas a strong oxidising agent in aqueous acidic medium allows oxidation to the acid.

Step 1: Choose the reagent for the aldehyde Use pyridinium chlorochromate (PCC), generally in an anhydrous organic solvent such as dichloromethane. PCC oxidises the primary alcohol to an aldehyde without further oxidation to the acid under these conditions:



The absence of water and the controlled action of PCC help preserve the aldehyde product.

Step 2: Choose the reagent for the carboxylic acid Use acidified potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, with heating under reflux. Acidified potassium permanganate, KMnO_4/H^+ , is another suitable strong oxidising reagent. The overall oxidation is



where $[\text{O}]$ represents an oxygen equivalent supplied by the oxidising reagent. The initially formed aldehyde is oxidised further in this aqueous medium.

Step 3: Conclusion (i) Pyridinium chlorochromate (PCC). (ii) Acidified potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, or acidified KMnO_4 .

Quick Tip to Solve: For a primary alcohol, choose PCC to stop at the aldehyde; choose a strong aqueous oxidant for the acid.

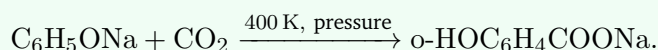
30(b). Write the reaction involved in Kolbe's reaction.

[1 mark]

Solution:**Concept:**

- In Kolbe's reaction of phenols, sodium phenoxide reacts with carbon dioxide under pressure; acidification gives salicylic acid.
- The phenoxide group activates the aromatic ring, and carboxylation occurs predominantly at the ortho position.

Step 1: Carboxylate sodium phenoxide Sodium phenoxide is heated with CO_2 at about 400 K under pressure. The major product is sodium salicylate:



The new carboxylate group is adjacent to the hydroxyl group.

Step 2: Acidify the salt Treatment with dilute acid converts the carboxylate salt into 2-hydroxybenzoic acid (salicylic acid):



This is Kolbe's carboxylation of phenoxide, distinct from the electrolysis reaction also associated with the name Kolbe.

Step 3: Conclusion $\text{C}_6\text{H}_5\text{ONa}$ reacts with CO_2 under pressure at 400 K, followed by acidification, to give $\text{o-HOC}_6\text{H}_4\text{COOH}$ (salicylic acid).

Quick Tip to Solve: Remember phenoxide plus carbon dioxide, then acidification: place COOH ortho to OH .

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

[1 mark]

Solution:**Concept:**

- Ordinary oxidation of an alcohol to a carbonyl compound requires removal of the hydroxyl hydrogen and a hydrogen from the carbon bearing the hydroxyl group.
- In a tertiary alcohol, R_3COH , that carbon is bonded to three carbon groups and has no hydrogen.

Step 1: Inspect the carbon bearing OH A tertiary alcohol has three alkyl groups attached to the carbon bearing $-\text{OH}$. Thus, unlike a primary or secondary alcohol, it has no hydrogen on this carbon (the required α -hydrogen).

Step 2: Explain why usual oxidation cannot proceed The usual conversion of the $\text{C}-\text{OH}$ group into a $\text{C}=\text{O}$ group therefore cannot occur by simple removal of two hydrogen atoms. Oxidation would require cleavage of a carbon-carbon bond, which does not occur readily with ordinary mild oxidising agents. Under drastic conditions tertiary alcohols can undergo oxidative bond cleavage, so their resistance applies to normal alcohol-oxidation conditions.

Quick Tip to Solve: Check the carbon attached to OH : no hydrogen on that carbon means no ordinary carbonyl-forming oxidation.

Step 3: Conclusion Tertiary alcohols resist ordinary oxidation because the carbon bearing -OH has no hydrogen; oxidation would require breaking a C-C bond.

Quick Tip to Solve: Check the carbon attached to OH : no hydrogen on that carbon means no ordinary carbonyl-forming oxidation.

