

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-4-1

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.

$16 \times 1 = 16$

1. Oxidation of chloroform by air in the presence of sunlight produces a poisonous gas known as: [1 mark]

- (A) Mustard gas
- (B) Tear gas
- (C) Chlorine gas
- (D) Phosgene gas

Correct Answer: (D) Phosgene gas

Solution:

Concept:

- Chloroform, CHCl_3 , undergoes slow oxidation by oxygen in air in the presence of sunlight.
- Phosgene is carbonyl chloride, COCl_2 , a highly poisonous gas.

Step 1: Identify the oxidation product The reaction is



The product containing the carbonyl group is carbonyl chloride, commonly called phosgene.

Step 2: Check the alternatives Mustard gas and tear gas are different substances and are not the products of this oxidation. Chlorine gas is also not formed by the displayed reaction; chlorine remains bonded in carbonyl chloride and hydrogen chloride.

Step 3: Conclusion The poisonous gas is phosgene, COCl_2 . Hence, the correct option is (D).

Quick Tip to Solve: Associate air and sunlight acting on chloroform with carbonyl chloride (phosgene).

2. Lucas reagent produces cloudiness immediately with:

[1 mark]

- (A) 2-methyl-1-propanol
- (B) Butan-2-ol
- (C) 2-methyl-2-propanol
- (D) Butan-1-ol

Correct Answer: (C) 2-methyl-2-propanol

Solution:

Concept:

- Lucas reagent is concentrated HCl with anhydrous ZnCl_2 . It converts alcohols into alkyl chlorides.
- Turbidity results from the insoluble alkyl chloride; tertiary alcohols give immediate turbidity at room temperature.

Step 1: Classify the alcohols 2-methyl-2-propanol has its hydroxyl-bearing carbon attached to three

Quick Tip to Solve: Count carbon groups on the carbon bearing OH: three means immediate Lucas turbidity.

carbon groups, so it is tertiary. Butan-2-ol is secondary, while 2-methyl-1-propanol and butan-1-ol are primary.

Step 2: Relate structure to the observation The tertiary alcohol readily forms a stable tertiary carbocation and reacts rapidly with Lucas reagent, producing an insoluble chloride immediately. The secondary alcohol produces turbidity after a delay; the primary alcohols do not give immediate turbidity at room temperature.

Step 3: Conclusion 2-methyl-2-propanol gives immediate cloudiness. Hence, the correct option is (C).

Quick Tip to Solve: Count carbon groups on the carbon bearing OH: three means immediate Lucas turbidity.

3. Which of the following d-orbitals experience more repulsion in the crystal field splitting of octahedral complex? [1 mark]

(A) d_{xy}, d_{yz}, d_{xz}

(B) $d_{x^2-y^2}, d_{z^2}$

(C) $d_{xy}, d_{x^2-y^2}$

(D) d_{xz}, d_{z^2}

Correct Answer: (B) $d_{x^2-y^2}, d_{z^2}$

Solution:

Concept:

- In an octahedral complex, six ligands approach along the positive and negative x , y and z axes.
- The e_g set consists of $d_{x^2-y^2}$ and d_{z^2} ; the t_{2g} set consists of d_{xy}, d_{yz}, d_{xz} .

Step 1: Locate the orbital lobes The lobes of $d_{x^2-y^2}$ point along the x and y axes, while those of d_{z^2} point along the z axis. They therefore face the approaching ligand electron pairs directly and experience greater electrostatic repulsion.

Step 2: Compare all listed sets The t_{2g} orbitals point between the axes and experience less repulsion. Option (A) contains only this lower-energy set. Options (C) and (D) each combine one lower-energy orbital with one higher-energy orbital; only (B) lists both higher-energy e_g orbitals.

Step 3: Conclusion $d_{x^2-y^2}$ and d_{z^2} experience more repulsion. Hence, the correct option is (B).

Quick Tip to Solve: In octahedral splitting, orbitals pointing along ligand axes form the higher-energy orbital set.

4. The chelating ligand used for the treatment of lead poisoning is:

[1 mark]

- (A) Ethane-1,2-diamine
- (B) Oxalate ion
- (C) Dimethylglyoxime
- (D) EDTA

Correct Answer: (D) EDTA

Solution:

Concept:

- A chelating ligand binds a metal ion through more than one donor atom, forming a stable complex.
- EDTA (ethylenediaminetetraacetate) is hexadentate: it binds through two nitrogen and four oxygen donor atoms.

Step 1: Identify the treatment ligand EDTA forms a stable chelate with Pb^{2+} . The calcium disodium salt of EDTA is used in treating lead poisoning; complex formation facilitates removal of lead from the body.

Step 2: Distinguish the other ligands Ethane-1,2-diamine and oxalate are bidentate ligands, but they are not the specified ligand used for this treatment. Dimethylglyoxime is familiar for forming a characteristic nickel complex and is likewise not the answer to lead-poisoning treatment.

Step 3: Conclusion The chelating ligand is EDTA. Hence, the correct option is (D).

Quick Tip to Solve: Remember the textbook pair: lead poisoning is treated using the EDTA chelating ligand.

5. Manganate ion is paramagnetic due to the presence of:

[1 mark]

- (A) one unpaired electron
- (B) two unpaired electrons
- (C) three unpaired electrons
- (D) fully paired electrons

Correct Answer: (A) one unpaired electron

Solution:

Concept:

- Paramagnetism arises from one or more unpaired electrons; fully paired electrons give diamagnetism.
- Manganate is MnO_4^{2-} . Each oxygen has oxidation number -2 .

Step 1: Find the oxidation state Let the oxidation state of manganese be x . Then

$$x + 4(-2) = -2 \Rightarrow x = +6.$$

Thus the ion contains manganese in the $+6$ oxidation state.

Step 2: Count the remaining d electrons Manganese has atomic configuration $[\text{Ar}]3d^54s^2$. Removing

Quick Tip to Solve: Distinguish manganate (Mn in $+6$, one d electron) from permanganate (Mn in $+7$, no d electrons).

six electrons (the two $4s$ electrons first) gives Mn^{6+} a $3d^1$ configuration. Its single d electron is unpaired. Therefore two or three unpaired electrons are incorrect, and fully paired electrons cannot account for paramagnetism.

Step 3: Conclusion Manganate contains one unpaired electron. Hence, the correct option is (A).

Quick Tip to Solve: Distinguish manganate (Mn in +6, one d electron) from permanganate (Mn in +7, no d electrons).

