

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

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

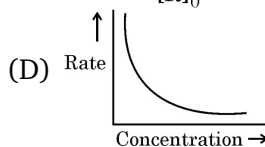
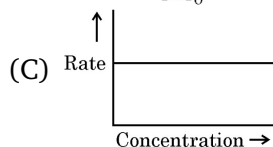
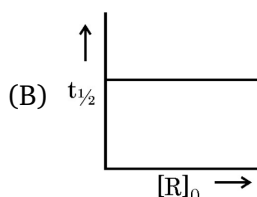
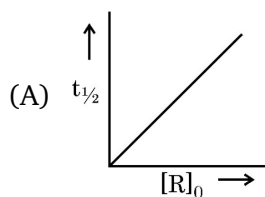
- (i) This question paper contains **33** questions. **All** questions are **compulsory**.
- (ii) This question paper is divided into **five** sections – Section **A, B, C, D** and **E**.
- (iii) **Section A** – questions number **1** to **16** are multiple choice type questions. Each question carries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

Section A (16 marks)

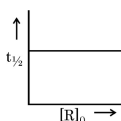
Questions No. 1 to 16 are Multiple Choice type questions carrying 1 mark each.

1. Which of the following curve represents the first order reaction?

[1 mark]



Correct Answer: (B)



Solution:

Concept:

- For a first-order reaction, the rate is $k[R]$, where k is the rate constant and $[R]$ is the reactant concentration.
- Its half-life is $t_{1/2} = \ln 2/k = 0.693/k$, independent of the initial concentration $[R]_0$.

Step 1: Relate half-life to initial concentration At a fixed temperature, k is constant. The first-order half-life therefore stays unchanged when $[R]_0$ changes. A plot of $t_{1/2}$ against $[R]_0$ must be a horizontal line.

Step 2: Compare the four curves Curve (B) has this constant half-life. Curve (A) shows $t_{1/2}$ proportional to $[R]_0$, as in a zero-order reaction. Curve (C) shows a rate independent of concentration, also characteristic of zero order. Curve (D) shows rate decreasing as concentration increases, whereas a first-order rate increases linearly with concentration.

Step 3: Conclusion The horizontal half-life versus initial-concentration graph represents a first-order reaction. Hence, the correct option is (B).

Quick Tip to Solve: Read both axes first: a horizontal half-life graph means first order, but a horizontal rate graph means zero order.

2. Which of the following solutions will have the lowest freezing point in water?

[1 mark]

- (A) 0.1 M Glucose
- (B) 0.1 M CaCl_2
- (C) 0.1 M KCl
- (D) 0.1 M Urea

Correct Answer: (B) 0.1 M CaCl_2

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the solvent cryoscopic constant and m the molality.
- For these dilute aqueous solutions of equal stated concentration, compare the number of dissolved particles furnished by each solute.

Step 1: Count particles from each solute Glucose and urea are non-electrolytes, so each has $i = 1$. Potassium chloride dissociates as $\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$, giving $i \approx 2$. Calcium chloride dissociates as $\text{CaCl}_2 \longrightarrow \text{Ca}^{2+} + 2\text{Cl}^-$, giving $i \approx 3$.

Step 2: Compare freezing-point depressions Using the usual dilute-solution comparison for equal 0.1 M concentrations in water, CaCl_2 supplies the largest particle concentration and hence the greatest ΔT_f . Since $T_f = T_f^0 - \Delta T_f$, greater depression means lower freezing point. KCl produces fewer ions; glucose and urea do not dissociate.

Step 3: Conclusion The 0.1 M solution of CaCl_2 has the lowest freezing point. Hence, the correct option is (B).

Quick Tip to Solve: For equally dilute aqueous solutions, count the ions per formula unit; more particles imply greater freezing-point depression.

3. Which of the following is not a transition metal?

[1 mark]

- (A) Sc
- (B) Ag
- (C) Hg
- (D) Cu

Correct Answer: (C) Hg

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its oxidation states.
- A completely filled d^{10} subshell in both the atom and its usual ions excludes an element from the transition-metal category.

Step 1: Examine mercury Mercury has configuration $[\text{Xe}]4f^{14}5d^{10}6s^2$, and its common Hg^{2+} ion has

Quick Tip to Solve: Apply the definition to both the atom and its ions; a filled atomic d subshell alone does not exclude copper or silver.

[Xe]4f¹⁴5d¹⁰. The 5d subshell remains full; mercury therefore fails the transition-element criterion.

Step 2: Check the remaining metals Scandium has 3d¹ in its atom, so it qualifies even though Sc³⁺ is d⁰. Copper forms Cu²⁺ with 3d⁹. Silver can form Ag²⁺ with 4d⁹, so its full 4d¹⁰ ground-state subshell alone does not exclude it. Thus (A), (B) and (D) are transition metals.

Step 3: Conclusion Hg is not a transition metal. Hence, the correct option is (C).

Quick Tip to Solve: Apply the definition to both the atom and its ions; a filled atomic d subshell alone does not exclude copper or silver.

4. Which of the following represents the fraction of molecules with energies equal to or greater than E_a ? [1 mark]

- (A) $+\frac{E_a}{RT}$
(B) $e^{-E_a/RT}$
(C) $-\frac{E_a}{RT}$
(D) $e^{+E_a/RT}$

Correct Answer: (B) $e^{-E_a/RT}$

Solution:

Concept:

- In the CBSE Arrhenius treatment, the fraction of molecules with energy at least the activation energy E_a is represented by the Boltzmann factor $e^{-E_a/(RT)}$.
- Here R is the gas constant and T is the absolute temperature; E_a and RT must have matching energy-per-mole units.

Step 1: Use the activation-energy factor The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the pre-exponential factor. Its negative exponential accounts for the fraction energetic enough to cross the activation-energy barrier. For positive E_a and T , this factor is between zero and one.

Step 2: Eliminate the other expressions Option (A), $+E_a/(RT)$, is only an energy ratio and need not be below one. Option (C), $-E_a/(RT)$, is negative and cannot be a fraction of molecules. Option (D), $e^{+E_a/(RT)}$, exceeds one. Only option (B) has the required negative-exponential form.

Step 3: Conclusion The required fraction is $e^{-E_a/(RT)}$. Hence, the correct option is (B).

Quick Tip to Solve: Check the sign in the exponent: raising the activation barrier must reduce the fraction of molecules able to react.

5. What will happen during the electrolysis of aqueous solution of CuCl_2 by using platinum electrodes?

[1 mark]

- (A) Cu will deposit at Anode
- (B) H_2 gas will be released at cathode
- (C) O_2 gas will be released at anode
- (D) Cl_2 gas will be released at anode

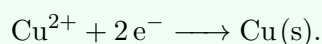
Correct Answer: (D) Cl_2 gas will be released at anode

Solution:

Concept:

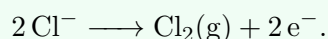
- In electrolysis, reduction occurs at the cathode and oxidation at the anode. Platinum electrodes are inert and do not supply metal ions.
- For aqueous CuCl_2 under the usual conditions, copper ions are reduced preferentially and chloride ions are oxidised to chlorine.

Step 1: Identify the cathode process Copper ions gain electrons at the cathode:



Copper is deposited at the cathode, not the anode, so (A) is wrong. Reduction of Cu^{2+} is preferred over hydrogen evolution here, so (B) is also wrong.

Step 2: Identify the anode process Chloride ions lose electrons at the platinum anode:



Although water oxidation is a competing process, the overpotential for oxygen evolution favours chlorine liberation in the standard aqueous chloride electrolysis described here. Thus oxygen evolution in (C) is not the expected observation.

Step 3: Conclusion Cl_2 gas is released at the anode. Hence, the correct option is (D).

Quick Tip to Solve: Write reduction at the cathode and oxidation at the anode first; then assign copper deposition and chlorine evolution to those electrodes.

6. Aspirin is obtained by acetylation of

[1 mark]

- (A) Phenol
- (B) Salicylaldehyde
- (C) 2-Hydroxybenzoic acid
- (D) Benzoic acid

Correct Answer: (C) 2-Hydroxybenzoic acid

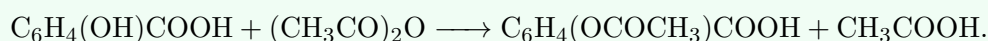
Solution:

Concept:

- Aspirin is acetylsalicylic acid, also called 2-acetoxybenzoic acid.
- Acetylation replaces the hydrogen of the phenolic –OH group with an acetyl group, forming an ester while retaining the carboxyl group.

Step 1: Identify the parent compound Salicylic acid is 2-hydroxybenzoic acid. It contains an –OH group ortho to a –COOH group on the benzene ring. Acetylating this phenolic group, commonly with acetic anhydride, gives aspirin.

Step 2: Follow the functional-group change The reaction can be represented in condensed form as



The ring substituents remain in the ortho positions. Phenol lacks the carboxyl group, salicylaldehyde has an aldehyde instead of a carboxyl group, and benzoic acid lacks the phenolic hydroxyl group. None of those gives aspirin by simple acetylation.

Step 3: Conclusion Aspirin is obtained by acetylation of 2-hydroxybenzoic acid. Hence, the correct option is (C).

Quick Tip to Solve: Recognise salicylic acid as 2-hydroxybenzoic acid: aspirin forms by acetylating its phenolic OH while leaving COOH intact.

7. The secondary valency of Co in the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ is

[1 mark]

- (A) 5
- (B) 1
- (C) 4
- (D) 6

Correct Answer: (D) 6

Solution:

Concept:

- In Werner's theory, secondary valency equals the coordination number: the number of ligand donor atoms directly bonded to the central metal.
- Primary valency corresponds to oxidation state and must not be confused with secondary valency.

Quick Tip to Solve: Count donor atoms for secondary valency; use ligand charges only when the question asks for oxidation state or primary valency.

Both NH_3 and NO_2^- are monodentate in this complex.

Step 1: Count directly attached donor atoms The complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ contains five ammonia ligands, each contributing one donor atom. The nitrite ligand contributes one donor atom. Although nitrite is ambidentate, it binds through one of its possible donor atoms at a time here. Hence the total donor count is $5 + 1 = 6$.

Step 2: Distinguish the other numerical choices The value 5 counts only the ammonia ligands and omits nitrite. The value 1 counts only the nitrite ligand; 4 is not the total number of donor atoms. The cobalt oxidation state follows $x + 5(0) - 1 = +2$, giving $x = +3$; this is primary valency, not the requested secondary valency.

Step 3: Conclusion The secondary valency of cobalt is 6. Hence, the correct option is (D).

Quick Tip to Solve: Count donor atoms for secondary valency; use ligand charges only when the question asks for oxidation state or primary valency.

8. At low temperature, phenol reacts with dil. HNO_3 to yield

[1 mark]

- (A) 2, 4, 6-Trinitrophenol
- (B) o-Nitrophenol only
- (C) p-Nitrophenol only
- (D) ortho- and para-nitrophenol

Correct Answer: (D) ortho- and para-nitrophenol

Solution:

Concept:

- The hydroxyl group in phenol donates an oxygen lone pair to the benzene ring by resonance, activating it towards electrophilic substitution.
- The $-\text{OH}$ group is ortho- and para-directing, so mild nitration introduces $-\text{NO}_2$ predominantly at these positions.

Step 1: Apply the directing effect Dilute HNO_3 at low temperature nitrates the activated phenol ring. Resonance increases electron density at both ortho and para positions, so both positions can undergo substitution. The products are 2-nitrophenol and 4-nitrophenol.

Step 2: Distinguish mild and strong nitration Options (B) and (C) incorrectly claim that only one of the two mononitrophenols forms. Option (A), 2,4,6-trinitrophenol or picric acid, is associated with concentrated nitric acid; the dilute acid and low temperature specified here favour mononitration.

Step 3: Conclusion Phenol gives a mixture of ortho- and para-nitrophenol. Hence, the correct option is (D).

Quick Tip to Solve: Link dilute, cold nitric acid with the two mononitrophenols; concentrated nitric acid gives picric acid.

9. Which of the following is 'not' true about enantiomers?

[1 mark]

- (A) They have the same chemical reactivity.
- (B) They have the same specific rotation.
- (C) They have the same melting or boiling point.
- (D) They have the same refractive index.

Correct Answer: (B) They have the same specific rotation.

