

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-1-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **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. On dissolving ammonium chloride in water at room temperature, the solution feels cool to touch. Under which of the following conditions does salt dissolve faster? [1 mark]

- (A) Powdered salt in cold water
- (B) Powdered salt in hot water
- (C) Salt crystals in cold water
- (D) Salt crystals in hot water

Correct Answer: (B) Powdered salt in hot water

Solution:

Concept:

- Dissolution of ammonium chloride is endothermic: the salt absorbs heat from its surroundings, so the solution feels cool.
- The rate of dissolution increases with temperature and with the surface area of salt exposed to water.

Step 1: Compare the physical forms Powdered salt consists of many small particles. For the same mass it exposes a larger total surface area to water than large salt crystals, so more solvent can contact the salt at once.

Step 2: Compare the temperatures and options Hot water increases molecular motion and speeds up dissolution. Option (A) has the surface-area advantage but uses cold water; (C) has neither advantage; (D) uses hot water but has less surface area. Only (B) combines powdered salt with hot water.

Step 3: Conclusion Ammonium chloride dissolves fastest as powdered salt in hot water. Hence, the correct option is (B).

Quick Tip to Solve: For fastest dissolution, combine small particles with a higher solvent temperature.

2. Lanthanoid contraction is due to increase in:

[1 mark]

- (A) atomic number
- (B) shielding by 4f electrons
- (C) effective nuclear charge
- (D) atomic radius

Correct Answer: (C) effective nuclear charge

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series.

Quick Tip to Solve: Link lanthanoid contraction to poor 4f shielding and the resulting stronger nuclear attraction.

- Effective nuclear charge is the net nuclear attraction felt by an electron after shielding by other electrons.

Step 1: Relate nuclear charge to shielding Across the lanthanoids, nuclear charge increases while the added electrons enter the inner 4f subshell. The 4f electrons shield one another poorly, so shielding does not fully compensate for the increase in nuclear charge.

Step 2: Test the proposed causes The resulting increase in effective nuclear charge pulls the electron cloud closer to the nucleus. Increasing atomic number alone does not specify the shielding balance, so (A) is less precise than (C). Option (B) incorrectly emphasises increased shielding as the cause, while (D) contradicts the observed decrease in radius.

Step 3: Conclusion Lanthanoid contraction is caused by increasing effective nuclear charge. Hence, the correct option is (C).

Quick Tip to Solve: Link lanthanoid contraction to poor 4f shielding and the resulting stronger nuclear attraction.

3. 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 amine contains one carbon atom fewer than the starting amide because the carbonyl carbon is removed.

Step 1: Identify the reaction and carbon skeleton The reactant is acetamide, CH_3CONH_2 , containing two carbon atoms. With Br_2/NaOH , it undergoes Hofmann bromamide degradation. Removal of its carbonyl carbon leaves the methyl group attached to nitrogen.

Step 2: Identify the product among the options The balanced overall reaction is



Option (A) is a carboxylate associated with amide hydrolysis. Option (C) is an alkyl bromide, not an amine. Option (D) retains two carbon atoms and therefore does not follow Hofmann degradation.

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

Quick Tip to Solve: In Hofmann degradation, delete the amide carbonyl carbon and retain the group bonded to it.

4. 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 constitute Lucas reagent and convert alcohols into alkyl chlorides.
- For ordinary aliphatic alcohols in this test, greater carbocation stability gives faster substitution.

Step 1: Explain the role of the reagent ZnCl_2 is a Lewis acid that coordinates with the alcohol oxygen and facilitates displacement of the hydroxyl group. Under these conditions tertiary alcohols react readily, secondary alcohols react more slowly, and primary alcohols react slowest at room temperature.

Step 2: Compare the orders in the options The stability of the corresponding carbocations decreases in the order tertiary, secondary, primary because alkyl groups stabilise positive charge through their electron-releasing effect and hyperconjugation. Thus the increasing reactivity order must be $1^\circ < 2^\circ < 3^\circ$. Options (B), (C) and (D) each place at least one less reactive alcohol above a more reactive one.

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

Quick Tip to Solve: With Lucas reagent, remember tertiary reacts first, secondary next, and primary last.

5. 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 isomerism occurs when a coordinated ligand and a counter-ion exchange positions between the coordination sphere and the ionisation sphere.
- Ionisation isomers yield different ions in solution despite having the same overall composition.

Step 1: Locate the coordinated and free anions In $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$, sulfate is within the coordination sphere and bromide is outside it. In $[\text{Co}(\text{Br})(\text{NH}_3)_5]\text{SO}_4$, bromide is coordinated and sulfate is the counter-ion. Thus the two anions have exchanged their positions.

Quick Tip to Solve: Check which anion lies outside the square brackets: different free anions indicate ionisation isomerism.

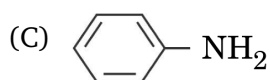
Step 2: Distinguish the other forms of isomerism The first compound releases bromide ions in solution, whereas the second releases sulfate ions. This is the defining difference of ionisation isomers. Optical isomerism concerns nonsuperimposable mirror images. Linkage isomerism changes the donor atom of an ambidentate ligand, and coordination isomerism exchanges ligands between complex cations and complex anions; neither occurs here.

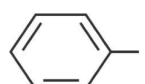
Step 3: Conclusion The compounds exhibit ionisation isomerism. Hence, the correct option is (C).

Quick Tip to Solve: Check which anion lies outside the square brackets: different free anions indicate ionisation isomerism.

6. Which of the following is least basic?

[1 mark]



Correct Answer: (C)  NH_2

Solution:

Concept:

- A base accepts a proton using an available lone pair; reduced availability of the nitrogen lone pair weakens basicity.
- In aniline, nitrogen is directly attached to a benzene ring, and its lone pair is delocalised by resonance into the ring.

Step 1: Compare aniline with ammonia In $\text{C}_6\text{H}_5\text{NH}_2$, the nitrogen lone pair participates in conjugation with the benzene ring and is less readily available to bind H^+ . Protonation removes this lone pair from conjugation, so aniline is less basic than ammonia, whose lone pair is localised.

Step 2: Compare the alkylamines and select the least basic The methyl groups in $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$ donate electron density through their positive inductive effect. Neither has aromatic resonance delocalisation of the nitrogen lone pair. Although solvation affects the relative basicity of alkylamines in water, both remain more basic than aniline; therefore options (A), (B) and (D) cannot be the least basic here.

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

Quick Tip to Solve: Look for a nitrogen lone pair conjugated with an aromatic ring before comparing alkyl substitution.

7. 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 essentially unbranched component of starch, made of α -D-glucose units.
- A glycosidic linkage joins the anomeric carbon of one sugar to an oxygen attached to another sugar carbon.

Step 1: Identify the carbons joined in amylose In amylose, the anomeric carbon C_1 of one glucose residue is joined through oxygen to C_4 of the next glucose residue. The configuration at the anomeric carbon is alpha, giving an $\alpha(1 \rightarrow 4)$ glycosidic linkage.

Step 2: Compare all printed alternatives Option (A), the alpha $C_1 - C_6$ linkage, occurs at branching points in amylopectin rather than along amylose. Option (B) has both the wrong carbon connection and the wrong configuration. Option (D), the beta $C_1 - C_4$ linkage, is characteristic of cellulose. Only option (C) has both the required $1 \rightarrow 4$ connection and alpha configuration.

Step 3: Conclusion Amylose contains $C_1 - C_4$ alpha glycosidic linkages, that is, $\alpha(1 \rightarrow 4)$. Hence, the correct option is (C).

Quick Tip to Solve: Remember: amylose is alpha 1-4, amylopectin branches are alpha 1-6, and cellulose is beta 1-4.

8. The order of the reaction $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$ is:

[1 mark]

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

Correct Answer: (C) 0

Solution:

Concept:

- Reaction order is the sum of the powers of reactant concentrations in the experimentally determined rate law.
- For this photochemical reaction, under fixed illumination the rate is governed by the absorbed light intensity rather than the reactant concentrations.

Step 1: Identify the controlling factor The symbol $h\nu$ above the arrow indicates a photochemical reaction. Light initiates the reaction between hydrogen and chlorine. In the standard kinetic

Quick Tip to Solve: When light controls this photochemical reaction, do not infer its order from the balanced equation.

description of this reaction under fixed illumination, the reaction rate depends on the incident light intensity.

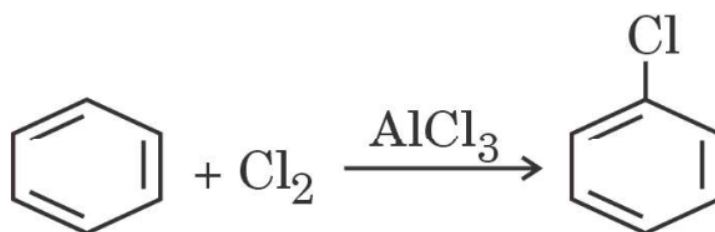
Step 2: Apply the definition of order The rate is independent of $[H_2]$ and $[Cl_2]$ under these conditions, so it can be written as $r = k[H_2]^0[Cl_2]^0 = k$. The total order is therefore $0 + 0 = 0$. The stoichiometric coefficients do not establish the rate-law powers: adding them to obtain 2 is incorrect, and neither 1 nor 3 describes this photochemical rate law.

Step 3: Conclusion The reaction is zero order. Hence, the correct option is (C), 0.

Quick Tip to Solve: When light controls this photochemical reaction, do not infer its order from the balanced equation.

9. The species that attacks benzene in the following is:

[1 mark]



- (A) Cl^-
- (B) $AlCl_4^-$
- (C) $AlCl_3$
- (D) Cl^+

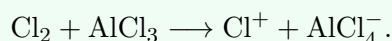
Correct Answer: (D) Cl^+

Solution:

Concept:

- Benzene undergoes electrophilic aromatic substitution because its π -electron cloud attracts an electron-deficient species.
- $AlCl_3$ acts as a Lewis acid, activating chlorine to provide the electrophile represented as Cl^+ .

Step 1: Generate the electrophile The Lewis acid $AlCl_3$ interacts with Cl_2 , strongly polarising the chlorine-chlorine bond. The usual CBSE representation of this activation is



The positive chlorine species is electron deficient.

Step 2: Identify the species that attacks benzene The benzene ring supplies π electrons to the electrophile Cl^+ , forming the intermediate in electrophilic substitution. Cl^- and $AlCl_4^-$ are negatively charged species, so neither is the attacking electrophile. $AlCl_3$ activates chlorine as the catalyst; it is not the chlorine species that substitutes for hydrogen on the ring.

Step 3: Conclusion The attacking species is Cl^+ . Hence, the correct option is (D).

Quick Tip to Solve: Identify the Lewis acid catalyst first, then choose the electron-deficient chlorine electrophile.