6. The correct order of decreasing basicities of $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $(\text{C}_2\text{H}_5)_3\text{N}$ in aqueous solution is: [1 mark]

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

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

(C) $\text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N}$

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

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

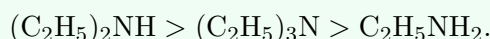
Solution:

Concept:

- An amine accepts a proton through the nitrogen lone pair; alkyl groups increase electron density by the $+I$ effect.
- In water, basicity depends on electron donation, solvation of the protonated ion and steric effects together.

Step 1: Balance the effects in water For ethylamines, the secondary amine benefits from two electron-donating ethyl groups while its conjugate acid can still be effectively hydrated. Adding a third ethyl group enhances electron donation but makes hydration less favourable and increases crowding, so the tertiary amine is less basic than the secondary amine.

Step 2: Apply the ethylamine order For these ethyl-substituted amines in aqueous solution, the tertiary amine nevertheless remains more basic than the primary amine. Thus the established order is



Option (A) wrongly puts the tertiary amine first; (B) reverses the tertiary-primary order, and (C) puts the primary amine first.

Step 3: Conclusion The decreasing order is $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2$. Hence, the correct option is (D).

Quick Tip to Solve: For aqueous ethylamines use secondary $>$ tertiary $>$ primary; do not use the methylamine order.

7. The boiling point of one molal NaCl solution, assuming NaCl to be completely dissociated in water is: (K_b for water = $0.52 \text{ K kg mol}^{-1}$) [1 mark]

- (A) 100.52°C
- (B) 101.04°C
- (C) 100.04°C
- (D) 101.52°C

Correct Answer: (B) 101.04°C

Solution:

Concept:

- Boiling-point elevation is $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality.
- Complete dissociation $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ gives two solute particles per formula unit, so $i = 2$.

Step 1: Calculate the elevation With $m = 1 \text{ mol kg}^{-1}$ and $K_b = 0.52 \text{ K kg mol}^{-1}$,

$$\Delta T_b = 2 \times 0.52 \times 1 = 1.04 \text{ K}.$$

The same numerical temperature increment is 1.04°C .

Step 2: Add the elevation to the solvent boiling point Using the normal boiling point of water,

$$T_b = 100 + 1.04 = 101.04^\circ\text{C}.$$

Option (A) ignores dissociation and uses $i = 1$. Options (C) and (D) do not match the calculated elevation of 1.04 K .

Step 3: Conclusion The boiling point is 101.04°C . Hence, the correct option is (B).

Quick Tip to Solve: Count ions before using the boiling-point elevation: complete NaCl dissociation doubles the elevation.

8. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased: [1 mark]

- (A) vapour pressure of the solution increases
- (B) heating occurs
- (C) cooling occurs
- (D) equilibrium remains unaffected

Correct Answer: (C) cooling occurs

Solution:

Concept:

- At liquid-vapour equilibrium, evaporation and condensation occur at equal rates.
- Evaporation requires latent heat; lowering pressure favours the vapour phase.

Step 1: Predict the response to the pressure decrease For the equilibrium liquid $\rightleftharpoons$ vapour, decreasing

Quick Tip to Solve: When pressure falls, identify the extra evaporation and then remember that evaporation absorbs latent heat.

pressure favours formation of the phase occupying the larger volume. More liquid therefore evaporates until equilibrium is re-established. The original equilibrium is disturbed, so option (D) cannot describe the immediate response.

Step 2: Account for the thermal effect The additional evaporation absorbs latent heat from the liquid and its surroundings, lowering the liquid temperature. Heating in (B) has the opposite sign. Option (A) is not the governing response: equilibrium vapour pressure depends on temperature, and the cooling tends to lower it rather than raise it.

Step 3: Conclusion Cooling occurs. Hence, the correct option is (C).

Quick Tip to Solve: When pressure falls, identify the extra evaporation and then remember that evaporation absorbs latent heat.

9. Consider the following cell at 298 K:



How can we increase the emf of the cell using the same substances?

[1 mark]

- (A) By decreasing only the $[\text{Mg}^{2+}]$ to 0.1 M
- (B) By decreasing only the $[\text{Cu}^{2+}]$ to 0.1 M
- (C) By increasing both $[\text{Mg}^{2+}]$ and $[\text{Cu}^{2+}]$ to 2.0 M
- (D) By increasing only the $[\text{Mg}^{2+}]$ to 2.0 M

Correct Answer: (A) By decreasing only the $[\text{Mg}^{2+}]$ to 0.1 M

Solution:

Concept:

- The cell reaction is $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$; two electrons are transferred.
- At 298 K, $E = E^\circ - \frac{0.0591}{2} \log Q$, where $Q = [\text{Mg}^{2+}]/[\text{Cu}^{2+}]$.

Step 1: Evaluate the change that increases emf Initially both ion concentrations are 1.0 M, so $Q = 1$ and $E = E^\circ$. In option (A), decreasing only $[\text{Mg}^{2+}]$ to 0.1 M gives $Q = 0.1$. Thus $\log Q = -1$, and $E = E^\circ + 0.02955 \text{ V}$.

Step 2: Test the remaining concentration changes Option (B) gives $Q = 10$, lowering emf by 0.02955 V. In (C), both concentrations become 2.0 M, so their ratio remains one and emf is unchanged. Option (D) gives $Q = 2$, making the logarithmic correction negative and lowering emf.

Step 3: Conclusion Decrease only $[\text{Mg}^{2+}]$ to 0.1 M. Hence, the correct option is (A).

Quick Tip to Solve: Write the product-ion concentration above the reactant-ion concentration; decreasing this ratio increases the cell emf.

10. The rate of a first order reaction is $5.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ when the concentration of reactant is 0.2 mol L^{-1} . The rate constant 'k' is:

[1 mark]

(A) $5.6 \times 10^{-3} \text{ s}^{-1}$

(B) $2.8 \times 10^{-4} \text{ s}^{-1}$

(C) $2.8 \times 10^{-5} \text{ s}^{-1}$

(D) $2.8 \times 10^{-3} \text{ s}^{-1}$

Correct Answer: (D) $2.8 \times 10^{-3} \text{ s}^{-1}$

Solution:

Concept:

- For a first-order reaction, $r = k[A]$, where r is the reaction rate and $[A]$ is the reactant concentration.
- Therefore $k = r/[A]$, and the units of k are s^{-1} .