Solution:

Concept:

- Enantiomers are non-superimposable mirror images. They have identical physical properties in an achiral environment, apart from the direction of optical rotation.
- Under identical measurement conditions, their specific rotations have equal magnitudes and opposite signs: $[\alpha]_1 = -[\alpha]_2$.

Step 1: Compare optical rotation One enantiomer rotates plane-polarised light clockwise, whereas its mirror image rotates it anticlockwise by the same amount. Specific rotation includes its sign; equal magnitude does not mean the same specific rotation. Thus the statement in option (B) is false.

Step 2: Check the remaining properties The pair has the same melting point, boiling point and refractive index, so (C) and (D) are true. Their chemical reactivity towards achiral reagents is also the same, as intended in (A). Chiral reagents or biological environments can distinguish enantiomers, but that exception does not change their equal-and-opposite optical rotations.

Step 3: Conclusion Enantiomers do not have the same signed specific rotation. Hence, the correct option is (B).

Quick Tip to Solve: In an enantiomer question, keep the sign of specific rotation: equal magnitudes with opposite signs are different values.

10. Aniline on direct nitration yields

[1 mark]

- (A) 51%-ortho, 47%-para, 2%-meta derivatives
- (B) 51%-meta, 47%-ortho, 2%-para derivatives
- (C) 51%-para, 47%-meta, 2%-ortho derivatives
- (D) 51%-ortho, 47%-meta, 2%-para derivatives

Correct Answer: (C) 51%-para, 47%-meta, 2%-ortho derivatives

Solution:

Concept:

- Free aniline has an electron-donating $-\text{NH}_2$ group and is ortho- and para-directing in electrophilic aromatic substitution.
- In the strongly acidic nitrating mixture, aniline is protonated to the anilinium ion, $\text{C}_6\text{H}_5\text{NH}_3^+$, whose positively charged group is meta-directing.

Step 1: Account for the meta product Direct nitration exposes aniline to strong acid. Protonation uses the nitrogen lone pair, preventing its donation into the ring. The resulting anilinium ion is

Quick Tip to Solve: For direct nitration of aniline, remember para and meta are nearly equal; ortho is only 2%.

deactivating and meta-directing, so a substantial amount of meta-nitroaniline is obtained rather than exclusively ortho and para products.

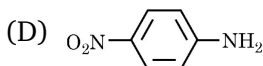
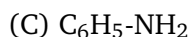
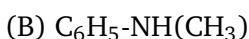
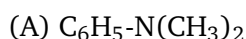
Step 2: Match the observed distribution The standard direct-nitration distribution is 51% para, 47% meta and 2% ortho. Option (A) wrongly makes meta only 2%; options (B) and (D) wrongly make para only 2%. The directing effects explain why meta is substantial; the percentages themselves are the observed product distribution.

Step 3: Conclusion The products are 51% para, 47% meta and 2% ortho derivatives. Hence, the correct option is (C).

Quick Tip to Solve: For direct nitration of aniline, remember para and meta are nearly equal; ortho is only 2%.

11. Which of the following amines has lowest pK_b value?

[1 mark]



Correct Answer: (A) $C_6H_5-N(CH_3)_2$

Solution:

Concept:

- Base strength increases with the availability of the nitrogen lone pair for protonation. Since $pK_b = -\log K_b$, the strongest base has the lowest pK_b .
- Methyl groups donate electron density by their positive inductive effect, while a para nitro group withdraws electron density by inductive and resonance effects.

Step 1: Compare the methyl-substituted anilines In aniline, the nitrogen lone pair is partly delocalised into the benzene ring. Adding methyl groups on nitrogen increases electron density through the $+I$ effect. Among the three listed anilines without a ring nitro group, $C_6H_5N(CH_3)_2$ is the strongest base, followed by $C_6H_5NHCH_3$ and then $C_6H_5NH_2$.

Step 2: Eliminate the nitro compound and invert the scale The para $-NO_2$ group in option (D) strongly withdraws electron density and decreases the availability of the amino nitrogen lone pair, making para-nitroaniline the weakest base listed. Hence the largest K_b belongs to option (A), and the negative logarithm gives it the smallest pK_b . Options (B), (C) and (D) all have higher pK_b values.

Step 3: Conclusion $C_6H_5N(CH_3)_2$, or *N,N*-dimethylaniline, has the lowest pK_b . Hence, the correct option is (A).

Quick Tip to Solve: First find the strongest base using electron donation; then reverse the ranking because lower pK_b means greater basicity.

12. The deficiency of which of the following vitamins causes increased fragility of red blood cells and muscular weakness?

[1 mark]

- (A) Vitamin A
- (B) Vitamin K
- (C) Vitamin E
- (D) Vitamin D

Correct Answer: (C) Vitamin E

Solution:

Concept:

- Vitamins are organic nutrients needed in small quantities for normal body functions; characteristic deficiency symptoms help identify a vitamin.
- Vitamin E is a fat-soluble antioxidant that protects cell membranes, including red blood cell membranes, against oxidative damage.

Step 1: Connect the symptoms with membrane protection A deficiency of vitamin E reduces protection of membrane lipids against oxidation. Red blood cells therefore become more fragile. Muscular weakness is another characteristic symptom associated with this deficiency. The pair of symptoms in the question identifies vitamin E.

Step 2: Compare the other deficiencies Vitamin A deficiency is mainly associated with night blindness and eye disorders. Vitamin K deficiency impairs blood clotting, while vitamin D deficiency causes defective bone mineralisation, such as rickets. These characteristic effects do not match the given combination of red blood cell fragility and muscular weakness.

Step 3: Conclusion The deficient nutrient is vitamin E. Hence, the correct option is (C).

Quick Tip to Solve: Match red blood cell fragility plus muscular weakness to vitamin E; abnormal blood clotting instead points to vitamin K.

13. Assertion (A): It is not possible to separate the components of an azeotrope by fractional distillation.

Reason (R): Components of an azeotrope have the same composition in liquid and vapour phase and boil at a constant temperature.

Select the correct answer from the codes (A), (B), (C) and (D).

[1 mark]

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

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

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

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

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

Solution:

Concept:

- An azeotrope is a mixture that boils at a constant temperature at a given pressure and has the same composition in its equilibrium liquid and vapour phases.
- Fractional distillation separates components by repeated vaporisation and condensation only when the vapour composition differs from that of the liquid.

Step 1: Evaluate the assertion At the azeotropic composition, ordinary fractional distillation cannot separate the mixture into its individual components. Successive vaporisation and condensation cycles do not enrich either component. Assertion (A) is therefore true.

Step 2: Evaluate the reason The composition of the vapour above an azeotropic liquid is identical to the liquid composition, and the mixture boils at a constant temperature at fixed pressure. Reason (R) correctly states these defining properties and is true.

Step 3: Test the explanatory link Condensing the vapour simply returns a liquid with the original composition. Repeating this process in a fractionating column still gives no composition change. Thus the equal-composition property in (R) directly explains the failure of separation in (A); the option claiming no explanatory link is incorrect.

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

Quick Tip to Solve: For an azeotrope, write liquid composition = vapour composition; no enrichment means no separation by fractional distillation.

14. Assertion (A): The presence of -OH group in phenols directs the incoming group to meta position in the ring.

Reason (R): -OH group in phenols activates the aromatic ring towards electrophilic substitution reaction.

Select the correct answer from the codes (A), (B), (C) and (D).

[1 mark]

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

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

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

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

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

Solution:

Concept:

- In phenol, an oxygen lone pair is delocalised into the aromatic ring. This positive resonance effect increases the ring's electron density.
- Resonance donation by -OH particularly increases electron density at the ortho and para positions and stabilises the intermediates of substitution at these positions.

Step 1: Evaluate the assertion The hydroxyl group directs an incoming electrophile preferentially to the ortho and para positions, not to the meta position. Thus the directing effect stated in Assertion (A) is incorrect, and the assertion is false.

Step 2: Evaluate the reason Although oxygen has an electron-withdrawing inductive effect, its electron-donating resonance effect predominates in phenol. The aromatic ring is consequently more reactive than benzene towards electrophilic substitution. Reason (R), which states that the hydroxyl group activates the ring, is true.

Step 3: Test the relationship Activation is consistent with ortho and para direction; it does not support the claimed meta direction. Since the assertion itself is false, neither option requiring both statements to be true can apply. The code must indicate a false assertion and a true reason.

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

Quick Tip to Solve: Pair phenolic -OH with activation and ortho/para direction; a statement claiming meta direction is false.

15. Assertion (A): Actinoids show wide range of oxidation states.

Reason (R): Actinoids are radioactive in nature.

Select the correct answer from the codes (A), (B), (C) and (D).

[1 mark]

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

Correct Answer: (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

Solution:

Concept:

- Oxidation states depend on the electrons available for chemical bonding, whereas radioactivity depends on nuclear instability.
- In actinoids the energies of the $5f$, $6d$ and $7s$ orbitals are comparable, so different numbers of electrons can participate in bonding.

Step 1: Evaluate the assertion The assertion is true. Actinoids exhibit a wide range of oxidation states because electrons from closely spaced $5f$, $6d$ and $7s$ levels can be used in bonding. Their accessible oxidation states therefore need not be limited to a single value.

Step 2: Evaluate the reason The reason is also true: all actinoid elements are radioactive. Their nuclei are unstable and undergo radioactive decay. This is a property of the nucleus, rather than an explanation of the energies of the valence orbitals.

Step 3: Test the explanatory link Radioactivity does not explain the variable number of electrons involved in chemical bonding. Thus the two statements are true but are not related as cause and explanation. Option (A) incorrectly claims an explanatory link, while (C) and (D) incorrectly declare one of the statements false.

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

Quick Tip to Solve: For actinoids, connect oxidation states with closely spaced valence orbitals and radioactivity with the nucleus; do not confuse these two properties.

16. Assertion (A): The pentaacetate of glucose does not react with $\text{H}_2\text{N-OH}$.

Reason (R): It indicates the presence of free $-\text{CHO}$ group in glucose.

Select the correct answer from the codes (A), (B), (C) and (D).

[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:

- Hydroxylamine, NH_2OH , reacts with an available aldehyde or ketone carbonyl group to form an oxime.
- Glucose pentaacetate has a cyclic structure with its anomeric hydroxyl group acetylated; it does not have a free aldehyde group available for oxime formation.

Step 1: Evaluate the assertion The assertion is true. On acetylation, the five hydroxyl groups of glucose are converted into acetate ester groups. The cyclic pentaacetate cannot open in the usual manner to give a free aldehyde group, so it does not react with hydroxylamine to form an oxime.

Step 2: Evaluate the reason The reason is false. The stated non-reaction does not indicate the presence of a free $-\text{CHO}$ group. It indicates the absence of an available aldehyde group in glucose pentaacetate. Glucose itself can furnish an open-chain aldehyde form, but that fact is not the inference from this pentaacetate experiment.

Step 3: Check the relation and the codes A reason that infers the presence of a reactive carbonyl from the failure of its characteristic reaction cannot explain the assertion. The codes requiring both statements to be true are eliminated, as is the code making the assertion false.

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

Quick Tip to Solve: Distinguish glucose from glucose pentaacetate: oxime formation requires an available carbonyl group, which the cyclic pentaacetate lacks.

Section B (10 marks)

17. What type of deviation from Raoult's law is shown by a mixture of phenol and aniline? Give reason. What will happen to the boiling point of the solution on mixing phenol and aniline? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal binary solution is $p = x_A p_A^\circ + x_B p_B^\circ$, where x_i is the liquid mole fraction and p_i° is the vapour pressure of pure component i at the same temperature.

Quick Tip to Solve: For phenol plus aniline, follow the chain: stronger hydrogen bonding, lower vapour pressure, and a higher temperature needed for boiling.

- Stronger attractions between unlike molecules reduce their escape into the vapour and produce negative deviation. A liquid boils when its vapour pressure equals the external pressure.

Step 1: Identify the intermolecular attraction Phenol and aniline form strong intermolecular hydrogen bonds with each other. The hydrogen of the phenolic –OH group interacts with the lone pair on the nitrogen atom of aniline. These unlike-molecule attractions are stronger than the average attractions in the separate liquids, so molecules are held more firmly in the mixture.