10. 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 predominantly form Ln^{3+} ions, where Ln denotes a lanthanoid element.
- An additional stabilisation from particular $4f$ configurations may permit +2 or +4 for some elements, but these are exceptions.

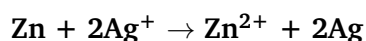
Step 1: Explain formation of the common ion Lanthanoids typically lose their two outer $6s$ electrons and one additional electron from a $5d$ or $4f$ orbital to form Ln^{3+} . The remaining $4f$ electrons are relatively less available for further removal, making the tripositive state predominant across the series.

Step 2: Compare the alternatives The +2 state occurs for some lanthanoids when the resulting electronic configuration is particularly favourable, while +4 occurs for some others, for example cerium. Neither state is the most common throughout the series. The +6 state is not the usual stable oxidation state of lanthanoids. Thus the general answer must be the predominant +3 state.

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

Quick Tip to Solve: For a general lanthanoid question choose +3; reserve +2 and +4 for specifically named exceptions.

11. 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) $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$

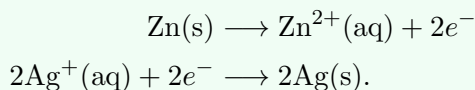
Solution:

Concept:

- In conventional cell notation, the anode (oxidation half-cell) is written on the left and the cathode (reduction half-cell) on the right.
- A single vertical line denotes a phase boundary, while a double vertical line represents the salt bridge.

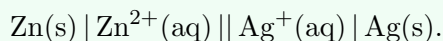
Quick Tip to Solve: Locate the species losing electrons and place its metal-ion half-cell first in the cell notation.

Step 1: Identify oxidation and reduction In the given reaction, zinc loses electrons and silver ions gain them:



Zinc is therefore the anode and silver is the cathode.

Step 2: Arrange the half-cells in the correct order Write the zinc metal and its ions on the left, followed by the salt bridge and the silver ions and silver metal on the right:



Options (A), (B) and (C) place the silver half-cell on the left, so they do not represent the given forward reaction by the conventional anode-left rule. The coefficient 2 in the silver half-reaction is not attached to the electrode in cell notation.

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

Quick Tip to Solve: Locate the species losing electrons and place its metal-ion half-cell first in the cell notation.

12. 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:

- A spontaneous reaction has a negative Gibbs energy change, $\Delta G < 0$, at constant temperature and pressure.
- The electrochemical relation is $\Delta G = -nFE_{\text{cell}}$, and under standard conditions $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$, with $n > 0$ and $F > 0$.

Step 1: Determine the Gibbs energy sign For a reaction proceeding spontaneously in the forward direction at constant temperature and pressure, Gibbs energy decreases. Therefore ΔG is negative. This eliminates options (A) and (D), which give a positive Gibbs energy change.

Step 2: Use the energy-potential relationship The negative sign in $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$ means that the standard Gibbs energy change and standard cell potential have opposite signs. For the spontaneous reaction in the standard-condition interpretation of this question, $\Delta G^{\circ} < 0$ requires $E^{\circ}_{\text{cell}} > 0$. Option (B), which makes both quantities negative, therefore has the incorrect potential sign. Away from standard conditions, spontaneity is tested using the actual E_{cell} and ΔG .

Step 3: Conclusion The required signs are negative and positive, respectively. Hence, the correct

Quick Tip to Solve: Use the minus sign in the Gibbs energy-cell potential relation to pair negative energy with positive emf.

option is (C).

Quick Tip to Solve: Use the minus sign in the Gibbs energy-cell potential relation to pair negative energy with positive emf.

13. 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 initial and final thermodynamic states, which are not changed by a catalyst.

Step 1: Identify the kinetic quantity Activation energy is the energy barrier between reactants and the activated configuration along a reaction pathway. By supplying an alternative pathway with a lower barrier, a catalyst increases the reaction rate at a given temperature. The kinetic quantity affected is therefore E_a .

Step 2: Check the thermodynamic alternatives A catalyst does not change the identities or thermodynamic states of reactants and products. Hence the reaction enthalpy change ΔH , Gibbs energy change ΔG , and entropy change ΔS remain unchanged. It accelerates attainment of equilibrium by increasing both forward and reverse rates, without changing the equilibrium position. Thus options (A), (B) and (D) are not correct.

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

Quick Tip to Solve: A catalyst changes the barrier between the endpoints, so select activation energy rather than a state-function change.

14. Which of the following is a non-reducing sugar?

[1 mark]

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

Correct Answer: (A) Sucrose

Solution:

Concept:

- A reducing sugar has a free anomeric centre that allows a ring-chain equilibrium with an oxidisable carbonyl group.
- A sugar is non-reducing when its anomeric centres are locked in the glycosidic linkage and cannot produce the free carbonyl form.

Step 1: Examine sucrose Sucrose consists of glucose and fructose joined through the anomeric carbon of each unit: C-1 of glucose and C-2 of fructose. Both anomeric centres participate in the glycosidic bond, so there is no free hemiacetal or hemiketal group. Sucrose therefore cannot open into a free aldehyde or ketone form and is non-reducing.

Step 2: Check the other sugars Maltose and lactose each retain one free anomeric centre, allowing ring opening and reducing behaviour. Glucose also has a free anomeric centre and equilibrates with its open-chain aldehyde form, so it is reducing. Consequently options (B), (C) and (D) do not satisfy the requirement of a non-reducing sugar.

Step 3: Conclusion Sucrose is the non-reducing sugar. Hence, the correct option is (A).

Quick Tip to Solve: For a disaccharide, check whether both anomeric carbons are bonded; if both are locked, it is non-reducing.

15. Assertion (A): Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.

Reason (R): Ammonolysis of alkyl halides yields mainly secondary amines.

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:

- Ammonolysis replaces a halogen in an alkyl halide by an amino group using alcoholic ammonia.
- The primary amine formed is also nucleophilic and can undergo further alkylation, so the reaction generally gives a mixture.

Step 1: Judge the assertion A primary amine, RNH_2 , is initially formed from RX . Its nitrogen lone pair allows it to react further with the alkyl halide, producing secondary and tertiary amines and finally a quaternary ammonium salt. Thus, obtaining a pure primary amine directly by ammonolysis is difficult. Assertion (A) is true.

Step 2: Judge the reason Ammonolysis does not invariably yield mainly secondary amines. The product distribution depends on the relative amounts of ammonia and alkyl halide; a large excess of ammonia favours the primary amine. The general result is a mixture, not predominantly secondary amine in every case. Reason (R) is false.

Step 3: Select the assertion-reason relationship Further alkylation and the resulting mixture explain the difficulty in preparing a pure primary amine. The printed reason incorrectly singles out secondary amines as the main product, so the choices requiring a true reason are excluded.

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

Quick Tip to Solve: For ammonolysis, distinguish a mixture of alkylated products from a claim that one class must predominate.

16. 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 participating in a single elementary step; it is a positive integer.
- The overall stoichiometric equation of a complex reaction does not determine its actual molecularity or its experimentally measured order.

Step 1: Judge the assertion In the written equation $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$, one molecule of hydrogen and one molecule of bromine occur on the reactant side. Simply counting these gives two, so the molecularity appears to be 2. The word “appears” is essential: this count is only a superficial inference from the overall equation. Assertion (A) is true.

Step 2: Judge the reason Formation of hydrogen bromide from hydrogen and bromine proceeds through a chain mechanism involving several elementary steps. The displayed overall reaction is not itself an elementary reaction. Thus the reason incorrectly identifies the overall equation as an elementary event, even though it shows two reactant molecules. Reason (R) is false.

Step 3: Decide whether the reason explains the assertion The apparent value comes from counting the species in the overall equation, not from establishing a simultaneous elementary collision. Because the reason contains a false claim about the reaction mechanism, neither choice requiring both statements to be true applies; the choice requiring a false assertion also fails.

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

Quick Tip to Solve: Count molecules only for an elementary step; an overall equation may merely suggest an apparent molecularity.

17. 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:

- The competition between crystal field splitting energy Δ and pairing energy P determines whether electrons pair or occupy higher energy orbitals.
- For comparable metal ions and ligands, tetrahedral splitting is small: $\Delta_t \approx \frac{4}{9}\Delta_o$, where the subscripts denote tetrahedral and octahedral fields.

Step 1: Judge the assertion In a tetrahedral field, the two e orbitals lie below the three t_2 orbitals. Electrons generally occupy the upper set before pairing in the lower set wherever that choice exists, producing a high spin arrangement. Consequently, low spin tetrahedral complexes are rarely observed. Assertion (A) is true.

Step 2: Judge the reason The tetrahedral crystal field splitting Δ_t is usually smaller than the electron pairing energy P . It therefore costs less energy to place an electron in an upper orbital than to pair it in a lower orbital. Reason (R) is true.

Step 3: Connect the energy comparison to spin The inequality $\Delta_t < P$ directly favours retaining unpaired electrons and hence a high spin configuration. This energy comparison explains why the alternative low spin arrangement is rare, rather than merely giving an unrelated fact. The choices denying either statement or denying the explanatory link are excluded.

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

Quick Tip to Solve: Compare splitting with pairing energy: a small tetrahedral splitting favours unpaired electrons and high spin.

18. 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.
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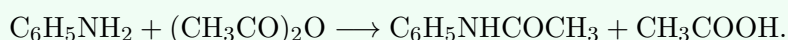
Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- Acetylation converts the $-\text{NH}_2$ group of aniline into the amide group $-\text{NHCOCH}_3$, forming acetanilide.
- In an amide, the nitrogen lone pair is also delocalised towards the carbonyl group, reducing its availability for activating the benzene ring.

Step 1: Judge the assertion Acetylation of aniline with acetic anhydride produces acetanilide:



The benzene ring in this product bears one acetamido substituent. Moreover, acetyl protection moderates ring activation and enables controlled monosubstitution in subsequent electrophilic substitution reactions. Assertion (A) is true.

Step 2: Judge the reason The $-\text{NHCOCH}_3$ group is less activating than $-\text{NH}_2$. Resonance of the nitrogen lone pair with the carbonyl group competes with donation into the benzene ring. The reason reverses this comparison by saying that the acetamido group is more activating. Reason (R) is false.

Step 3: Select the relationship Reduced activation after acetylation explains the controlled substitution behaviour of acetanilide. The printed claim of greater activation cannot provide that explanation. Therefore, the choices treating the reason as true, including the choice with a false assertion, do not fit.

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

Quick Tip to Solve: Acetyl protection ties up part of the nitrogen lone pair in the carbonyl group, so ring activation decreases.