OR

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



[1 mark]

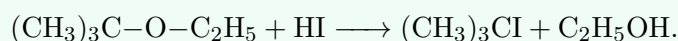
Solution:

Concept:

- HI cleaves ethers after protonation of the ether oxygen. Cleavage involving a tertiary alkyl group occurs through a stable tertiary carbocation.
- For an ether containing a tertiary group, iodide forms the tertiary alkyl iodide and the other fragment leaves as an alcohol.

Step 1: Identify the favoured bond cleavage The ether is tert-butyl ethyl ether, $(\text{CH}_3)_3\text{C-O-C}_2\text{H}_5$. Protonation by HI makes oxygen a better leaving group. The bond between oxygen and the tert-butyl carbon breaks because it generates the relatively stable tertiary carbocation, $(\text{CH}_3)_3\text{C}^+$, along with ethanol.

Step 2: Form the products Iodide captures this carbocation, giving tert-butyl iodide (2-iodo-2-methylpropane). The overall reaction is



Here the tertiary group determines the cleavage route; the ordinary preference for attack at a less hindered primary carbon does not apply to this tertiary ether. Further conversion of ethanol to ethyl iodide would require additional HI and is not the single cleavage shown.

Step 3: Conclusion The products are tert-butyl iodide, $(\text{CH}_3)_3\text{CI}$, and ethanol, $\text{C}_2\text{H}_5\text{OH}$.

Quick Tip to Solve: If either ether carbon is tertiary, form the tertiary iodide and retain the other alkyl group as an alcohol.

Section E (15 marks)

31(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:

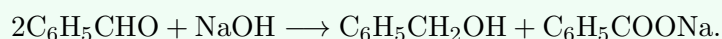
- Acid-catalysed addition of one molecule of an alcohol to an aldehyde gives a hemiacetal, in which the former carbonyl carbon bears both $-\text{OH}$ and $-\text{OR}$ groups.
- An aldehyde without an α -hydrogen undergoes the Cannizzaro reaction in concentrated alkali: one molecule is reduced to an alcohol while another is oxidised to a carboxylate salt.
- P_2O_5 is a dehydrating agent. The iodoform test detects the $\text{CH}_3\text{CO}-$ group, including ethanal, whereas pyridinium chlorochromate (PCC) oxidises a primary alcohol to an aldehyde.

Step 1: (a)(i)(I) Add one equivalent of methanol to ethanal Dry HCl supplies the acid catalyst for nucleophilic addition of methanol to the carbonyl group. Since the stated proportion is one mole of methanol per mole of ethanal, the product is the hemiacetal, 1-methoxyethan-1-ol:



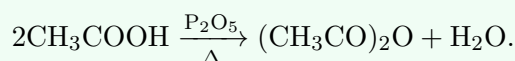
The product retains an $-\text{OH}$ group on the same carbon as $-\text{OCH}_3$. A full acetal, $\text{CH}_3\text{CH}(\text{OCH}_3)_2$, would require two alcohol molecules per aldehyde molecule; it is not the product corresponding to the stated one-equivalent addition.

Step 2: (a)(i)(II) Apply the Cannizzaro reaction Benzaldehyde has no α -hydrogen and therefore undergoes disproportionation with concentrated NaOH . The products in the alkaline reaction mixture are benzyl alcohol and sodium benzoate:



One benzaldehyde molecule is reduced to $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$; the other is oxidised to $\text{C}_6\text{H}_5\text{COO}^-$. Benzoic acid would be obtained only after acidifying the benzoate, which is not specified here.

Step 3: (a)(i)(III) Dehydrate ethanoic acid On heating with P_2O_5 , two molecules of ethanoic acid lose the elements of one molecule of water to form ethanoic anhydride (acetic anhydride):



This equation shows the net dehydration; the dehydrating agent removes the water formed and favours anhydride formation.