Step 2: Relate the attraction to vapour pressure Fewer molecules escape into the vapour at a given temperature. The observed total vapour pressure is therefore lower than the ideal Raoult's-law value at the same composition:

$$p_{\text{observed}} < x_A p_A^\circ + x_B p_B^\circ.$$

This is a negative deviation from Raoult's law.

Step 3: Predict the boiling-point change At a fixed external pressure, the reduction in vapour pressure means that the solution must be heated to a higher temperature to reach the boiling condition. Thus mixing produces an increase in boiling point relative to ideal-solution behaviour at the same composition.

Step 4: Conclusion The phenol-aniline mixture shows negative deviation because of strong hydrogen bonding between unlike molecules. Its vapour pressure decreases and its boiling point increases.

Quick Tip to Solve: For phenol plus aniline, follow the chain: stronger hydrogen bonding, lower vapour pressure, and a higher temperature needed for boiling.

18. Why are haloarenes less reactive towards nucleophilic substitution reaction? Give two reasons.

[2 marks]

Solution:

Concept:

- Nucleophilic substitution requires cleavage of the carbon-halogen bond. A shorter, stronger bond is more difficult to break.
- In haloarenes, the halogen is attached directly to an sp^2 -hybridised ring carbon, and its lone pair can participate in conjugation with the aromatic ring.

Step 1: Explain the effect of resonance A lone pair on the halogen overlaps with the delocalised π -electron system of the benzene ring. Resonance gives the carbon-halogen bond partial double-bond character. This makes the bond shorter and stronger than a normal carbon-halogen single bond in a haloalkane, so its cleavage during nucleophilic substitution is difficult.

Step 2: Explain the effect of carbon hybridisation The carbon bonded to halogen in a haloarene is sp^2 -hybridised, whereas the corresponding carbon in a haloalkane is sp^3 -hybridised. An sp^2 orbital has greater s-character: about 33%, compared with 25% for sp^3 . The bonding electrons are held closer to the carbon nucleus, giving a shorter, stronger carbon-halogen bond that is harder for a substitution reaction to cleave.

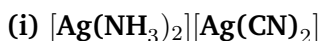
Step 3: Conclusion Haloarenes are less reactive towards nucleophilic substitution because resonance

Quick Tip to Solve: State two separate causes of the strong aryl-halogen bond: resonance and the greater s-character of the ring carbon's sp^2 orbital.

gives their carbon-halogen bond partial double-bond character, and attachment to an sp^2 carbon further strengthens and shortens that bond.

Quick Tip to Solve: State two separate causes of the strong aryl-halogen bond: resonance and the greater s-character of the ring carbon's sp^2 orbital.

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



[2 marks]

Solution:

Concept:

- Name the cation before the anion. Within a complex, name the ligands first and then the metal with its oxidation state in Roman numerals.
- NH_3 is a neutral ammine ligand, CN^- is cyanido and $\text{C}_2\text{O}_4^{2-}$ is oxalato. An anionic metal complex takes the suffix “ate”; silver and iron then become argentate and ferrate.

Step 1: Name the silver coordination salt In $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$, the complex cation is $[\text{Ag}(\text{NH}_3)_2]^+$. Since both ammine ligands are neutral, silver has oxidation state +1, giving diammine silver(I), written as diamminesilver(I). The complex anion is $[\text{Ag}(\text{CN})_2]^-$. If silver has oxidation state x , then

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

Two cyanido ligands and the anionic metal name give dicyanidoargentate(I). Combining cation and anion gives diamminesilver(I) dicyanidoargentate(I).

Step 2: Name the potassium coordination salt The three K^+ ions in $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ require the complex ion to carry charge -3 . Each oxalato ligand carries charge -2 , so the oxidation state of iron follows from

$$x + 3(-2) = -3 \Rightarrow x = +3.$$

The anionic iron complex is named ferrate(III). For three oxalato ligands use tris(oxalato), and place the potassium cation first. The name is potassium tris(oxalato)ferrate(III).

Step 3: Conclusion (i) Diamminesilver(I) dicyanidoargentate(I).

(ii) Potassium tris(oxalato)ferrate(III).

Quick Tip to Solve: Calculate the charge of each complex before naming its metal; use argentate and ferrate only for the negatively charged coordination entities.

19(b). (i) Give a chemical test to show that $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ are ionisation isomers.

(ii) What is meant by the 'Chelate effect'? Give an example.

[2 marks]

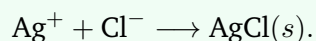
Solution:

Concept:

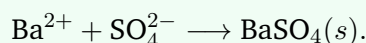
- Ionisation isomers have the same overall composition but exchange a coordinated ligand with a counter-ion, so they release different ions in aqueous solution.
- A chelating ligand binds through two or more donor atoms to the same metal ion and forms one or more rings; this generally increases complex stability.

Step 1: (i) Identify the ions outside the coordination sphere In $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$, chloride is the counter-ion and is released as free Cl^- . In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$, sulfate is the counter-ion and is released as free SO_4^{2-} . The ions inside square brackets remain coordinated during the usual immediate tests.

Step 2: (i) Perform precipitation tests on separate portions Add aqueous silver nitrate to fresh aqueous samples. The first compound gives a white precipitate of silver chloride immediately, whereas the second does not give this immediate chloride test:



As a complementary test, add barium chloride to separate portions. The second compound gives a white precipitate of barium sulfate; the first does not give this immediate sulfate test:



Step 3: (ii) Explain the chelate effect with an example The chelate effect is the enhanced stability of a complex containing chelating ligands compared with a comparable complex containing only monodentate ligands. For example, $[\text{Ni}(\text{en})_3]^{2+}$ is more stable than $[\text{Ni}(\text{NH}_3)_6]^{2+}$, where en is ethane-1,2-diamine. Each en ligand binds through two nitrogen donor atoms and forms a five-membered chelate ring with nickel.

Step 4: Conclusion The first complex gives the immediate AgCl test and the second gives the immediate BaSO_4 test, confirming different counter-ions and hence ionisation isomerism. Enhanced stability due to chelation is illustrated by $[\text{Ni}(\text{en})_3]^{2+}$.

Quick Tip to Solve: Check the ion outside the square brackets before choosing a precipitation test; coordinated chloride or sulfate is not immediately available as a free ion.

20. Differentiate between the following:

(i) Peptide linkage and Glycosidic linkage

(ii) Essential amino acids and Non-essential amino acids

[2 marks]

Solution:

Concept:

- Biological polymers contain characteristic covalent linkages: proteins contain peptide bonds, while oligosaccharides and polysaccharides contain glycosidic bonds.
- The nutritional classification of amino acids depends on whether the human body can synthesise enough of them, rather than on whether they are necessary for proteins.

Step 1: (i) Distinguish the two linkages A peptide linkage is the amide group $-\text{CO}-\text{NH}-$, formed when the carboxyl group of one amino acid combines with the amino group of another with elimination of water. It joins amino acid residues in peptides and proteins. For example, glycine and alanine form a dipeptide containing this bond.

A glycosidic linkage is an oxygen bridge, $\text{C}-\text{O}-\text{C}$, joining two monosaccharide units, with participation of an anomeric carbon. It forms by elimination of water between suitable hydroxyl groups. For example, the two glucose units in maltose are joined by an $\alpha(1 \rightarrow 4)$ glycosidic linkage. Thus the linked units and the chemical nature of the bonds differ.

Step 2: (ii) Distinguish the two classes of amino acids Essential amino acids cannot be synthesised by the human body in sufficient amounts and therefore must be supplied in the diet. Examples include valine and lysine.

Non-essential amino acids can be synthesised by the body in adequate amounts under normal conditions, so they need not necessarily be supplied in the diet. Examples include glycine and alanine. The word non-essential does not mean that these amino acids are unnecessary; they are also required for protein synthesis.

Step 3: Conclusion Peptide linkages join amino acid residues through $-\text{CO}-\text{NH}-$, while glycosidic linkages join monosaccharide units through an oxygen bridge. Essential amino acids require dietary supply; non-essential amino acids can normally be made by the body.

Quick Tip to Solve: Associate peptide with amino acids and glycosidic with sugars; for essential amino acids, ask whether the body can supply enough by synthesis.

21. Following reaction takes place in one step:



How will the rate of above reaction change if the volume of the reaction vessel is decreased to one third of its original volume? Will there be any change in the order of reaction with the reduced volume? [2 marks]

Solution:

Concept:

- For an elementary reaction occurring in a single step, the concentration powers in the rate law equal the stoichiometric coefficients of the reactants.
- Concentration is amount divided by volume, $[A] = n_A/V$. At unchanged temperature, changing the volume changes reactant concentrations but not the rate constant or the reaction order.

Step 1: Write the rate law for the one-step reaction Because $2A + B \rightarrow 2C$ occurs in one elementary step, its rate law is

$$r = k[A]^2[B],$$

where k is the rate constant and $[A]$, $[B]$ are the reactant concentrations. The powers are justified by the one-step information; they could not in general be read from the overall equation of a multistep reaction. The overall order is the sum of the concentration powers, $2 + 1$.

Step 2: Substitute the concentrations after compression Immediately after the vessel volume becomes $V' = V/3$, the amounts of both reactants are unchanged. Hence

$$[A]' = \frac{n_A}{V/3} = 3[A], \quad [B]' = 3[B].$$

At the same temperature, k is unchanged. Comparing the new rate r' with the original rate gives

$$\frac{r'}{r} = \frac{k(3[A])^2(3[B])}{k[A]^2[B]} = 3^2 \times 3 = 27.$$

Compression affects the numerical concentrations, but it does not alter their exponents in the rate law or the elementary reaction mechanism.

Step 3: Conclusion The reaction rate becomes 27 times its original value. The order remains $2 + 1 = 3$; there is no change in reaction order.

Quick Tip to Solve: When all reactant concentrations increase by the same factor, raise that factor to the total order: here the rate factor is 3^3 .

Section C (21 marks)

22. For the first order thermal decomposition reaction, following data was obtained:



Calculate rate constant. [Given: $\log 3 = 0.48$]

[3 marks]

S. No.	Time(s)	Total Pressure (atm)
1	0	0.30
2	30	0.50

Solution:

Concept:

- For a first-order reaction, $k = (2.303/t) \log_{10}([A]_0/[A]_t)$, where $[A]_0$ and $[A]_t$ are initial and remaining reactant concentrations.
- At constant temperature and volume, a gas's partial pressure is proportional to its concentration. Total pressure includes all gases and cannot directly replace reactant concentration.

Step 1: Relate total pressure to decomposition Initially only ethyl chloride is present, at $P_0 = 0.30$ atm. Let x atm be the decrease in its partial pressure after 30 s. One mole each of ethene and hydrogen chloride forms per mole of reactant consumed. The partial pressures are therefore $P_0 - x$, x and x , respectively. Adding them gives

$$P_t = (P_0 - x) + x + x = P_0 + x.$$

The total pressure rises because each reactant molecule produces two gaseous molecules.

Step 2: Find the remaining reactant pressure At 30 s, the measured total pressure is 0.50 atm. Thus

$$\begin{aligned} x &= P_t - P_0 = 0.50 - 0.30 = 0.20 \text{ atm,} \\ P_A &= P_0 - x = 0.30 - 0.20 = 0.10 \text{ atm.} \end{aligned}$$

Equivalently, the required reactant partial pressure is $P_A = 2P_0 - P_t$, not P_t .

Step 3: Apply the integrated first-order rate equation Substitute the initial and remaining partial pressures, using the given $\log 3 = 0.48$:

$$\begin{aligned} k &= \frac{2.303}{30} \log_{10} \frac{0.30}{0.10} \\ &= \frac{2.303 \times 0.48}{30} = 0.036848 \text{ s}^{-1}. \end{aligned}$$

The pressure ratio is dimensionless, and time in seconds gives k in s^{-1} .

Step 4: Conclusion The rate constant is $k \approx 3.68 \times 10^{-2} \text{ s}^{-1}$.

Quick Tip to Solve: For one gaseous reactant forming two gaseous products, first find $P_A = 2P_0 - P_t$, then use this remaining reactant pressure in the rate equation.

23(a). Answer the following:

(i) Why is the Equilibrium Constant (K_c) related to E_{cell}° and not to E_{cell} ?