Step 1: Substitute the given rate and concentration The printed rate is $5.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, and the concentration is 0.2 mol L^{-1} . Thus

$$k = \frac{5.6 \times 10^{-4}}{0.2} = 28 \times 10^{-4} = 2.8 \times 10^{-3} \text{ s}^{-1}.$$

The concentration units cancel, leaving inverse seconds.

Step 2: Check the printed choices Option (A), $5.6 \times 10^{-3} \text{ s}^{-1}$, is twice the calculated value. Option (B), $2.8 \times 10^{-4} \text{ s}^{-1}$, is ten times too small; option (C), $2.8 \times 10^{-5} \text{ s}^{-1}$, is one hundred times too small. Only option (D) matches the division and the required unit.

Step 3: Conclusion $k = 2.8 \times 10^{-3} \text{ s}^{-1}$. Hence, the correct option is (D).

Quick Tip to Solve: Dividing by 0.2 multiplies the rate by five; normalise the resulting power of ten before choosing the option.

11. Nucleic acids are polymers of:

[1 mark]

(A) amino acids

(B) nucleosides

(C) nucleotides

(D) pentose sugar

Correct Answer: (C) nucleotides

Solution:

Concept:

- A nucleotide consists of a nitrogenous base, a pentose sugar and a phosphate group.
- Nucleotides are linked by phosphodiester bonds to form DNA or RNA chains.

Step 1: Identify the complete repeating units Nucleic acids are polynucleotides. Their sugar-phosphate backbone forms when phosphate groups join the pentose sugars of adjacent nucleotide units through phosphodiester linkages. Each repeating unit includes its nitrogenous base as well as sugar and

Quick Tip to Solve: Use the phosphate group to distinguish a nucleotide from a nucleoside when identifying DNA and RNA monomers.

phosphate.

Step 2: Distinguish the other options Amino acids in (A) are the monomers of proteins. A nucleoside in (B) contains only a base and sugar; it lacks the phosphate group needed for the nucleic-acid backbone. Pentose sugar in (D) is just one constituent of a nucleotide, rather than the complete monomer.

Step 3: Conclusion Nucleic acids are polymers of nucleotides. Hence, the correct option is (C).

Quick Tip to Solve: Use the phosphate group to distinguish a nucleotide from a nucleoside when identifying DNA and RNA monomers.

12. In the reaction of NaOBr with amide, the carbonyl carbon is lost as:

[1 mark]

- (A) HCO_3^-
- (B) CO_3^{2-}
- (C) CO_2
- (D) CO

Correct Answer: (B) CO_3^{2-}

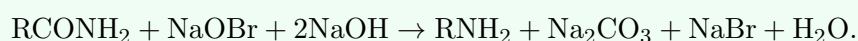
Solution:

Concept:

- Hofmann bromamide degradation converts RCONH_2 into RNH_2 , removing the carbonyl carbon.
- The reaction occurs in alkaline hypobromite; carbon dioxide produced during hydrolysis is trapped as carbonate.

Step 1: Trace the carbonyl carbon The primary amide rearranges through an isocyanate intermediate, RNCO . Hydrolysis gives an unstable carbamic acid, which decomposes to the primary amine and carbon dioxide. The amine therefore contains one carbon atom fewer than the original amide.

Step 2: Identify its form in the alkaline reaction mixture In the strongly alkaline medium, $\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$. The overall hypobromite equation is



Thus free carbon dioxide (C) is an intermediate description, bicarbonate (A) is not the final form under these conditions, and carbon monoxide (D) is not formed.

Step 3: Conclusion The carbonyl carbon is lost as CO_3^{2-} . Hence, the correct option is (B).

Quick Tip to Solve: For Hofmann degradation in alkaline hypobromite, track the lost carbon into carbonate in the overall equation.

13. Assertion (A): Alcohols act as Bronsted bases as well as Bronsted acids.

Reason (R): It is due to the presence of unshared electron pairs on oxygen atom and presence of polar O-H bond. [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:

- A Bronsted acid donates a proton; a Bronsted base accepts a proton.
- Alcohol oxygen has lone pairs, while its polar O – H bond permits proton donation.

Step 1: Judge the assertion Alcohols can accept a proton to give an oxonium ion, $\text{ROH} + \text{H}^+ \rightarrow \text{ROH}_2^+$. They can also donate the hydroxyl proton to a sufficiently strong base, forming RO^- . Their behaviour depends on the reacting species, so the assertion is true.

Step 2: Judge the reason The oxygen atom possesses unshared electron pairs which can bind an incoming proton. Oxygen also draws electron density away from hydrogen in the polar O – H bond, enabling proton loss. Both structural features stated in the reason are present, so the reason is true.

Step 3: Check the explanatory link The lone pair explains proton acceptance and therefore basic behaviour; the polar hydroxyl bond explains proton donation and therefore acidic behaviour. The reason directly accounts for both parts of the assertion. This rules out (B), while the truth of both statements rules out (C) and (D).

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

Quick Tip to Solve: Match oxygen lone pairs with proton acceptance, and the polar O-H bond with proton donation.

14. Assertion (A): Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Reason (R): Diazonium salts of aliphatic amines undergo resonance.

[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:

- Aromatic diazonium ions are stabilised by conjugation of the diazonium group with the aromatic ring.
- Aliphatic diazonium ions lack this aromatic conjugation and readily lose N_2 .

Step 1: Judge the assertion Aromatic diazonium salts are comparatively more stable and can be maintained in cold solution, typically at 273–278 K. The aromatic ring provides resonance stabilisation of the diazonium group. Aliphatic diazonium salts decompose readily with loss of nitrogen, so the assertion is true.

Step 2: Judge the reason The relevant resonance stabilisation is supplied by conjugation with an aromatic ring. An alkyl group has no aromatic pi system to provide this stabilisation. The reason incorrectly attributes the stabilising resonance to the aliphatic diazonium salts and is therefore false.

Step 3: Relate the statements to the answer codes A false reason cannot explain the true assertion. Options (A) and (B) require both statements to be true, while (D) requires the assertion to be false. These conditions are not satisfied by the relative stability and conjugation of the two classes of salts.

Step 4: Conclusion A is true, but R is false. Hence, the correct option is (C).

Quick Tip to Solve: Associate diazonium stability with an aromatic ring conjugated to the diazonium group; alkyl diazonium ions lose nitrogen readily.