Step 4: (a)(ii) Distinguish the aldehydes using the iodoform test Warm separate samples with iodine

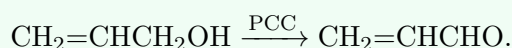
Quick Tip to Solve: Count the alcohol equivalents before choosing hemiacetal or acetal; for two aldehydes, use the iodoform test to identify ethanal specifically.

solution and aqueous NaOH. Ethanal gives a yellow precipitate of iodoform, CHI_3 , whereas propanal gives no yellow precipitate. The reaction for ethanal is



Ethanal has the required $\text{CH}_3\text{CO}-$ arrangement, but propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, does not. Tollens' reagent is unsuitable for distinguishing this pair because both compounds are aldehydes and both give a positive test.

Step 5: (a)(iii) Select a reagent for oxidation of allyl alcohol Use pyridinium chlorochromate (PCC), preferably in a nonaqueous solvent such as dichloromethane. It oxidises the primary alcohol group to an aldehyde while retaining the carbon-carbon double bond:



Thus allyl alcohol (prop-2-en-1-ol) gives propenal (prop-2-enal). A controlled oxidant is chosen so that oxidation stops at the aldehyde stage.

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 yellow iodoform with I_2/NaOH ; propanal does not. (iii) The reagent is pyridinium chlorochromate (PCC).

Quick Tip to Solve: Count the alcohol equivalents before choosing hemiacetal or acetal; for two aldehydes, use the iodoform test to identify ethanal specifically.

OR

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

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

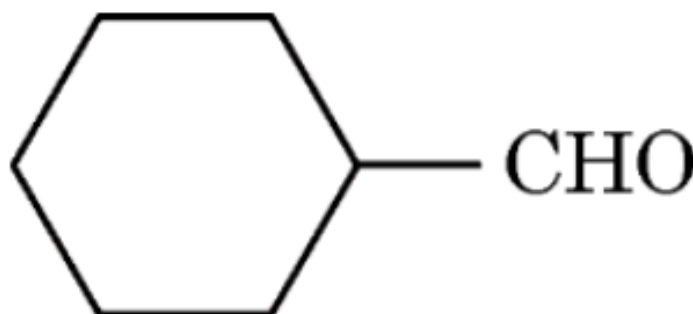
(iii) Arrange the following compounds in increasing order of their reactivity towards HCN:

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

(iv) Write the reaction involved in Etard reaction.

(v) Write the product when the compound shown reacts with $\text{Zn}(\text{Hg})/\text{conc. HCl}$.

[5 marks]

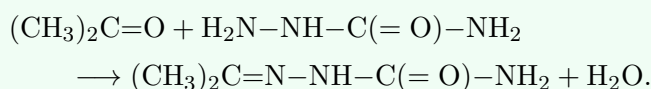


Solution:

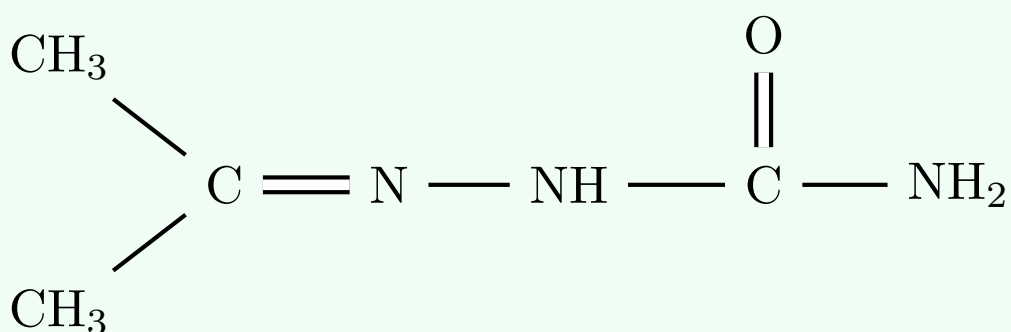
Concept:

- Semicarbazide, $\text{H}_2\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$, condenses with a carbonyl compound through its terminal amino group to form a semicarbazone, eliminating water.
- An α -hydrogen is bonded to the carbon next to a carbonyl group. Its removal gives a resonance-stabilised enolate ion.
- Cyanide attacks the electrophilic carbonyl carbon. Electron-donating alkyl groups and steric crowding reduce the rate of this nucleophilic addition.
- Etard oxidation converts the methyl side chain of toluene into an aldehyde; Clemmensen reduction with $\text{Zn}(\text{Hg})/\text{concentrated HCl}$ converts a carbonyl group to a methylene group.