(ii) Two metals 'A' and 'B' have standard electrode potential values of -0.24 V and $+0.80$ V respectively. Which of these will liberate hydrogen gas from dil. H_2SO_4 ?

(iii) Write the cell reaction which occurs in lead storage battery when it is in charging.

[3 marks]

Solution:

Concept:

- The standard Gibbs energy change and equilibrium constant satisfy $\Delta_r G^\circ = -RT \ln K_c = -nFE_{cell}^\circ$, where n is the number of transferred electrons and F is the Faraday constant.
- A metal liberates H_2 from dilute acid when its oxidation coupled with reduction of H^+ is spontaneous; the standard hydrogen electrode has reduction potential zero.
- Charging a secondary battery reverses its discharge reaction by supplying electrical energy from an external source.

Step 1: (i) Relate equilibrium to the standard cell potential Combining the two expressions for standard Gibbs energy gives

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

At a fixed temperature, K_c is fixed for the reaction. The non-standard potential E_{cell} , however, depends on the current reactant and product activities through the reaction quotient Q :

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

At equilibrium $Q = K_c$ and $E_{cell} = 0$. Thus the value of the equilibrium constant is related to the standard potential, whereas the actual cell potential changes as the reaction proceeds.

Step 2: (ii) Compare each metal with the hydrogen electrode Hydrogen ions are reduced at the cathode and the metal is oxidised at the anode. Hence

$$E_{cell}^\circ = E_{H^+/H_2}^\circ - E_{metal}^\circ.$$

For A, this is $0 - (-0.24) = +0.24$ V, making the reaction spontaneous. For B, it is $0 - (+0.80) = -0.80$ V, so hydrogen displacement is not spontaneous under standard conditions. Therefore metal A liberates hydrogen from dilute H_2SO_4 .

Step 3: (iii) Reverse the lead storage battery discharge reaction During charging, lead sulphate on the two electrodes is converted back to lead and lead dioxide, and sulphuric acid is regenerated:



The external source supplies the energy needed to drive this reverse reaction; the acid concentration increases during charging.

Step 4: Conclusion K_c is linked to E_{cell}° by $\ln K_c = nFE_{cell}^\circ/(RT)$. Metal A releases H_2 . On charging, $2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4$.

Quick Tip to Solve: For acid displacement calculate $0 - E_{metal}^\circ$; for lead-battery charging, put lead sulphate on the reactant side and regenerate sulphuric acid.

23(b). What type of battery is Mercury cell? Why it is more advantageous than dry cell? Write overall reaction taking place in Mercury cell. [3 marks]

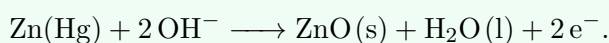
Solution:

Concept:

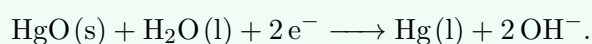
- A primary cell supplies electrical energy through a chemical reaction and is not designed to be recharged for repeated use.
- Cell potential depends on the activities of the species in the overall cell reaction. Pure solids have constant unit activity, so their amounts do not enter the reaction quotient.

Step 1: Identify the battery and its components The mercury cell is a primary battery. Its anode is zinc amalgam, its cathode is a paste of mercuric oxide, HgO , and carbon, and its electrolyte is a paste containing KOH and ZnO . The zinc is oxidised while mercury(II) oxide is reduced. The cell is suitable for low-current devices such as watches and hearing aids.

Step 2: Write and combine the electrode reactions In the alkaline electrolyte, the anode reaction is



The cathode reaction is



On addition, the electrons, hydroxide ions and water cancel, giving the overall reaction



Thus the reacting zinc is converted into zinc oxide, and mercury is formed at the cathode.

Step 3: Explain the advantage over a dry cell The mercury cell delivers an approximately constant potential of 1.35 V throughout its useful life. The net reaction does not involve an ion in solution whose concentration changes during discharge; hydroxide ions consumed at the anode are regenerated at the cathode. Consequently, concentration changes in the electrolyte do not progressively lower its voltage. This stable output is advantageous over the ordinary dry cell, whose potential falls during use.

Step 4: Conclusion A mercury cell is a primary battery with a nearly constant 1.35 V output. Its overall reaction is $\text{Zn(Hg)} + \text{HgO(s)} \longrightarrow \text{ZnO(s)} + \text{Hg(l)}$; the absence of changing ionic concentrations in this net reaction accounts for its voltage stability.

Quick Tip to Solve: Add the two alkaline half-reactions and cancel OH^- and water; their absence from the net reaction explains the mercury cell's constant voltage.

24. Calculate the boiling point of a solution containing 0.61 g of benzoic acid (Molar mass = 122 g mol⁻¹) in 5 g of CS₂ in which it dimerises to the extent of 88%. The boiling point and K_b of CS₂ are 46.2 °C and 2.3 K kg mol⁻¹ respectively. [3 marks]

Solution:

Concept:

- Boiling-point elevation is $\Delta T_b = iK_b m$, where m is the molality calculated from the original solute amount and i is the van't Hoff factor accounting for association.
- Dimerisation joins two solute molecules into one particle. If a fraction α of the original molecules associates, then $i = 1 - \alpha/2$.

Step 1: Calculate the original molality The amount of benzoic acid before allowing for association is

$$n = \frac{0.61 \text{ g}}{122 \text{ g mol}^{-1}} = 0.005 \text{ mol.}$$

The solvent mass is 5 g = 0.005 kg. Therefore

$$m = \frac{0.005 \text{ mol}}{0.005 \text{ kg}} = 1.00 \text{ mol kg}^{-1}.$$

Use the mass of the solvent, CS₂, rather than the total mass of the solution in this calculation.

Step 2: Count the particles after dimerisation Benzoic acid associates according to $2 \text{ C}_6\text{H}_5\text{COOH} \rightleftharpoons (\text{C}_6\text{H}_5\text{COOH})_2$. For one mole of original molecules, $1 - \alpha$ mole remains as monomers and $\alpha/2$ mole of dimers forms. Thus the total number of solute particles relative to the initial number is

$$i = (1 - \alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}.$$

Here $\alpha = 88/100 = 0.88$, giving

$$i = 1 - \frac{0.88}{2} = 0.56.$$

The factor is less than unity because association reduces the number of independently moving solute particles.

Step 3: Find the elevation and add it to the solvent boiling point Substituting the molality and van't Hoff factor gives

$$\Delta T_b = (0.56)(2.3 \text{ K kg mol}^{-1})(1.00 \text{ mol kg}^{-1}) = 1.288 \text{ K.}$$

A temperature rise of 1.288 K equals a rise of 1.288 °C. Therefore

$$T_b = 46.2 + 1.288 = 47.488 \text{ °C.}$$

The elevation is smaller than the 2.3 K that an unassociated solute of the same original molality would produce.

Step 4: Conclusion The boiling point of the solution is 47.488 °C, approximately 47.49 °C, with $i = 0.56$.

Quick Tip to Solve: For 88 percent dimerisation, count 12 monomers plus 44 dimers per 100 original molecules: $i = 56/100$. Multiply the elevation by this factor only once.

25. Write the reactions of D-Glucose with the following:

(a) HI

(b) Br₂ water

(c) Conc. HNO₃

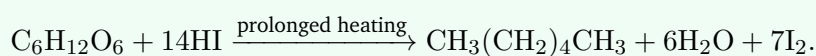
[3 marks]

Solution:

Concept:

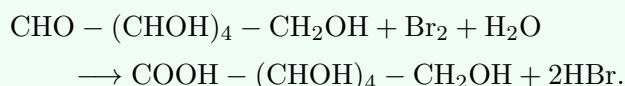
- Open-chain D-glucose has the structure CHO – (CHOH)₄ – CH₂OH: it contains an aldehyde group at one end and a primary alcohol group at the other.
- Prolonged heating with HI reduces glucose to a hydrocarbon. Bromine water mildly oxidises its aldehyde group, whereas concentrated nitric acid oxidises both terminal groups.

Step 1: (a) Reduction with HI On prolonged heating with excess HI, all the oxygen-containing groups are reduced, giving normal hexane:



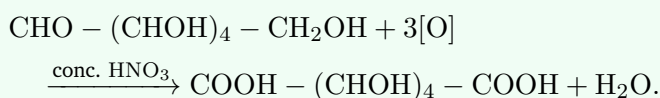
The product is *n*-hexane. Its formation shows that the six carbon atoms of glucose form an unbranched chain; reduction does not change that carbon skeleton.

Step 2: (b) Oxidation with bromine water Bromine water oxidises the aldehyde group to a carboxyl group while leaving the terminal primary alcohol group unchanged:



The organic product is D-gluconic acid, a monocarboxylic acid. This mild oxidation provides evidence for the aldehyde group in open-chain glucose.

Step 3: (c) Oxidation with concentrated nitric acid Concentrated nitric acid is a stronger oxidising agent. It converts both –CHO and the terminal –CH₂OH into –COOH:



Here [O] denotes oxygen supplied by the oxidising agent. The product is saccharic acid (D-glucaric acid), a dicarboxylic acid; the four internal –CHOH– groups are retained in this standard transformation.

Step 4: Conclusion D-glucose gives (a) *n*-hexane with HI on prolonged heating, (b) D-gluconic acid with bromine water, and (c) saccharic acid with concentrated HNO₃.

Quick Tip to Solve: Track the two ends of glucose: bromine water changes only CHO to COOH; concentrated nitric acid changes both ends to COOH; HI removes oxygen to give the six-carbon alkane.

26. Give reasons for the following:

- (a) Carboxylic acids have higher boiling point than alcohols of comparable molecular masses.
(b) Alpha (α) hydrogens of aldehydes and ketones are acidic in nature.
(c) Nucleophilic addition of ammonia and its derivatives does not occur with carbonyl group in strongly acidic medium.

[3 marks]

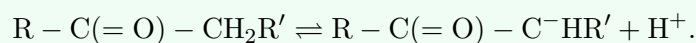
Solution:

Concept:

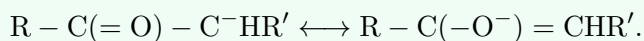
- Stronger intermolecular association requires more energy for vaporisation and generally raises the boiling point.
- Acidity increases with conjugate-base stability. An enolate delocalises its negative charge between the alpha carbon and oxygen.
- A nitrogen nucleophile must have an available lone pair to attack a carbonyl carbon. Protonation of nitrogen reduces the concentration of the reactive nucleophile.

Step 1: (a) Stronger association of carboxylic acids Carboxylic acids form cyclic dimers held together by two intermolecular hydrogen bonds, using the O-H group and carbonyl oxygen of each molecule. Although alcohols also form hydrogen bonds, acids have stronger association through this dimer formation. More energy is required to overcome these attractions during vaporisation; hence acids have higher boiling points than alcohols of comparable molecular masses.

Step 2: (b) Stabilisation of the conjugate base An alpha hydrogen is attached to the carbon adjacent to the carbonyl group. Removal of this hydrogen as H^+ gives an enolate ion, illustrated for a carbonyl compound as follows:



Its two principal resonance contributors are



Thus the negative charge is delocalised, including onto the more electronegative oxygen atom. This resonance stabilisation, together with the electron-withdrawing inductive effect of the carbonyl group, makes alpha hydrogens acidic relative to ordinary alkane hydrogens.

Step 3: (c) Protonation of ammonia and its derivatives In a strongly acidic medium, ammonia and its derivatives become protonated, for example:



Protonation uses the nitrogen lone pair, making it unavailable for attack on the carbonyl carbon. Strong acid suppresses the concentration of unprotonated nucleophile and prevents addition. Mild acid can activate the carbonyl, but excessive acidity deactivates the nitrogen reagent.

Step 4: Conclusion (a) Carboxylic acids form strongly hydrogen-bonded dimers. (b) Loss of an alpha proton gives a resonance-stabilised enolate ion. (c) Strong acid protonates nitrogen nucleophiles, making their lone pairs unavailable for carbonyl addition.

Quick Tip to Solve: For these three reasons, identify the stabilised species: the acid dimer raises boiling point, the enolate stabilises proton loss, and the ammonium ion removes the reactive nitrogen lone pair.