15. Assertion (A): For complex reaction, order of reaction is given by the slowest step.

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

[1 mark]

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

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

Solution:

Concept:

- The order is the sum of concentration powers in the experimentally determined rate law: for $r = k[A]^m[B]^n$, order is $m + n$.
- In a multistep reaction, the slowest, rate-determining step controls the overall rate; the mechanism must agree with experiment.

Step 1: Judge Assertion (A) Assertion (A) is true in the standard rate-determining-step description of a complex reaction. The slowest step limits the overall rate, so the rate law associated with that step determines the observed order, after any intermediates are expressed in terms of reactants.

Step 2: Judge Reason (R) Reason (R) is true. The powers in a rate law are obtained from measured rates and concentrations; they cannot generally be read from the balanced overall equation.

Step 3: Check the explanatory connection The experimental nature of order does not explain why the slowest step controls a complex reaction. That control follows from the relative speeds of the successive steps. Thus (A) incorrectly claims an explanatory connection, while (C) and (D) incorrectly declare one statement false.

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

Quick Tip to Solve: First identify the rate-determining step; then distinguish experimental determination of order from its mechanistic explanation.

16. Assertion (A): $E_{\text{Sc}^{3+}/\text{Sc}^{2+}}^{\circ}$ has low value.

Reason (R): Because of the stability of Sc^{3+} ion which has a noble gas configuration.

[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:

- A low standard reduction potential indicates an unfavourable tendency to accept electrons under standard conditions.
- Scandium has configuration $[\text{Ar}]3d^14s^2$; Sc^{3+} has the closed-shell configuration $[\text{Ar}]$.

Step 1: Judge Assertion (A) The printed couple corresponds to $\text{Sc}^{3+} + e^{-} \rightarrow \text{Sc}^{2+}$. Its standard reduction potential has a low value because reduction of the stable trivalent ion to the divalent state is unfavourable. Assertion (A) is therefore true.

Step 2: Judge Reason (R) Removing the three outer electrons of scandium gives $\text{Sc}^{3+} : [\text{Ar}]$, a noble-gas configuration. In contrast, Sc^{2+} has $[\text{Ar}]3d^1$. Thus Reason (R) correctly identifies the special stability of the trivalent ion.

Step 3: Check the explanatory connection Adding an electron destroys the closed-shell configuration of Sc^{3+} . Its stability therefore accounts for the low tendency toward reduction and directly explains the low potential. Option (B) misses this connection; (C) and (D) wrongly reject a true statement.

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

Quick Tip to Solve: Write the two ion configurations: the stable closed shell belongs to Sc^{3+} , so reduction away from it is unfavourable.

Section B (10 marks)

17. (a) Reactions of which order will show the rate to be independent of the concentration of the reactant? Give one example of this order.

(b) State the condition under which a bimolecular reaction may be kinetically a first order reaction.

[2 marks]

Solution:

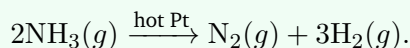
Concept:

- For a zero-order reaction, $r = k[A]^0 = k$, where r is rate and k is the rate constant.

Quick Tip to Solve: Zero order means concentration drops out of the rate law; pseudo-first order means one concentration is absorbed into the observed rate constant.

- For a bimolecular reaction with rate $r = k[A][B]$, keeping $[B]$ practically constant gives an observed first-order law.

Step 1: (a) Identify the order and give an example The required reactions are zero-order reactions: changing the reactant concentration does not change the rate under the conditions in which the zero-order law applies. An example is the decomposition of ammonia on a hot platinum surface when the surface is saturated with ammonia:



All active surface sites are occupied, so increasing ammonia concentration does not increase the rate.

Step 2: (b) State the pseudo-first-order condition A bimolecular reaction becomes kinetically first order when one reactant is present in such large excess that its concentration changes negligibly during the reaction. For $r = k[A][B]$, take $[B] \approx [B]_0$ and define $k_{\text{obs}} = k[B]_0$. Then

$$r = k_{\text{obs}}[A].$$

The measured rate depends on the concentration of only the other reactant, although the underlying reaction remains bimolecular.

Step 3: Conclusion (a) Zero order; ammonia decomposition on hot, saturated platinum is an example. (b) One reactant must be in large excess, giving effectively constant concentration and pseudo-first-order kinetics.

Quick Tip to Solve: Zero order means concentration drops out of the rate law; pseudo-first order means one concentration is absorbed into the observed rate constant.

18(a). Explain the following with the help of Henry's law:

(i) Bends

(ii) Anoxia

[2 marks]

Solution:

Concept:

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

Step 1: (i) Explain bends A diver at depth experiences high pressure. The increased partial pressure of nitrogen causes more nitrogen from the breathing mixture to dissolve in blood and tissues. On a rapid ascent, the external pressure falls abruptly, so nitrogen solubility decreases. Dissolved nitrogen escapes as bubbles, causing painful and potentially dangerous decompression sickness called bends. A slow ascent allows nitrogen to leave gradually instead of forming bubbles.

Step 2: (ii) Explain anoxia At high altitude the atmospheric pressure is lower, and therefore the partial pressure of oxygen is lower even though its proportion in air is approximately unchanged. By Henry's law, less oxygen can dissolve in blood at the lower oxygen partial pressure. The resulting

Quick Tip to Solve: Use partial pressure: high pressure dissolves more nitrogen at depth, while low oxygen partial pressure at altitude reduces oxygen uptake.

inadequate oxygen supply to body tissues is called anoxia and can cause weakness and impaired thinking. Thus bends involves a sudden fall in nitrogen solubility, whereas anoxia involves reduced oxygen availability.

Step 3: Conclusion Bends arises from nitrogen bubbles after rapid decompression; anoxia at high altitude arises from insufficient oxygen supply caused by low oxygen partial pressure.

Quick Tip to Solve: Use partial pressure: high pressure dissolves more nitrogen at depth, while low oxygen partial pressure at altitude reduces oxygen uptake.

OR

18(b). How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Write the name of the colligative property involved in this process. [2 marks]

Solution:

Concept:

- A dissolved nonvolatile solute lowers the freezing point of a solvent; this is the colligative property called depression of freezing point.
- For a dilute solution, $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the solvent cryoscopic constant and m the solute molality.

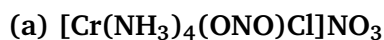
Step 1: Formation of salt solution on the snow A small amount of liquid water is generally present at the surface of snow or ice. Sprinkled salt dissolves in this water to form brine. Since dissolved salt supplies solute particles, the freezing point of the resulting aqueous solution is lower than that of pure water, whose normal freezing point is 0°C . For sodium chloride, dissociation into sodium and chloride ions increases the number of dissolved particles.

