

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-1-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **35** questions. All questions are **compulsory**.
- (ii) This question paper is divided into **five** Sections – **A, B, C, D** and **E**.
- (iii) In **Section A** – Questions no. **1 to 18** are multiple choice (MCQ) type questions, carrying **1** mark each.
- (iv) In **Section B** – Questions no. **19 to 25** very short answer (VSA) type questions, carrying **2** marks each.
- (v) In **Section C** – Questions no. **26 to 30** are short answer (SA) type questions, carrying **3** marks each.
- (vi) In **Section D** – Questions no. **31 and 32** are case-based questions carrying **4** marks each.
- (vii) In **Section E** – Questions no. **33 to 35** are long answer (LA) type questions carrying **5** marks each.
- (viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section B, 2 questions in Section C, 2 questions in Section D and 2 questions in Section E.
- (ix) Use of calculators is not allowed.

Section A (18 marks)

Questions no. 1 to 18 are Multiple Choice (MCQ) type Questions, carrying 1 mark each.

1. The colligative property used for the determination of molar mass of polymers and proteins is: [1 mark]

- (A) Osmotic pressure
- (B) Depression in freezing point
- (C) Relative lowering in vapour pressure
- (D) Elevation in boiling point

Correct Answer: (A) Osmotic pressure

Solution:

Concept:

- Osmotic pressure obeys $\pi = CRT$, where C is molar concentration, R is the gas constant and T is absolute temperature.
- For solute mass w in solution volume V , molar mass is $M = wRT/(\pi V)$.

Step 1: Compare the measurable effects Polymers and proteins have very large molar masses, so even an appreciable mass produces a very small molar concentration. Their freezing-point depression, boiling-point elevation and relative lowering of vapour pressure are consequently very small and difficult to measure accurately.

Step 2: Choose a suitable measurement Osmotic pressure remains appreciable in dilute macromolecular solutions and can be measured at room temperature. This also avoids heating delicate proteins. The other three options are colligative properties, but their tiny changes make them less suitable for this determination.

Step 3: Conclusion Osmotic pressure is used to determine the molar masses of polymers and proteins. Hence, the correct option is (A).

Quick Tip to Solve: For a very large molar mass, choose the colligative property measurable in dilute solution at room temperature.

2. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to: [1 mark]

- (A) high atmospheric pressure
- (B) low temperature
- (C) low atmospheric pressure
- (D) both low temperature and high atmospheric pressure

Correct Answer: (C) low atmospheric pressure

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the gas partial pressure, x its mole fraction dissolved in liquid and K_H the Henry constant.
- At a fixed temperature, the amount of gas dissolved increases with its partial pressure.

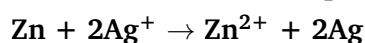
Step 1: Find the pressure change Atmospheric pressure decreases as altitude increases. Since the proportion of oxygen in air is approximately unchanged, the partial pressure of oxygen also decreases. The oxygen supply therefore has a smaller driving pressure for entering the blood.

Step 2: Relate pressure to oxygen concentration By Henry's law, lower oxygen partial pressure gives less dissolved oxygen at the same temperature. This leads to a lower oxygen concentration in blood and tissues. High atmospheric pressure would have the opposite effect, so (A) and (D) fail; low temperature alone in (B) does not explain the altitude effect.

Step 3: Conclusion Low atmospheric pressure is responsible. Hence, the correct option is (C).

Quick Tip to Solve: At high altitude first track oxygen partial pressure: lower pressure means less oxygen dissolved in blood.

3. The correct cell to represent the following reaction is:



[1 mark]

- (A) $2\text{Ag} \mid \text{Ag}^+ \parallel \text{Zn} \mid \text{Zn}^{2+}$
- (B) $\text{Ag}^+ \mid \text{Ag} \parallel \text{Zn}^{2+} \mid \text{Zn}$
- (C) $\text{Ag} \mid \text{Ag}^+ \parallel \text{Zn} \mid \text{Zn}^{2+}$
- (D) $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$

Correct Answer: (D) $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$

Solution:

Concept:

- In cell notation, oxidation at the anode is written on the left and reduction at the cathode on the right.
- A single vertical line denotes a phase boundary; a double line denotes the salt bridge.

Step 1: Identify the half-reactions Zinc loses electrons: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. Silver ions gain electrons: $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$. Thus zinc is the anode and the silver electrode is the cathode.

Quick Tip to Solve: Find the species losing electrons, put its metal-ion pair on the left, and place the reduced metal on the far right.

Step 2: Place the phases in cell order The anode metal and its ions appear as $\text{Zn} \mid \text{Zn}^{2+}$, followed by the salt bridge and $\text{Ag}^+ \mid \text{Ag}$ at the cathode. Options (A) and (C) put silver on the left and also reverse the zinc phase order; (B) has silver on the left and represents the reverse reaction. Stoichiometric coefficients such as 2 are not placed before the electrode metal in standard notation.

Step 3: Conclusion The cell is $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$. Hence, the correct option is (D).

Quick Tip to Solve: Find the species losing electrons, put its metal-ion pair on the left, and place the reduced metal on the far right.

4. ΔG and E°_{cell} for a spontaneous reaction will be:

[1 mark]

- (A) positive, negative
- (B) negative, negative
- (C) negative, positive
- (D) positive, positive

Correct Answer: (C) negative, positive

Solution:

Concept:

- For a cell reaction, $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where n is the electron number and F is Faraday's constant.
- A spontaneous process has negative Gibbs energy change; a galvanic cell has positive cell potential.

Step 1: Determine the Gibbs energy sign For a reaction proceeding spontaneously at constant temperature and pressure, the Gibbs energy decreases, so $\Delta G < 0$. Therefore, the positive Gibbs energy choices (A) and (D) cannot describe a spontaneous reaction.

Step 2: Determine the corresponding cell potential The factor nF is positive, so Gibbs energy and cell potential have opposite signs. For spontaneity under standard conditions, $\Delta G^\circ < 0$ requires $E^\circ_{\text{cell}} > 0$. Choice (B), which gives both signs negative, conflicts with this relation. The question asks for the usual standard-cell sign combination.

Step 3: Conclusion Gibbs energy is negative and standard cell potential is positive. Hence, the correct option is (C).

Quick Tip to Solve: Use the minus sign in $\Delta G^\circ = -nFE^\circ$: the two quantities must have opposite signs.

5. Which of the following is affected by catalyst?

[1 mark]

- (A) ΔH
- (B) ΔG
- (C) E_a
- (D) ΔS

Correct Answer: (C) E_a

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with a lower activation energy E_a .
- ΔH , ΔG and ΔS depend on the reactant and product states, not on the reaction pathway.

Step 1: Identify the kinetic quantity Activation energy is the energy barrier that reactant particles must overcome to react. A catalyst changes the mechanism and reduces this barrier, so a larger fraction of particles can react at a given temperature and the reaction rate increases.

Step 2: Eliminate the thermodynamic quantities The initial reactants and final products remain the same when a catalyst is used. Consequently, their enthalpy, Gibbs energy and entropy differences are unchanged. Thus options (A), (B) and (D) are unaffected, even though the rate changes. A catalyst speeds up attainment of equilibrium without changing its position.

Step 3: Conclusion The activation energy E_a is affected by a catalyst. Hence, the correct option is (C).

Quick Tip to Solve: Separate the reaction barrier from state-function changes: a catalyst lowers the barrier but preserves the endpoints.

6. The order of the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{h\nu} 2\text{HCl}(\text{g})$ is:

[1 mark]

- (A) 2
- (B) 1
- (C) 0
- (D) 3

Correct Answer: (C) 0

Solution:

Concept:

- Reaction order is the sum of concentration powers in the experimental rate law, not the sum of stoichiometric coefficients.
- The light-driven combination of H_2 and Cl_2 is treated as a zero-order photochemical reaction in the standard CBSE example.

Step 1: Identify what controls the rate The symbol $h\nu$ above the arrow indicates that light initiates the reaction. Under the conditions of this zero-order photochemical example, the rate is controlled by the light energy supplied and is independent of the concentrations of hydrogen and chlorine.

Quick Tip to Solve: For this standard photochemical example, look at fixed illumination rather than adding the balanced-equation coefficients.

Step 2: Apply the rate-law definition The rate is written $r = k[\text{H}_2]^0[\text{Cl}_2]^0 = k$ for fixed illumination. The sum of the concentration exponents is therefore zero. Adding the reactant coefficients to obtain 2 is invalid, since the overall equation does not determine reaction order. Neither a first-order nor a third-order concentration dependence is indicated by this standard example.

Step 3: Conclusion The reaction is of zero order. Hence, the correct option is (C).

Quick Tip to Solve: For this standard photochemical example, look at fixed illumination rather than adding the balanced-equation coefficients.

7. The most common and stable oxidation state of a Lanthanoid is:

[1 mark]

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

Correct Answer: (B) +3

Solution:

Concept:

- Lanthanoids most commonly form Ln^{3+} ions by losing two $6s$ electrons and one additional electron.
- Special stability of empty, half-filled or filled $4f$ subshells can permit some +2 or +4 ions.

Step 1: Identify the general oxidation state For the lanthanoid series, removal of three outer electrons produces the characteristic trivalent ions. Their chemistry is therefore dominated by the +3 oxidation state, which occurs throughout the series and is the most common stable state.

Step 2: Compare the alternatives The +2 state occurs for a few members, such as europium, and +4 occurs for a few members, such as cerium, because particular electronic configurations gain extra stability. These exceptions do not replace the general trivalent state. The +6 state is not the characteristic stable oxidation state of lanthanoids.

Step 3: Conclusion The most common and stable lanthanoid oxidation state is +3. Hence, the correct option is (B).

Quick Tip to Solve: Remember lanthanoids as predominantly trivalent; special +2 and +4 configurations are exceptions.

8. The compounds $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ and $[\text{Co}(\text{Br})(\text{NH}_3)_5]\text{SO}_4$ represent:

[1 mark]

- (A) optical isomerism
- (B) linkage isomerism
- (C) ionisation isomerism
- (D) coordination isomerism

Correct Answer: (C) ionisation isomerism

Solution:

Concept:

- Ionisation isomers exchange a ligand inside the coordination sphere with a counter-ion outside it.
- Square brackets identify coordinated ligands; the counter-ion outside the brackets is liberated in solution.

Step 1: Compare the coordination spheres In $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$, sulfate is inside the brackets and bromide is outside. In $[\text{Co}(\text{Br})(\text{NH}_3)_5]\text{SO}_4$, bromide is coordinated and sulfate is the counter-ion. The five ammonia ligands remain unchanged.

Step 2: Identify the exchanged ions The interchange of coordinated sulfate with external bromide changes the ions released on dissolution. This is the characteristic test for ionisation isomerism. Linkage isomerism instead changes the donor atom of the same ambidentate ligand; coordination isomerism exchanges ligands between complex cations and anions. No mirror-image relationship is involved here.

Step 3: Conclusion The compounds represent ionisation isomerism. Hence, the correct option is (C).

Quick Tip to Solve: Compare the species inside and outside the square brackets: their exchange signals ionisation isomerism.

9. The synthesis of alkyl fluoride is best obtained from:

[1 mark]

- (A) Free radicals
- (B) Swartz reaction
- (C) Sandmeyer reaction
- (D) Finkelstein reaction

Correct Answer: (B) Swartz reaction

Solution:

Concept:

- Swarts reaction prepares alkyl fluorides by replacing chlorine or bromine in an alkyl halide with fluorine.
- Metallic fluorides such as AgF , Hg_2F_2 , CoF_2 or SbF_3 supply the fluoride needed for halogen exchange.

Step 1: Select the fluorination reaction Heating an alkyl chloride or bromide with a suitable metallic

Quick Tip to Solve: Associate Swarts with alkyl fluoride and Finkelstein with alkyl iodide before comparing the other choices.

fluoride gives the corresponding alkyl fluoride. For example,



The carbon skeleton is retained while the halogen changes to fluorine.