Section B (14 marks)

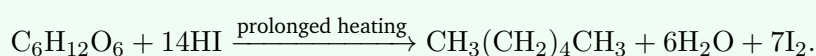
19. (a) Write chemical reaction to show that open structure of D-glucose contains the straight chain.
 (b) What type of linkage is responsible for the formation of protein? [2 marks]

Solution:

Concept:

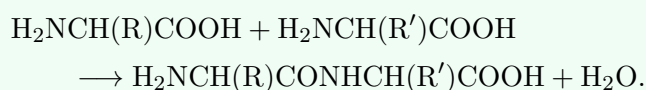
- Prolonged heating of glucose with hydroiodic acid reduces its oxygen-containing groups and yields a hydrocarbon that reveals its carbon skeleton.
- Proteins consist of amino acid residues connected by peptide bonds, $-\text{CO}-\text{NH}-$, formed by condensation of amino and carboxyl groups.

Step 1: Show the straight carbon chain in glucose (a) On prolonged heating with excess hydroiodic acid, D-glucose yields *n*-hexane. A balanced equation representing the reduction is



The product has six carbon atoms in one unbranched chain. Since reduction removes the oxygen-containing groups without changing the carbon skeleton, formation of *n*-hexane establishes that all six carbons of glucose lie in a straight chain.

Step 2: Identify the linkage in proteins (b) The carboxyl group of one amino acid condenses with the amino group of another, eliminating a molecule of water:



The newly formed $-\text{CO}-\text{NH}-$ group is a peptide (amide) linkage. Repeated condensation produces the polypeptide chain of a protein; *R* and *R'* denote the amino acid side chains.

Step 3: Conclusion (a) D-glucose gives *n*-hexane on prolonged heating with HI, confirming a straight six-carbon chain. (b) Proteins are formed through peptide linkages, $-\text{CO}-\text{NH}-$.

Quick Tip to Solve: Use the unbranched hydrocarbon product to identify glucose's skeleton, and write the peptide bond as $-\text{CO}-\text{NH}-$.

20(a). Calculate $\Delta_r G^\circ$ for the cell reaction at 25°C :



Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = 0.40 \text{ V}$; $1 \text{ F} = 96500 \text{ C mol}^{-1}$

[2 marks]

Solution:

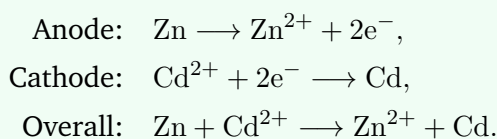
Concept:

- For a cell written with the anode on the left and cathode on the right, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.

Quick Tip to Solve: Use the printed cadmium potential and count two transferred electrons before substituting in $-nFE$.

- Standard Gibbs energy and cell potential are related by $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons transferred and F is the Faraday constant.

Step 1: Write the electrode reactions In the given cell, zinc is oxidised at the left electrode and cadmium ions are reduced at the right electrode:



Hence $n = 2$. Use the electrode potentials supplied in the question, including the positive sign of the cadmium value.

Step 2: Calculate the standard cell potential Both listed electrode potentials are reduction potentials, so subtract the anode value from the cathode value:

$$E_{\text{cell}}^\circ = 0.40 - (-0.76) = 1.16 \text{ V}.$$

The minus sign of the zinc potential must be retained; subtracting this negative number adds 0.76 V.

Step 3: Evaluate the standard Gibbs energy Substituting $F = 96500 \text{ C mol}^{-1}$ and using $1 \text{ C V} = 1 \text{ J}$,

$$\begin{aligned}\Delta_r G^\circ &= -2 \times 96500 \times 1.16 \\ &= -223880 \text{ J mol}^{-1} \\ &= -223.88 \text{ kJ mol}^{-1}.\end{aligned}$$

The negative sign agrees with the positive standard cell potential and indicates a thermodynamically favourable cell reaction under standard conditions.

Step 4: Conclusion For the given cell reaction at 25°C , $\Delta_r G^\circ = -223.88 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Use the printed cadmium potential and count two transferred electrons before substituting in $-nFE$.

OR

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:

- Resistance is related to resistivity by $R = \rho l/A$, where l is the length of the solution column and A its cross-sectional area.
- Conductivity is the reciprocal of resistivity: $\kappa = 1/\rho = l/(RA)$. Using length in cm gives conductivity in S cm^{-1} .

Step 1: Calculate the cross-sectional area The column is cylindrical. Its diameter is $d = 1 \text{ cm}$, so its

Quick Tip to Solve: Convert diameter to radius before calculating area, and use $\kappa = (l/A)/R$; concentration enters only if molar conductivity is requested.

radius is $r = 0.5$ cm. Therefore,

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

The cell constant is $l/A = 50/0.7854 = 63.66 \text{ cm}^{-1}$. The given concentration describes the solution; it is not required separately when its resistance and cell dimensions are known.

Step 2: Substitute in the conductivity formula With $R = 5.55 \times 10^3 \Omega$ and $l = 50$ cm,

$$\begin{aligned}\kappa &= \frac{l}{RA} \\ &= \frac{50}{(5.55 \times 10^3)(0.7854)} \\ &= 1.147 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}.\end{aligned}$$

Here Ω^{-1} is the siemens (S). This calculation gives conductivity, so no molar-conductivity conversion using concentration is needed.

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

Quick Tip to Solve: Convert diameter to radius before calculating area, and use $\kappa = (l/A)/R$; concentration enters only if molar conductivity is requested.

21(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.

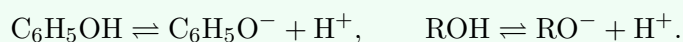
[2 marks]

Solution:

Concept:

- Acid strength depends on the stability of the conjugate base: greater stabilisation of the anion favours release of H^+ .
- For isomeric alcohols with comparable hydrogen bonding, boiling points also depend on London dispersion forces, which decrease as branching reduces molecular surface area.

Step 1: Explain the greater acidity of phenol Phenol loses a proton to give the phenoxide ion, whereas an alcohol gives an alkoxide ion:



In phenoxide, the negative charge is delocalised by resonance between oxygen and the ortho and para positions of the benzene ring. An alkoxide ion has no comparable resonance stabilisation: its negative charge remains localised on oxygen. Furthermore, the electron-releasing inductive effect of an alkyl group increases electron density on oxygen and destabilises the alkoxide ion. The greater relative stability of phenoxide favours proton loss from phenol.

Step 2: Explain the effect of branching on boiling point Among alcohols with the same molecular

Quick Tip to Solve: For acidity compare the conjugate bases; for branching compare the molecular surface areas of alcohols with the same molecular formula.

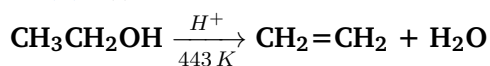
formula, increased branching makes the molecule more compact and reduces the surface area available for contact with neighbouring molecules. Consequently, the intermolecular London dispersion attractions become weaker. Less energy is required to separate the molecules into the vapour phase, so the boiling point decreases. The alcohols still form intermolecular hydrogen bonds through their hydroxyl groups; the branching trend arises from the reduced dispersion contribution.

Step 3: Conclusion (i) Phenol is more acidic because its conjugate base, phenoxide, is resonance stabilised. (ii) Branching lowers the boiling point of isomeric alcohols by reducing their surface area and intermolecular dispersion forces.

Quick Tip to Solve: For acidity compare the conjugate bases; for branching compare the molecular surface areas of alcohols with the same molecular formula.

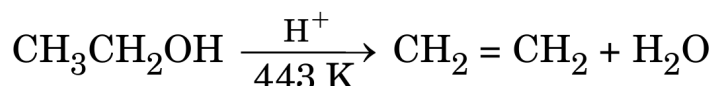
OR

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



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

[2 marks]

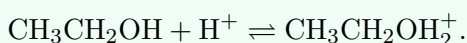


Solution:

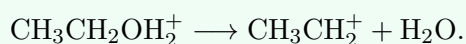
Concept:

- Acid-catalysed dehydration of an alcohol converts its hydroxyl group into a better leaving group by protonation; elimination at 443 K gives an alkene.
- The Reimer-Tiemann reaction introduces a formyl group, $-\text{CHO}$, mainly at the ortho position of phenol using chloroform and aqueous alkali, followed by acidification.

Step 1: Show the acid-catalysed dehydration mechanism First, a lone pair on the ethanol oxygen accepts a proton. This produces the ethyloxonium ion and converts the poor hydroxyl leaving group into water:



In the standard textbook representation, loss of water gives the carbocation intermediate:



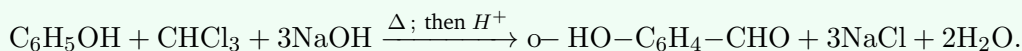
A proton is then removed from the adjacent carbon. The electrons of that carbon-hydrogen bond form the carbon-carbon double bond:



Thus the acid catalyst is regenerated, and overall ethanol loses one molecule of water to form ethene at 443 K.

Quick Tip to Solve: In dehydration, protonate oxygen first and regenerate the acid last; in Reimer-Tiemann, place the new $-\text{CHO}$ group ortho to $-\text{OH}$.

Step 2: Write the Reimer–Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide, and the reaction mixture is then acidified. The major product is 2-hydroxybenzaldehyde (salicylaldehyde):



The –OH and –CHO groups occupy adjacent positions on the benzene ring. A small amount of the para isomer may also form; the characteristic main product is the ortho aldehyde.

Step 3: Conclusion (i) Ethanol undergoes protonation, water loss and proton elimination to give ethene, regenerating H^+ . (ii) The Reimer–Tiemann reaction gives mainly salicylaldehyde from phenol, chloroform and aqueous NaOH followed by acidification.

Quick Tip to Solve: In dehydration, protonate oxygen first and regenerate the acid last; in Reimer–Tiemann, place the new –CHO group ortho to –OH.

22. Write the main product formed when:

(a) n-Butyl chloride is treated with alc. KOH.

(b) 2,4,6-Trinitrochlorobenzene is subjected to hydrolysis.

[2 marks]

Solution:

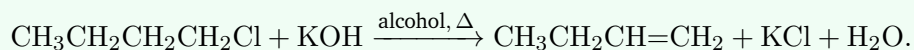
Concept:

- Alcoholic KOH favours beta-elimination from a haloalkane: hydrogen is removed from a carbon adjacent to the carbon bearing the halogen, giving an alkene.
- Electron-withdrawing nitro groups at the ortho and para positions activate an aryl chloride towards nucleophilic substitution. Hydrolysis replaces chlorine by a hydroxyl group.

Step 1: Treat n-butyl chloride with alcoholic KOH n-Butyl chloride is 1-chlorobutane. Its formula is

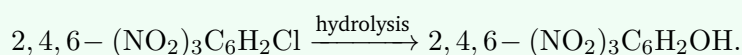


On heating with alcoholic KOH, a beta hydrogen is removed from the adjacent carbon while chloride leaves the terminal carbon. There is only one adjacent carbon from which the required hydrogen can be removed, so a double bond forms between carbons 1 and 2:



The organic product is but-1-ene. The alcoholic medium favours elimination, whereas aqueous KOH would favour formation of the corresponding alcohol by substitution.