27. Write the reaction involved in the following:

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Friedel-Crafts acylation of anisole

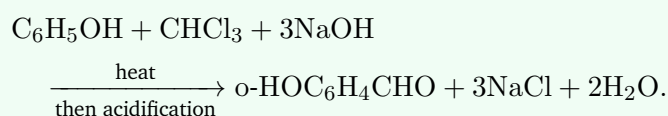
[3 marks]

Solution:

Concept:

- Reimer-Tiemann introduces $-\text{CHO}$ into phenol; Kolbe's reaction introduces $-\text{COOH}$ via sodium phenoxide.
- Friedel-Crafts acylation uses an acyl chloride and anhydrous AlCl_3 to introduce an acyl group $-\text{COR}$ into an activated aromatic ring.

Step 1: (a) Reimer-Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide, then acidified. The main product is salicylaldehyde (2-hydroxybenzaldehyde). The overall reaction is

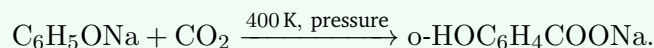


The electrophile is dichlorocarbene, generated from chloroform and base. The ortho aldehyde is the major product.

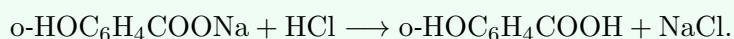
Step 2: (b) Kolbe's reaction Phenol first reacts with sodium hydroxide to form sodium phenoxide:



Sodium phenoxide reacts with carbon dioxide under pressure at about 400 K, giving sodium salicylate:

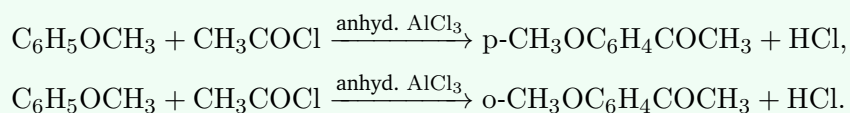


Acidification liberates salicylic acid (2-hydroxybenzoic acid):



The carboxyl group is introduced predominantly ortho to the hydroxyl group.

Step 3: (c) Friedel-Crafts acylation of anisole Anisole reacts with acetyl chloride in the presence of anhydrous aluminium chloride. The alternative product channels are



The products are 4-methoxyacetophenone (major) and 2-methoxyacetophenone (minor). Methoxy directs acylation to ortho and para positions; the less hindered para position is favoured.

Step 4: Conclusion The principal products are (a) salicylaldehyde, (b) salicylic acid after acidification, and (c) para-methoxyacetophenone together with a smaller amount of the ortho isomer.

Quick Tip to Solve: Remember the group introduced: Reimer-Tiemann gives CHO , Kolbe gives COOH , and anisole with acetyl chloride gives COCH_3 , mainly at the para position.

28. Compound 'X' with molecular formula C_4H_9Br reacts with aqueous KOH to give an alcohol. The rate of this reaction depends only on the concentration of the compound 'X'. When an optically active isomer 'Y' of the compound 'X' was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound 'Y' and aqueous KOH both.

(a) Write down the structural formula of both 'X' and 'Y'.

(b) Out of 'X' and 'Y', which one will undergo racemisation and why?

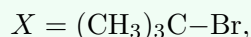
(c) Out of 'X' and 'Y', which one will form product with inversion of configuration and why? [3 marks]

Solution:

Concept:

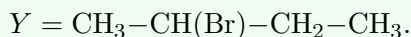
- An S_N1 substitution has rate $k[X]$: ionisation to a carbocation is the rate-determining step. A tertiary alkyl halide favours this pathway.
- An S_N2 substitution has rate $k[Y][OH^-]$: nucleophile attack and leaving-group departure occur together, giving inversion at a reacting stereocentre.
- Racemisation requires an initially optically active substrate. A planar carbocation permits attack from either face, but an achiral substrate cannot become racemised.

Step 1: Identify X from the first-order rate law The rate depends only on X, so the reaction is assigned the S_N1 mechanism. Among the isomers of C_4H_9Br , the tertiary bromide readily forms a tertiary carbocation. Thus the structural formula is



namely 2-bromo-2-methylpropane. Its hydrolysis forms $(CH_3)_3COH$, 2-methylpropan-2-ol.

Step 2: Identify Y and explain inversion The optically active isomer must contain a carbon attached to four different groups. It is one enantiomer of 2-bromobutane,



The second carbon is attached to H, Br, CH_3 and C_2H_5 . The given dependence on both Y and OH^- identifies S_N2 substitution. Backside attack by OH^- , opposite the departing Br^- , reverses the spatial arrangement at this carbon. The resulting butan-2-ol therefore has inversion of configuration.

Step 3: Examine the racemisation demand in part (b) The mechanism conventionally associated with racemisation is S_N1 , so the intended mechanistic choice is X: a planar carbocation can be attacked from either face. However, the actual $X = (CH_3)_3CBr$ is achiral because its central carbon bears three identical methyl groups. Its alcohol is also achiral, so these attacks give the same product, not a pair of enantiomers. Consequently neither specified compound undergoes actual racemisation under the stated mechanisms: X is achiral and Y undergoes inversion. The printed part (b) incorrectly presupposes that one of them racemises.

Step 4: Conclusion (a) $X = (CH_3)_3CBr$, and $Y = CH_3CH(Br)CH_2CH_3$, taken as an optically active enantiomer. (b) X follows the S_N1 pathway associated with racemisation of chiral substrates, but actual racemisation is impossible here because X is achiral. (c) Y gives inversion by S_N2 backside attack.

Quick Tip to Solve: Use the rate law to identify the substitution mechanism, then separately check chirality before claiming racemisation.

Section D (8 marks)

The following questions are case-based questions. Each question has an internal choice and carries 4(2 + 1 + 1) marks each. Read the passage carefully and answer the questions that follow.

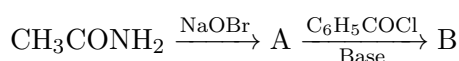
29. The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Aliphatic amines are stronger bases than ammonia whereas aromatic amines are weaker bases than ammonia. Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their high reactivity. Substitution tends to occur at ortho- and para-positions. Hinsberg reagent is used for the identification and distinction of primary, secondary and tertiary amines. Aryldiazonium salts, usually obtained from arylamines, undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes.

Answer the following questions:

[4 marks]

29(a). (i) Why CH_3-NH_2 is a stronger base than $(\text{CH}_3)_3\text{N}$ in aqueous solution?

(ii) Write structural formulae of the compound A and B:



[2 marks]

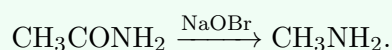
Solution:

Concept:

- In water, amine basicity depends on electron donation and hydration of the conjugate ammonium ion; stronger hydration stabilises the protonated base.
- Hofmann bromamide degradation converts RCONH_2 into RNH_2 with loss of the carbonyl carbon. An amine then undergoes benzylation with $\text{C}_6\text{H}_5\text{COCl}$ in base.

Step 1: Compare hydration in aqueous solution For protonation, $\text{RNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_3^+ + \text{OH}^-$. The conjugate acid CH_3NH_3^+ has three N–H bonds and is better hydrated than the bulky $(\text{CH}_3)_3\text{NH}^+$, which has only one N–H bond. This greater hydration stabilisation more than compensates for the stronger electron-donating effect of the three methyl groups in trimethylamine. Hence methylamine is the stronger base in aqueous solution.

Step 2: Identify A by Hofmann degradation The starting compound is ethanamide, CH_3CONH_2 . Treatment with NaOBr removes its carbonyl carbon, leaving the methyl group bonded to nitrogen:



Thus A is methylamine, CH_3-NH_2 ; it contains one carbon rather than the two carbons of the starting amide.

Step 3: Identify B by benzylation Methylamine reacts with benzoyl chloride by replacing the acyl

Quick Tip to Solve: For NaOBr on an amide, remove the carbonyl carbon first; then attach the benzoyl group to the remaining amine nitrogen.

chloride's chlorine with the methylamino group. The base neutralises the acid produced:



Thus B is N-methylbenzamide, whose condensed structural formula is $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}-\text{CH}_3$.

Step 4: Conclusion (i) Better hydration of CH_3NH_3^+ makes CH_3NH_2 the stronger aqueous base. (ii) $A = \text{CH}_3-\text{NH}_2$ and $B = \text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}-\text{CH}_3$.

Quick Tip to Solve: For NaOBr on an amide, remove the carbonyl carbon first; then attach the benzoyl group to the remaining amine nitrogen.

29(b). A compound 'X' with molecular formula $\text{C}_3\text{H}_9\text{N}$ reacts with Hinsberg reagent to give a product insoluble in alkali. Identify 'X'. [1 mark]

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. Primary and secondary amines form sulphonamides, while tertiary amines do not form these derivatives.
- A secondary amine gives an N,N-disubstituted sulphonamide without an acidic N–H bond, so its product is insoluble in alkali.

Step 1: Infer the amine class Since X reacts with Hinsberg reagent, it cannot be the tertiary isomer trimethylamine. The product is insoluble in alkali, so it has no acidic hydrogen on nitrogen. A primary amine would give a sulphonamide with an N–H bond that dissolves in alkali. Therefore X is a secondary amine.

Step 2: Distribute the three carbons between two groups A secondary amine has two alkyl groups and one hydrogen on nitrogen. With three carbons in total, the groups must be methyl and ethyl:



Its Hinsberg product is $\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)$, which has no N–H bond and therefore cannot form the alkali-soluble sulphonamide salt.

Step 3: Conclusion X is N-methylethanamine (ethylmethylaniline), $\text{CH}_3-\text{NH}-\text{CH}_2-\text{CH}_3$.

Quick Tip to Solve: An alkali-insoluble Hinsberg reaction product identifies a secondary amine; split three carbons as methyl plus ethyl.

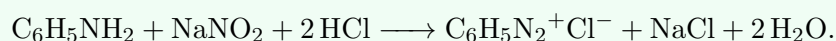
29(b). How can you convert aniline to benzonitrile?

[1 mark]

Solution:**Concept:**

- Aniline undergoes diazotisation with nitrous acid generated from NaNO_2 and HCl at 273–278 K.
- In the Sandmeyer reaction, CuCN replaces an aryl diazonium group by CN , with evolution of nitrogen gas.

Step 1: Prepare benzenediazonium chloride Keep aniline in aqueous hydrochloric acid cold at 273–278 K and add sodium nitrite. The nitrous acid formed in situ diazotises aniline:



The low temperature preserves the diazonium salt until the replacement reaction.

Step 2: Replace the diazonium group by cyanide Treat the freshly prepared benzenediazonium chloride with cuprous cyanide, CuCN . Nitrogen is expelled and the cyanide carbon bonds to the ring:



This is the Sandmeyer cyanation step; direct treatment of aniline with an alkali cyanide would not replace its amino group.

Step 3: Conclusion Convert aniline to benzenediazonium chloride using NaNO_2/HCl at 273–278 K, then use CuCN to obtain benzonitrile, $\text{C}_6\text{H}_5\text{CN}$.

Quick Tip to Solve: For aniline to an aryl nitrile, first diazotise cold, then replace the diazonium group with CuCN .

29(c). Why is $-\text{NH}_2$ group of aniline acetylated before carrying out nitration?

[1 mark]

Solution:**Concept:**

- The free $-\text{NH}_2$ group strongly activates the benzene ring; acidic nitrating mixtures also protonate it to the meta-directing $-\text{NH}_3^+$ group.
- Acetylation converts $-\text{NH}_2$ to $-\text{NHCOCH}_3$. Resonance with the carbonyl reduces nitrogen lone-pair donation to the ring and moderates activation.

Step 1: Identify the problems with direct nitration Direct nitration of aniline can cause oxidation and poorly controlled substitution because the amino group strongly activates the ring. In the strongly acidic nitrating mixture, some aniline becomes anilinium ion, $\text{C}_6\text{H}_5\text{NH}_3^+$, which directs substitution to the meta position and gives an unwanted mixture.

Step 2: Protect the amino group before nitration Acetylation forms acetanilide, $\text{C}_6\text{H}_5\text{NHCOCH}_3$. Its acetylamino group activates the ring less strongly, reduces protonation of nitrogen, and still

Quick Tip to Solve: Protect aniline as acetanilide before nitration, then hydrolyse the acetyl group after introducing the nitro group.

directs nitration mainly to ortho and para positions. Steric hindrance favours the para product. After controlled nitration, hydrolysis removes the acetyl group to regenerate $-\text{NH}_2$.