Step 2: Compare the other methods Finkelstein reaction normally prepares alkyl iodides using NaI in dry acetone. Sandmeyer reaction replaces the diazonium group of an aromatic diazonium salt, typically with chlorine, bromine or cyanide; it is not the standard method for alkyl fluorides. Free-radical fluorination is too vigorous and difficult to control for this selective preparation.

Step 3: Conclusion The required method is Swarts reaction, printed as “Swartz reaction” in the option. Hence, the correct option is (B).

Quick Tip to Solve: Associate Swarts with alkyl fluoride and Finkelstein with alkyl iodide before comparing the other choices.

10. In the reaction $\text{R-OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{RCl} + \text{H}_2\text{O}$, what is the correct order of reactivity of alcohol?

[1 mark]

- (A) $1^\circ < 2^\circ < 3^\circ$
- (B) $1^\circ > 3^\circ > 2^\circ$
- (C) $1^\circ > 2^\circ > 3^\circ$
- (D) $3^\circ > 1^\circ > 2^\circ$

Correct Answer: (A) $1^\circ < 2^\circ < 3^\circ$

Solution:

Concept:

- Concentrated HCl and anhydrous ZnCl_2 form Lucas reagent, which converts alcohols into alkyl chlorides.
- For ordinary primary, secondary and tertiary alcohols, the ease of substitution follows the stability of the developing carbocation: $3^\circ > 2^\circ > 1^\circ$.

Step 1: Examine the role of the reagent ZnCl_2 assists the conversion of the poor leaving hydroxyl group into a group that can leave readily. In the acidic medium, water leaves and chloride replaces it. Tertiary alcohols react fastest because the tertiary carbocation is stabilised most strongly by alkyl groups.

Step 2: Arrange the alcohol classes Secondary alcohols react more slowly than tertiary alcohols, while ordinary primary alcohols react very slowly at room temperature. The increasing order is therefore $1^\circ < 2^\circ < 3^\circ$. Options (B) and (C) incorrectly put primary alcohols first in decreasing reactivity, and (D) incorrectly makes primary alcohols faster than secondary alcohols.

Step 3: Conclusion The correct increasing order is $1^\circ < 2^\circ < 3^\circ$. Hence, the correct option is (A).

Quick Tip to Solve: For Lucas reagent, remember that tertiary alcohol gives immediate turbidity, secondary is slower and primary is slowest.

11. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives:

[1 mark]

- (A) CH_3COONa
- (B) CH_3NH_2
- (C) $\text{CH}_3\text{CH}_2\text{Br}$
- (D) $\text{CH}_3\text{CH}_2\text{NH}_2$

Correct Answer: (B) CH_3NH_2

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine using bromine and sodium hydroxide.
- The product has one fewer carbon atom than the starting amide because the carbonyl carbon is removed.

Step 1: Identify the amide and the reaction The starting compound CH_3CONH_2 is ethanamide. With Br_2 and NaOH , it undergoes Hofmann bromamide degradation rather than simple hydrolysis. The alkyl group attached to the carbonyl carbon becomes attached to nitrogen.

Step 2: Count the product carbons Ethanamide has two carbon atoms, but the carbonyl carbon is lost, so the amine has only one carbon atom. The balanced net reaction is



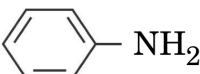
Sodium ethanoate would result from alkaline hydrolysis alone. Bromoethane is not an amine, and ethylamine retains two carbons, so neither is the Hofmann degradation product.

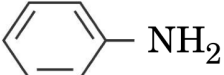
Step 3: Conclusion The product is methylamine, CH_3NH_2 . Hence, the correct option is (B).

Quick Tip to Solve: In Hofmann bromamide degradation, delete the carbonyl carbon and attach the remaining alkyl group directly to nitrogen.

12. Which of the following is least basic?

[1 mark]

- (A) $(\text{CH}_3)_2\text{NH}$
- (B) NH_3
- (C) 
- (D) $(\text{CH}_3)_3\text{N}$

Correct Answer: (C) 

Solution:

Concept:

- A base accepts a proton using an available electron pair; amine basicity depends on the availability of the nitrogen lone pair.

Quick Tip to Solve: First identify a nitrogen attached directly to a benzene ring: its lone pair is delocalised, making aniline weakly basic.

- Resonance in aniline delocalises the nitrogen lone pair into the benzene ring, reducing its availability for protonation.

Step 1: Examine the aromatic amine Option (C), $\text{C}_6\text{H}_5\text{NH}_2$, is aniline. Its nitrogen lone pair participates in conjugation with the aromatic ring. This resonance stabilises the unprotonated molecule, whereas protonation removes that lone pair from conjugation. Proton acceptance is therefore less favourable than in ammonia or the listed methylamines.

Step 2: Compare the remaining bases In ammonia, NH_3 , the lone pair is localised on nitrogen. In dimethylamine and trimethylamine, methyl groups donate electron density through the inductive effect. Although solvation affects the relative basicities of different alkylamines, none of these options has the strong lone-pair delocalisation of aniline. Thus options (A), (B) and (D) are more basic than the aromatic amine.

Step 3: Conclusion Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, is the least basic compound listed. Hence, the correct option is (C).

Quick Tip to Solve: First identify a nitrogen attached directly to a benzene ring: its lone pair is delocalised, making aniline weakly basic.

13. The glycosidic linkage involved in linking the glucose units in amylose part of starch is: [1 mark]

- (A) C_1-C_6 α linkage
- (B) C_1-C_6 β linkage
- (C) C_1-C_4 α linkage
- (D) C_1-C_4 β linkage

Correct Answer: (C) C_1-C_4 α linkage

Solution:

Concept:

- Amylose is the unbranched component of starch, formed from α -D-glucose units.
- An $\alpha(1 \rightarrow 4)$ glycosidic bond connects the anomeric carbon, C_1 , of one glucose unit through oxygen to C_4 of the next.

Step 1: Identify the chain structure Amylose contains a continuous, unbranched chain of glucose residues. Its glucose units are joined by the oxygen bridge formed between the hydroxyl groups associated with carbon 1 of one unit and carbon 4 of the following unit. The configuration at the anomeric carbon is alpha.

Step 2: Distinguish branching and beta bonds A C_1-C_6 alpha linkage occurs at branch points of amylopectin, the branched starch component, rather than along an amylose chain. A C_1-C_4 beta linkage characterises cellulose. The beta C_1-C_6 alternative also does not describe amylose. Hence both the carbon positions and alpha configuration must be selected together.

Step 3: Conclusion Amylose has C_1-C_4 α glycosidic linkages. Hence, the correct option is (C).

Quick Tip to Solve: Remember amylose as an unbranched alpha-1,4 chain; alpha-1,6 links instead identify amylopectin branch points.

14. An α -helix is a structural feature of:

[1 mark]

- (A) Sucrose
- (B) Starch
- (C) Polypeptides
- (D) Nucleotides

Correct Answer: (C) Polypeptides

Solution:

Concept:

- The secondary structure of proteins describes regular folding of the polypeptide backbone, including the α -helix and β -pleated sheet.
- Hydrogen bonding between backbone carbonyl and amide groups stabilises the α -helical arrangement.

Step 1: Identify the helical backbone In an α -helix, a polypeptide chain coils into a regular helix. Hydrogen bonds form between the backbone carbonyl oxygen of one residue and the amide hydrogen of a residue farther along the same chain, commonly four residues ahead. Thus the helix is a feature of protein secondary structure.

Step 2: Eliminate the other biomolecules Sucrose is a disaccharide and has no polypeptide backbone. Starch is a polysaccharide of glucose units; although amylose can adopt a helical arrangement, it is not the protein α -helix. Nucleotides are the building units of nucleic acids, whose helices have a different backbone and bonding pattern. Only polypeptides fit the stated structural feature.

Step 3: Conclusion An α -helix is a structural feature of polypeptides. Hence, the correct option is (C).

Quick Tip to Solve: Link the terms alpha-helix and beta-pleated sheet specifically with the secondary structure of proteins.

15. Assertion (A): -NH_2 group is o- and p-directing in electrophilic substitution reactions.

Reason (R): Aniline cannot undergo Friedel-Crafts reaction.

Select the correct answer:

[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:

- The amino group donates its nitrogen lone pair into the benzene ring by resonance, increasing electron density especially at the ortho and para positions.
- Aniline is a Lewis base; the nitrogen lone pair forms a salt or complex with the Lewis-acid catalyst used for a Friedel-Crafts reaction.

Step 1: Judge Assertion (A) The assertion is true. In aniline, resonance donation from -NH_2 stabilises the intermediates for ortho and para electrophilic substitution more effectively than the meta intermediate. Hence this group is ortho- and para-directing.

Step 2: Judge Reason (R) The reason is also true. Aniline coordinates to AlCl_3 , the Lewis-acid catalyst, through its nitrogen lone pair. The resulting salt or complex strongly deactivates the ring, so aniline does not undergo the usual Friedel-Crafts alkylation or acylation.

Step 3: Test the explanation The failure of Friedel-Crafts reaction follows from interaction with its catalyst; it does not explain the directing effect of a free amino group. That directing effect is explained by resonance donation. Thus (A) is excluded because the explanation link is wrong, and (C) and (D) are excluded because both statements are true.

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

Quick Tip to Solve: For this pair, separate resonance directing effects from the amino-group interaction with the Friedel-Crafts catalyst.

16. Assertion (A): Acetylation of aniline gives a monosubstituted product.

Reason (R): Activating effect of $-\text{NHCOCH}_3$ group is more than that of amino group.

Select the correct answer:

[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:

- Acetylation converts the amino group of aniline into the acetamido group, $-\text{NHCOCH}_3$.
- The nitrogen lone pair in acetanilide is shared with the carbonyl group as well as the ring; its ring-activating effect is therefore weaker than that of $-\text{NH}_2$.

Step 1: Judge Assertion (A) The assertion is true. Acetylation of aniline gives acetanilide, $\text{C}_6\text{H}_5\text{NHCOCH}_3$, which has a single acetamido substituent on the benzene ring. Protection of the amino group by acetylation also controls subsequent electrophilic substitution, favouring a monosubstituted ring product rather than the extensive substitution caused by free aniline.

Step 2: Judge Reason (R) The reason is false. The activating effect of $-\text{NHCOCH}_3$ is less than that of the amino group, not more. The adjacent carbonyl withdraws electron density and competes for the nitrogen lone pair, reducing donation into the aromatic ring.

Step 3: Choose the matching code Since A is true and R is false, codes (A) and (B), which require both statements to be true, do not apply. Code (D) reverses their truth values. The correct combination is therefore code (C).

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

Quick Tip to Solve: An acetyl group protects aniline by reducing nitrogen lone-pair donation to the ring; acetamido is a weaker activator than amino.

17. Assertion (A): The molecularity of the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ appears to be 2.

Reason (R): Two molecules of the reactants are involved in the given elementary reaction.

Select the correct answer:

[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:

- Molecularity counts the reacting species in one elementary step; it is not assigned from the balanced equation of a complex reaction.
- The hydrogen–bromine reaction is a chain reaction with several elementary steps, although its overall equation suggests two reactant molecules.

Step 1: Judge Assertion (A) The assertion says the molecularity *appears* to be 2. This apparent count is true: the overall equation $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ contains one hydrogen molecule and one bromine molecule on its left-hand side. Their stoichiometric coefficients add to $1 + 1 = 2$. This appearance must not be confused with a molecularity of the overall reaction.

Step 2: Judge Reason (R) The reason is false because it calls the given reaction elementary. Formation of hydrogen bromide from hydrogen and bromine proceeds through a radical chain mechanism with several steps. The displayed equation represents the overall chemical change, not one elementary collision involving exactly those two molecules.

Step 3: Test the explanation and select the code An apparent count from the equation does not establish an elementary mechanism. Thus the reason cannot explain the assertion: its premise is false. Options (A) and (B) incorrectly call R true, while (D) incorrectly calls A false. The printed wording therefore gives the true-A, false-R combination.