Step 2: Hydrolyse 2,4,6-trinitrochlorobenzene The three nitro groups at positions 2, 4 and 6 strongly withdraw electron density and stabilise the intermediate formed during attack by hydroxide. Thus replacement of the chlorine atom by a hydroxyl group occurs readily:



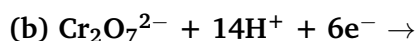
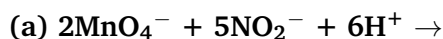
Quick Tip to Solve: For alcoholic KOH identify the beta carbon before drawing the alkene; for activated aryl chlorides replace only Cl by OH, keeping the nitro positions fixed.

The product is 2,4,6-trinitrophenol, commonly called picric acid. Under alkaline hydrolysis conditions it initially exists as the picrate salt; acidification gives the phenol shown above. The positions of the three nitro groups remain unchanged.

Step 3: Conclusion (a) The main product is but-1-ene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$. (b) Hydrolysis gives 2,4,6-trinitrophenol (picric acid).

Quick Tip to Solve: For alcoholic KOH identify the beta carbon before drawing the alkene; for activated aryl chlorides replace only Cl by OH, keeping the nitro positions fixed.

23. Complete the following equations:



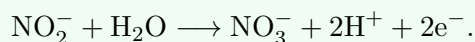
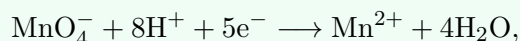
[2 marks]

Solution:

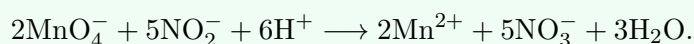
Concept:

- In acidic solution, permanganate is reduced from Mn(VII) to Mn(II), while nitrite is oxidised from N(III) to N(V).
- Balance oxygen with H_2O , hydrogen with H^+ , and charge with electrons; electrons cancel in the complete redox equation.

Step 1: Complete equation (a) The acidic half-reactions are

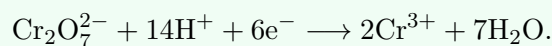


Multiply the first by 2 and the second by 5. On adding, cancel ten electrons, five water molecules and ten hydrogen ions:



Both sides have charge -1 ; oxygen and hydrogen are also balanced.

Step 2: Complete equation (b) Each chromium atom changes from oxidation state $+6$ to $+3$, so the two chromium atoms accept six electrons. Seven oxygen atoms form seven water molecules using the fourteen hydrogen ions supplied:

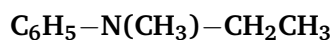


The net charge is $+6$ on each side, confirming the balance.

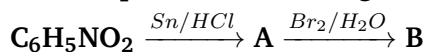
Step 3: Conclusion The products are (a) $2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$ and (b) $2\text{Cr}^{3+} + 7\text{H}_2\text{O}$.

Quick Tip to Solve: In acidic medium, use Mn(II) for permanganate and Cr(III) for dichromate; check total charge after balancing atoms.

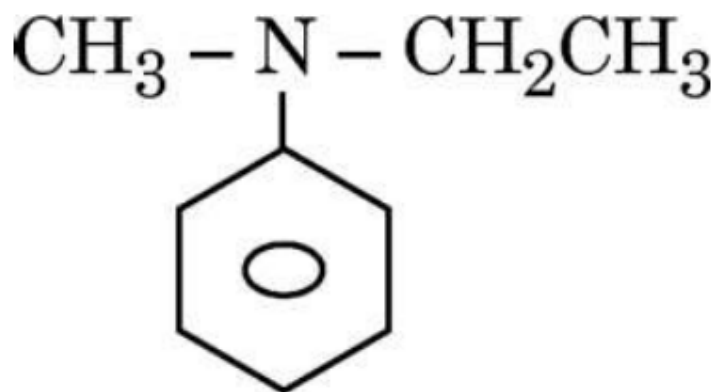
24. (a) Write the IUPAC name for the following organic compound:



(b) Complete the following:



[2 marks]



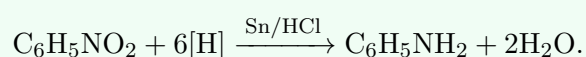
Solution:

Concept:

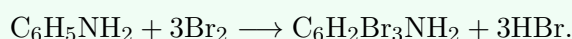
- Aniline is benzenamine. Alkyl groups attached directly to its nitrogen are indicated with the locant *N*, and their names are placed in alphabetical order.
- Tin and hydrochloric acid reduce an aromatic nitro group to an amino group. The amino group activates the benzene ring towards electrophilic substitution at the ortho and para positions.

Step 1: Name the compound in part (a) The nitrogen is bonded to the benzene ring, one methyl group and one ethyl group. Take benzenamine as the parent, and indicate that both alkyl substituents are on nitrogen. Ethyl precedes methyl alphabetically. Thus the IUPAC name is *N*-ethyl-*N*-methylbenzenamine (also written *N*-ethyl-*N*-methylaniline). The compound is a tertiary amine because nitrogen has three carbon-containing groups and no hydrogen.

Step 2: Identify A and B in part (b) Reduction of nitrobenzene gives aniline, A:



Aniline reacts readily with bromine water. Bromine substitutes at both ortho positions and at the para position relative to $-\text{NH}_2$:



Hence B is 2,4,6-tribromoaniline, obtained as a white precipitate. Bromine water gives the trisubstituted product, rather than a single brominated derivative.

Step 3: Conclusion (a) *N*-ethyl-*N*-methylbenzenamine. (b) A is aniline, $\text{C}_6\text{H}_5\text{NH}_2$, and B is 2,4,6-tribromoaniline, $\text{C}_6\text{H}_2\text{Br}_3\text{NH}_2$.

Quick Tip to Solve: Put N before each alkyl substituent attached to nitrogen; aniline with bromine water gives bromination at 2, 4 and 6.

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

[2 marks]

Solution:

Concept:

- Henry's law relates the equilibrium solubility of a gas in a liquid to the partial pressure of that gas above the liquid at a fixed temperature.
- In the CBSE convention, $p = K_H x$, where p is the gas partial pressure, x its mole fraction in solution, and K_H the Henry's law constant for the gas-solvent pair at that temperature.

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

$$p = K_H x, \quad x = \frac{p}{K_H}.$$

Thus, for a given gas and solvent at the same temperature, raising the gas pressure increases the amount of gas dissolved. The temperature must be specified because K_H depends on it.

Step 2: Apply the law to carbonated drinks Soft drinks and soda water are bottled under high carbon dioxide pressure. The greater partial pressure increases the dissolved mole fraction of CO_2 , producing carbonation. When the bottle is opened, the pressure above the liquid drops. The equilibrium solubility then decreases, and the excess dissolved carbon dioxide escapes as bubbles. This explains both the high-pressure bottling process and the fizz on opening.

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

Quick Tip to Solve: Write $p = K_H x$ and say constant temperature; link high-pressure soda bottling to increased dissolved carbon dioxide.

Section C (15 marks)

26. Write the main product formed when:

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

[3 marks]

Solution:

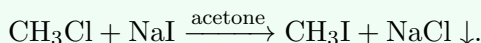
Concept:

- Sodium iodide in dry acetone exchanges iodine for chlorine in an alkyl chloride; precipitation of sodium chloride drives the Finkelstein reaction forward.
- Nitro groups at ortho and para positions facilitate nucleophilic substitution in aryl halides. Hydrolysis replaces chlorine with a hydroxyl group.
- Alcoholic potassium hydroxide favours beta-elimination: hydrogen is removed from a carbon adjacent to the one carrying halogen, and an alkene is formed.

Step 1: (a) Treat methyl chloride with NaI in acetone Iodide displaces chloride from methyl chloride

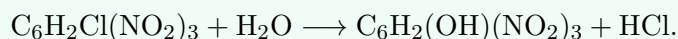
Quick Tip to Solve: Match the reagent to its action: NaI /acetone exchanges halogen, hydrolysis gives OH , and alcoholic KOH removes HCl to form an alkene.

through nucleophilic substitution:



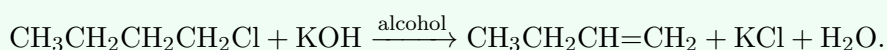
The main organic product is methyl iodide (iodomethane), CH_3I . Sodium chloride is poorly soluble in acetone and precipitates, promoting the exchange. Methyl chloride cannot undergo beta-elimination because it has no beta carbon.

Step 2: (b) Hydrolyse 2,4,6-trinitrochlorobenzene The three electron-withdrawing nitro groups activate the carbon bonded to chlorine towards nucleophilic attack. Hydrolysis replaces only the chlorine substituent with $-\text{OH}$; the nitro groups remain at positions 2, 4 and 6:



The main product is 2,4,6-trinitrophenol, commonly called picric acid. If hydrolysis is performed in alkali, the phenoxide salt forms first and yields the phenol on acidification.

Step 3: (c) Treat n-butyl chloride with alcoholic KOH The starting compound is 1-chlorobutane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$. Alcoholic KOH removes a beta hydrogen from carbon 2 while chloride leaves carbon 1. A double bond forms between these two carbons:



The product is but-1-ene. There is only one adjacent beta-carbon position in this primary chloride, so elimination produces the terminal alkene.

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

Quick Tip to Solve: Match the reagent to its action: NaI/acetone exchanges halogen, hydrolysis gives OH, and alcoholic KOH removes HCl to form an alkene.

27. 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:

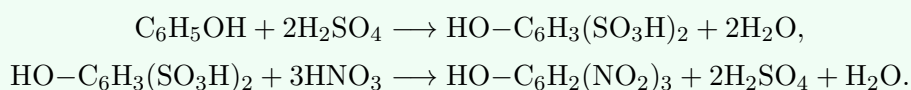
Concept:

- Phenol activates its ring towards electrophilic substitution and directs substitution to the ortho and para positions.
- A Grignard reagent adds an alkyl group to a carbonyl carbon; hydrolysis of the resulting magnesium alkoxide gives an alcohol.
- Williamson synthesis joins an alkoxide or phenoxide ion to a primary alkyl halide. Hydroboration-

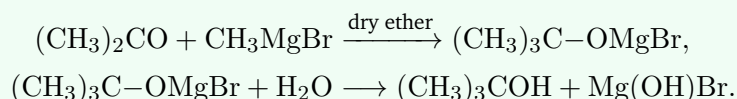
Quick Tip to Solve: For propan-1-ol choose hydroboration-oxidation; ordinary acid-catalysed hydration of propene gives propan-2-ol.

oxidation gives an anti-Markovnikov alcohol from an alkene.