Step 3: Conclusion Aniline is acetylated to protect $-\text{NH}_2$, reduce excessive activation and oxidation, and obtain mainly the para-nitrated product by controlled nitration.

Quick Tip to Solve: Protect aniline as acetanilide before nitration, then hydrolyse the acetyl group after introducing the nitro group.

30. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometry of coordination compounds. The Crystal Field Theory (CFT) of coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields.

Answer the following questions :

[4 marks]

30(a). In octahedral crystal field, energies of which d-orbitals will be raised when ligands approach the central metal atom/ion ? Give reason in support of your answer.

[2 marks]

Solution:

Concept:

- In an octahedral complex, six ligands approach the metal along the positive and negative directions of the three Cartesian axes.
- Electrostatic repulsion between ligand electron pairs and metal d electrons splits the five degenerate d orbitals into the higher e_g and lower t_{2g} sets.

Step 1: Identify the orbitals directed towards ligands The lobes of $d_{x^2-y^2}$ point along the x and y axes, and the major lobes of d_{z^2} point along the z axis. These two orbitals therefore face the incoming ligands directly. They experience greater electrostatic repulsion than the other three d orbitals, whose lobes lie between the axes.

Step 2: Compare the energies of the two sets The two directly repelled orbitals form the e_g set and rise in energy relative to the barycentre. The d_{xy} , d_{xz} and d_{yz} orbitals form the lower t_{2g} set. If the octahedral splitting is Δ_o , their relative energies are

$$E(e_g) = +\frac{3}{5}\Delta_o, \quad E(t_{2g}) = -\frac{2}{5}\Delta_o.$$

The weighted mean remains unchanged because $2(3/5) + 3(-2/5) = 0$.

Step 3: Conclusion The $d_{x^2-y^2}$ and d_{z^2} orbitals, collectively e_g , are raised in energy because their lobes point directly towards the approaching octahedral ligands and experience stronger repulsion.

Quick Tip to Solve: Place octahedral ligands on the coordinate axes: orbitals aimed along those axes form the higher-energy pair.

(b) Using crystal field theory, write the electronic configuration of central metal atom/ion of the following : 1

30(b)(i). $[\text{CoF}_6]^{3-}$

Solution:

Concept:

- The metal oxidation state follows from the complex charge and ligand charges. Cobalt has atomic number 27 and loses its 4s electrons before its 3d electrons.
- In an octahedral weak field, $\Delta_o < P$, where P is the pairing energy; electrons occupy the higher e_g orbitals before pairing extensively in t_{2g} .

Step 1: Determine the metal d-electron count Each fluoride ligand has charge -1 . If the cobalt oxidation state is x , then $x + 6(-1) = -3$, giving $x = +3$. Neutral cobalt is $[\text{Ar}]3d^74s^2$, so Co^{3+} is $[\text{Ar}]3d^6$.

Step 2: Fill the orbitals in the weak crystal field Fluoride is a weak-field ligand. The first five d electrons occupy the three t_{2g} and two e_g orbitals singly; the sixth pairs in one t_{2g} orbital. This gives the high-spin occupancy $t_{2g}^4e_g^2$, with four unpaired electrons. Filling all six electrons into t_{2g} would instead require a sufficiently strong field to favour pairing.

Step 3: Conclusion In $[\text{CoF}_6]^{3-}$, cobalt is Co^{3+} with $3d^6$ configuration; its octahedral crystal-field configuration is $t_{2g}^4e_g^2$ (high spin).

Quick Tip to Solve: For this fluoride complex, first find Co(III), then distribute its six d electrons using weak-field high-spin filling.

30(b)(ii). $[\text{Co}(\text{NH}_3)_6]^{3+}$

[At. No. : Co = 27]

Solution:

Concept:

- Ammonia is a neutral ligand, so the oxidation state of the metal equals the charge on $[\text{Co}(\text{NH}_3)_6]^{3+}$.
- When octahedral splitting Δ_o exceeds pairing energy P , d electrons pair in the lower t_{2g} orbitals before occupying e_g ; this is low-spin filling.

Step 1: Count the metal d electrons Because all six ammonia ligands are neutral, cobalt is in the $+3$ oxidation state. Its neutral electronic configuration is $[\text{Ar}]3d^74s^2$. Removal of two 4s electrons and one 3d electron gives Co^{3+} with configuration $[\text{Ar}]3d^6$.

Step 2: Apply the strong-field filling pattern For ammonia coordinated to Co^{3+} , the octahedral splitting is large enough to favour pairing: $\Delta_o > P$. All six d electrons occupy the three lower t_{2g} orbitals as three pairs; the two e_g orbitals remain empty. Thus the crystal-field occupancy is $t_{2g}^6e_g^0$, with no unpaired electrons.

Step 3: Conclusion The cobalt ion in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is $3d^6$, with low-spin crystal-field configuration $t_{2g}^6e_g^0$.

Quick Tip to Solve: In this Co(III) ammine complex, pair the six d electrons in the lower triplet before filling the upper doublet.

30(c). $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why ?
[Atomic No. : Ni = 28] [1 mark]

Solution:

Concept:

- Paramagnetism requires unpaired electrons; a complex with all electrons paired is diamagnetic. Geometry alone does not determine magnetic behaviour.
- The metal oxidation state fixes its d-electron count. Chloride is an anionic ligand, whereas carbon monoxide is neutral.

Step 1: Count electrons in the chloride complex In $[\text{NiCl}_4]^{2-}$, $x + 4(-1) = -2$, so nickel is Ni^{2+} . Nickel has atomic number 28; loss of its two 4s electrons gives $3d^8$. In the tetrahedral weak field, these eight electrons leave two unpaired electrons (occupancy $e^4 t_2^4$). Their magnetic moments make the complex paramagnetic.

Step 2: Count electrons in the carbonyl complex In neutral $[\text{Ni}(\text{CO})_4]$, each carbon monoxide ligand has zero charge, so nickel has oxidation state zero. In forming this complex the metal has a filled $3d^{10}$ set; all its d electrons are paired. The four ligand pairs occupy bonds described by sp^3 hybridisation in VBT. No unpaired electrons remain, so the complex is diamagnetic despite being tetrahedral.

Step 3: Conclusion $[\text{NiCl}_4]^{2-}$ contains Ni^{2+} (d^8) with two unpaired electrons; $[\text{Ni}(\text{CO})_4]$ has $\text{Ni}(0)$ with a filled d^{10} set and no unpaired electrons. Hence their magnetic behaviours differ.

Quick Tip to Solve: Compare nickel oxidation states before comparing shapes: chloride gives Ni(II), whereas neutral CO leaves nickel in oxidation state zero.

OR

30(c). Write hybridization and magnetic behaviour of the complex $[\text{Fe}(\text{CN})_6]^{3-}$. [Atomic No. : Fe = 26] [1 mark]

Solution:

Concept:

- Cyanide is a strong-field ligand: in an octahedral complex it can favour pairing in the lower-energy t_{2g} orbitals.
- An inner-orbital octahedral complex uses two 3d, one 4s and three 4p orbitals for $d^2 sp^3$ hybridisation. Unpaired electrons cause paramagnetism.

Step 1: Establish the oxidation state and d count Each cyanide ligand has charge -1 . For $[\text{Fe}(\text{CN})_6]^{3-}$, $x + 6(-1) = -3$, so iron is Fe^{3+} . Iron has atomic number 26 and neutral configuration $[\text{Ar}]3d^6 4s^2$; removing three electrons gives $[\text{Ar}]3d^5$.

Step 2: Apply pairing and identify the bonding orbitals The strong field of cyanide gives low-spin filling $t_{2g}^5 e_g^0$. The five d electrons occupy three orbitals as two pairs and one single electron. Two inner 3d orbitals are therefore available for VBT hybridisation with one 4s and three 4p orbitals, producing $d^2 sp^3$ hybridisation. The remaining single electron makes the complex paramagnetic; strong-field pairing cannot pair all five electrons.

Quick Tip to Solve: Use the printed 3- charge to obtain Fe(III), d5; even strong-field pairing leaves one electron unpaired.

Step 3: Conclusion $[\text{Fe}(\text{CN})_6]^{3-}$ has d^2sp^3 hybridisation and is paramagnetic, with one unpaired electron in the low-spin t_{2g}^5 configuration.

Quick Tip to Solve: Use the printed 3- charge to obtain Fe(III), d^5 ; even strong-field pairing leaves one electron unpaired.

Section E (15 marks)

31(a). (i) An organic compound (X) has the molecular formula $\text{C}_5\text{H}_{10}\text{O}$. Draw structures for (X) if it:

(I) does not give Tollen's test but gives a positive iodoform test.

(II) does not give Tollen's test and iodoform test but undergoes Aldol condensation.

(III) undergoes Cannizzaro's reaction.

(ii) Show how each of the following compounds can be converted to benzoic acid:

(I) Acetophenone (II) Ethyl benzene

[5 marks]

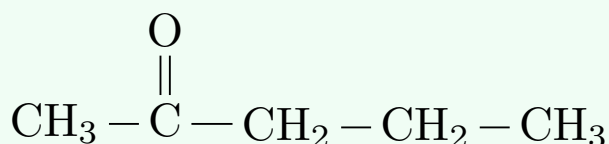
Solution:

Concept:

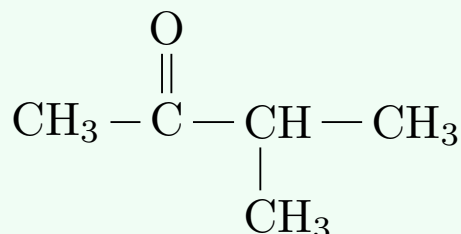
- Tollens' reagent oxidises aldehydes, whereas ordinary ketones do not give this test. A positive iodoform test identifies the methyl ketone group $\text{CH}_3\text{CO}-$ in a ketone.
- Aldol condensation requires at least one hydrogen on a carbon adjacent to the carbonyl group (an α -hydrogen). Cannizzaro's reaction occurs with aldehydes having no α -hydrogen.
- Haloform cleavage converts a methyl ketone into a carboxylate containing one fewer carbon atom. Strong oxidation of an alkylbenzene having a benzylic hydrogen converts its side chain into a carboxyl group.

Step 1: (i)(I) Identify a methyl ketone The negative Tollens' test excludes an aldehyde. To give iodoform, the ketone must contain $\text{CH}_3\text{CO}-$. With molecular formula $\text{C}_5\text{H}_{10}\text{O}$, one suitable structure is pentan-2-one, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$. Another valid structure is 3-methylbutan-2-one, $\text{CH}_3\text{COCH}(\text{CH}_3)_2$. Both have five carbon atoms and ten hydrogen atoms, and both contain the required methyl ketone group. Either structure meets the stated tests; their structures are shown below.

Quick Tip to Solve: For the three structure tests, check the carbonyl type first, then the methyl ketone group, then alpha-hydrogens. Always acidify a benzoate salt to obtain benzoic acid.



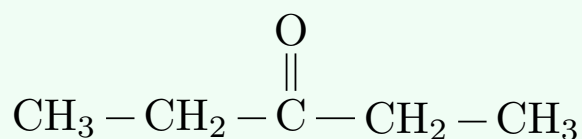
Pentan-2-one



3-Methylbutan-2-one

Two valid structures for (i)(I)

Step 2: (i)(II) Select a ketone without a methyl ketone group Pentan-3-one, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$, gives neither Tollens' test nor the iodoform test. Its carbonyl carbon is bonded to two ethyl groups, so it has no $\text{CH}_3\text{CO}-$ group. Each adjacent CH_2 group has α -hydrogens, however, so it can form an enolate and undergo aldol condensation. Thus it satisfies all three conditions simultaneously.



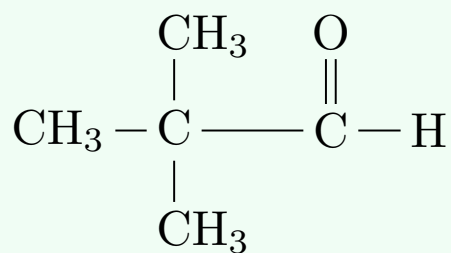
Pentan-3-one for (i)(II)

Step 3: (i)(III) Select an aldehyde without alpha-hydrogen Choose 2,2-dimethylpropanal, $(\text{CH}_3)_3\text{CCHO}$. The carbon adjacent to $-\text{CHO}$ is bonded to three methyl groups and therefore bears no hydrogen. It undergoes disproportionation in concentrated alkali: one aldehyde molecule is oxidised to the carboxylate while another is reduced to the alcohol.