Step 1: (i) Form the semicarbazone of acetone Acetone reacts with semicarbazide as follows:

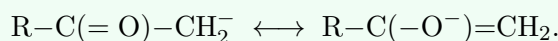


The carbonyl oxygen of acetone is replaced by $=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$. Both methyl groups remain attached to the same carbon. The labelled structure is drawn below. The amino group directly bonded to the carbonyl carbon of semicarbazide is resonance-deactivated and does not form the new imine bond.



Structure of the semicarbazone of acetone

Step 2: (ii) Explain the acidity of alpha-hydrogens On removal of an α -hydrogen as H^+ , the remaining electron pair gives an enolate ion. For a representative aldehyde or ketone, its resonance forms are



Here R is hydrogen or an alkyl group. The negative charge is delocalised between the alpha-carbon and the electronegative oxygen. This stabilisation of the conjugate base, together with the electron-withdrawing effect of the carbonyl group, makes these hydrogens acidic compared with ordinary alkane hydrogens.

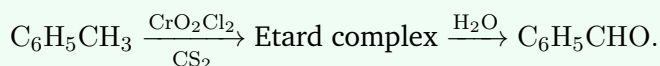
Step 3: (iii) Compare addition of HCN In HCN addition, CN^- attacks the carbonyl carbon and the resulting alkoxide is protonated to give a cyanohydrin. Ethanal has only one electron-donating methyl group and a small hydrogen, so its carbonyl carbon is more electrophilic and more accessible than

Quick Tip to Solve: Keep the semicarbazone chain in the order $\text{C}=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$. For the last reaction, replace only the ring's CHO substituent by CH_3 ; $\text{Zn}(\text{Hg})/\text{HCl}$ retains its carbon.

that of acetone. Acetone has two methyl groups. The tert-butyl methyl ketone has a much bulkier tert-butyl group, which hinders the attack still more. Thus the increasing order is

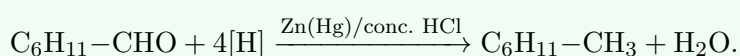


Step 4: (iv) Write the Etard reaction Toluene is treated with chromyl chloride in a non-aqueous solvent such as carbon disulphide. The Etard complex formed is then hydrolysed to benzaldehyde:



Controlled oxidation changes the side-chain $-\text{CH}_3$ group into $-\text{CHO}$, retaining the benzene ring.

Step 5: (v) Apply Clemmensen reduction to the printed structure The figure shows cyclohexanecarbaldehyde, $\text{C}_6\text{H}_{11}-\text{CHO}$: the aldehyde group is attached to a saturated cyclohexane ring. Zn(Hg) in concentrated HCl reduces its aldehyde group to a methyl group:



The ring remains saturated and intact. The product is methylcyclohexane; the aldehyde carbon is retained as the carbon of the methyl substituent.

Step 6: Conclusion (i) Acetone semicarbazone: $(\text{CH}_3)_2\text{C}=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$. (ii) Alpha-hydrogens are acidic because their removal produces resonance-stabilised enolate ions. (iii) $(\text{CH}_3)_3\text{C}-\text{CO}-\text{CH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO}$. (iv) Etard oxidation converts toluene to benzaldehyde using CrO_2Cl_2 , followed by hydrolysis. (v) The product is methylcyclohexane, $\text{C}_6\text{H}_{11}\text{CH}_3$.

Quick Tip to Solve: Keep the semicarbazone chain in the order $\text{C}=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$. For the last reaction, replace only the ring's CHO substituent by CH_3 ; Zn(Hg)/HCl retains its carbon.