Step 2: Explain melting and identify the property If the road temperature is below 0°C but above the freezing point of the brine, the salty water can remain liquid. Snow or ice then melts into this solution, helping to loosen and clear the covering. The salt also makes refreezing less likely under these conditions. The relevant colligative property is depression of freezing point, because the effect depends on the number of dissolved solute particles.

Step 3: Conclusion Salt forms brine with a freezing point below that of pure water, allowing snow to melt at suitable subzero temperatures. The property is depression of freezing point.

Quick Tip to Solve: Connect road salt to freezing-point depression: it lowers the temperature at which the water can freeze rather than simply heating the snow.

19. Write IUPAC names of the following compounds:



[2 marks]

Solution:

Concept:

- For a complex ion, determine the metal oxidation state from the total charge and ligand charges before naming it.
- Ligands are named alphabetically: ammine for NH_3 , chlorido for Cl^- , nitrito-O for O-bonded ONO^- , and cyanido for CN^- .

Step 1: (a) Name the chromium complex The nitrate outside the coordination sphere is NO_3^- , so the complex cation has charge +1. The four ammine ligands are neutral; chlorido and nitrito-O each carry charge -1 . If the oxidation state of chromium is x , then

$$x + 4(0) - 1 - 1 = +1 \Rightarrow x = +3.$$

Alphabetical ligand order is ammine, chlorido, nitrito-O. The multiplier tetra does not affect alphabetisation. The O-bonded ligand must be distinguished from N-bonded nitro.

Step 2: (b) Name the silver complex Sodium has charge +1; hence $[\text{Ag}(\text{CN})_2]^-$ is an anion. With two cyanido ligands,

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

An anionic silver complex takes the metal name argentate, followed by its oxidation state in Roman numerals. The cation sodium is named first.

Step 3: Conclusion (a) Tetraamminechloridonitrito-O-chromium(III) nitrate.

(b) Sodium dicyanidoargentate(I).

Quick Tip to Solve: Use the ion outside the square brackets to find the complex charge; ONO explicitly indicates oxygen coordination.

20. What are the hydrolysis products of the following?

(a) Lactose

(b) DNA containing Thymine

[2 marks]

Solution:

Concept:

- Hydrolysis cleaves glycosidic bonds in disaccharides and breaks nucleic acids into their constituent sugar, phosphate and nitrogenous bases.
- Lactose contains glucose and galactose units; the pentose sugar in DNA is 2-deoxyribose.

Step 1: (a) Hydrolyse lactose Lactose is a reducing disaccharide made of D-galactose and D-glucose joined by a β -(1 $\rightarrow$ 4) glycosidic linkage. Hydrolysis adds water across this linkage and releases one molecule of each monosaccharide:



The products are two different hexoses; fructose is the hydrolysis partner of glucose in sucrose, not in lactose.

Step 2: (b) Hydrolyse DNA Complete hydrolysis of DNA breaks the sugar-phosphate backbone and the bonds joining bases to the sugar. The constituent products are 2-deoxy-D-ribose, phosphoric acid and nitrogenous bases. DNA containing thymine gives thymine among its base products, together with adenine, guanine and cytosine in ordinary DNA. Its sugar is deoxyribose, not ribose, and thymine is not converted into uracil during hydrolysis.

Step 3: Conclusion (a) D-glucose and D-galactose.

(b) 2-deoxy-D-ribose, phosphoric acid and the DNA bases adenine, guanine, cytosine and thymine.

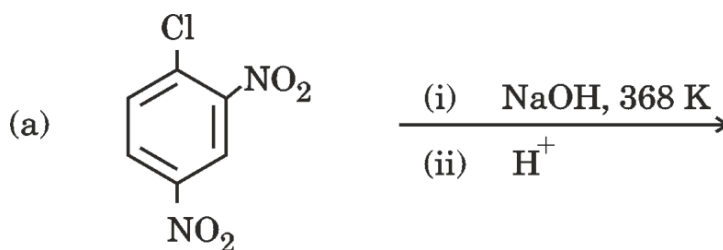
Quick Tip to Solve: Remember lactose as glucose plus galactose; identify DNA by deoxyribose and thymine.

21. Draw the structures of major product(s) in each of the following reactions:

(a) 2,4-dinitrochlorobenzene treated with (i) NaOH at 368 K followed by (ii) H^+ .

(b) $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{HBr} \rightarrow$

[2 marks]



Solution:

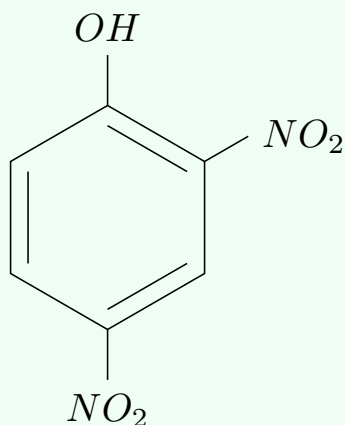
Concept:

- Ortho and para nitro groups activate aryl halides towards nucleophilic substitution by stabilising the intermediate.

Quick Tip to Solve: For HBr addition, place H to form the most stable carbocation, then attach Br at that carbocation carbon.

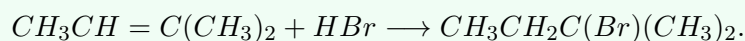
- Without peroxide, HBr adds to an unsymmetrical alkene by the Markovnikov rule through the more stable carbocation.

Step 1: (a) Substitute chlorine and acidify In 2,4-dinitrochlorobenzene, the two electron-withdrawing nitro groups are ortho and para to chlorine. They facilitate attack by hydroxide at the carbon carrying chlorine. Chloride is displaced and the basic reaction mixture contains sodium 2,4-dinitrophenoxide. Subsequent acidification protonates the phenoxide oxygen, yielding 2,4-dinitrophenol. Both nitro groups remain in their original positions; the only net structural change is *Cl* to *OH*.

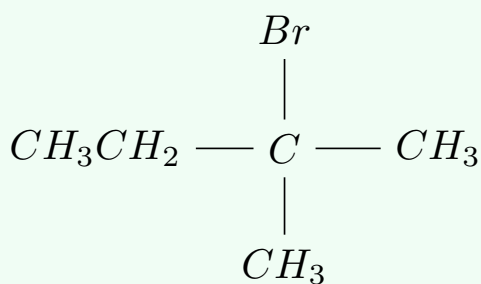


Product (a): 2,4-dinitrophenol

Step 2: (b) Add HBr to the alkene In $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$, the left alkene carbon bears a hydrogen, while the right carbon bears two methyl groups. Proton addition to the left carbon produces the more stable tertiary carbocation on the right carbon. Bromide then attacks that carbon:



The reverse orientation would involve a less stable secondary carbocation. No peroxide is specified, so the anti-Markovnikov radical pathway is not applicable.