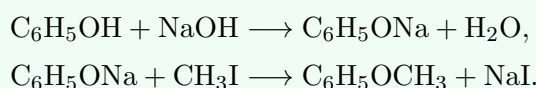
Step 1: (a) Convert phenol into picric acid Sulphonate phenol first with concentrated sulphuric acid, then nitrate the phenol-2,4-disulphonic acid with concentrated nitric acid. The sulphonic acid groups are replaced and nitration gives 2,4,6-trinitrophenol (picric acid):



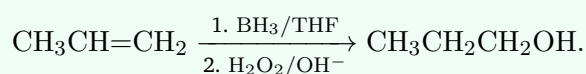
Step 2: (b) Add a methyl group to propanone Treat propanone with methylmagnesium bromide in dry ether and hydrolyse the product with dilute acid:



Step 3: (c) Prepare anisole by Williamson synthesis Convert phenol to sodium phenoxide using sodium hydroxide, then react the phenoxide with methyl iodide:



Step 4: (d) Obtain propan-1-ol from propene Use hydroboration with BH_3 in tetrahydrofuran (THF), followed by oxidation with alkaline hydrogen peroxide:



Oxidation replaces terminal boron by hydroxyl, giving the anti-Markovnikov product.

Step 5: Conclusion The conversions give picric acid by sulphonation-nitration, 2-methylpropan-2-ol by methyl Grignard addition, anisole by Williamson synthesis, and propan-1-ol by hydroboration-oxidation. Any three of these routes satisfy the question.

Quick Tip to Solve: For propan-1-ol choose hydroboration-oxidation; ordinary acid-catalysed hydration of propene gives propan-2-ol.

28. (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:

- Raoult's law states that the partial vapour pressure of a volatile component is $p_i = x_i p_i^0$, where x_i is its liquid-phase mole fraction and p_i^0 its pure vapour pressure at the same temperature.

Quick Tip to Solve: Calculate water's mole fraction using 47 mol of water and 0.5 mol of urea; multiply it by 23.8 mm Hg.

- Ideal solutions obey Raoult's law throughout the composition range. Their enthalpy and volume changes on mixing are zero.
- Urea is a non-volatile, non-electrolyte solute. The solution vapour pressure therefore equals the water vapour pressure, calculated using the mole fraction of water.

Step 1: (a) Distinguish ideal and non-ideal solutions An ideal solution obeys Raoult's law at all compositions, has $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$, and has unlike-molecule interactions approximately equal in strength to like-molecule interactions. A benzene-toluene mixture is an example.

A non-ideal solution deviates positively or negatively from Raoult's law because unlike-molecule interactions differ from like-molecule interactions. Generally $\Delta H_{\text{mix}} \neq 0$ and $\Delta V_{\text{mix}} \neq 0$. Weaker unlike interactions cause positive deviation, as in ethanol-acetone; stronger unlike interactions cause negative deviation, as in chloroform-acetone.

Step 2: (b) Calculate the mole fraction of water Use molar masses $M_{\text{urea}} = 60 \text{ g mol}^{-1}$ and $M_{\text{water}} = 18 \text{ g mol}^{-1}$:

$$\begin{aligned}n_{\text{urea}} &= \frac{30}{60} = 0.500 \text{ mol}, \\n_{\text{water}} &= \frac{846}{18} = 47.0 \text{ mol}, \\x_{\text{water}} &= \frac{47.0}{47.0 + 0.500} = \frac{94}{95}.\end{aligned}$$

Mole fractions require moles of both components, rather than a ratio of their masses.

Step 3: Apply Raoult's law at 298 K Taking the solution to obey Raoult's law and using the supplied pure-water vapour pressure,

$$p_{\text{water}} = x_{\text{water}} p_{\text{water}}^0 = \frac{94}{95} \times 23.8 = 23.549 \dots \text{ mm Hg}.$$

The lowering is $23.8 - 23.549 \dots = 0.2505 \dots \text{ mm Hg}$, consistent with the small mole fraction of non-volatile urea.

Step 4: Conclusion Ideal solutions obey Raoult's law at all compositions with zero enthalpy and volume changes on mixing; non-ideal solutions deviate from it. The vapour pressure of water in the given urea solution is approximately 23.55 mm Hg at 298 K.

Quick Tip to Solve: Calculate water's mole fraction using 47 mol of water and 0.5 mol of urea; multiply it by 23.8 mm Hg.

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]

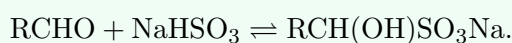
Solution:

Concept:

- The carboxyl group $-\text{COOH}$ withdraws electron density from an aromatic ring through its negative inductive and resonance effects.
- Aldehydes and many ketones undergo reversible nucleophilic addition with sodium hydrogen sulphite (sodium bisulphite), forming crystalline addition products.
- Resonance donation by the hydroxyl oxygen in a carboxylic acid reduces the electrophilicity of its carbonyl carbon compared with aldehydes and ketones.

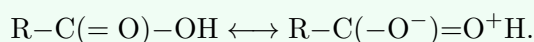
Step 1: (i) Explain the meta-directing carboxyl group In benzoic acid, $-\text{COOH}$ withdraws electrons by both $-I$ and $-R$ effects, deactivating the benzene ring towards electrophilic substitution. Ortho and para attack give arenium-ion intermediates with a resonance contributor having a positive charge on the ring carbon attached to the electron-withdrawing carboxyl group. This contributor is particularly unstable. The intermediate formed by meta attack avoids this extra destabilisation, so meta substitution is favoured.

Step 2: (ii) Explain purification using sodium bisulphite Aldehydes and suitable ketones form crystalline bisulphite addition compounds, which can be separated from impurities by filtration and washed. For an aldehyde, the reversible reaction is



Treating the isolated crystals with dilute acid or alkali decomposes the addition compound and regenerates the pure carbonyl compound. Purification is possible because formation and decomposition of the addition product are reversible; ketones that do not form such an adduct cannot be purified by this method.

Step 3: (iii) Explain the different behaviour of carboxylic acids In RCOOH , a lone pair on the hydroxyl oxygen is delocalised into the carbonyl group:



This resonance reduces the positive character of the carbonyl carbon, making nucleophilic attack less favourable than in aldehydes and ketones. Carboxylic acids therefore do not undergo their characteristic nucleophilic addition reactions. Under suitable conditions, acids instead undergo reactions such as esterification, involving substitution at the acyl group.

Step 4: Conclusion The carboxyl group favours meta substitution by destabilising ortho and para intermediates; reversible crystalline bisulphite adducts permit carbonyl purification; and resonance donation in $-\text{COOH}$ suppresses the characteristic carbonyl addition reactions.

Quick Tip to Solve: Link meta direction to electron withdrawal, bisulphite purification to reversible crystallisation, and acid behaviour to resonance donation from OH.

29(b). Give chemical equation for the following reactions:

(i) Propanone is treated with dil. $\text{Ba}(\text{OH})_2$.

(ii) Acetophenone is treated with $\text{Zn}(\text{Hg})/\text{Conc. HCl}$.

(iii) Benzoyl chloride is hydrogenated in presence of $\text{Pd}-\text{BaSO}_4$.

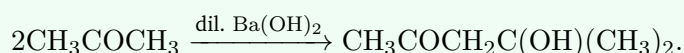
[3 marks]

Solution:

Concept:

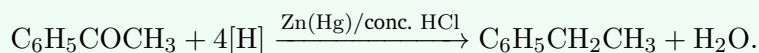
- Ketones containing an α -hydrogen undergo aldol addition in dilute base: two molecules combine to form a β -hydroxy ketone.
- Clemmensen reduction uses $\text{Zn}(\text{Hg})$ and concentrated HCl to convert a carbonyl group into a methylene group.
- Rosenmund reduction uses hydrogen over poisoned Pd/BaSO_4 to convert an acid chloride into an aldehyde.

Step 1: (i) Aldol addition of propanone Propanone has hydrogen atoms on the carbons adjacent to its carbonyl group. In dilute $\text{Ba}(\text{OH})_2$, an enolate of one molecule adds to the carbonyl carbon of another. Protonation gives the addition product, diacetone alcohol (4-hydroxy-4-methylpentan-2-one):



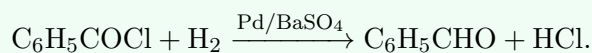
No heating is specified, so the product retains its hydroxyl group; dehydration to an unsaturated ketone is not required.

Step 2: (ii) Clemmensen reduction of acetophenone Acetophenone is $\text{C}_6\text{H}_5\text{COCH}_3$. Its carbonyl oxygen is removed during reduction, and the carbonyl carbon becomes $-\text{CH}_2-$, giving ethylbenzene:



Here $[\text{H}]$ denotes reducing equivalents supplied by the reagent. The benzene ring is retained.

Step 3: (iii) Rosenmund reduction of benzoyl chloride Controlled hydrogenation replaces the chlorine of the acid chloride by hydrogen, yielding benzaldehyde:



The poisoned catalyst limits further reduction, allowing isolation of the aldehyde rather than benzyl alcohol.

Step 4: Conclusion The products are (i) diacetone alcohol, $\text{CH}_3\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$; (ii) ethylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$; and (iii) benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$.

Quick Tip to Solve: Match the reagents first: dilute base gives aldol addition, $\text{Zn}(\text{Hg})/\text{HCl}$ removes carbonyl oxygen, and Pd/BaSO_4 stops an acid chloride at the aldehyde.

30. (a) Write the product when D-glucose reacts with conc. HNO_3 .

(b) Amino acids show amphoteric behaviour. Why?

(c) Write one difference between α -helix and β -pleated structure of protein.

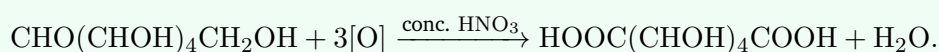
[3 marks]

Solution:

Concept:

- Concentrated nitric acid oxidises both the aldehyde end and the primary alcohol end of open-chain D-glucose to carboxyl groups.
- An amino acid contains a basic amino group and an acidic carboxyl group; in aqueous solution it commonly exists as a zwitterion.
- An α -helix and a β -pleated sheet are secondary structures of proteins stabilised by hydrogen bonding between peptide groups.

Step 1: (a) Oxidation product of D-glucose Open-chain D-glucose has an aldehyde group at C-1 and a primary alcohol group at C-6. Concentrated HNO_3 oxidises both ends, while the four intervening CHOH groups remain:



The dicarboxylic acid obtained is saccharic acid, also called D-glucaric acid.

Step 2: (b) Reason for amphoteric behaviour The carboxyl group can donate a proton, whereas the amino group can accept a proton. Thus amino acids react with both acids and bases. For a general amino acid, internal proton transfer gives the zwitterion $\text{H}_3\text{N}^+ - \text{CH}(\text{R}) - \text{COO}^-$. In acid it accepts a proton at the carboxylate group; in base it loses a proton from the ammonium group. Therefore the same molecule displays both acidic and basic behaviour.