Step 4: Conclusion the assertion, with the word “appears, is true, but the reason is false. The correct option is (C).

Quick Tip to Solve: Do not assign molecularity from an overall equation: the hydrogen–bromine reaction is a chain reaction, despite its apparent count of two.

18. Assertion (A): Low spin tetrahedral complexes are rarely observed.

Reason (R): Crystal field splitting energy is less than pairing energy for tetrahedral complexes.

Select the correct answer:

[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:

- Crystal-field splitting separates tetrahedral d orbitals into lower-energy e and higher-energy t_2 sets; the gap is Δ_t .
- Pairing energy P is the energy needed to pair electrons in one orbital. When $\Delta_t < P$, occupying a higher orbital costs less than pairing.

Step 1: Judge Assertion (A) The assertion is true. Tetrahedral complexes generally have small crystal-field splitting and consequently favour high-spin arrangements wherever distinct high- and low-spin configurations are possible. Low-spin tetrahedral complexes are therefore rarely observed.

Step 2: Judge Reason (R) The reason is true in the usual tetrahedral case: $\Delta_t < P$. For comparable metal ions and ligands, tetrahedral splitting is approximately $\Delta_t = \frac{4}{9}\Delta_o$, where Δ_o is the octahedral splitting. Thus it is generally too small to induce electron pairing.

Step 3: Test whether R explains A Because entering a higher-energy tetrahedral orbital costs less energy than pairing in a lower orbital, electrons remain unpaired as far as possible. This directly produces the high-spin preference and explains why low-spin arrangements are rare. Code (B) incorrectly denies this explanatory connection; (C) and (D) incorrectly reject a true statement.

Step 4: Conclusion Both Assertion (A) and Reason (R) are true, and Reason (R) correctly explains Assertion (A). The correct option is (A).

Quick Tip to Solve: Compare Δ_t with pairing energy: the smaller splitting favours occupation of higher orbitals and hence high spin.

Section B (14 marks)

19. What is Henry's law? Give one application of it.

[2 marks]

Solution:

Concept:

- At constant temperature, the amount of a gas dissolved in a liquid increases with its partial pressure above the liquid.
- Henry's law is $p = K_H x$, where p is gas partial pressure, x its mole fraction in solution and K_H the Henry-law constant for that gas, solvent and temperature.

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

$$p = K_H x \quad \text{or} \quad x = \frac{p}{K_H}.$$

Holding the temperature fixed keeps K_H fixed, so increasing p increases the gas solubility expressed by x . The pressure here is the partial pressure of the particular gas, rather than the total pressure of an arbitrary gas mixture.

Step 2: Give an application: carbonated drinks Soft drinks and soda water are bottled under a high pressure of carbon dioxide. The high CO_2 partial pressure makes a larger amount dissolve in the liquid. Opening the bottle lowers the pressure above the drink, so its equilibrium carbon dioxide solubility falls and excess gas escapes as bubbles. This is why the bottle is sealed under pressure during manufacture.

Step 3: Conclusion Henry's law is $p = K_H x$ at constant temperature. An application is dissolving carbon dioxide in soft drinks by bottling them under high pressure.

Quick Tip to Solve: For a sealed soda bottle, use $x = p/K_H$: higher carbon dioxide pressure means more dissolved gas; opening reverses this.

20(a). On diluting two electrolytes 'A' and 'B', the Λ_m of 'A' increases 25 times while that of 'B' increases by 1.5 times. Which of the two electrolytes is strong? Justify your answer graphically.

[2 marks]

Solution:

Concept:

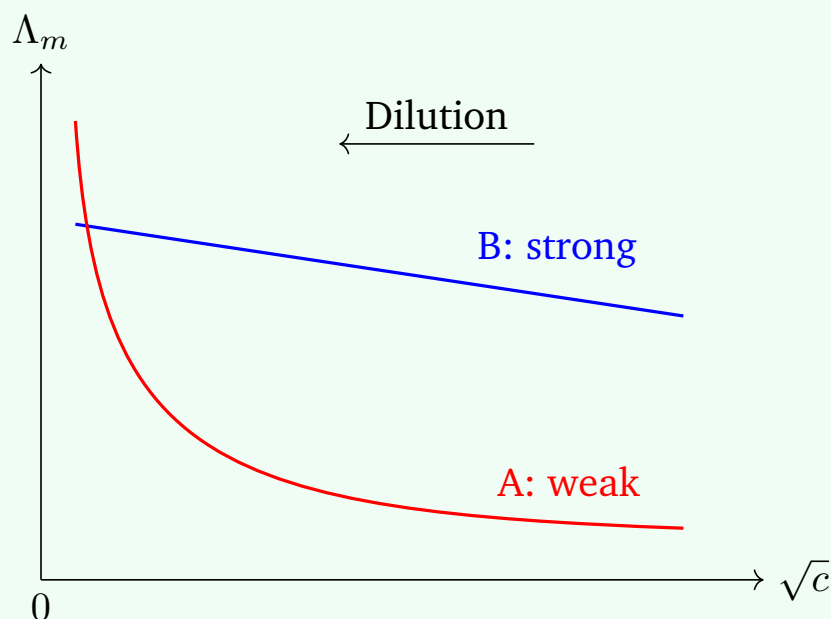
- Molar conductivity Λ_m measures the conductance associated with one mole of electrolyte and increases on dilution.
- A strong electrolyte is already almost completely dissociated; dilution mainly reduces interionic interactions. A weak electrolyte also undergoes a large increase in ionisation.
- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - K\sqrt{c}$, with concentration c , limiting molar conductivity Λ_m° , and a positive constant K .

Step 1: Compare the increases on dilution Electrolyte A shows a very large, 25-fold increase in Λ_m .

Quick Tip to Solve: On a Λ_m versus $\sqrt{c}$ graph, dilution moves left: a modest straight-line rise indicates the strong electrolyte B.

This indicates a substantial rise in the number of ions supplied per mole as dilution increases its degree of ionisation, characteristic of a weak electrolyte. Electrolyte B shows only a 1.5-fold increase. Its ions already exist in solution to a large extent, and dilution mainly increases their mobility by reducing interionic interactions.

Step 2: Justify with the conductivity graph Plot Λ_m against $\sqrt{c}$. For the strong electrolyte B, the dilute-solution plot is approximately a straight line with negative slope; dilution means moving left, towards smaller $\sqrt{c}$, and gives a gradual increase in Λ_m . For the weak electrolyte A, the curve rises sharply towards very low concentration because ionisation increases markedly. The schematic graph shows the distinct trends; it does not imply specific measured concentrations or a common numerical limiting conductivity.



Schematic molar conductivity trends: dilution proceeds towards lower concentration.

Step 3: Conclusion Electrolyte B is strong; electrolyte A is weak. The modest 1.5-fold increase for B and steep increase for A on dilution are consistent with their respective straight and curved conductivity plots.

Quick Tip to Solve: On a Λ_m versus $\sqrt{c}$ graph, dilution moves left: a modest straight-line rise indicates the strong electrolyte B.

20(b). The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate the conductivity. [2 marks]

Solution:

Concept:

- Conductivity is the reciprocal of resistivity: $\kappa = 1/\rho$. For a uniform solution column, $R = \rho l/A$, so $\kappa = l/(RA)$, where l is its length and A its cross-sectional area.
- The cell constant is l/A . When lengths are in centimetres and resistance in ohms, conductivity is obtained in S cm^{-1} .

Step 1: Calculate the cross-sectional area The diameter is $d = 1 \text{ cm}$, so the radius is $r = d/2 = 0.5 \text{ cm}$. Thus,

$$A = \pi r^2 = \pi(0.5)^2 = 0.7854 \text{ cm}^2.$$

The length of the solution column is $l = 50 \text{ cm}$, giving a cell constant $l/A = 50/0.7854 = 63.66 \text{ cm}^{-1}$.

Step 2: Substitute the resistance in the conductivity relation Using $R = 5.55 \times 10^3 \Omega$,

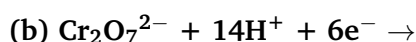
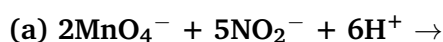
$$\kappa = \frac{l/A}{R} = \frac{63.66}{5.55 \times 10^3} = 1.147 \times 10^{-2} \text{ S cm}^{-1}.$$

The given concentration is not needed here because the question asks for conductivity, which follows directly from the resistance and geometry. It would be needed for a calculation of molar conductivity.

Step 3: Conclusion The conductivity of the NaOH solution is $\kappa \approx 1.15 \times 10^{-2} \text{ S cm}^{-1}$, equivalent to 1.15 S m^{-1} .

Quick Tip to Solve: Halve the diameter before calculating area, and use centimetres consistently to obtain conductivity in S cm^{-1} .

21. Complete the following equations:



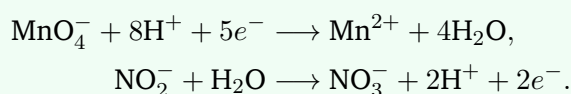
[2 marks]

Solution:

Concept:

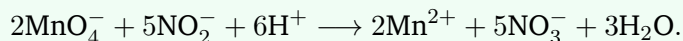
- In an acidic medium, permanganate is reduced from Mn(VII) to Mn^{2+} , while nitrite is oxidised from N(III) to nitrate, N(V).
- Balance redox equations by conserving atoms and total charge. In acidic solution, use H_2O to balance oxygen, H^+ to balance hydrogen, and electrons to balance charge.

Step 1: Complete the permanganate–nitrite reaction The reduction and oxidation half-reactions are



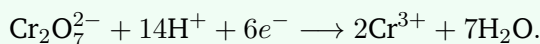
Quick Tip to Solve: In acidic medium, remember the terminal ions Mn^{2+} and Cr^{3+} , then check charge as well as atoms.

Multiply the first by 2 and the second by 5, add them and cancel electrons, water and hydrogen ions. This gives



Both sides have total charge -1 and contain the same numbers of Mn, N, O and H atoms.

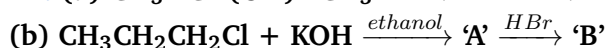
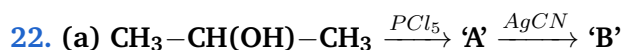
Step 2: Complete the dichromate reduction half-reaction Each chromium atom changes from oxidation state $+6$ to $+3$. The two chromium atoms therefore gain six electrons in total. The seven oxygen atoms form seven water molecules using the fourteen hydrogen ions supplied:



The net charge on the left is $-2 + 14 - 6 = +6$, equal to that of 2Cr^{3+} on the right.

Step 3: Conclusion The required products are (a) $2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$ and (b) $2\text{Cr}^{3+} + 7\text{H}_2\text{O}$.

Quick Tip to Solve: In acidic medium, remember the terminal ions Mn^{2+} and Cr^{3+} , then check charge as well as atoms.



Identify 'A' and 'B' in the above reactions.

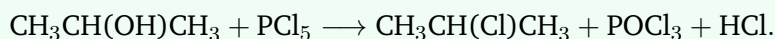
[2 marks]

Solution:

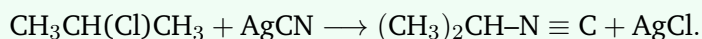
Concept:

- PCl_5 converts an alcohol into the corresponding chloroalkane by replacing its $-\text{OH}$ group with $-\text{Cl}$. Covalent AgCN reacts predominantly through nitrogen to form an isocyanide, $\text{R}-\text{N} \equiv \text{C}$.
- Alcoholic KOH promotes elimination of HCl from a haloalkane to form an alkene. In the absence of peroxide, HBr adds to an unsymmetrical alkene according to Markovnikov's rule.