32(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:

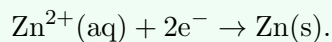
Concept:

- The potential of a metal electrode is quoted for reduction. For $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(s)}$, the Nernst equation at 298 K is $E = E^\circ - (0.0591/2) \log Q$, where Q is the reaction quotient and the activity of solid zinc is unity.
- A dry cell converts the oxidation of its zinc container and the reduction of manganese dioxide into electrical energy. The moist ammonium chloride paste supplies ions; the carbon rod collects current from the cathode mixture.

Quick Tip to Solve: For a metal-ion reduction electrode use $Q = 1/[\text{metal ion}]$; dilution therefore lowers its reduction potential. Cancel electrons before combining dry-cell half-reactions.

- Standard free energy, standard cell potential and the equilibrium constant satisfy $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ = -RT \ln K_c$, where n is the number of electrons transferred and F is the Faraday constant.

Step 1: (i) Identify the reduction reaction and its reaction quotient Write the zinc electrode reaction in the reduction direction:



Zinc sulphate supplies Zn^{2+} , so its ion concentration is 0.01 mol L^{-1} . The solid metal does not appear as a variable concentration in the reaction quotient. Thus, using the usual dilute-solution approximation,

$$Q = \frac{1}{[\text{Zn}^{2+}]} = \frac{1}{0.01} = 100.$$

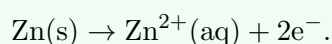
Two electrons are involved, hence $n = 2$. The given temperature 25°C corresponds to approximately 298 K.

Step 2: (i) Substitute in the Nernst equation

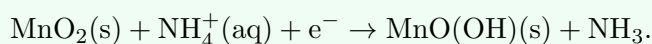
$$\begin{aligned} E &= E^\circ - \frac{0.0591}{2} \log Q \\ &= -0.76 - \frac{0.0591}{2} \log 100 \\ &= -0.76 - \frac{0.0591}{2} (2) \\ &= -0.8191 \text{ V}. \end{aligned}$$

The dilute zinc-ion solution makes the reduction potential more negative than the standard value: fewer zinc ions are available to accept electrons. This also checks the sign of the concentration correction.

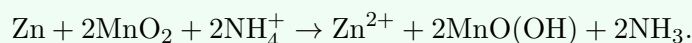
Step 3: (ii) Write the dry-cell electrode reactions and add them At the zinc anode, oxidation occurs:



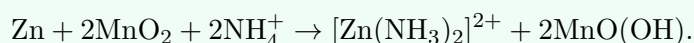
At the cathode, manganese dioxide is reduced in the presence of ammonium ions:



Multiply the cathode reaction by two and add it to the anode reaction. The electrons cancel, giving the overall ionic reaction:



The ammonia formed complexes with zinc ions, forming $[\text{Zn}(\text{NH}_3)_2]^{2+}$. Therefore the overall reaction may also be represented with this complex as the zinc-containing product:



Step 4: (iii) Explain why the equilibrium constant uses the standard potential Combine the two

Quick Tip to Solve: For a metal-ion reduction electrode use $Q = 1/[\text{metal ion}]$; dilution therefore lowers its reduction potential. Cancel electrons before combining dry-cell half-reactions.

expressions for standard reaction free energy:

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

Consequently, $E_{\text{cell}}^{\circ} = (RT/nF) \ln K_c$. Both K_c and the standard cell potential are fixed for the given reaction at a fixed temperature. In contrast, the operating potential obeys

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q,$$

and therefore varies with the instantaneous concentrations through Q . At equilibrium $Q = K_c$ and $E_{\text{cell}} = 0$; the concentration-dependent operating potential cannot by itself determine the equilibrium constant.

Step 5: Conclusion (i) The zinc half-cell reduction potential is -0.8191 V , approximately -0.82 V . (ii) Zinc is oxidised at the anode and MnO_2 is reduced to $\text{MnO}(\text{OH})$ at the cathode; their balanced reactions give the overall dry-cell reaction above. (iii) K_c is related to E_{cell}° through standard free energy, whereas E_{cell} also depends on the current reaction quotient.