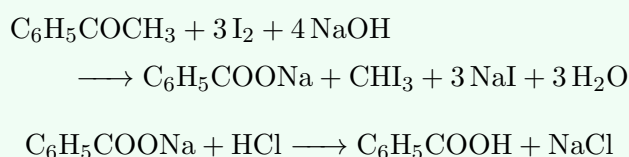
Counting the three methyl groups, the central carbon and the aldehyde carbon confirms $\text{C}_5\text{H}_{10}\text{O}$.

Quick Tip to Solve: For the three structure tests, check the carbonyl type first, then the methyl ketone group, then alpha-hydrogens. Always acidify a benzoate salt to obtain benzoic acid.



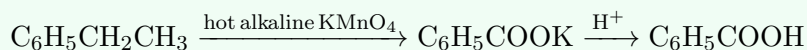
2,2-Dimethylpropanal for (i)(III)

Step 4: (ii)(I) Convert acetophenone by haloform cleavage Treat acetophenone with iodine and aqueous sodium hydroxide, then acidify the sodium benzoate obtained. The methyl group of the methyl ketone leaves as yellow iodoform; the carbonyl carbon remains in the benzoate ion.



Acidification is necessary because the alkaline reaction initially produces a salt, not free benzoic acid.

Step 5: (ii)(II) Oxidise the ethyl side chain Heat ethylbenzene with alkaline potassium permanganate and then acidify. The benzylic CH_2 group supplies the required benzylic hydrogen, allowing oxidation of the side chain to benzoate. Acidification yields benzoic acid.



The carbon directly attached to the ring becomes the carboxyl carbon; the terminal side-chain carbon is removed during strong oxidation.

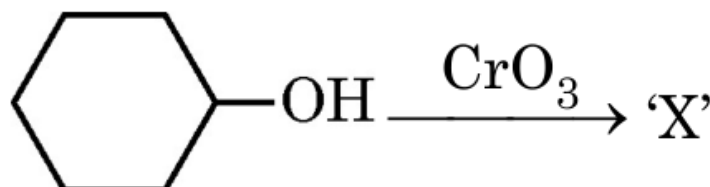
Step 6: Conclusion Suitable structures for (i) are (I) pentan-2-one (also 3-methylbutan-2-one), (II) pentan-3-one, and (III) 2,2-dimethylpropanal. For (ii), acetophenone gives benzoic acid by iodoform cleavage followed by acidification; ethylbenzene gives it by hot alkaline permanganate oxidation followed by acidification.

Quick Tip to Solve: For the three structure tests, check the carbonyl type first, then the methyl ketone group, then alpha-hydrogens. Always acidify a benzoate salt to obtain benzoic acid.

31(b). Answer the following questions:

- Draw structure of the 2, 4-dinitrophenyl hydrazone derivative of benzaldehyde.
- Arrange the following in increasing order of their reactivity towards HCN: Di-tert. butyl ketone, Acetaldehyde, Acetone.
- Give a simple chemical test to distinguish between benzoic acid and ethyl benzoate.
- Write the name of the reagent to convert Ethanenitrile to Ethanal.
- Draw the structure of 'X' in the following reaction:

[5 marks]

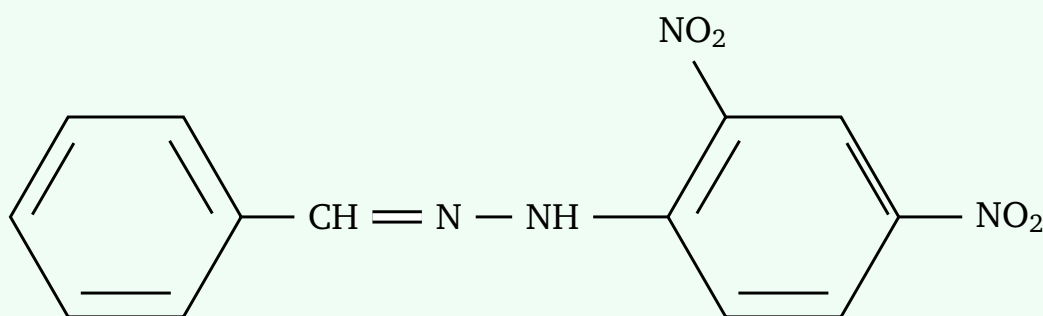


Solution:

Concept:

- Carbonyl compounds condense with 2,4-dinitrophenylhydrazine: the carbonyl group becomes $C=N-NH-Ar$, where Ar is the 2,4-dinitrophenyl group, with elimination of water.
- Nucleophilic addition of CN^- is favoured by a more electrophilic and less sterically hindered carbonyl carbon.
- Carboxylic acids release CO_2 with sodium hydrogen carbonate; ordinary esters do not give this effervescence.
- Controlled reduction of a nitrile followed by hydrolysis gives an aldehyde. Oxidation of a secondary alcohol gives a ketone without changing the carbon skeleton.

Step 1: (i) Form the benzaldehyde hydrazone The reagent's terminal $-NH_2$ group reacts with the carbonyl group of benzaldehyde. Removal of water produces the $CH=N-NH$ linkage. The two nitro groups remain at positions 2 and 4 relative to the hydrazone attachment on the reagent's benzene ring. Thus the product is $C_6H_5CH=N-NHC_6H_3(NO_2)_2$, drawn below with both rings and the ortho and para nitro groups shown.



Benzaldehyde 2,4-dinitrophenylhydrazone; the nitro groups are ortho and para to the hydrazone attachment.

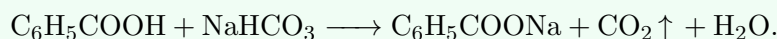
Step 2: (ii) Compare HCN addition reactivity Acetaldehyde has only one electron-releasing alkyl group and offers less steric hindrance than acetone, so nucleophilic attack occurs more readily. Acetone

Quick Tip to Solve: For the hydrazone, retain the aldehyde carbon's H and replace its O by $N-NH-Ar$; for cyclohexanol, replace the secondary $CHOH$ unit by $C=O$ without opening the ring.

has two methyl groups, which reduce carbonyl electrophilicity and increase crowding. In di-tert-butyl ketone, the two bulky tert-butyl groups strongly hinder attack on the carbonyl carbon. Hence the increasing order is

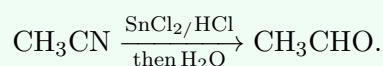


Step 3: (iii) Use the sodium hydrogen carbonate test Add aqueous sodium hydrogen carbonate separately to the two samples. Benzoic acid gives brisk effervescence of carbon dioxide, whereas ethyl benzoate gives no such effervescence under these test conditions. The acid reacts as follows:



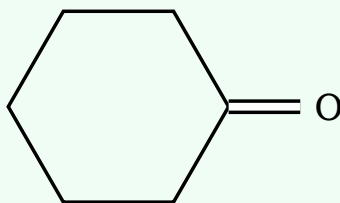
The gas can be confirmed by passing it through limewater, which turns milky. This directly distinguishes the acidic carboxyl group from the ester group.

Step 4: (iv) Carry out Stephen reduction Use stannous chloride, SnCl_2 , and hydrochloric acid, followed by hydrolysis. This is Stephen reduction. The nitrile is first reduced to an iminium salt; hydrolysis then releases ethanal. The overall conversion is



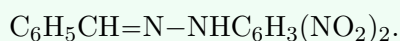
Controlled reduction is essential: a reagent such as LiAlH_4 would reduce the nitrile further to a primary amine instead of giving the required aldehyde.

Step 5: (v) Oxidise the cyclic secondary alcohol The printed reactant is cyclohexanol and the oxidising reagent is CrO_3 . The carbon bearing the hydroxyl group is joined to two ring carbons, so it is a secondary alcohol. Oxidation removes the hydroxyl hydrogen and the hydrogen on that carbon, producing a carbonyl group at the same ring position. The six-membered ring remains intact, and X is cyclohexanone, whose structure is drawn below.



Product X: cyclohexanone.

Step 6: Conclusion (i) The required hydrazone has the structure drawn above:



(ii) Di-tert-butyl ketone < acetone < acetaldehyde.

(iii) Benzoic acid evolves CO_2 with NaHCO_3 ; ethyl benzoate does not.

(iv) Use SnCl_2/HCl , followed by hydrolysis.

(v) X is cyclohexanone, as drawn.

Quick Tip to Solve: For the hydrazone, retain the aldehyde carbon's H and replace its O by $\text{N}-\text{NH}-\text{Ar}$; for cyclohexanol, replace the secondary CHOH unit by $\text{C}=\text{O}$ without opening the ring.

32(a). (i) From the given data of E° values, answer the following questions:

$E^\circ_{M^{2+}/M}$	V	Cr	Mn	Fe	Co	Ni	Cu
	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

(I) Why $E^\circ_{M^{2+}/M}$ show irregular trend in the above values?

(II) Why is $E^\circ_{Cu^{2+}/Cu}$ value exceptionally positive?

(III) Why $E^\circ_{Mn^{2+}/Mn}$ value is highly negative?

(ii) Write the ionic equations for the oxidising action of potassium permanganate for its reaction with I^- in both acidic and alkaline solutions. [5 marks]

Solution:

Concept:

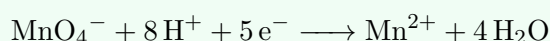
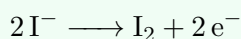
- The standard reduction potential for $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ depends on the overall energy balance involving atomisation of the metal, its first two ionisation enthalpies and hydration of the gaseous divalent ion.
- A particularly stable electronic configuration can favour formation of an ion. The half-filled $3d^5$ configuration stabilises Mn^{2+} .
- Permanganate is reduced to Mn^{2+} in acidic solution, and to MnO_2 in the usual neutral or alkaline oxidation of iodide. Balance both atoms and total charge in an ionic equation.

Step 1: (i)(I) Explain the irregular potentials Forming $M^{2+}(aq)$ from the solid requires atomisation and removal of two electrons, followed by hydration of the ion. The first two processes require energy, while hydration releases energy. Atomisation, ionisation and hydration enthalpies do not change uniformly across the series because the electronic configurations and metallic bonding change. Their combined effect, together with the corresponding entropy contribution to free energy, therefore gives an irregular trend in $E^\circ_{M^{2+}/M}$; it cannot be predicted from ionisation enthalpy alone.

Step 2: (i)(II) Account for the positive copper value Copper has a high atomisation enthalpy and a high energy requirement for conversion to Cu^{2+} . In particular, the second ionisation removes an electron from the stable $3d^{10}$ configuration of Cu^+ . The energy needed for atomisation and ionisation is not compensated by the hydration enthalpy of Cu^{2+} . Oxidation of copper to its aqueous divalent ion is consequently unfavourable relative to the standard hydrogen electrode, and the reverse reduction has the positive potential +0.34 V.

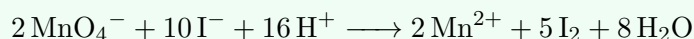
Step 3: (i)(III) Explain the negative manganese value Manganese has configuration $[Ar]3d^54s^2$. Loss of its two 4s electrons produces Mn^{2+} , with the particularly stable half-filled configuration $[Ar]3d^5$. Formation of this stable ion is favoured, whereas reducing it back to the metal is relatively difficult. Thus its standard reduction potential is highly negative, -1.18 V.

Step 4: (ii) Balance the oxidation in acidic solution Iodide loses electrons to form iodine, while manganese changes from +7 to +2:



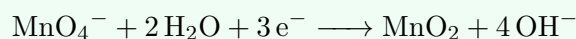
Quick Tip to Solve: First choose the medium: pair acidic Mn^{2+} with iodine, and alkaline MnO_2 with iodate; then balance electrons and check total charge.

Multiply the first half-reaction by 5 and the second by 2 to cancel 10 electrons:

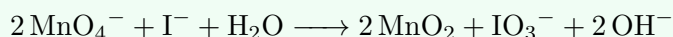


The charge on each side is +4, and both oxygen and hydrogen are balanced.