Step 1: Identify the products of sequence (a) The starting alcohol is propan-2-ol. Replacement of its hydroxyl group by chlorine gives 2-chloropropane:

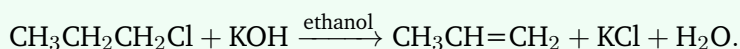


Thus, $\text{A} = \text{CH}_3\text{CH}(\text{Cl})\text{CH}_3$. Reaction with AgCN gives the isocyanide, since nitrogen is the attacking end:



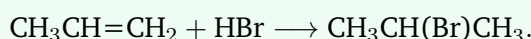
Hence B is isopropyl isocyanide (propan-2-yl isocyanide). A nitrile with a carbon-carbon bond to CN would instead be the usual product with KCN .

Step 2: Identify the products of sequence (b) Ethanolic KOH removes a hydrogen from the carbon adjacent to the chlorine-bearing carbon of 1-chloropropane, eliminating HCl :



Quick Tip to Solve: Check both the cyanide reagent and the KOH solvent: AgCN gives an isocyanide, while ethanolic KOH gives elimination.

Therefore A is propene. Addition of HBr puts hydrogen on the terminal carbon and bromine on the more substituted middle carbon:



Thus B is 2-bromopropane; the peroxide effect does not apply because no peroxide is specified.

Step 3: Conclusion In (a), $A = \text{CH}_3\text{CH}(\text{Cl})\text{CH}_3$, $B = (\text{CH}_3)_2\text{CH}-\text{N} \equiv \text{C}$. In (b), $A = \text{CH}_3\text{CH}=\text{CH}_2$, $B = \text{CH}_3\text{CH}(\text{Br})\text{CH}_3$.

Quick Tip to Solve: Check both the cyanide reagent and the KOH solvent: AgCN gives an isocyanide, while ethanolic KOH gives elimination.

23(a). Account for the following:

(i) Phenol is a stronger acid than an alcohol.

(ii) The boiling point of alcohols decreases with increase in branching of alkyl chain.

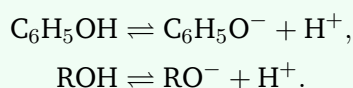
[2 marks]

Solution:

Concept:

- Acid strength depends on the stability of the conjugate base formed after loss of H^+ . Greater stabilisation of the conjugate base favours acid dissociation.
- Boiling requires overcoming intermolecular attractions. Among isomeric alcohols, branching makes molecules more compact and reduces their effective surface area for intermolecular contact.

Step 1: Explain why phenol is more acidic than an alcohol The dissociation equilibria can be written as



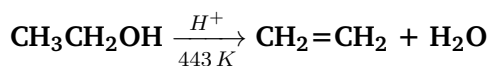
In the phenoxide ion, the negative charge is delocalised by resonance over oxygen and the ortho and para carbon atoms of the benzene ring. This stabilises the conjugate base. An alkoxide ion has no such resonance stabilisation; its negative charge remains localised on oxygen. The alkyl group's electron-releasing inductive effect further increases electron density on that oxygen. Therefore phenol loses a proton more readily than an alcohol.

Step 2: Explain the effect of branching on boiling point For alcohols of comparable molecular mass, increased branching makes the alkyl portion more compact and reduces the surface area available for contact between molecules. Consequently, London dispersion forces become weaker. Although alcohol molecules form hydrogen bonds through their hydroxyl groups, the reduced dispersion attraction lowers the overall intermolecular cohesion as branching increases. Less energy is then required to separate the molecules into the vapour phase, so the boiling point decreases.

Step 3: Conclusion (i) Phenol is the stronger acid because its conjugate base, phenoxide, is resonance-stabilised, whereas an alkoxide is not. (ii) Increased branching reduces molecular surface contact and dispersion forces, thereby lowering the boiling point of comparable alcohols.

Quick Tip to Solve: For acidity compare the conjugate bases; for branching and boiling point compare the molecular surface area and dispersion forces.

23(b). (i) Write the mechanism of the following reaction:



(ii) Write the equation involved in Reimer-Tiemann reaction.

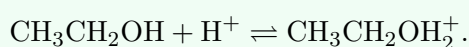
[2 marks]

Solution:

Concept:

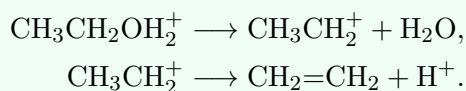
- Acid-catalysed dehydration removes water from an alcohol to form an alkene; protonation converts the hydroxyl group into a better leaving group.
- The Reimer-Tiemann reaction introduces a formyl group into phenol, mainly at the ortho position, using chloroform and aqueous sodium hydroxide followed by acidification.

Step 1: (i) Protonate ethanol The oxygen atom accepts a proton from the acid catalyst:



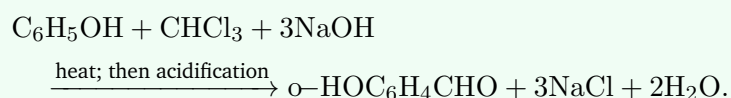
The protonated hydroxyl group can leave as neutral water.

Step 2: (i) Eliminate water and regenerate the acid In the standard stepwise mechanism, loss of water is followed by loss of a proton from the adjacent carbon:



Thus ethene is formed at 443 K, and H^+ is regenerated.

Step 3: (ii) Write the Reimer-Tiemann equation Phenol reacts with chloroform in aqueous alkali on heating. After acid work-up, the major product is salicylaldehyde (2-hydroxybenzaldehyde). The net equation is



A small amount of the para-formyl product may also form.

Step 4: Conclusion (i) Ethanol undergoes protonation, water loss and deprotonation to give ethene. (ii) Reimer-Tiemann reaction gives mainly *o*-hydroxybenzaldehyde from phenol.

Quick Tip to Solve: For dehydration, show regeneration of H^+ ; for Reimer-Tiemann, place $-\text{CHO}$ ortho to $-\text{OH}$.

24. Explain briefly:

(a) Carbylamine reaction

(b) Gabriel phthalimide synthesis

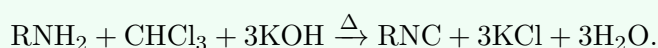
[2 marks]

Solution:

Concept:

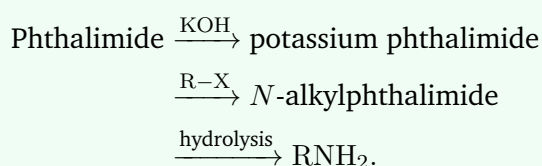
- Only primary amines give the carbylamine test: heating with chloroform and alcoholic alkali produces a foul-smelling isocyanide.
- Gabriel synthesis uses the nucleophilic nitrogen of potassium phthalimide to prepare primary aliphatic amines from alkyl halides.

Step 1: (a) Carbylamine reaction An aliphatic or aromatic primary amine reacts with chloroform and alcoholic potassium hydroxide on heating to give an isocyanide:



The unpleasant odour of RNC is the characteristic positive test. Secondary and tertiary amines do not undergo this reaction.

Step 2: (b) Gabriel phthalimide synthesis Phthalimide is treated with alcoholic KOH to form potassium phthalimide. This salt reacts with an alkyl halide R–X by nucleophilic substitution, producing *N*-alkylphthalimide. Hydrolysis then releases RNH₂:



Here R is an alkyl group and X is a halogen. The reaction gives a primary aliphatic amine without further alkylation of the liberated amine. Aryl halides do not normally undergo this substitution, so aromatic primary amines cannot be prepared by this method.

Step 3: Conclusion Carbylamine reaction identifies primary amines by isocyanide formation. Gabriel synthesis prepares primary aliphatic amines through *N*-alkylphthalimide.

Quick Tip to Solve: Remember the distinction: aromatic primary amines give the carbylamine test, but Gabriel synthesis does not prepare them.

25. (a) Write chemical reaction to show that open structure of D-glucose contains the straight chain.

(b) What type of linkage is responsible for the formation of protein?

[2 marks]

Solution:

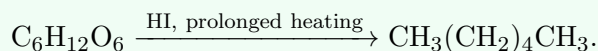
Concept:

- Prolonged heating of glucose with hydrogen iodide removes its oxygen-containing groups and gives *n*-hexane, revealing its unbranched six-carbon skeleton.

Quick Tip to Solve: Use the specific product *n*-hexane as the evidence, and write the peptide linkage in its carbonyl-containing form.

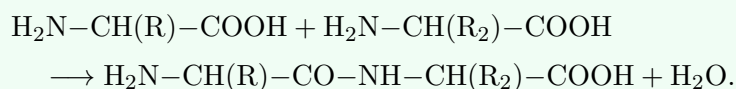
- A peptide linkage, $-\text{CO} - \text{NH}-$, joins amino-acid residues through condensation of a carboxyl group and an amino group.

Step 1: (a) Establish the straight carbon chain On prolonged heating with hydrogen iodide, D-glucose is converted into *n*-hexane:



The product has all six carbon atoms arranged in one unbranched chain. This reaction therefore provides evidence that the carbon skeleton of open-chain D-glucose is straight, rather than branched. It establishes the skeleton; it does not by itself determine the positions of all the hydroxyl groups.

Step 2: (b) Identify the linkage in proteins Proteins contain peptide bonds, also called amide linkages. The $-\text{COOH}$ group of one amino acid reacts with the $-\text{NH}_2$ group of another, eliminating water:



Repeated condensation produces the polypeptide backbone, whose successive residues are joined through $-\text{CO} - \text{NH}-$.

Step 3: Conclusion (a) Glucose gives *n*-hexane on prolonged heating with HI, indicating a straight six-carbon chain. (b) The linkage responsible for protein formation is the peptide bond, $-\text{CO} - \text{NH}-$.

Quick Tip to Solve: Use the specific product *n*-hexane as the evidence, and write the peptide linkage in its carbonyl-containing form.

Section C (15 marks)

26. (a) Differentiate between Ideal solution and Non-ideal solution.

(b) 30 g of urea is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg. [3 marks]

Solution:

Concept:

- An ideal solution obeys Raoult's law over the entire composition range; mixing has $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$.
- For a non-volatile solute, $p_{\text{water}} = x_{\text{water}} p_{\text{water}}^\circ$, where x_{water} is the mole fraction of water and p_{water}° its pure vapour pressure.

Step 1: (a) Compare ideal and non-ideal solutions An ideal solution obeys $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$ throughout its composition range. Its unlike-molecule interactions $A-B$ are approximately as strong as $A-A$ and $B-B$ interactions, and both enthalpy and volume changes on mixing are zero. A non-ideal solution departs from Raoult's law. Its unlike-molecule interactions differ appreciably from like-molecule interactions, so ΔH_{mix} and ΔV_{mix} are generally nonzero. Weaker unlike interactions give positive deviation; stronger unlike interactions give negative deviation.

Quick Tip to Solve: Convert masses to moles before forming the mole fraction; use the water mole fraction, not the urea mole fraction, for vapour pressure.

Step 2: (b) Calculate the mole fraction of water Urea is non-volatile. Taking molar masses as 60 g mol^{-1} for urea and 18 g mol^{-1} for water,

$$\begin{aligned}n_{\text{urea}} &= \frac{30}{60} = 0.50 \text{ mol}, \\n_{\text{water}} &= \frac{846}{18} = 47.0 \text{ mol}, \\x_{\text{water}} &= \frac{47.0}{47.0 + 0.50} = \frac{94}{95}.\end{aligned}$$

The denominator contains the moles of both components.

Step 3: (b) Apply Raoult's law Using the given pure-water vapour pressure at 298 K,

$$\begin{aligned}p_{\text{water}} &= x_{\text{water}} p_{\text{water}}^{\circ} \\&= \frac{94}{95} \times 23.8 \\&= 23.5495 \text{ mm Hg} \approx 23.55 \text{ mm Hg}.\end{aligned}$$

As a check, adding a non-volatile solute must lower the solvent vapour pressure below 23.8 mm Hg, which this value does.

Step 4: Conclusion (a) Ideal solutions obey Raoult's law with zero enthalpy and volume changes on mixing; non-ideal solutions show deviations. (b) The vapour pressure of water in the solution is 23.55 mm Hg.