Step 3: (c) Difference between the two secondary structures In an α -helix, one polypeptide chain coils into a helix, stabilised by hydrogen bonds between peptide groups within that helical chain. In a β -pleated sheet, extended polypeptide strands lie alongside one another and are linked by hydrogen bonds between adjacent strands. Such strands may belong to different chains or to different folded segments of one chain. The essential difference is a coiled helical arrangement versus an extended, pleated sheet arrangement.

Step 4: Conclusion (a) D-glucose gives saccharic acid, $\text{HOOC}(\text{CHOH})_4\text{COOH}$. (b) Amino acids are amphoteric because they contain acidic $-\text{COOH}$ and basic $-\text{NH}_2$ groups. (c) An α -helix is coiled, whereas a β -pleated sheet consists of adjacent extended strands.

Quick Tip to Solve: For glucose oxidation, check both terminal groups; for protein structure, compare a coiled chain with adjacent extended strands.

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 reaction rate measures the change in concentration over a finite time interval $\Delta t = t_2 - t_1$.
- Reactant concentration decreases, so its rate expression needs a minus sign; product concentration increases, so its expression has a plus sign.

Step 1: Define the finite-interval rate The average rate of a reaction is the decrease in concentration of a reactant, or the increase in concentration of a product, per unit time over a specified time interval. It describes the whole interval, rather than the rate at one instant.

Step 2: Express the definition mathematically For $R \rightarrow P$, with unit stoichiometric coefficients,

$$r_{\text{avg}} = -\frac{[R]_2 - [R]_1}{t_2 - t_1} = \frac{[P]_2 - [P]_1}{t_2 - t_1}.$$

Square brackets denote molar concentration. When time is in seconds, the unit is $\text{mol L}^{-1} \text{s}^{-1}$. For other stoichiometric coefficients, divide each species rate by its coefficient to obtain the common reaction rate.

Step 3: Conclusion Average reaction rate is the concentration change per unit time over a finite interval: $r_{\text{avg}} = -\Delta[R]/\Delta t$ for a reactant, or $+\Delta[P]/\Delta t$ for a product of unit stoichiometric coefficient.

Quick Tip to Solve: Use the two endpoint concentrations and the elapsed time; include a minus sign when calculating from the disappearing reactant.

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

[1 mark]

Solution:

Concept:

- Reaction rate depends on how frequently reacting particles undergo effective collisions.
- Reactant concentration affects collision frequency; temperature affects particle energy and the fraction of collisions that can overcome the activation barrier.

Step 1: Factor 1: Reactant concentration The concentration of the reactants affects the rate. For a reaction with positive order in a reactant, increasing its concentration increases the rate because more

Quick Tip to Solve: Name concentration and temperature as two distinct factors; remember that concentration dependence is governed by the reaction order.

reacting particles occupy the same volume and collisions are more frequent. The precise dependence follows the rate law; a zero-order reaction is independent of concentration within its zero-order range.

Step 2: Factor 2: Temperature The temperature of the reaction mixture also affects the rate. Increasing temperature generally increases the rate constant because a greater fraction of particles have sufficient energy to cross the activation energy barrier. Thus effective collisions occur more often. Temperature and concentration are two separate factors and each directly answers the question.

Step 3: Conclusion Two factors that affect the rate of reaction are (1) concentration of the reactants and (2) temperature of the reaction mixture.

Quick Tip to Solve: Name concentration and temperature as two distinct factors; remember that concentration dependence is governed by the reaction order.

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 the reaction rate and k is the rate constant.
- Rate has the dimensions concentration per unit time; hence a zero-order rate constant has the same units as rate.

Step 1: Determine the effect of concentration The exponent of reactant concentration is zero, so $[A]^0 = 1$ within the range over which zero-order kinetics applies. Thus

$$r = k.$$

Changing the reactant concentration does not change the rate. At a fixed temperature and under the same reaction conditions, the rate remains constant while the reaction follows this rate law; it does not progressively decrease merely because the reactant concentration falls.

Step 2: Obtain the unit of the rate constant Since $k = r$, the unit follows directly from concentration divided by time. Taking concentration in mol L^{-1} and time in seconds,

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

Unlike a first-order rate constant, this constant does not have the unit s^{-1} , because the concentration factor has not been divided out of the rate.

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

Quick Tip to Solve: For zero order, set the concentration factor equal to 1; then both the value and the units of rate equal those of k .

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

Solution:

Concept:

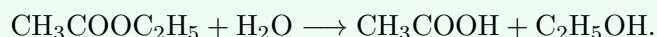
- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- A pseudo first-order reaction has a higher-order rate law but behaves as first order when the concentration of another reactant is effectively constant.

Step 1: Add the exponents in the given rate law For $r = k[P]^{1/2}[Q]^1$, the partial order with respect to P is $1/2$ and that with respect to Q is 1. Therefore the overall order is

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

The coefficient 2 in the balanced equation is not used to determine order: stoichiometric coefficients do not in general equal the exponents in an experimental rate law.

Step 2: Define pseudo first order and give an example A reaction that is actually of higher order but behaves kinetically as first order because one reactant is present in large excess is called a pseudo first-order reaction. For example, acid-catalysed hydrolysis of ethyl ethanoate in excess water is



At fixed acid concentration, $r = k[\text{ester}][\text{H}_2\text{O}]$. Since the concentration of excess water remains practically constant, $r = k'[\text{ester}]$, where $k' = k[\text{H}_2\text{O}]$. Hence the observed kinetics is first order in the ester.

Step 3: Conclusion (1) Order = $\boxed{3/2}$. (2) A higher-order reaction behaving as first order because an excess reactant has nearly constant concentration is pseudo first order; hydrolysis of ethyl ethanoate in excess water is an example.

Quick Tip to Solve: Add powers in the rate law for order, and absorb the nearly constant concentration of an excess reactant into the apparent rate constant.

32(i). Case Study: 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:

- Chloride ions outside the coordination sphere ionise in solution and give a precipitate of AgCl with AgNO_3 .
- Ligands bound directly to the metal are placed inside square brackets in the formula of a coordination compound.

Step 1: Use the silver nitrate observation The compound does not react with silver nitrate, so neither of its two chloride ions is available as a free, ionisable counter-ion. Both chloride ions must therefore be coordinated directly to platinum.

Step 2: Place all the ligands within the coordination sphere The two neutral ammonia molecules are also coordinated to platinum. Putting both ammine ligands and both chlorido ligands within the brackets gives $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. Platinum is in the +2 oxidation state, and the two chlorido ligands balance this charge, so the complex is neutral and needs no counter-ion outside the brackets.

Step 3: Conclusion The formula is $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Quick Tip to Solve: No AgCl precipitate means there is no chloride outside the square brackets; put 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 secondary valency equals the coordination number: the number of donor atoms bonded directly to the central metal.
- Ethylenediamine, abbreviated en, is a neutral bidentate ligand; each molecule binds through two nitrogen donor atoms.

Step 1: Count donor atoms per ligand Each ethylenediamine ligand contains two nitrogen atoms with lone pairs available for coordination. One en ligand therefore satisfies two secondary valencies of cobalt, rather than just one.

Step 2: Count the total coordination number The complex contains three such ligands, so the number of coordinated donor atoms is

$$3 \times 2 = 6.$$

The overall 3+ charge of the complex indicates the cobalt oxidation state because the ligands are neutral. That charge is not its secondary valency; secondary valency counts metal-donor bonds.

Quick Tip to Solve: For a chelating ligand, multiply the number of ligands by its denticity; three bidentate en ligands provide six donor atoms.

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

Quick Tip to Solve: For a chelating ligand, multiply the number of ligands by its denticity; three bidentate en ligands provide six donor atoms.

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 charge on a complex equals the metal oxidation state plus the sum of ligand charges; each cyanido or chlorido ligand has charge -1 , while ammonia is neutral.
- For a neutral salt, total positive and negative charges balance. In IUPAC naming, ligands precede the metal name and its oxidation state.

Step 1: Write iron(III) hexacyanidoferrate(II) Iron(III) is the cation Fe^{3+} . Hexacyanidoferrate(II) contains iron in the $+2$ state with six CN^- ligands, giving the complex charge

$$+2 + 6(-1) = -4.$$

Thus the anion is $[\text{Fe}(\text{CN})_6]^{4-}$. The least common multiple of 3 and 4 is 12, so four iron(III) cations balance three complex anions. The resulting neutral salt has formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

Step 2: Name the cobalt complex In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, the two outside chloride ions show that the complex cation has charge $+2$. If the cobalt oxidation state is x , the neutral ammine ligands and one chlorido ligand give

$$x + 5(0) - 1 = +2, \quad x = +3.$$

Name the five ammonia ligands pentaammine and the coordinated chloride chlorido, in alphabetical ligand order. Since the complex is cationic, the metal name remains cobalt. Include its oxidation state as (III), followed by chloride for the counter-ion; multiplicative prefixes are not used for the outside chloride ions.

Step 3: Conclusion (1) The formula is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

(2) The IUPAC name is pentaamminechloridocobalt(III) chloride.

Quick Tip to Solve: First determine each complex charge, then balance the salt; for naming, determine cobalt oxidation state using only ligand and counter-ion charges.

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 a metal is obtained by adding the charges of its ligands to the metal charge and equating the sum to the overall complex charge. Each cyanido ligand, CN^- , has charge -1 .
- Cyanide is a strong-field ligand. For a d^8 nickel(II) ion it promotes pairing of the $3d$ electrons, permitting dsp^2 hybridisation and a square-planar arrangement.
- A species with no unpaired electrons is diamagnetic; unpaired electrons produce paramagnetic behaviour.

Step 1: Determine the oxidation state and electron configuration Let the oxidation state of nickel be x . In $[\text{Ni}(\text{CN})_4]^{2-}$,

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

Nickel has atomic number 28, so neutral Ni has configuration $[\text{Ar}]3d^84s^2$. Removal of the two $4s$ electrons gives $\text{Ni}^{2+} : [\text{Ar}]3d^8$.

Step 2: Apply strong-field pairing and identify the magnetic behaviour The strong-field CN^- ligands cause the eight $3d$ electrons to pair in four orbitals, leaving one $3d$ orbital vacant. This vacant orbital, the $4s$ orbital and two $4p$ orbitals form four dsp^2 hybrid orbitals. The four ligands donate lone pairs into these orbitals, giving square-planar geometry. All the metal electrons are paired, so the number of unpaired electrons is zero and the complex is diamagnetic. A tetrahedral sp^3 description is therefore inappropriate for this strong-field nickel complex.

Step 3: Conclusion $[\text{Ni}(\text{CN})_4]^{2-}$ has dsp^2 hybridisation, square-planar geometry and diamagnetic behaviour.

Quick Tip to Solve: First establish Ni^{2+} as d^8 ; then remember that strong-field cyanide pairs the electrons to give square-planar dsp^2 nickel.