Product (b): 2-bromo-2-methylbutane

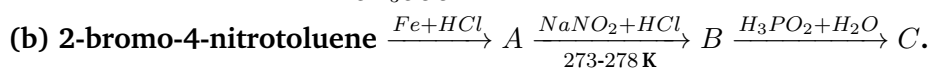
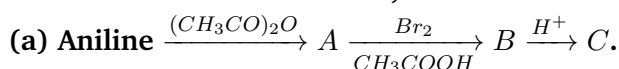
Step 3: Conclusion (a) 2,4-Dinitrophenol.

(b) $\text{CH}_3\text{CH}_2\text{C}(\text{Br})(\text{CH}_3)_2$, 2-bromo-2-methylbutane.

Quick Tip to Solve: For HBr addition, place H to form the most stable carbocation, then attach Br at that carbocation carbon.

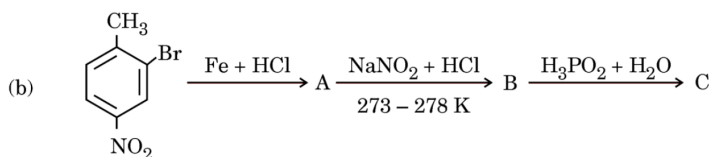
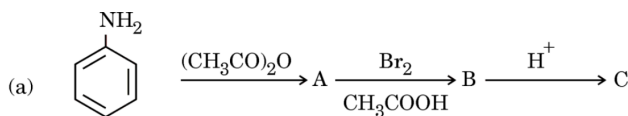
Section C (21 marks)

22. Write the structures of A, B and C in the following reactions:



[3 marks]

Write the structures of A, B and C in the following reactions : $2 \times 1 \frac{1}{2} =$



Solution:

Concept:

- Acetylation protects the strongly activating amino group; bromination of acetanilide mainly occurs para to the protected amino group.
- Fe/HCl reduces an aromatic nitro group to an amino group; cold nitrous acid converts a primary aromatic amine to a diazonium salt.
- Hypophosphorous acid replaces the diazonium group by hydrogen; the other ring substituents retain their positions.

Step 1: (a) Identify the protected and brominated compounds Aniline reacts with acetic anhydride by acetylation of nitrogen. Thus A is acetanilide, $C_6H_5NHC(=O)CH_3$. The $-NHC(=O)CH_3$ group remains ortho/para directing, but is less activating than a free amino group. Bromination in acetic acid gives mainly the less hindered para product. Therefore B is p-bromoacetanilide, $p\text{-}BrC_6H_4NHC(=O)CH_3$. Acidic hydrolysis removes the acetyl protecting group and restores $-NH_2$, so C is p-bromoaniline, $p\text{-}BrC_6H_4NH_2$.

Step 2: (b) Reduce and diazotise the nitro compound Read the printed starting ring with methyl at position 1, bromine at position 2 and nitro at position 4. Fe/HCl reduces only $-NO_2$ to $-NH_2$, leaving the aryl bromine and methyl groups intact. A is therefore 2-bromo-4-aminotoluene, equivalently 3-bromo-4-methylaniline. Its condensed structure is $C_6H_3(1-CH_3)(2-Br)(4-NH_2)$. Treatment with $NaNO_2/HCl$ at 273-278 K converts the amino group into $-N_2^+Cl^-$. B is $C_6H_3(1-CH_3)(2-Br)(4-N_2^+)Cl^-$, 3-bromo-4-methylbenzenediazonium chloride.

Step 3: (b) Replace the diazonium group by hydrogen Hypophosphorous acid in water removes the diazonium group with evolution of nitrogen and replaces it by hydrogen. The carbon that originally bore $-NO_2$, and then $-NH_2$, now bears H. Neither bromine nor methyl is removed. C is consequently o- $BrC_6H_4CH_3$, 2-bromotoluene. The positional relationship between bromine and methyl is ortho throughout this sequence.

Step 4: Conclusion (a) A: $C_6H_5NHC(=O)CH_3$; B: $p\text{-}BrC_6H_4NHC(=O)CH_3$; C: $p\text{-}BrC_6H_4NH_2$.

Quick Tip to Solve: Keep the printed ring positions fixed while changing the functional group: NO_2 to NH_2 to diazonium to H.

(b) A: $C_6H_3(1-CH_3)(2-Br)(4-NH_2)$; B: $C_6H_3(1-CH_3)(2-Br)(4-N_2^+)Cl^-$; C: $o-BrC_6H_4CH_3$.

Quick Tip to Solve: Keep the printed ring positions fixed while changing the functional group: NO₂ to NH₂ to diazonium to H.

23. What happens when:

(a) Propanenitrile is treated with phenyl magnesium bromide followed by hydrolysis?

(b) p-fluorotoluene is treated with CrO₃ in the presence of acetic anhydride followed by hydrolysis with aqueous acid.

(c) Phthalic acid is treated with NH₃ followed by heating?

Write chemical reactions in support of your answer.

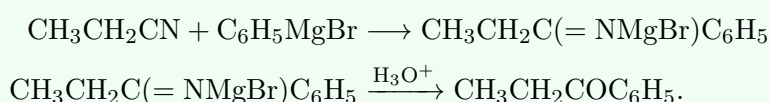
[3 marks]

Solution:

Concept:

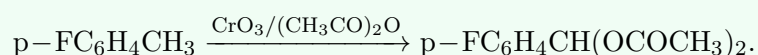
- Nitriles react with Grignard reagents through an imine magnesium salt, whose acidic hydrolysis gives a ketone.
- Chromium trioxide in acetic anhydride converts a benzylic methyl group into an aldehyde diacetate, which hydrolyses to the aldehyde.
- An ortho-dicarboxylic acid reacts with ammonia and loses water on heating to form a cyclic imide.