Quick Tip to Solve: Convert masses to moles before forming the mole fraction; use the water mole fraction, not the urea mole fraction, for vapour pressure.

27. Write the main product formed when:

- (a) Methyl chloride is treated with NaI/Acetone.
- (b) 2,4,6-trinitrochlorobenzene is subjected to hydrolysis.
- (c) n-Butyl chloride is treated with alcoholic KOH.

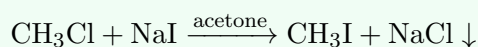
[3 marks]

Solution:

Concept:

- Sodium iodide in dry acetone brings about halogen exchange (the Finkelstein reaction), replacing chlorine in an alkyl chloride by iodine.
- Nitro groups at the ortho and para positions activate an aryl chloride towards nucleophilic substitution; hydrolysis replaces chlorine by hydroxyl.
- Alcoholic KOH favours elimination of hydrogen halide from a haloalkane. Hydrogen is removed from a carbon adjacent to the carbon carrying the halogen.

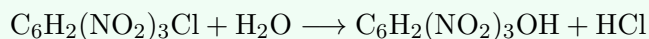
Step 1: (a) Halogen exchange in methyl chloride Iodide ion substitutes for chloride ion in methyl chloride:



Quick Tip to Solve: Identify the reagent first: NaI/acetone exchanges halogens, hydrolysis replaces Cl by OH, and alcoholic KOH forms an alkene.

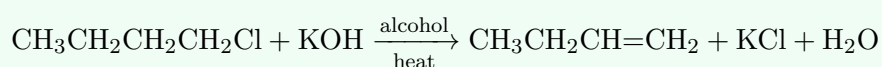
The product is methyl iodide (iodomethane). Sodium chloride is insoluble in acetone and precipitates, helping the reaction proceed towards the products.

Step 2: (b) Hydrolysis of the activated aryl chloride The three electron-withdrawing nitro groups make the chlorine-bearing ring carbon susceptible to attack by hydroxide. Hydrolysis, followed by acidification if an alkaline medium is used, gives 2,4,6-trinitrophenol:



This product is commonly called picric acid. The positions of the nitro groups remain 2, 4 and 6 relative to the new hydroxyl group.

Step 3: (c) Elimination from n-butyl chloride In 1-chlorobutane, the carbon adjacent to the chlorine-bearing terminal carbon is carbon 2. Alcoholic KOH removes a hydrogen from carbon 2 while chlorine leaves carbon 1:



A double bond therefore forms between carbons 1 and 2, giving but-1-ene. Aqueous KOH would instead favour substitution to an alcohol.

Step 4: Conclusion The main products are (a) methyl iodide, CH_3I ; (b) picric acid, or 2,4,6-trinitrophenol; and (c) but-1-ene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$.

Quick Tip to Solve: Identify the reagent first: NaI/acetone exchanges halogens, hydrolysis replaces Cl by OH, and alcoholic KOH forms an alkene.

28. How do you convert the following: (Any three)

(a) Phenol to picric acid

(b) Propanone to 2-Methylpropan-2-ol

(c) Phenol to anisole

(d) Propene to Propan-1-ol

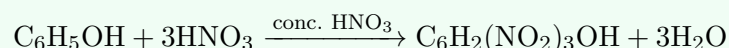
[3 marks]

Solution:

Concept:

- Exhaustive nitration of phenol at its ortho and para positions gives picric acid.
- Grignard addition to a carbonyl group followed by acidic hydrolysis gives an alcohol.
- Williamson ether synthesis couples a phenoxide ion with a primary alkyl halide. Hydroboration-oxidation adds water across an alkene with anti-Markovnikov orientation.

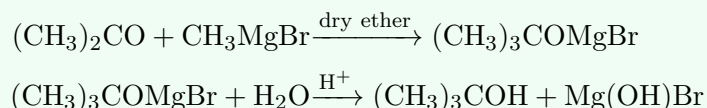
Step 1: (a) Phenol to picric acid Treat phenol with concentrated nitric acid to introduce nitro groups at both ortho positions and the para position:



The product is 2,4,6-trinitrophenol, called picric acid.

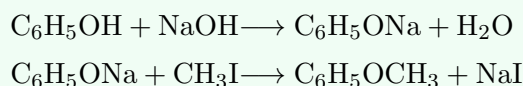
Quick Tip to Solve: To obtain the terminal alcohol from propene, use hydroboration-oxidation; ordinary acid-catalysed hydration gives the wrong positional isomer.

Step 2: (b) Propanone to 2-methylpropan-2-ol React propanone with methylmagnesium bromide in dry ether, then hydrolyse the resulting alkoxide with dilute acid:



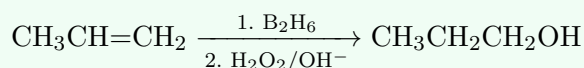
The added methyl group gives a four-carbon tertiary alcohol.

Step 3: (c) Phenol to anisole First form sodium phenoxide, then methylate it with methyl iodide:



This Williamson reaction gives anisole (methoxybenzene).

Step 4: (d) Propene to propan-1-ol Carry out hydroboration with diborane, followed by oxidation using hydrogen peroxide in alkaline solution:



Boron attaches to the terminal carbon and is replaced by OH during oxidation, giving propan-1-ol. Acid-catalysed hydration would instead give propan-2-ol.

Step 5: Conclusion The required routes are (a) nitration with concentrated HNO_3 , (b) CH_3MgBr in dry ether followed by acidic hydrolysis, (c) sodium phenoxide followed by CH_3I , and (d) hydroboration–oxidation. Any three of these conversions may be written.

Quick Tip to Solve: To obtain the terminal alcohol from propene, use hydroboration–oxidation; ordinary acid-catalysed hydration gives the wrong positional isomer.

29(a). Explain why:

- (i) Carboxyl group in benzoic acid is meta directing.
- (ii) Sodium bisulphite is used for the purification of aldehydes and ketones.
- (iii) Carboxylic acids do not give characteristic reactions of carbonyl group.

[3 marks]

Solution:

Concept:

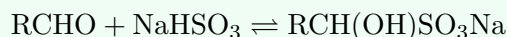
- Electrophilic aromatic substitution is directed by the relative stability of the intermediate carbocations. Electron-withdrawing groups generally deactivate the ring.
- Aldehydes and suitable ketones form crystalline addition compounds with sodium hydrogen sulphite (sodium bisulphite), and this reaction can be reversed.
- Resonance within a carboxyl group reduces the electrophilicity of its carbonyl carbon compared with that of an aldehyde or ketone.

Step 1: (i) Why the carboxyl group directs substitution to meta The $-\text{COOH}$ group withdraws

Quick Tip to Solve: Distinguish the two resonance effects: COOH withdraws electrons from a benzene ring, while its OH oxygen donates into its own carbonyl group.

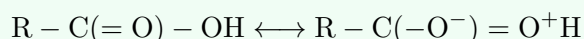
electron density from the benzene ring through both its negative inductive effect and its negative resonance effect. For attack at an ortho or para position, the intermediate has a resonance contributor with positive charge on the ring carbon attached to the electron-withdrawing carboxyl group. The meta intermediate avoids this unfavourable contributor, so meta substitution is favoured.

Step 2: (ii) Why sodium bisulphite is useful for purification Aldehydes and ketones that undergo this reaction form crystalline bisulphite addition compounds:



For a ketone, the analogous adduct is $\text{RR}'\text{C(OH)SO}_3\text{Na}$. The solid adduct can be separated by filtration from impurities that do not form such compounds, and washed. Treatment of the purified adduct with dilute acid or alkali decomposes it and regenerates the original carbonyl compound.

Step 3: (iii) Why carboxylic acids lack the usual carbonyl addition reactions In a carboxylic acid, a lone pair on the hydroxyl oxygen is delocalised into the carbonyl group:



This resonance donation reduces the positive character, and therefore the electrophilicity, of the carbonyl carbon. Consequently, carboxylic acids do not show the characteristic nucleophilic addition reactions of aldehydes and ketones, such as ordinary cyanohydrin or bisulphite-adduct formation.

Step 4: Conclusion (i) The electron-withdrawing $-\text{COOH}$ group destabilises ortho/para intermediates more than the meta intermediate. (ii) Reversible crystalline bisulphite-adduct formation allows separation and recovery of a pure carbonyl compound. (iii) Carboxyl-group resonance reduces carbonyl electrophilicity, suppressing characteristic aldehyde/ketone addition reactions.

Quick Tip to Solve: Distinguish the two resonance effects: COOH withdraws electrons from a benzene ring, while its OH oxygen donates into its own carbonyl group.

OR

29(b). An organic compound 'A', having the molecular formula $\text{C}_3\text{H}_8\text{O}$ on treatment with Cu at 573 K, gives 'B'. 'B' does not reduce Fehling's solution but gives a yellow precipitate of the compound 'C' with I_2/NaOH . Deduce the structures of A, B and C.

[3 marks]

Solution:

Concept:

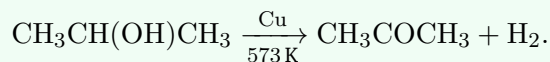
- Alcohol vapours passed over heated copper at 573 K undergo dehydrogenation: a primary alcohol forms an aldehyde, whereas a secondary alcohol forms a ketone.
- Fehling's solution is reduced by aliphatic aldehydes but not by ordinary ketones. A methyl ketone, containing $\text{CH}_3\text{CO}-$, gives yellow iodoform, CHI_3 , with I_2/NaOH .

Step 1: Identify the carbonyl compound B The formula $\text{C}_3\text{H}_8\text{O}$ permits propan-1-ol and propan-2-ol as alcohols. Dehydrogenation of propan-1-ol would give propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, which would reduce

Quick Tip to Solve: Combine a negative Fehling test with a positive iodoform test to identify a methyl ketone, then work backward to its secondary alcohol.

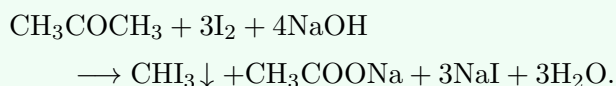
Fehling's solution. Since B does not reduce this reagent, B is the ketone propanone, CH_3COCH_3 . Its methyl ketone group also accounts for the positive iodoform test. An ether of this formula cannot account for the stated alcohol-to-carbonyl conversion.

Step 2: Deduce A from the copper reaction Propanone is formed by removing two hydrogen atoms from the secondary alcohol propan-2-ol, one from the hydroxyl group and one from its carbon:



Thus A has its hydroxyl group attached to the middle carbon, rather than to a terminal carbon.

Step 3: Identify the yellow precipitate C Propanone reacts with iodine in alkali to give iodoform and sodium ethanoate:



The precipitate is the carbon bonded to one hydrogen and three iodine atoms. The soluble ethanoate salt is a coproduct, not the yellow solid.

Step 4: Conclusion $\boxed{\text{A} = \text{CH}_3\text{CH}(\text{OH})\text{CH}_3}$ (propan-2-ol), $\boxed{\text{B} = \text{CH}_3\text{COCH}_3}$ (propanone), and $\boxed{\text{C} = \text{CHI}_3}$ (iodoform).

Quick Tip to Solve: Combine a negative Fehling test with a positive iodoform test to identify a methyl ketone, then work backward to its secondary alcohol.

30. (a) What are the hydrolysis products of (i) Lactose, (ii) Maltose?

(b) Give the basic structural difference between starch and cellulose.

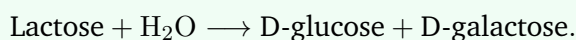
[3 marks]

Solution:

Concept:

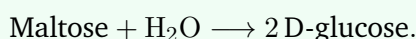
- Hydrolysis breaks the glycosidic linkage of a disaccharide by adding water and releases its constituent monosaccharides.
- Starch and cellulose are glucose polymers, but the configuration of glucose and the glycosidic linkages differ. These differences determine their chain shapes and properties.