Step 5: (ii) Balance the oxidation in alkaline solution Here iodide is oxidised to iodate, with iodine changing from -1 to $+5$, while manganese is reduced from $+7$ to $+4$:



Double the second half-reaction and add, cancelling electrons, water and hydroxide ions common to the two sides:



The charge on each side is -3 ; the insoluble reduction product is manganese dioxide.

Step 6: Conclusion The potentials reflect the combined atomisation, ionisation and hydration effects. Copper has insufficient hydration compensation, while manganese favours the stable $3d^5$ divalent ion. Acidic permanganate oxidises iodide to I_2 ; alkaline permanganate oxidises it to IO_3^- , with the balanced equations shown above.

Quick Tip to Solve: First choose the medium: pair acidic Mn^{2+} with iodine, and alkaline MnO_2 with iodate; then balance electrons and check total charge.

OR

32(b). Answer the following questions:

(i) Name a member of the lanthanoid series

(I) which exhibits $+4$ oxidation state

(II) which exhibits $+2$ oxidation state.

(ii) Why transition metals act as good catalyst?

(iii) Why Cr has higher melting point than Mn?

(iv) What happens when acidic solution of potassium permanganate is allowed to stand for sometime?

Give the equation involved. What is this type of reaction called?

[5 marks]

Solution:

Concept:

- Although $+3$ is the common lanthanoid oxidation state, empty, half-filled and filled $4f$ subshells can stabilise other oxidation states.
- Transition-metal catalysis is associated with accessible oxidation states, formation of intermediate complexes and adsorption of reactants on a metal surface.
- Metallic-bond strength depends on the availability of valence electrons for bonding. Stronger

Quick Tip to Solve: For the last part, check the ion first: MnO_4^- has Mn at $+7$. Classify the written equation by oxidation-state changes, not by confusing permanganate with manganate.

metallic bonding generally leads to a higher melting point.

- In a redox decomposition, reduction and oxidation occur within the decomposing system. Disproportionation specifically requires the same element in one oxidation state to form both a higher and a lower oxidation state.

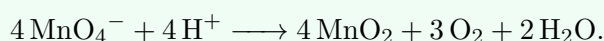
Step 1: (i) Name the lanthanoids (I) **Cerium**, Ce, exhibits the +4 oxidation state. The Ce^{4+} ion has the noble-gas configuration [Xe], with an empty $4f$ subshell.

(II) **Europium**, Eu, exhibits the +2 oxidation state. The Eu^{2+} ion has configuration $[\text{Xe}]4f^7$, whose half-filled $4f$ subshell provides additional stability. Thus both choices can be understood using electronic configurations rather than memorising the names alone.

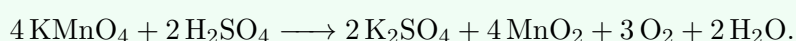
Step 2: (ii) Explain transition-metal catalysis The similar energies of the $(n-1)d$ and ns electrons allow transition metals to exhibit variable oxidation states. They can accept and donate electrons, form intermediate compounds or complexes with reactants, and provide a reaction pathway of lower activation energy. In heterogeneous catalysis, adsorption on the metal surface brings reactants together and weakens bonds before reaction. The catalyst is regenerated at the end of the catalytic cycle.

Step 3: (iii) Compare chromium and manganese Chromium has configuration $[\text{Ar}]3d^54s^1$, with six unpaired valence electrons, while manganese has $[\text{Ar}]3d^54s^2$, with five. Chromium has more unpaired electrons available for interatomic metallic bonding. The particularly stable half-filled $3d^5$ configuration of manganese also contributes to its anomalously weaker metallic bonding. More energy is therefore needed to disrupt the chromium lattice, explaining why chromium has a higher melting point than manganese.

Step 4: (iv) Describe standing acidic permanganate On prolonged standing, an acidic potassium permanganate solution undergoes slow decomposition: its purple colour fades, brown MnO_2 forms and oxygen is liberated. The ionic equation is



For a solution acidified with dilute sulphuric acid, the corresponding molecular equation is



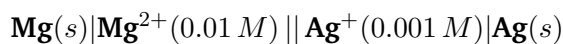
In the ionic equation, charge is zero on both sides; the 16 oxygen atoms on the left become 8 in MnO_2 , 6 in oxygen gas and 2 in water.

Step 5: (iv) Identify the reaction type Manganese is reduced from +7 in MnO_4^- to +4 in MnO_2 . Oxygen forming O_2 is oxidised from -2 to 0 . Four manganese atoms gain 12 electrons in total and six oxygen atoms lose 12 electrons. This is a **redox decomposition (internal oxidation–reduction)**. It is not disproportionation: manganese forms only a lower oxidation state, not both a higher and a lower one. The distinction matters because the question specifies potassium permanganate, KMnO_4 .

Step 6: Conclusion (i) Cerium shows +4, and europium shows +2. (ii) Variable oxidation states and intermediate formation account for catalytic action. (iii) Chromium has stronger metallic bonding than manganese. (iv) Standing acidic permanganate slowly forms MnO_2 , O_2 and water by redox decomposition.

Quick Tip to Solve: For the last part, check the ion first: MnO_4^- has Mn at +7. Classify the written equation by oxidation-state changes, not by confusing permanganate with manganate.

33(a). Calculate emf and ΔG for the following cell at 298 K:



Given: $E_{\text{Mg}^{2+}/\text{Mg}}^\circ = -2.37 \text{ V}$, $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$

[1 F = 96500 C mol⁻¹, log 10 = 1]

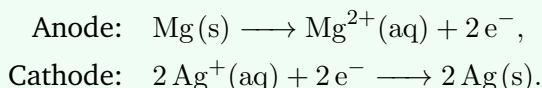
[5 marks]

Solution:

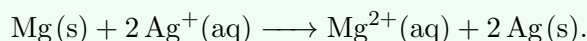
Concept:

- A galvanic cell oxidises the anode and reduces the cathode. Its standard emf is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using both electrode potentials as reduction potentials.
- 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 and Q is the reaction quotient; pure solids have unit activity.
- The Gibbs energy change under the stated conditions is $\Delta G = -nFE_{\text{cell}}$, where $F = 96500 \text{ C mol}^{-1}$. Use the actual cell emf here because the question asks for ΔG , not ΔG° .

Step 1: Write the balanced electrode reactions In the cell notation, magnesium forms the left electrode (anode) and silver forms the right electrode (cathode). Magnesium loses two electrons, while each silver ion gains one:



Adding the half-reactions gives



Thus $n = 2$. Multiplying the silver half-reaction by two balances electrons but does not multiply its electrode potential.

Step 2: Find the standard emf and reaction quotient The given values are standard reduction potentials, so subtract the anode value, retaining its negative sign:

$$E_{\text{cell}}^\circ = 0.80 - (-2.37) = 3.17 \text{ V}.$$

The stoichiometric coefficient of the silver ion becomes an exponent in Q . Omitting the solid magnesium and silver and using the given molar concentrations gives

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.01}{(0.001)^2} = 10^4.$$

Concentrations are understood relative to the standard concentration, so this reaction quotient is dimensionless. Hence $\log Q = 4$.

Step 3: Apply the Nernst equation Substitute the standard emf, electron count and reaction quotient at the stated temperature:

$$\begin{aligned}E_{\text{cell}} &= 3.17 - \frac{0.0591}{2} \times 4 \\ &= 3.17 - 0.1182 = 3.0518 \text{ V}.\end{aligned}$$

Since $Q > 1$, the Nernst correction lowers the emf from its standard value, which is consistent with

Quick Tip to Solve: Balance electrons first: $n = 2$, and the silver-ion concentration is squared in Q . Use the Nernst-corrected emf, not 3.17 V, to calculate the requested ΔG .

the calculated sign of the correction.

Step 4: Calculate the Gibbs energy change Use the unrounded non-standard emf in the energy relation:

$$\begin{aligned}\Delta G &= -2(96500)(3.0518) \\ &= -588997.4 \text{ J mol}^{-1} \\ &= -588.9974 \text{ kJ mol}^{-1}.\end{aligned}$$

Here $C \times V = J$, and the molar energy refers to one mole of the overall reaction as balanced above. A positive cell emf gives a negative Gibbs energy change, so the forward cell reaction is spontaneous under these conditions.

Step 5: Conclusion At 298 K, the cell emf is $E_{\text{cell}} \approx 3.052 \text{ V}$, and $\Delta G \approx -589.0 \text{ kJ mol}^{-1}$ for the reaction $\text{Mg} + 2 \text{Ag}^+ \longrightarrow \text{Mg}^{2+} + 2 \text{Ag}$.

Quick Tip to Solve: Balance electrons first: $n = 2$, and the silver-ion concentration is squared in Q . Use the Nernst-corrected emf, not 3.17 V, to calculate the requested ΔG .

OR

33(b). For the reaction:



Calculate emf of the cell at 25 °C.

Given: $\Delta G^\circ = -43500 \text{ J mol}^{-1}$

[$\log 10 = 1$, $1 \text{ F} = 96500 \text{ C mol}^{-1}$]

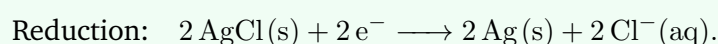
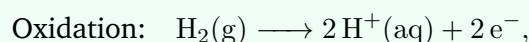
[5 marks]

Solution:

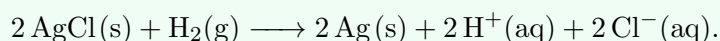
Concept:

- Standard Gibbs energy and standard cell emf are related by $\Delta G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons transferred in the balanced cell reaction and F is the Faraday constant.
- At 25 °C, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$, where Q contains dissolved species and gases raised to their stoichiometric powers.
- Pure solids have unit activity and do not appear explicitly in Q . Approximate aqueous activities by the given molar concentrations relative to their standard state and gas activity by its pressure relative to the standard pressure.

Step 1: Identify the electron transfer Hydrogen is oxidised to hydrogen ions, while silver in silver chloride is reduced to metallic silver. The half-reactions are



Their sum is the reaction in the question:



Quick Tip to Solve: In this reaction, square both $[\text{H}^+]$ and $[\text{Cl}^-]$, omit both solids and divide by hydrogen pressure. Since $Q = 10^{-3}$, the Nernst correction must increase the standard emf.

Therefore two electrons are transferred per reaction as written, so $n = 2$. The supplied molar Gibbs energy belongs to this same balanced reaction.

Step 2: Obtain the standard cell emf Rearrange the Gibbs energy relation before substituting the negative value of ΔG° :

$$\begin{aligned} E_{\text{cell}}^\circ &= -\frac{\Delta G^\circ}{nF} \\ &= -\frac{-43500}{2 \times 96500} \\ &= 0.22539 \text{ V.} \end{aligned}$$

The two minus signs cancel. This is the emf at standard conditions; the stated ion concentrations and hydrogen pressure require a further Nernst correction.

Step 3: Form the reaction quotient Both ion products have coefficient two, so both their concentrations are squared. Hydrogen is a reactant and appears in the denominator with power one. The two solids, AgCl and Ag, each have unit activity:

$$\begin{aligned} Q &= \frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{p_{\text{H}_2}} \\ &= \frac{(0.1)^2 (0.2)^2}{0.4} \\ &= \frac{0.0004}{0.4} = 0.001 = 10^{-3}. \end{aligned}$$

The numerical pressure is expressed relative to the standard pressure in the same unit. Thus Q is dimensionless and $\log Q = -3$, using $\log 10 = 1$.

Step 4: Apply the concentration and pressure correction At 25°C , substitute $n = 2$ and the negative logarithm into the Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= 0.22539 - \frac{0.0591}{2}(-3) \\ &= 0.22539 + 0.08865 \\ &= 0.31404 \text{ V.} \end{aligned}$$

The correction is positive because $Q < 1$. The product-ion activities are low enough, relative to the supplied hydrogen pressure, to increase the forward reaction's emf above its standard value. Keeping the negative sign in $\log Q$ is essential to this result.

Step 5: Conclusion The emf of the cell under the given conditions at 25°C is $E_{\text{cell}} \approx 0.314 \text{ V}$.

Quick Tip to Solve: In this reaction, square both $[\text{H}^+]$ and $[\text{Cl}^-]$, omit both solids and divide by hydrogen pressure. Since $Q = 10^{-3}$, the Nernst correction must increase the standard emf.