Step 1: (a) Reaction of propanenitrile The phenyl group adds to the nitrile carbon. Hydrolysis replaces the nitrogen-containing group of the imine salt by oxygen:

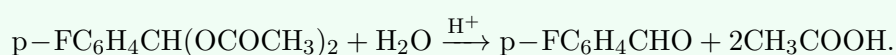


The organic product is 1-phenylpropan-1-one (propiophenone). The ethyl group originally attached to the nitrile carbon remains attached to the carbonyl carbon.

Step 2: (b) Controlled oxidation of p-fluorotoluene The methyl group is oxidised while fluorine remains attached to the ring. Acetic anhydride traps the aldehyde as its geminal diacetate:

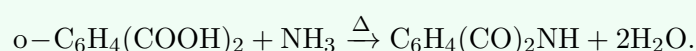


Acidic hydrolysis releases p-fluorobenzaldehyde:



These controlled conditions give the aldehyde rather than complete oxidation of the side chain to a carboxylic acid.

Step 3: (c) Formation of phthalimide Ammonia first forms an ammonium salt with phthalic acid. On heating, dehydration produces the five-membered cyclic imide, phthalimide. The overall balanced reaction is



Quick Tip to Solve: For nitrile plus Grignard reagent, place the nitrile's alkyl group and the reagent's organic group on opposite sides of the final carbonyl.

In the product, the same NH group is bonded to both adjacent carbonyl carbon atoms, closing the imide ring.

Step 4: Conclusion The products are (a) propiophenone, (b) p-fluorobenzaldehyde after diacetate hydrolysis, and (c) phthalimide on heating.

Quick Tip to Solve: For nitrile plus Grignard reagent, place the nitrile's alkyl group and the reagent's organic group on opposite sides of the final carbonyl.

24. Answer the following questions:

- (a) Why is direct current (DC) not used to measure the resistance of an ionic solution?
(b) Why are the products of electrolysis different for the electrolysis of aqueous solution of AgNO_3 with silver electrodes and electrolysis of aqueous solution of AgNO_3 with platinum electrodes?
(c) Why are magnesium blocks fixed to the iron pipelines carrying water? [3 marks]

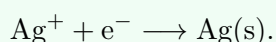
Solution:

Concept:

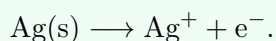
- Measuring the resistance of an electrolyte requires its composition and electrode conditions to remain unchanged.
- Electrolysis products depend on the species available for discharge and whether the electrodes are active or inert.
- A metal more easily oxidised than iron can protect iron by acting as a sacrificial anode.

Step 1: (a) Why DC is unsuitable Direct current drives sustained electrolysis. Ions are discharged at the electrodes, changing the solution's composition and concentration near them. Electrode polarisation also develops and introduces an opposing potential. Consequently, the measured value no longer represents only the resistance of the original ionic solution. Alternating current is used because frequent reversal greatly reduces net electrolysis and polarisation during the measurement.

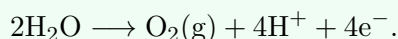
Step 2: (b) Active silver and inert platinum electrodes In both cases, silver ions are reduced at the cathode:



With silver electrodes, the silver anode itself oxidises:



Thus silver transfers from anode to cathode and the silver ions removed at the cathode are replenished. With platinum electrodes, the anode is inert and does not supply silver ions. Water is oxidised instead, producing oxygen:



Nitrate ions remain in solution. Hence the cathodic deposit is silver in both arrangements, but the anodic product is silver ions with a silver anode and oxygen gas with a platinum anode.

Step 3: (c) Sacrificial protection of iron pipelines Magnesium is more readily oxidised than iron.

Quick Tip to Solve: Compare the anodes first: silver can dissolve, platinum cannot, and magnesium oxidises preferentially when connected to iron.

When magnesium blocks are electrically connected to the pipeline, magnesium acts as the anode:



Its electrons flow to the iron, making the pipeline the cathode and suppressing the oxidation of iron to iron ions. Magnesium is consumed preferentially, so the blocks are sacrificial anodes and must be replaced periodically. This is cathodic protection against corrosion.

Step 4: Conclusion DC causes electrolysis and polarisation; electrode participation changes the anodic products of silver nitrate electrolysis; magnesium corrodes sacrificially to protect the iron pipeline.

Quick Tip to Solve: Compare the anodes first: silver can dissolve, platinum cannot, and magnesium oxidises preferentially when connected to iron.

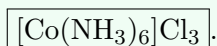
25(a). When a coordination compound $\text{CoCl}_3 \cdot 6\text{NH}_3$ is mixed with excess of AgNO_3 solution, 3 moles of AgCl are precipitated per mole of the compound. Write the structural formula of the complex, IUPAC name, its hybridisation and magnetic behaviour on the basis of valence bond theory. [3 marks]

Solution:

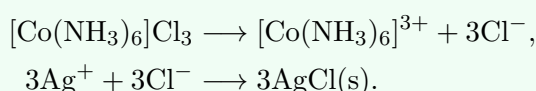
Concept:

- Chloride ions outside the coordination sphere ionise in solution and precipitate as silver chloride; coordinated chloride does not precipitate directly.
- Ammonia is a neutral ligand. The oxidation state and d-electron configuration of cobalt determine the valence-bond description.
- Six donor pairs occupy six hybrid orbitals in an octahedral complex; paired d electrons give diamagnetic behaviour.

Step 1: Establish the structural formula Three moles of AgCl per mole of compound show that all three chloride ions are outside the coordination sphere. All six ammonia molecules are coordinated to cobalt:



Its dissociation and chloride precipitation are



Thus the complex cation has coordination number six and charge +3.

Step 2: Write the IUPAC name Since ammonia is neutral, cobalt in $[\text{Co}(\text{NH}_3)_6]^{3+}$ has oxidation state +3. The ligand name is ammine and six such ligands give the prefix hexaammine. The compound is named **hexaamminecobalt(III) chloride**. Chloride is the counter-ion and is named after the complex cation.

Step 3: Explain hybridisation and magnetism by VBT Neutral cobalt has configuration $[\text{Ar}]3d^74s^2$. Removal of two 4s electrons and one 3d electron gives Co^{3+} the configuration $[\text{Ar}]3d^6$. In this cobalt(III) complex, ammonia causes the six 3d electrons to pair in three 3d orbitals, leaving two 3d

Quick Tip to Solve: Use the AgCl yield to count external chloride ions first, then obtain cobalt's charge before writing its d-electron configuration.

orbitals vacant. These two inner 3d orbitals combine with one 4s and three 4p orbitals to form six d^2sp^3 hybrid orbitals. Each accepts one lone pair from an ammonia ligand, producing an octahedral inner-orbital complex. All six d electrons are paired, so there are no unpaired electrons and the complex is diamagnetic.