Step 1: Give the hydrolysis products of lactose Lactose is composed of a D-galactose unit and a D-glucose unit. On hydrolysis its glycosidic bond breaks, giving one molecule of each:



Hence the two monosaccharides released are glucose and galactose; lactose does not yield two glucose molecules.

Step 2: Give the hydrolysis products of maltose Maltose contains two D-glucose units joined by an $\alpha(1 \rightarrow 4)$ glycosidic bond. Hydrolysis adds water across this bond and produces two molecules of D-glucose:



Quick Tip to Solve: Remember lactose as glucose plus galactose, maltose as glucose plus glucose, and distinguish starch from cellulose by alpha versus beta linkages.

Both lactose and maltose are disaccharides, but their different constituent units explain the difference in hydrolysis products.

Step 3: Compare the basic structures of starch and cellulose Starch is a polymer of α -D-glucose. Its amylose component contains $\alpha(1 \rightarrow 4)$ linkages and forms a helical chain. Amylopectin contains $\alpha(1 \rightarrow 4)$ linkages in its chains and $\alpha(1 \rightarrow 6)$ linkages at branch points. Cellulose, in contrast, consists of β -D-glucose units joined by $\beta(1 \rightarrow 4)$ linkages, forming straight, unbranched chains. Thus the fundamental distinction is the alpha linkage in starch versus the beta linkage in cellulose, rather than a different elemental composition.

Step 4: Conclusion (a) Lactose yields D-glucose and D-galactose; maltose yields two D-glucose molecules. (b) Starch has α -glucose units with alpha glycosidic bonds, whereas cellulose has β -glucose units with $\beta(1 \rightarrow 4)$ bonds.

Quick Tip to Solve: Remember lactose as glucose plus galactose, maltose as glucose plus glucose, and distinguish starch from cellulose by alpha versus beta linkages.

Section D (8 marks)

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

31(i). Case Study: The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. Mathematical representation of rate of reaction is given by rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation.

(i) What is average rate of reaction?

[1 mark]

Solution:

Concept:

- Average rate measures the change in concentration over a finite time interval. Reactant concentration decreases, so its change is taken with a negative sign to give a positive rate.
- For a reaction $aA \rightarrow bB$, division by the stoichiometric coefficient gives a single reaction rate independent of which species is measured.

Step 1: Select a finite time interval Let concentrations be measured at times t_1 and t_2 . The elapsed time is $\Delta t = t_2 - t_1$, and the concentration change is the final concentration minus the initial concentration, $\Delta[A] = [A]_{t_2} - [A]_{t_1}$.

Step 2: Express the rate using the concentration change For a reactant A, its average rate of disappearance is $-\Delta[A]/\Delta t$; for a product B, its average rate of appearance is $\Delta[B]/\Delta t$. These expressions refer to a whole time interval, unlike instantaneous rate, which refers to one instant. For $aA \rightarrow bB$, the average reaction rate is

$$r_{av} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t}.$$

Quick Tip to Solve: Use final minus initial concentration and place a minus sign before a reactant's change to keep the reaction rate positive.

Step 3: Conclusion Average rate is the decrease in reactant concentration or increase in product concentration per unit time over a specified finite time interval, with stoichiometric normalization when required.

Quick Tip to Solve: Use final minus initial concentration and place a minus sign before a reactant's change to keep the reaction rate positive.

31(ii). Write two factors that affect the rate of reaction.

[1 mark]

Solution:

Concept:

- A chemical reaction requires effective collisions between reacting particles. Collision frequency and the fraction of collisions with sufficient energy affect its rate.
- The rate law relates rate to reactant concentration, while the rate constant depends on temperature.

Step 1: State the concentration factor The concentration of reactants affects reaction rate. Increasing concentration generally brings more reacting particles into a given volume and increases collision frequency. The precise concentration dependence is specified by the reaction's rate law; for example, $r = k[A]$ shows a direct dependence on $[A]$. A zero-order reaction is a special case in which rate is independent of reactant concentration over its zero-order range.

Step 2: State the temperature factor Temperature affects reaction rate. Raising temperature generally increases the fraction of reacting particles that can overcome the activation-energy barrier, so the rate constant and reaction rate increase. This concerns successful collisions, not merely the total number of collisions.

Step 3: Conclusion Two factors affecting the rate of reaction are **reactant concentration** and **temperature**.

Quick Tip to Solve: Name concentration and temperature, then connect them respectively to collision frequency and the fraction of particles overcoming activation energy.

31(iii). (1) What happens to rate of reaction for zero order reaction?

(2) What is the unit of k for zero order reaction?

[2 marks]

Solution:

Concept:

- For a zero order reaction, the rate law is $r = k[A]^0 = k$, where r is reaction rate, k is the rate constant and $[A]$ is reactant concentration.
- Reaction rate has dimensions of concentration divided by time. Since $r = k$ for zero order, the rate constant has these same dimensions.

Step 1: (1) Effect on the rate The concentration term has exponent zero and therefore equals unity. Hence increasing or decreasing the reactant concentration does not change the rate, provided the reaction continues to follow zero order kinetics and temperature and other conditions remain fixed.

Quick Tip to Solve: Write the rate law first: for zero order, rate equals k, so copy the units of rate directly to k.

The rate remains constant at k as the reaction proceeds within this regime; it does not become zero simply because the order is zero.

Step 2: (2) Determine the unit of the rate constant From $k = r$, the units are

$$[k] = \frac{\text{mol L}^{-1}}{\text{s}} = \text{mol L}^{-1} \text{s}^{-1}.$$

Equivalently, one may write M s^{-1} , with M denoting molarity. The unit s^{-1} alone belongs to a first order rate constant, so it would omit the concentration dimension required here.

Step 3: Conclusion (1) The rate remains constant and independent of reactant concentration under fixed conditions. (2) The unit of k is $\boxed{\text{mol L}^{-1} \text{s}^{-1}}$.

Quick Tip to Solve: Write the rate law first: for zero order, rate equals k , so copy the units of rate directly to k .

OR

31(iii). (1) For a reaction $\text{P} + 2\text{Q} \rightarrow \text{Products}$, $\text{Rate} = k[\text{P}]^{1/2}[\text{Q}]^1$. What is the order of the reaction?

(2) Define pseudo first order reaction with an example.

[2 marks]

Solution:

Concept:

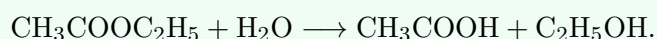
- The overall order is the sum of the powers of reactant concentrations in the experimentally determined rate law; these powers need not equal the stoichiometric coefficients.
- A pseudo first order reaction has a higher actual order but behaves as first order when another reactant is present in large excess, making its concentration practically constant.

Step 1: (1) Add the rate-law exponents The given rate law is $r = k[\text{P}]^{1/2}[\text{Q}]^1$. Its order with respect to P is $1/2$, and that with respect to Q is 1. Thus the overall order is

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

The coefficient 2 of Q in the balanced reaction does not make its partial order 2; the exponent in the supplied rate law, not the reaction coefficient, determines that order.

Step 2: (2) Define pseudo first order and give an example In a pseudo first order reaction, one reactant is taken in such large excess that its concentration changes negligibly during the reaction. The remaining concentration dependence then gives an apparent first order rate law. For example, hydrolysis of ethyl acetate in excess water, under constant acid catalyst concentration, is



Its rate can be written $r = k[\text{ester}][\text{H}_2\text{O}]$. Since water is in excess, $k[\text{H}_2\text{O}] = k'$ is effectively constant, giving $r = k'[\text{ester}]$, the pseudo first order form.

Step 3: Conclusion (1) The reaction order is $\boxed{3/2}$. (2) A higher-order reaction that behaves as first

Quick Tip to Solve: Add only the concentration exponents for order; for pseudo first order, identify the excess reactant absorbed into k' .

order because another reactant is in large excess is pseudo first order; ethyl acetate hydrolysis in excess water is an example.

Quick Tip to Solve: Add only the concentration exponents for order; for pseudo first order, identify the excess reactant absorbed into k' .

32(i). In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape of the complexes.

(i) If $\text{PtCl}_2 \cdot 2\text{NH}_3$ does not react with AgNO_3 , what will be its formula?

[1 mark]

Solution:

Concept:

- The coordination sphere is enclosed in square brackets and contains the metal together with its directly attached ligands.
- Silver nitrate precipitates ionisable chloride outside the coordination sphere as AgCl ; coordinated chloride does not give this immediate precipitation test.

Step 1: Locate the chloride ions The compound $\text{PtCl}_2 \cdot 2\text{NH}_3$ does not react with AgNO_3 . Therefore it has no freely ionisable chloride counterions. Both chloride groups must be directly bonded to platinum within the coordination sphere, rather than placed outside the brackets.

Step 2: Write the coordination formula Include platinum, the two neutral ammonia ligands and the two chlorido ligands within one pair of brackets. This gives $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. Charge balance also agrees: two chlorido ligands contribute -2 , ammonia is neutral, and platinum is in oxidation state $+2$, making the complex neutral.

Step 3: Conclusion The formula is $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$; both chlorides are coordinated and neither is an ionisable counterion.

Quick Tip to Solve: No AgCl precipitation means no free chloride outside the brackets; place both chlorides inside the coordination sphere.

32(ii). What is the secondary valency of $[\text{Co}(\text{en})_3]^{3+}$?

[1 mark]

Solution:

Concept:

- Werner's secondary valency equals the coordination number, which counts the donor atoms directly bonded to the central metal ion.
- Ethane-1,2-diamine, abbreviated en, is a neutral bidentate ligand: its two nitrogen atoms each donate a lone pair to the metal.

Step 1: Identify the donor atoms in one ligand In en, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, both nitrogen atoms

Quick Tip to Solve: Multiply the number of en ligands by two donor atoms; distinguish coordination number 6 from the complex charge $+3$.

coordinate to cobalt. Thus each en ligand occupies two coordination positions. Counting ligand molecules alone would miss the second donor atom of each bidentate ligand.

Step 2: Count the total coordination positions The complex $[\text{Co}(\text{en})_3]^{3+}$ has three en ligands, each supplying two nitrogen donors. Consequently, the coordination number is $3 \times 2 = 6$. The charge +3 identifies the primary valency or oxidation state of cobalt here; it is not the secondary valency.

Step 3: Conclusion The secondary valency of cobalt in $[\text{Co}(\text{en})_3]^{3+}$ is 6.

Quick Tip to Solve: Multiply the number of en ligands by two donor atoms; distinguish coordination number 6 from the complex charge +3.

32(iii). (1) Write the formula of Iron(III)hexacyanidoferrate(II).

(2) Write the IUPAC name of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

[2 marks]

Solution:

Concept:

- The formula of a coordination salt must balance the charges of the cation and complex anion. Cyanido ligands carry charge -1 .
- IUPAC names list ligands alphabetically before the metal; the oxidation state is written in Roman numerals. Neutral ammonia is named ammine and coordinated chloride is chlorido.

Step 1: (1) Determine the charge of hexacyanidoferrate(II) In $[\text{Fe}(\text{CN})_6]$, iron(II) has charge +2 and the six cyanido ligands contribute -6 . Hence the complex ion is $[\text{Fe}(\text{CN})_6]^{4-}$. Iron(III) outside this complex is the cation Fe^{3+} . The least common multiple of 3 and 4 is 12, so four iron(III) ions balance three complex anions:

$$4(+3) + 3(-4) = 0.$$

Thus the neutral salt contains four external Fe atoms and three hexacyanidoferrate groups: $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

Step 2: (2) Name the cobalt coordination salt In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, the two outer chloride ions require the complex cation to have charge +2. If cobalt's oxidation state is x , then $x + 5(0) - 1 = +2$, giving $x = +3$. The coordinated ligands are five ammines and one chlorido, named alphabetically as pentaamminechlorido. Since the coordination entity is cationic, use cobalt rather than cobaltate. Append the oxidation state (III), then name the outside anion chloride.