Quick Tip to Solve: For a metal-ion reduction electrode use $Q = 1/[\text{metal ion}]$; dilution therefore lowers its reduction potential. Cancel electrons before combining dry-cell half-reactions.

OR

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

(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 $\Lambda_m = \kappa \times 1000/c$, when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} . The factor 1000 converts litres into cubic centimetres.
- 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 $\alpha = \Lambda_m/\Lambda_m^{\circ}$, where the superscript $\circ$ denotes the limiting value at infinite dilution.
- A cell potential depends on the reaction quotient through the Nernst equation. Pure solids have unit activity, so an overall cell reaction involving only solids has no changing concentration term.
- A salt bridge carries ionic current between the half-cells and maintains electrical neutrality, allowing electrons to keep flowing through the external wire.

Step 1: (i) **Calculate the molar conductivity** The supplied conductivity is $\kappa = 3.905 \times 10^{-5} \text{ S cm}^{-1}$,

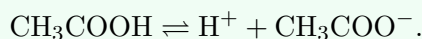
Quick Tip to Solve: Keep the factor 1000 in the conductivity formula when c is in mol/L ; then divide by the sum of the two limiting ionic conductivities to obtain α .

and the acid concentration is $c = 0.001 \text{ mol L}^{-1}$. Therefore,

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

The unit follows because conductivity is multiplied by the volume containing one mole. Using concentration in moles per litre without the factor 1000 would give an incorrect value.

Step 2: (i) Obtain limiting molar conductivity and degree of dissociation Acetic acid dissociates as



Each dissociated molecule gives one ion of each type, so their limiting ionic conductivities add:

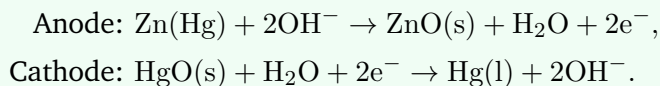
$$\begin{aligned}\Lambda_m^\circ &= 349.6 + 40.9 \\ &= 390.5 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

For this weak acid,

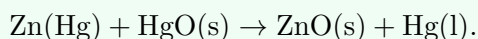
$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{39.05}{390.5} = 0.100.$$

Thus the degree of dissociation is 0.10, or 10%. It is dimensionless, since the conductivity units cancel. The substantially smaller observed conductivity compared with the limiting value is consistent with only partial dissociation at this concentration.

Step 3: (ii)(I) Explain the constant voltage of a mercury cell The mercury cell uses zinc amalgam as the anode and mercury(II) oxide as the cathode in an alkaline electrolyte. The electrode reactions are



Addition cancels electrons, water and hydroxide ions:



No ion whose concentration changes during discharge appears in the overall reaction. The condensed electrode substances have effectively constant activities. Hence the reaction quotient, and therefore the cell potential, remains effectively constant throughout its useful life, until the active materials are exhausted. Its usual voltage is about 1.35 V.

Step 4: (ii)(II) Explain the role of the salt bridge At the anode, oxidation tends to produce excess positive charge in the solution; at the cathode, reduction can remove positive ions and leave excess negative charge. Without ionic migration, this charge separation quickly opposes further electron flow and the cell stops operating. Salt-bridge anions migrate towards the anode compartment, while its cations migrate towards the cathode compartment, maintaining electrical neutrality in both half-cells. The bridge therefore completes the internal circuit by ionic conduction while the external wire carries

Quick Tip to Solve: Keep the factor 1000 in the conductivity formula when c is in mol/L; then divide by the sum of the two limiting ionic conductivities to obtain alpha.

electrons. It also limits direct mixing of the half-cell solutions and minimises the liquid-junction potential. Its electrolyte should not react with the electrode materials or solution ions.