Section E (15 marks)

33(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'.

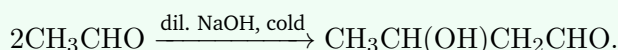
[5 marks]

Solution:

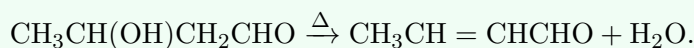
Concept:

- Aldehydes with an α -hydrogen undergo 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 with halogen using Cl_2 and red phosphorus, followed by hydrolysis.
- Reductive ozonolysis cleaves an alkene's $C = C$ bond, converting each double-bond carbon into a carbonyl carbon. Fehling's solution identifies an aliphatic aldehyde, while iodine in alkali gives iodoform with ethanal and methyl ketones.

Step 1: (i)(1) Convert ethanal into but-2-en-1-al Treat ethanal with cold dilute NaOH. Two ethanal molecules undergo aldol addition to form 3-hydroxybutanal:

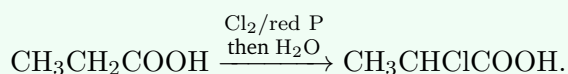


Heat the aldol product to eliminate water:



Numbering from the aldehyde carbon places the double bond between carbons 2 and 3. Thus this four-carbon product is the required but-2-en-1-al (crotonaldehyde).

Step 2: (i)(2) Convert propanoic acid into 2-chloropropanoic acid Chlorinate propanoic acid with chlorine in the presence of red phosphorus, then hydrolyse. This is the Hell-Volhard-Zelinsky reaction:

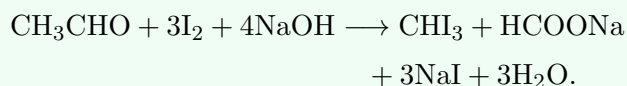


The carbon adjacent to $-COOH$ is the α -carbon, numbered 2. Replacement of one of its hydrogens with chlorine therefore gives 2-chloropropanoic acid.

Step 3: (ii) Identify the aldehyde B from its two tests A positive Fehling test points to an aliphatic aldehyde, which reduces the copper(II) reagent to a brick-red precipitate of Cu_2O . Among aldehydes, ethanal gives the iodoform reaction because it contains the CH_3CO- unit. Hence B is ethanal,

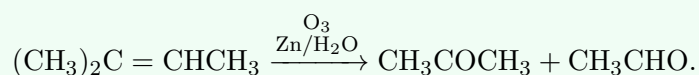
Quick Tip to Solve: An aldehyde positive in both Fehling and iodoform tests is ethanal; count the remaining carbons, then join the two carbonyl carbons to reconstruct the alkene.

CH_3CHO . Its reaction with iodine and sodium hydroxide is



The yellow precipitate is iodoform, CHI_3 .

Step 4: (ii) Identify C and reconstruct alkene A C gives iodoform but does not reduce Fehling's solution, so it is a methyl ketone. A has five carbon atoms, and B accounts for two of them. Ozonolysis does not change the total carbon count, leaving three carbon atoms in C. Therefore C is propanone, CH_3COCH_3 . To reconstruct A, remove the carbonyl oxygens and join the two carbonyl carbons with a double bond. The ethanal carbon bears H and CH_3 , while the propanone carbon bears two CH_3 groups. The resulting alkene is $(\text{CH}_3)_2\text{C} = \text{CHCH}_3$, 2-methylbut-2-ene:



This alkene has formula C_5H_{10} , and both products satisfy their respective chemical tests.

Step 5: Conclusion (i) Ethanal gives $\text{CH}_3\text{CH} = \text{CHCHO}$ by aldol addition followed by dehydration; propanoic acid gives $\text{CH}_3\text{CHClCOOH}$ by the Hell-Volhard-Zelinsky reaction. (ii)

A = 2-methylbut-2-ene, B = ethanal, and C = propanone.

Quick Tip to Solve: An aldehyde positive in both Fehling and iodoform tests is ethanal; count the remaining carbons, then join the two carbonyl carbons to reconstruct the alkene.

OR

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

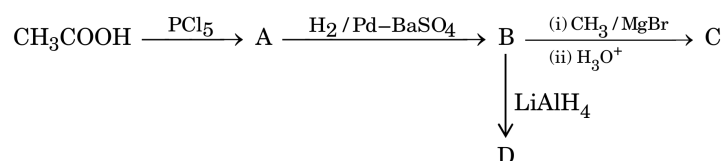
(1) $\text{CH}_3\text{COCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

(2) Ethanal and Ethanoic acid

(ii) Write the structure of oxime of acetone.

(iii) Identify A to D in the reaction scheme shown below.

[5 marks]



Solution:

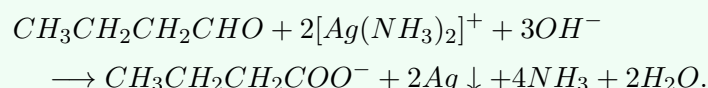
Concept:

- Aldehydes reduce Tollens' reagent, an alkaline solution containing $[\text{Ag}(\text{NH}_3)_2]^+$, to metallic silver; ordinary ketones do not.
- Carboxylic acids react with sodium hydrogen carbonate to liberate carbon dioxide, whereas aldehydes do not give this acid-base test.

Quick Tip to Solve: Track the carbon count through the scheme: Rosenmund reduction and LiAlH_4 retain two carbons, but CH_3MgBr adds one carbon to give a three-carbon secondary alcohol.

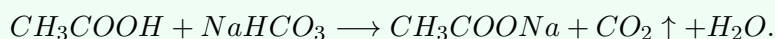
- Hydroxylamine, NH_2OH , converts a carbonyl group into an oxime group, $C = N - OH$, with elimination of water.
- PCl_5 converts a carboxylic acid into an acyl chloride. Rosenmund reduction converts the acyl chloride into an aldehyde; a Grignard reagent adds an alkyl group to the carbonyl carbon, while $LiAlH_4$ reduces an aldehyde to a primary alcohol.

Step 1: (i)(1) Distinguish butan-2-one from butanal Warm separate samples gently with freshly prepared Tollens' reagent. Butanal, $CH_3CH_2CH_2CHO$, gives a silver mirror on the wall of the test tube because its aldehyde group is oxidised to a carboxylate ion while silver(I) is reduced to metallic silver:



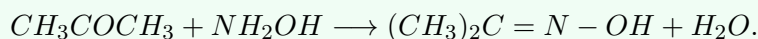
Butan-2-one, $CH_3COCH_2CH_3$, gives no silver mirror because it is a ketone and is not oxidised by this mild reagent. Thus a positive silver-mirror test identifies butanal, and the negative sample is butan-2-one.

Step 2: (i)(2) Distinguish ethanal from ethanoic acid Add aqueous sodium hydrogen carbonate, $NaHCO_3$, separately to the two samples. Ethanoic acid gives brisk effervescence of carbon dioxide:



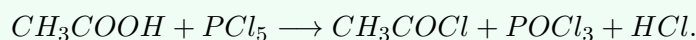
The evolved gas turns limewater milky, confirming CO_2 . Ethanal, CH_3CHO , gives no such effervescence because it lacks a carboxylic acid group and does not displace carbonic acid from bicarbonate. Hence the effervescent sample is ethanoic acid.

Step 3: (ii) Write the oxime of acetone Acetone reacts with hydroxylamine by condensation at its carbonyl group:

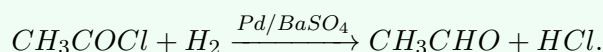


The required condensed structural formula is $CH_3 - C(=N - OH) - CH_3$. Both methyl groups remain attached to the same carbon; the oxygen of the original carbonyl group is replaced by the $=N - OH$ group. The hydroxyl group is attached to nitrogen, not directly to carbon.

Step 4: (iii) Identify A and B Ethanoic acid reacts with phosphorus pentachloride to form ethanoyl chloride, so $A = CH_3COCl$:



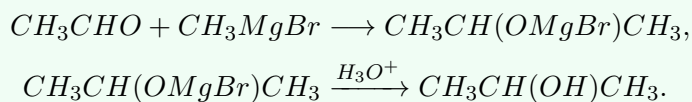
Hydrogen over palladium supported on barium sulphate carries out Rosenmund reduction. This controlled reduction stops at the aldehyde, giving $B = CH_3CHO$, ethanal:



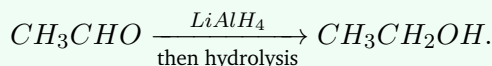
Step 5: (iii) Identify C and D Methylmagnesium bromide adds a methyl group to ethanal in dry ether,

Quick Tip to Solve: Track the carbon count through the scheme: Rosenmund reduction and $LiAlH_4$ retain two carbons, but CH_3MgBr adds one carbon to give a three-carbon secondary alcohol.

forming a magnesium alkoxide. Acidic hydrolysis then gives propan-2-ol:



Therefore $C = \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. The product is a secondary alcohol with three carbon atoms because the Grignard reagent supplies one additional carbon atom. In the other branch, lithium aluminium hydride reduces ethanal's aldehyde group to $-\text{CH}_2\text{OH}$, followed by hydrolysis of the intermediate:



Thus $D = \text{CH}_3\text{CH}_2\text{OH}$, ethanol; this reduction retains the two-carbon skeleton.

Step 6: Conclusion (i) Butanal gives a silver mirror with Tollens' reagent; butan-2-one does not. Ethanoic acid gives CO_2 effervescence with NaHCO_3 ; ethanal does not. (ii) Acetone oxime is $(\text{CH}_3)_2\text{C} = \text{N} - \text{OH}$. (iii) $A = \text{CH}_3\text{COCl}$, $B = \text{CH}_3\text{CHO}$, $C = \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$, and $D = \text{CH}_3\text{CH}_2\text{OH}$.

Quick Tip to Solve: Track the carbon count through the scheme: Rosenmund reduction and LiAlH_4 retain two carbons, but CH_3MgBr adds one carbon to give a three-carbon secondary alcohol.

34. (a) (i) In 3d series, which transition element has positive $E^\circ_{\text{M}^{2+}/\text{M}}$ value and why?

(ii) Name a member of lanthanide series which is well-known to show +4 oxidation state.

(b) Give reason:

(i) The highest oxidation state is exhibited in oxoanions of transition metals.

(ii) HCl is not used to acidify KMnO_4 solution.

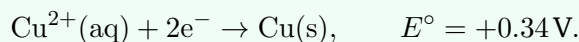
[5 marks]

Solution:

Concept:

- The standard reduction potential $E^\circ_{\text{M}^{2+}/\text{M}}$ refers to $\text{M}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{M}(\text{s})$. Its sign depends on the balance between atomisation, ionisation and hydration energies.
- Stable electronic configurations help explain lanthanide oxidation states. Removal of four electrons from cerium gives Ce^{4+} with the xenon-core configuration, $[\text{Xe}]$, or $4f^0$.
- Oxygen stabilises high oxidation states of transition metals by forming strong metal-oxygen bonds. Acidified permanganate is a powerful oxidising agent and can oxidise chloride ions to chlorine.