Step 3: Conclusion (1) Iron(III) hexacyanidoferrate(II) is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. (2) The IUPAC name is pentaamminechloridocobalt(III) chloride.

Quick Tip to Solve: Balance the $3+$ and $4-$ ions using their least common multiple; for cobalt, distinguish inside chlorido from outside chloride.

32(iii). Write the hybridization and magnetic behaviour of $[\text{Ni}(\text{CN})_4]^{2-}$. [Atomic number: Ni = 28] [2 marks]

Solution:

Concept:

- The oxidation state of the metal is found from the total charge and the charges on its ligands. Each cyanido ligand, CN^- , has charge -1 .
- Cyanide is a strong-field ligand. For Ni^{2+} , it pairs the $3d$ electrons, leaving one inner d orbital available for dsp^2 hybridisation.
- A complex with no unpaired electrons is diamagnetic; magnetic behaviour depends on the unpaired electrons, not merely on the coordination number.

Step 1: Determine the nickel ion configuration Let the oxidation state of nickel be x . The complex charge gives $x + 4(-1) = -2$, so $x = +2$. With atomic number 28, neutral nickel has configuration $[\text{Ar}] 3d^8 4s^2$. Removal of the two $4s$ electrons gives $\text{Ni}^{2+} : [\text{Ar}] 3d^8$.

Step 2: Apply the strong-field effect of cyanide The four strong-field CN^- ligands cause the eight $3d$ electrons to pair in four $3d$ orbitals. The remaining vacant $3d$ orbital, one $4s$ orbital and two $4p$ orbitals combine to form four dsp^2 hybrid orbitals, which accept the four ligand lone pairs. These orbitals are directed towards the corners of a square, giving square-planar geometry. All the metal electrons are paired, so the number of unpaired electrons is zero. Unlike a weak-field tetrahedral nickel(II) complex, this complex has no spin contribution to paramagnetism.

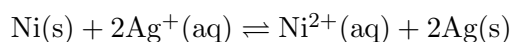
Step 3: Conclusion $[\text{Ni}(\text{CN})_4]^{2-}$ has dsp^2 hybridisation and square-planar geometry. It is **diamagnetic** because it has no unpaired electrons.

Quick Tip to Solve: First identify Ni(II) as a $d8$ ion; strong-field cyanide then points to paired electrons and square-planar dsp^2 hybridisation.

Section E (15 marks)

33(a). (i) State Kohlrausch's law of independent migration of ions. Write an expression for the limiting molar conductivity of acetic acid according to Kohlrausch's law.

(ii) Calculate the maximum work and $\log K_c$ for the given reaction at 298 K:



Given: $E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}$, $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$; $1 F = 96500 \text{ C mol}^{-1}$.

[5 marks]

Solution:

Concept:

- Kohlrausch's law states that at infinite dilution, each ion contributes independently to the molar conductivity of an electrolyte, irrespective of the nature of the other ion. The limiting molar conductivity is the sum of these ionic contributions, multiplied by their stoichiometric numbers.
- Standard cell potential is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using reduction potentials for both electrodes.

Quick Tip to Solve: Balance electrons to get $n = 2$, subtract the negative nickel reduction potential, and keep the sign of Gibbs energy distinct from the positive work delivered.

- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$. The maximum electrical work delivered by the cell is $-\Delta_r G^\circ$, where n is the number of electrons exchanged per reaction as written and F is the Faraday constant.
- Combining $\Delta_r G^\circ = -RT \ln K_c$ with the cell-energy relation gives $\log_{10} K_c = nFE_{\text{cell}}^\circ / (2.303RT)$, or $nE_{\text{cell}}^\circ / 0.0591$ at 298 K in the usual CBSE approximation.

Step 1: (i) Apply Kohlrausch's law to acetic acid Acetic acid dissociates into H^+ and CH_3COO^- . At infinite dilution the ions contribute independently, so

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{CH}_3\text{COO}^-).$$

Here λ° denotes the limiting ionic molar conductivity and Λ_m° the limiting molar conductivity of the electrolyte. Since acetic acid is a weak electrolyte, its limiting value can also be obtained by combining values for strong electrolytes:

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

The sodium and chloride ionic contributions cancel, leaving just the hydrogen and acetate contributions.

Step 2: (ii) Identify the electrodes and electron transfer Nickel undergoes oxidation, $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$, at the anode. Silver ions undergo reduction, $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$, at the cathode. Thus $n = 2$ for the reaction as printed. The standard cell potential is

$$E_{\text{cell}}^\circ = 0.80 - (-0.25) = 1.05 \text{ V}.$$

The silver reduction potential is not multiplied by two: electrode potentials are intensive quantities, even when the half-reaction is multiplied to balance electrons.

Step 3: Calculate the maximum electrical work Substituting the supplied Faraday constant gives

$$\begin{aligned}\Delta_r G^\circ &= -2 \times 96500 \times 1.05 \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1}.\end{aligned}$$

The negative Gibbs energy change indicates that the forward reaction is spontaneous under standard conditions. The maximum useful electrical work *delivered* by the reversible cell is its positive magnitude, 202.65 kJ per mole of reaction. With the convention of work done *on* the system, the corresponding signed work is $-202.65 \text{ kJ mol}^{-1}$.

Step 4: Calculate the equilibrium constant logarithm At 298 K, using the base-10 logarithm,

$$\log_{10} K_c = \frac{nE_{\text{cell}}^\circ}{0.0591} = \frac{2 \times 1.05}{0.0591} \approx 35.53.$$

Using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ directly in $nFE^\circ / (2.303RT)$ gives about 35.51, the small difference being due to the rounded 298 K factor. In either evaluation the very large equilibrium constant is

Quick Tip to Solve: Balance electrons to get $n = 2$, subtract the negative nickel reduction potential, and keep the sign of Gibbs energy distinct from the positive work delivered.

consistent with the positive cell potential and the negative standard Gibbs energy change.

Step 5: Conclusion $\Delta_m^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{CH}_3\text{COO}^-)$. The maximum electrical work delivered is $202.65 \text{ kJ mol}^{-1}$, with $\Delta_r G^\circ = -202.65 \text{ kJ mol}^{-1}$, and $\log_{10} K_c \approx 35.5$ (35.53 using the factor 0.0591 V).

Quick Tip to Solve: Balance electrons to get $n = 2$, subtract the negative nickel reduction potential, and keep the sign of Gibbs energy distinct from the positive work delivered.

OR

33(b). (i) State Faraday's first law of electrolysis. How much charge, in terms of Faraday, is required for the reduction of 1 mol Cu^{2+} to Cu?

(ii) Calculate emf of the following cell at 298 K for



$[E^\circ_{\text{cell}} = +2.71 \text{ V}, 1 \text{ F} = 96500 \text{ C mol}^{-1}, \log 10 = 1]$

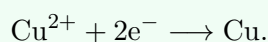
[5 marks]

Solution:

Concept:

- Faraday's first law states that the mass m of a substance deposited or liberated at an electrode is directly proportional to the charge q passed through the electrolyte: $m = Zq = Zit$. Here Z is the electrochemical equivalent, I is the current and t is the time.
- One Faraday is the charge carried by one mole of electrons: $F = 96500 \text{ C mol}^{-1}$. A reduction requiring z electrons per ion needs z moles of electrons for one mole of that ion.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, where n is the number of electrons transferred in the balanced cell reaction and Q is its reaction quotient. Pure solid electrodes have unit activity and are omitted from Q .

Step 1: (i) State the law and identify the electron requirement Faraday's first law of electrolysis: the mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Thus, for a given substance, $m \propto q$, or $m = Zq$. If a constant current is passed for time t , then $q = It$. The reduction half-reaction is



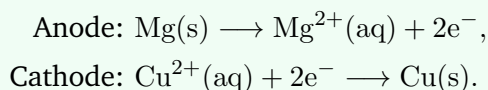
Each copper(II) ion accepts two electrons, so reducing one mole of Cu^{2+} requires two moles of electrons. The required charge is therefore

$$q = 2F = 2(96500) = 193000 \text{ C}.$$

Step 2: (ii) Write the cell reaction and reaction quotient In the cell as written, magnesium is the

Quick Tip to Solve: Balance the electrode reactions first: the two electrons give both the required $2F$ charge and $n = 2$ in the Nernst equation. For this cell, place magnesium ion concentration above copper ion concentration in Q .

anode and copper is the cathode. The electrode reactions are



Adding them gives $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$, so $n = 2$. With the aqueous concentrations expressed relative to the standard concentration, the quotient is

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.1}{0.01} = 10.$$

The solid magnesium and copper do not appear in this quotient.

Step 3: Substitute in the Nernst equation Using the given standard emf and $\log 10 = 1$,

$$\begin{aligned}E_{\text{cell}} &= 2.71 - \frac{0.0591}{2} \log 10 \\ &= 2.71 - 0.02955 \\ &= 2.68045 \text{ V}.\end{aligned}$$

Since $Q > 1$, the logarithmic correction is positive and is subtracted from the standard emf. This confirms that the calculated emf is slightly below 2.71 V, as expected for the stated concentrations.

Step 4: Conclusion (i) Faraday's first law is $m \propto q$; reducing 1 mol of Cu^{2+} requires $2F$, or $1.93 \times 10^5 \text{ C}$. (ii) The cell emf at 298 K is $E_{\text{cell}} \approx 2.68 \text{ V}$.

Quick Tip to Solve: Balance the electrode reactions first: the two electrons give both the required $2F$ charge and $n = 2$ in the Nernst equation. For this cell, place magnesium ion concentration above copper ion concentration in Q .

34. Assign reason for each of the following:

- (i) Manganese exhibits the highest oxidation state of +7 among the 3d series of transition elements.
- (ii) Transition metals and their compounds are generally found to be good catalysts in chemical reactions.
- (iii) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4) Mn^{3+} is an oxidising agent.
- (iv) Zn has lowest enthalpy of atomization.
- (v) Cu^+ is unstable in an aqueous solution.

[5 marks]

Solution:

Concept:

- Transition-metal properties depend on the energies and occupancies of the $3d$ and $4s$ orbitals. These orbitals can supply electrons for bonding and allow variable oxidation states.
- Oxidation is loss of electrons and reduction is gain of electrons. A reducing agent is itself oxidised; an oxidising agent is itself reduced. Stability of the product ion helps determine the preferred

Quick Tip to Solve: For the two d-four ions, write the product configurations first: Cr(III) is d-three and Mn(II) is d-five. For Cu(I) in water, compare hydration stability instead of judging only its filled d subshell.

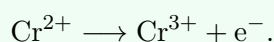
change.

- Metallic bonding determines the enthalpy of atomization, while hydration stabilises dissolved ions. For copper, the hydration enthalpy of Cu^{2+} makes its formation favourable in water.

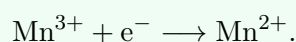
Step 1: (i) Highest oxidation state of manganese Manganese has electronic configuration $[\text{Ar}] 3d^5 4s^2$. It has five $3d$ electrons and two $4s$ electrons, making seven valence electrons available for participation in bonding. Consequently it can exhibit the oxidation state $+7$, as in MnO_4^- . This is the highest oxidation state exhibited among the $3d$ transition elements. The oxidation state is a formal electron-counting assignment; it does not mean that an isolated Mn^{7+} ion exists in aqueous solution.

Step 2: (ii) Catalytic activity of transition metals Transition metals can change oxidation states readily because the energies of their valence orbitals are close. Their compounds can therefore form intermediate species and undergo electron transfer with reactants, then return to the original state at the end of a catalytic cycle. Such intermediates provide a reaction pathway of lower activation energy. In heterogeneous catalysis, metal surfaces also adsorb reactants, bring them together and weaken their bonds. These features explain the catalytic activity of many transition metals and their compounds.