Step 5: Conclusion (i) $\Lambda_m = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$ and $\alpha = 0.100 = 10\%$. (ii)(I) A mercury cell gives constant voltage because its overall reaction has no changing ionic-concentration term. (ii)(II) A salt bridge maintains electrical neutrality and completes the internal ionic circuit, sustaining the galvanic-cell reaction.

Quick Tip to Solve: Keep the factor 1000 in the conductivity formula when c is in mol/L; then divide by the sum of the two limiting ionic conductivities to obtain α .

33(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:

- Transition-metal melting points depend on the strength of metallic bonding; participation of unpaired d electrons usually strengthens this bonding.
- Aqueous transition-metal ions can show colour through electronic transitions between split d orbitals. An ion with a partially filled d subshell can undergo d-d transitions, whereas a d^0 ion cannot.
- The third ionisation enthalpy removes an electron from the gaseous M^{2+} ion. Removal from a stable completely filled d^{10} configuration requires particularly high energy.
- In acidic medium, permanganate is reduced according to $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$. The electrons gained must equal those lost by the reducing agent.

Step 1: (a)(i)(I) Compare the metallic bonding Iron has configuration $[\text{Ar}] 3d^6 4s^2$, with more unpaired d electrons than copper, $[\text{Ar}] 3d^{10} 4s^1$. Its greater participation of d electrons in metallic bonding makes the bonding stronger. Consequently, more thermal energy is needed to disrupt the metallic lattice of iron. Thus Fe has the higher melting point of this pair.

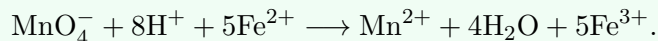
Step 2: (a)(i)(II) Examine the d-electron configurations Ti^{3+} has configuration $[\text{Ar}] 3d^1$, while Sc^{3+} has configuration $[\text{Ar}] 3d^0$. In the aqueous titanium(III) complex, absorption of visible light can promote the d electron between the ligand-field-split d levels; the transmitted light gives the solution its colour. Scandium(III) has no d electron to undergo such a transition, so its aqueous solution is colourless. Hence the coloured ion is Ti^{3+} .

Step 3: (a)(i)(III) Identify the electron removed in the third ionisation For chromium, the first two electrons removed leave Cr^{2+} with configuration $[\text{Ar}] 3d^4$; the third ionisation produces Cr^{3+} , $[\text{Ar}] 3d^3$.

Quick Tip to Solve: For the third ionisation compare the configurations of the divalent ions; for acidic permanganate use five electrons per permanganate ion.

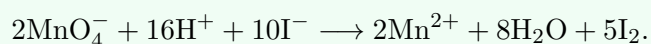
For zinc, Zn^{2+} has the stable, completely filled configuration $[\text{Ar}] 3d^{10}$. Its third ionisation must break this filled subshell to form $3d^9$. Therefore Zn has the higher third ionisation enthalpy. The comparison concerns the divalent ions, not simply the configurations of the neutral atoms.

Step 4: (a)(ii)(I) Balance oxidation of iron(II) Each iron(II) ion loses one electron: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$. Multiply this half-equation by five and combine it with the acidic permanganate reduction half-equation:



The four oxygen atoms become four water molecules, requiring eight hydrogen ions. Both sides have total charge +17, confirming the ionic balance.

Step 5: (a)(ii)(II) Balance oxidation of iodide Iodide is oxidised to iodine: $2\text{I}^- \rightarrow \text{I}_2 + 2e^-$. The least common multiple of five and two electrons is ten. Multiply the permanganate half-equation by two and the iodide half-equation by five:



Manganese gains ten electrons in total while iodide loses ten. Both sides have charge +4, and Mn, O, H and I are each conserved.

Step 6: Conclusion (i) The required choices are (I) Fe, (II) Ti^{3+} , and (III) Zn. (ii) Acidic permanganate oxidises Fe^{2+} to Fe^{3+} and I^- to I_2 , with the balanced ionic equations given above.

Quick Tip to Solve: For the third ionisation compare the configurations of the divalent ions; for acidic permanganate use five electrons per permanganate ion.