Step 1: (a)(i) Identify the metal with a positive reduction potential Copper, Cu, has a positive standard reduction potential in the 3d transition series:



Converting copper metal into $\text{Cu}^{2+}(\text{aq})$ requires atomisation of the metal followed by its first and second ionisations. Copper has a high atomisation enthalpy, and its second ionisation is particularly costly because it removes an electron from the stable $3d^{10}$ configuration of Cu^+ . The energy required

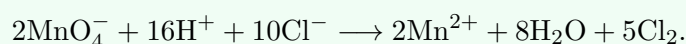
Quick Tip to Solve: For the acid choice, check whether its anion can itself be oxidised: chloride reacts with acidified permanganate, so use dilute sulphuric acid.

for these processes is not compensated by the hydration enthalpy released on forming $\text{Cu}^{2+}(\text{aq})$. Thus oxidation of copper to the aqueous divalent ion is energetically unfavourable relative to the standard hydrogen electrode, giving the reverse reduction a positive E° .

Step 2: (a)(ii) Identify the lanthanide showing the +4 state Cerium, Ce, is well known to show the +4 oxidation state. Its ground-state configuration is $[\text{Xe}]4f^15d^16s^2$. Loss of four valence electrons gives Ce^{4+} with the stable noble-gas-core configuration $[\text{Xe}]$. This accounts for the occurrence of the +4 state, for example in CeO_2 , in addition to the common lanthanide +3 state.

Step 3: (b)(i) Explain high oxidation states in oxoanions Oxygen is highly electronegative and forms strong bonds with transition metals, including metal–oxygen multiple bonding. These bonds stabilise the metal in a very high positive oxidation state. Consequently, the highest oxidation states are commonly found in oxoanions such as MnO_4^- and CrO_4^{2-} . Taking oxygen as -2 , the oxidation state x of manganese satisfies $x + 4(-2) = -1$, giving $x = +7$; for chromium, $x + 4(-2) = -2$, giving $x = +6$. These examples illustrate oxygen's ability to stabilise the high oxidation state.

Step 4: (b)(ii) Explain why hydrochloric acid is unsuitable Hydrochloric acid supplies chloride ions, which acidified potassium permanganate oxidises to chlorine. Permanganate is therefore consumed in an unwanted side reaction instead of only oxidising the intended substance:



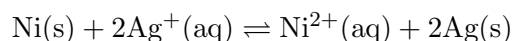
This changes the amount of permanganate available and causes an error in redox titrations. Dilute sulphuric acid is used for acidification because it supplies the necessary hydrogen ions without this chloride oxidation reaction.

Step 5: Conclusion (a)(i) Copper: its atomisation and ionisation energy requirements are not compensated by hydration, so $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is positive. (a)(ii) Cerium. (b)(i) Strong metal–oxygen bonding stabilises high oxidation states in oxoanions. (b)(ii) Acidified KMnO_4 oxidises chloride from HCl to Cl_2 , consuming permanganate.

Quick Tip to Solve: For the acid choice, check whether its anion can itself be oxidised: chloride reacts with acidified permanganate, so use dilute sulphuric acid.

35(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: $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$, $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$; $1 F = 96500 \text{ C mol}^{-1}$.

[5 marks]

Solution:

Concept:

- At infinite dilution, each ion contributes independently to the limiting molar conductivity. If λ_i° is the limiting ionic molar conductivity, then $\Lambda_m^\circ = \sum_i \nu_i \lambda_i^\circ$, where ν_i counts each ion in the electrolyte formula.

Quick Tip to Solve: Balance the electrons first to obtain $n = 2$, subtract reduction potentials without multiplying them, and distinguish the negative Gibbs energy change from the positive magnitude of work delivered.

- The standard cell potential is $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$, using both electrode potentials as reduction potentials.
- Standard Gibbs energy and maximum electrical work are related by $\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$. The maximum work delivered by the cell has magnitude $nFE_{\text{cell}}^{\circ}$; n is the number of electrons transferred and F is the Faraday constant.
- At equilibrium, $\Delta_r G^{\circ} = -2.303RT \log K_c$, so $\log K_c = nFE_{\text{cell}}^{\circ}/(2.303RT)$, with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T in kelvin.

Step 1: (i) State Kohlrausch's law and apply it to acetic acid Kohlrausch's law of independent migration of ions states that at infinite dilution, the limiting molar conductivity of an electrolyte is the sum of the individual contributions of its constituent ions. Each ion's contribution is independent of the nature of the other ion present. Acetic acid gives one hydrogen ion and one acetate ion per formula unit. Therefore,

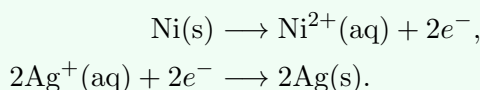
$$\Lambda_m^{\circ}(\text{CH}_3\text{COOH}) = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{CH}_3\text{COO}^-}^{\circ}$$

Equivalently, using strong electrolytes whose limiting conductivities can be measured,

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

In this combination, the sodium and chloride ion contributions cancel, leaving exactly the hydrogen and acetate contributions. This is useful because acetic acid is a weak electrolyte and its limiting conductivity cannot be found by directly extrapolating the usual conductivity plot for strong electrolytes.

Step 2: (ii) Identify the electron transfer and standard cell potential Nickel is oxidised while silver ions are reduced. The half-reactions for the reaction as written are



Thus $n = 2$, the silver electrode is the cathode, and the nickel electrode is the anode. Using the given reduction potentials,

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

Electrode potentials are not multiplied by stoichiometric coefficients: the coefficient 2 for silver determines electron balance, not a doubling of its potential.

Step 3: Calculate the maximum work For one mole of reaction as written, the standard Gibbs energy change is

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

Therefore the cell can deliver 202.65 kJ of maximum electrical work per mole of the reaction under standard reversible conditions. Under the convention that work done on the system is positive, the

Quick Tip to Solve: Balance the electrons first to obtain $n = 2$, subtract reduction potentials without multiplying them, and distinguish the negative Gibbs energy change from the positive magnitude of work delivered.

corresponding maximum reversible electrical work is $-202.65 \text{ kJ mol}^{-1}$. The negative Gibbs energy change is consistent with the positive standard cell potential.

Step 4: Calculate the equilibrium constant logarithm Combine the Gibbs energy expressions at 298 K:

$$\begin{aligned}\log K_c &= \frac{nF E_{\text{cell}}^{\circ}}{2.303RT} \\ &= \frac{2(96500)(1.05)}{2.303(8.314)(298)} \\ &\simeq 35.52.\end{aligned}$$

Using the usual rounded factor $2.303RT/F = 0.0591 \text{ V}$ at 298 K gives $\log K_c = 2(1.05)/0.0591 \simeq 35.53$, the same result to the precision of the constants. Pure nickel and silver solids have unit activity and do not appear in the equilibrium expression. Hence K_c corresponds to the ratio $[\text{Ni}^{2+}]/[\text{Ag}^+]^2$ in the standard concentration treatment; its very large value indicates that the forward reaction is strongly favoured.

Step 5: Conclusion $\Delta_m^{\circ}(\text{CH}_3\text{COOH}) = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{CH}_3\text{COO}^-}^{\circ}$. For the nickel-silver reaction, $E_{\text{cell}}^{\circ} = 1.05 \text{ V}$, $\Delta_r G^{\circ} = -202.65 \text{ kJ mol}^{-1}$, maximum work delivered is $202.65 \text{ kJ mol}^{-1}$, and $\log K_c \simeq 35.5$.

Quick Tip to Solve: Balance the electrons first to obtain $n = 2$, subtract reduction potentials without multiplying them, and distinguish the negative Gibbs energy change from the positive magnitude of work delivered.

OR

35(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

$\text{Mg(s)} \mid \text{Mg}^{2+}(0.1 \text{ M}) \parallel \text{Cu}^{2+}(0.01 \text{ M}) \mid \text{Cu(s)}$

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

[5 marks]

Solution:

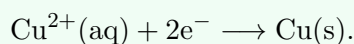
Concept:

- Faraday's first law states that the mass m of a substance deposited or liberated at an electrode is directly proportional to the electric charge q passed through the electrolyte: $m = Zq = ZIt$. Here Z is the electrochemical equivalent, I the current and t the time.
- One Faraday is the charge carried by one mole of electrons, $F = 96500 \text{ C mol}^{-1}$. The electron requirement follows from the balanced electrode reaction.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$, where n is the number of electrons transferred per balanced cell reaction and Q is its reaction quotient. Pure solid metals have unit activity.

Step 1: (i) State the law and determine the electron requirement Faraday's first law of electrolysis: the mass of a substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte. Thus, $m \propto q$, or $m = Zq$. The reduction of copper(II)

Quick Tip to Solve: For the Mg-Cu cell, balance electrons first: $n = 2$. Put the product ion concentration over the reactant ion concentration, giving $Q = 0.1/0.01 = 10$.

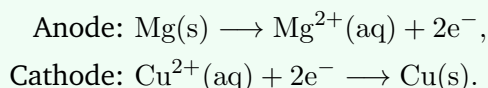
ions is



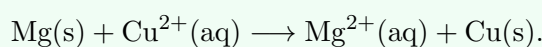
Each copper(II) ion accepts two electrons. Therefore, reduction of 1 mol of Cu^{2+} requires 2 mol of electrons. Since one mole of electrons carries one Faraday of charge, the required charge is

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

Step 2: (ii) Write the cell reaction and reaction quotient Magnesium is oxidised at the anode and copper(II) ions are reduced at the cathode:



Adding the half-reactions gives



Two electrons are transferred, so $n = 2$. Solids do not appear in the concentration quotient. Using the stated molar concentrations,

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

Step 3: Substitute into the Nernst equation at 298 K With $E_{\text{cell}}^{\circ} = +2.71 \text{ V}$, $n = 2$ and $\log 10 = 1$,

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

The quotient exceeds unity, so the non-standard emf is slightly smaller than the standard emf, consistent with the negative Nernst correction.

Step 4: Conclusion (i) Faraday's first law is $m \propto q$ or $m = ZIt$; reduction of 1 mol of Cu^{2+} requires 2 F of charge, equivalent to $1.93 \times 10^5 \text{ C}$. (ii) The cell emf at 298 K is $E_{\text{cell}} = 2.68045 \text{ V} \approx 2.68 \text{ V}$.

Quick Tip to Solve: For the Mg-Cu cell, balance electrons first: $n = 2$. Put the product ion concentration over the reactant ion concentration, giving $Q = 0.1/0.01 = 10$.