Step 3: (iii) Opposite redox behaviour of the two d-four ions Although both ions have d^4 configurations, their favourable product configurations differ. Chromium(II) loses an electron to form chromium(III):



The resulting Cr^{3+} has the stable d^3 configuration, corresponding to t_{2g}^3 in an octahedral field. Thus Cr^{2+} readily undergoes oxidation and acts as a reducing agent. Manganese(III), by contrast, gains an electron:



The product Mn^{2+} has the especially stable half-filled d^5 configuration. Hence Mn^{3+} undergoes reduction and acts as an oxidising agent.

Step 4: (iv) Low enthalpy of atomization of zinc Zinc has configuration $[\text{Ar}] 3d^{10} 4s^2$, with a completely filled $3d$ subshell and no unpaired d electrons. Its filled d orbitals contribute little to strong metallic bonding compared with the partly filled d orbitals of other $3d$ -series metals. The metallic bonding in zinc is therefore relatively weak. Less energy is required to separate its metal atoms into gaseous atoms, so zinc has the lowest enthalpy of atomization in this series.

Step 5: (v) Instability of copper(I) in aqueous solution In water, copper(I) undergoes disproportionation, in which the same species is both oxidised and reduced:



One Cu^+ ion loses an electron to become Cu^{2+} , while another gains that electron to become copper metal. The much more negative hydration enthalpy of Cu^{2+} , compared with Cu^+ , more than compensates for the energy needed to ionise Cu^+ further. The hydrated divalent ion is strongly stabilised, making disproportionation favourable despite the d^{10} configuration of Cu^+ .

Step 6: Conclusion The reasons are: (i) manganese can use seven valence electrons in bonding; (ii) transition metals offer variable oxidation states, intermediate formation and surface adsorption; (iii)

Quick Tip to Solve: For the two d-four ions, write the product configurations first: Cr(III) is d-three and Mn(II) is d-five. For Cu(I) in water, compare hydration stability instead of judging only its filled d subshell.

Cr^{2+} forms stable d^3 Cr^{3+} , whereas Mn^{3+} forms stable d^5 Mn^{2+} ; (iv) zinc has weak metallic bonding owing to its filled $3d$ subshell; and (v) copper(I) disproportionates because aqueous copper(II) is strongly stabilised by hydration.

Quick Tip to Solve: For the two d-four ions, write the product configurations first: Cr(III) is d-three and Mn(II) is d-five. For Cu(I) in water, compare hydration stability instead of judging only its filled d subshell.

35(a). (i) Carry out the following conversions:

(1) Ethanal to But-2-en-1-al

(2) Propanoic acid to 2-chloropropanoic acid

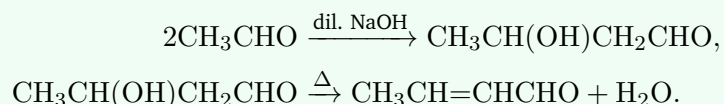
(ii) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling solution test but forms iodoform. Identify the compounds 'A', 'B' and 'C'. [5 marks]

Solution:

Concept:

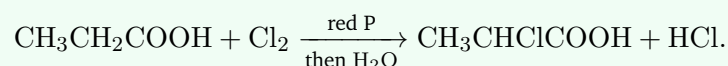
- An aldehyde with an α -hydrogen undergoes aldol addition in dilute alkali. Heating the resulting β -hydroxy aldehyde removes water to give an α, β -unsaturated aldehyde.
- The Hell-Volhard-Zelinsky reaction replaces an α -hydrogen of a carboxylic acid by halogen using chlorine or bromine in the presence of red phosphorus, followed by hydrolysis.
- Ozonolysis cleaves a carbon-carbon double bond into carbonyl groups. A positive Fehling test identifies an aliphatic aldehyde; the iodoform test identifies the $\text{CH}_3\text{CO}-$ group, including ethanal.

Step 1: (i)(1) Convert ethanal into but-2-en-1-al Treat ethanal with dilute NaOH to carry out self-aldol addition. Two molecules combine to form 3-hydroxybutanal. Heat this product to dehydrate it:



The aldehyde carbon is numbered 1, so the final four-carbon product has its double bond between carbons 2 and 3: but-2-en-1-al (crotonaldehyde). Mild conditions first give the aldol; heating is needed for the requested unsaturated product.

Step 2: (i)(2) Chlorinate propanoic acid at the alpha carbon Use the Hell-Volhard-Zelinsky reaction: treat propanoic acid with chlorine in the presence of red phosphorus, then hydrolyse the intermediate acid chloride.



The carbon adjacent to COOH is carbon 2. Replacing one hydrogen there by chlorine therefore gives 2-chloropropanoic acid. This is alpha-halogenation, not substitution at the terminal methyl group.

Step 3: (ii) Identify B using the two positive tests Since B reduces Fehling solution, it is an aliphatic aldehyde. Among aldehydes, ethanal has the $\text{CH}_3\text{CO}-$ arrangement needed to form iodoform with

Quick Tip to Solve: Identify ethanal from the combined Fehling and iodoform tests, then use the five-carbon total to identify acetone; reconnect the two carbonyl carbons to recover the alkene.

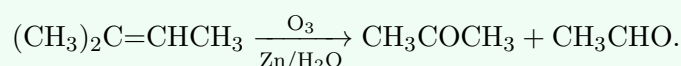
iodine and NaOH. Thus B = CH₃CHO, ethanal. Its iodoform reaction is



The yellow precipitate of CHI₃ is the positive iodoform observation.

Step 4: (ii) Identify C and reconstruct the alkene A C does not reduce Fehling solution but gives the iodoform test, so it is a methyl ketone. B contains two carbons and A contains five; hence C must contain the remaining three carbons. The required methyl ketone is CH₃COCH₃, propanone (acetone).

Join the carbonyl carbon of ethanal, bearing H and CH₃, to the carbonyl carbon of propanone, bearing two CH₃ groups, by a double bond. This gives (CH₃)₂C=CHCH₃. Check it by reductive ozonolysis:



This alkene is 2-methylbut-2-ene, has formula C₅H₁₀, and reproduces both identified products.

Step 5: Conclusion (i) Ethanal gives but-2-en-1-al by aldol addition followed by dehydration; propanoic acid gives 2-chloropropanoic acid by Cl₂/red phosphorus followed by hydrolysis. (ii) A = (CH₃)₂C=CHCH₃, 2-methylbut-2-ene; B = CH₃CHO, ethanal; and C = CH₃COCH₃, propanone.

Quick Tip to Solve: Identify ethanal from the combined Fehling and iodoform tests, then use the five-carbon total to identify acetone; reconnect the two carbonyl carbons to recover the alkene.

OR

35(b). (i) Distinguish with a suitable chemical test:

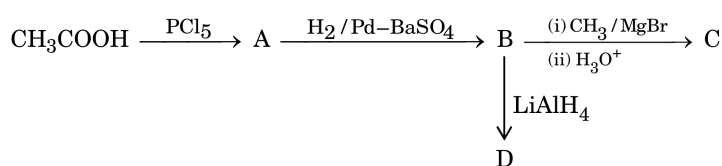
(1) CH₃COCH₂CH₃ and CH₃CH₂CH₂CHO

(2) Ethanal and Ethanoic acid

(ii) Write the structure of oxime of acetone.

(iii) Identify A to D.

[5 marks]



Solution:

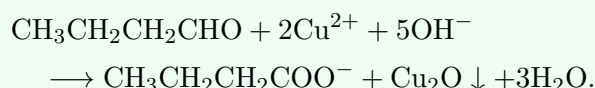
Concept:

- Aliphatic aldehydes reduce Fehling's solution on warming to brick-red Cu₂O; ordinary ketones do not. The aldehyde is oxidised to its carboxylate ion.
- Carboxylic acids liberate CO₂ from aqueous sodium hydrogen carbonate, whereas aldehydes do not. The escaping gas turns limewater milky.

Quick Tip to Solve: Track the carbon count after B: methylmagnesium bromide adds one carbon to give a three-carbon secondary alcohol, while LiAlH₄ keeps two carbons and gives a primary alcohol.

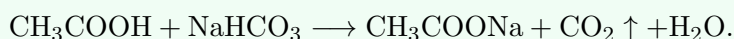
- Hydroxylamine, NH_2OH , condenses with a carbonyl compound to give an oxime containing $\text{C} = \text{N} - \text{OH}$, with elimination of water.
- PCl_5 converts a carboxylic acid into an acyl chloride. Rosenmund reduction gives an aldehyde; a Grignard reagent adds an alkyl group to its carbonyl carbon, while LiAlH_4 reduces it to a primary alcohol.

Step 1: (i)(1) Distinguish butan-2-one and butanal Add freshly mixed Fehling's solution to separate samples and warm gently. Butanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, gives a brick-red precipitate of copper(I) oxide. Butan-2-one, $\text{CH}_3\text{COCH}_2\text{CH}_3$, gives no such precipitate: its ketone group does not reduce this reagent. The balanced ionic equation for butanal is



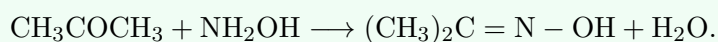
Thus the positive Fehling test identifies the aldehyde in this pair.

Step 2: (i)(2) Distinguish ethanal and ethanoic acid Add aqueous sodium hydrogen carbonate to separate samples. Ethanoic acid produces brisk effervescence of carbon dioxide, whereas ethanal gives no effervescence. The reaction is



Passing the gas through limewater gives a milky precipitate of CaCO_3 , confirming CO_2 . This test detects the acidic carboxyl group, so the observed effervescence distinguishes ethanoic acid directly from ethanal.

Step 3: (ii) Form the oxime of acetone Acetone reacts with hydroxylamine by condensation. The carbonyl oxygen is replaced by the $= \text{N} - \text{OH}$ group:

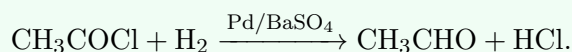


Both methyl groups remain bonded to the same carbon atom; the hydroxyl group is bonded to nitrogen through oxygen. Therefore the structural formula of acetone oxime is $\text{CH}_3 - \text{C}(= \text{N} - \text{OH}) - \text{CH}_3$.

Step 4: (iii) Identify the acyl chloride and aldehyde Treatment of ethanoic acid with PCl_5 replaces the acidic hydroxyl group by chlorine:



Hence A is ethanoyl chloride, CH_3COCl . Hydrogen with palladium supported on barium sulphate gives Rosenmund reduction:

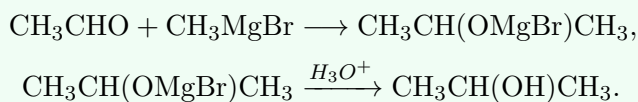


The moderated catalyst stops the reduction at the aldehyde stage, so B is ethanal, CH_3CHO .

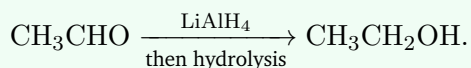
Step 5: (iii) Identify the two alcohol products Methylmagnesium bromide adds a methyl group to

Quick Tip to Solve: Track the carbon count after B: methylmagnesium bromide adds one carbon to give a three-carbon secondary alcohol, while LiAlH_4 keeps two carbons and gives a primary alcohol.

ethanal in dry ether. Acidic hydrolysis then protonates the alkoxide:



Thus C is propan-2-ol, a secondary alcohol with one more carbon atom than B. In the separate downward branch, LiAlH_4 reduces ethanal, followed by hydrolysis, without adding carbon:



Hence D is ethanol, a primary alcohol.

Step 6: Conclusion Butanal gives a positive Fehling test, while butan-2-one does not; ethanoic acid gives CO_2 with NaHCO_3 , while ethanal does not. Acetone oxime is $(\text{CH}_3)_2\text{C}=\text{N}-\text{OH}$. The products are A: CH_3COCl , B: CH_3CHO , C: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, and D: $\text{CH}_3\text{CH}_2\text{OH}$.

Quick Tip to Solve: Track the carbon count after B: methylmagnesium bromide adds one carbon to give a three-carbon secondary alcohol, while LiAlH_4 keeps two carbons and gives a primary alcohol.