OR

33(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:

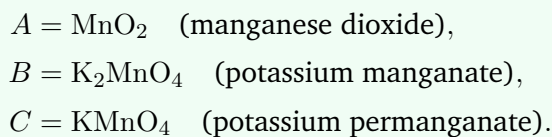
Concept:

- Manganese dioxide, MnO_2 , contains Mn in oxidation state +4. Oxidative fusion with potassium hydroxide in air produces green potassium manganate, K_2MnO_4 , containing Mn in oxidation state +6.
- Electrolytic oxidation removes an electron from each manganate ion, converting MnO_4^{2-} into permanganate, MnO_4^- , in which Mn has oxidation state +7.
- In disproportionation, the same element in one oxidation state is simultaneously oxidised and reduced. Manganate is stable in strongly alkaline solution but disproportionates on acidification.

Step 1: (b)(i) Identify the three manganese compounds The black-brown starting solid is manganese

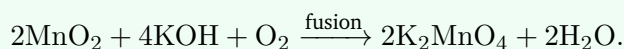
Quick Tip to Solve: Track manganese as $+4 \rightarrow +6 \rightarrow +7$ in preparation; on acidification, +6 splits into +7 and +4, identifying disproportionation.

dioxide. The green salt formed on oxidative fusion is potassium manganate, and the dark purple salt obtained by further oxidation is potassium permanganate:



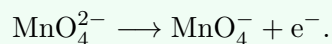
The oxidation states +4, +6, and +7, respectively, establish that both preparation stages involve oxidation of manganese.

Step 2: Write the oxidative fusion reaction Air supplies oxygen, which oxidises manganese dioxide in hot potassium hydroxide:

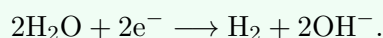


Each Mn atom increases its oxidation state from +4 to +6, losing two electrons. The oxygen molecule accepts the four electrons lost by the two Mn atoms. The balanced equation conserves two Mn atoms, four K atoms, four H atoms and ten O atoms on either side.

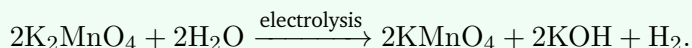
Step 3: Write the electrolytic oxidation reaction At the anode in alkaline medium, manganate loses one electron per ion:



The corresponding salt conversion is $\text{K}_2\text{MnO}_4 \longrightarrow \text{KMnO}_4$ under electrolytic oxidation. Water is reduced at the cathode according to

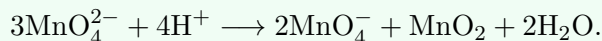


Combining twice the anode equation with the cathode equation gives the overall balanced process:



Thus the green manganate is converted into dark purple permanganate, while the solution remains alkaline.

Step 4: (b)(ii) Explain the change on standing in acidic solution The green manganate solution becomes purple as permanganate forms, and a brown precipitate of manganese dioxide separates. The ionic equation is



Of the three Mn atoms initially in oxidation state +6, two are oxidised to +7, losing two electrons altogether. The third is reduced to +4, gaining those two electrons. This simultaneous oxidation and reduction of manganate is called disproportionation. The equation is charge-balanced: each side has total charge -2 . All three manganese atoms, twelve oxygen atoms and four hydrogen atoms are also conserved.

Step 5: Conclusion $A = \text{MnO}_2$, $B = \text{K}_2\text{MnO}_4$, and $C = \text{KMnO}_4$. Acidified green manganate disproportionates into purple permanganate and brown MnO_2 , according to the balanced ionic

Quick Tip to Solve: Track manganese as $+4 \rightarrow +6 \rightarrow +7$ in preparation; on acidification, +6 splits into +7 and +4, identifying disproportionation.

equation above.

Quick Tip to Solve: Track manganese as $+4 \rightarrow +6 \rightarrow +7$ in preparation; on acidification, $+6$ splits into $+7$ and $+4$, identifying disproportionation.