Step 4: Conclusion The complex is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, hexaamminecobalt(III) chloride; it has d^2sp^3 hybridisation, octahedral geometry and diamagnetic behaviour.

Quick Tip to Solve: Use the AgCl yield to count external chloride ions first, then obtain cobalt's charge before writing its d-electron configuration.

OR

25(b). (i) How many geometrical isomers are possible in each of the following complexes?

(I) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

(II) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

(ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex. Why? [Atomic number: Co = 27, Ni = 28]

(iii) Write the formula of Wilkinson catalyst and its use.

[3 marks]

Solution:

Concept:

- Geometrical isomers have different relative positions of ligands; optical isomers are counted separately.
- An inner orbital octahedral complex uses two vacant 3d orbitals in d^2sp^3 hybridisation; an outer orbital complex uses 4d orbitals in sp^3d^2 hybridisation.

Step 1: Determine the geometrical isomers in part (i) (I) In $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, three identical bidentate oxalate ligands occupy the six octahedral coordination positions. There is only one geometrical arrangement, so it has no geometrical isomerism (one geometrical form). Its two optical forms do not constitute different geometrical isomers.

(II) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ has two geometrical isomers: facial (fac), in which the three identical ligands occupy one triangular face and are mutually cis, and meridional (mer), in which they lie on a meridian with one identical pair trans.

Step 2: Explain the orbital choice in part (ii) Cobalt has configuration $[\text{Ar}]3d^74s^2$, so Co^{3+} is $3d^6$. In its ammine complex, the six electrons pair in three 3d orbitals, leaving two vacant 3d orbitals. These combine with one 4s and three 4p orbitals to give d^2sp^3 hybridisation. Hence it is an inner orbital complex.

Nickel has configuration $[\text{Ar}]3d^84s^2$, so Ni^{2+} is $3d^8$. Eight electrons cannot leave two of the five 3d orbitals vacant, even after maximum pairing. Therefore the octahedral ammine complex uses two 4d, one 4s and three 4p orbitals for sp^3d^2 hybridisation and is an outer orbital complex.

Step 3: Give Wilkinson catalyst and its use in part (iii) Wilkinson catalyst is a rhodium(I) complex containing one chlorido ligand and three triphenylphosphine ligands, $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$. It is a

Quick Tip to Solve: For the orbital comparison, first remove the two 4s electrons and then ask whether two 3d orbitals can be vacant.

homogeneous catalyst used for hydrogenation of alkenes to alkanes: hydrogen adds across the carbon-carbon double bond.

Step 4: Conclusion (i) One geometrical form (no geometrical isomerism) and two (fac and mer), respectively. (ii) Co^{3+} permits d^2sp^3 hybridisation; Ni^{2+} requires sp^3d^2 . (iii) Wilkinson catalyst: $[\text{RhCl}(\text{PPh}_3)_3]$, used for alkene hydrogenation.

Quick Tip to Solve: For the orbital comparison, first remove the two 4s electrons and then ask whether two 3d orbitals can be vacant.

26. Calculate the vapour pressure of a solution containing 61 g of benzoic acid (molar mass = 122 g mol⁻¹) dissolved in 500 g of benzene when the vapour pressure of pure benzene at this temperature of experiment is 66 torr. Assume complete dimerization of benzoic acid in benzene. [3 marks]

Solution:

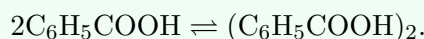
Concept:

- Raoult's law for a nonvolatile solute is $p = x_{\text{benzene}}p^0$, where p^0 is pure-solvent vapour pressure and x is solvent mole fraction.
- Complete dimerisation converts two solute molecules into one particle: the van't Hoff factor is $i = 1/2$. Mole fraction must use the actual number of dissolved particles.

Step 1: Calculate solute particles after dimerisation The analytical amount of benzoic acid is

$$n_{\text{acid}} = \frac{61 \text{ g}}{122 \text{ g mol}^{-1}} = 0.500 \text{ mol.}$$

In benzene, two benzoic acid molecules associate through hydrogen bonding to form each dimer:



Since dimerisation is complete, no monomer remains and the effective amount of solute particles is $n_{\text{dimer}} = 0.500/2 = 0.250 \text{ mol}$. The mass remains 61 g; only the particle count is halved.

Step 2: Calculate the benzene mole fraction Using the molar mass of benzene C_6H_6 , $M = 78 \text{ g mol}^{-1}$, the solvent amount is

$$n_{\text{benzene}} = \frac{500}{78} = 6.41026 \text{ mol.}$$

Therefore the solvent mole fraction, using dimers rather than the original acid molecules, is

$$x_{\text{benzene}} = \frac{6.41026}{6.41026 + 0.250} = \frac{500}{519.5} = 0.96246.$$

The denominator includes both solvent molecules and the actual associated solute particles.

Step 3: Apply Raoult's law Benzoic acid is treated as a nonvolatile solute, so the vapour pressure above the solution is due to benzene:

$$p = x_{\text{benzene}}p^0 = \frac{500}{519.5} \times 66 \text{ torr} = 63.5226 \text{ torr.}$$

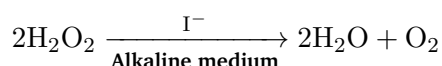
Quick Tip to Solve: Halve the acid moles before forming the solvent mole fraction; do not halve the final vapour pressure.

The pressure is below 66 torr, as expected on adding a nonvolatile solute. Association makes the lowering smaller than it would be for 0.500 mol of unassociated acid.

Step 4: Conclusion The vapour pressure of the solution is 63.52 torr.

Quick Tip to Solve: Halve the acid moles before forming the solvent mole fraction; do not halve the final vapour pressure.

27. Consider the decomposition of hydrogen peroxide (H_2O_2) as per the equation given below:



The mechanism for this reaction was found to be:

Step I: $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$ (slow)

Step II: $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2$ (fast)

(a) Write the rate law expression.

(b) Determine the order of reaction with respect to H_2O_2 , I^- and overall order of reaction.

(c) What is the molecularity of the reaction in Step II?

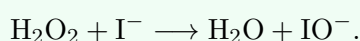
[3 marks]

Solution:

Concept:

- The rate-determining step is the slow elementary step. Its reactant stoichiometry gives its rate law, with k the rate constant at the stated temperature.
- Reaction order is the sum of concentration exponents in the rate law. Molecularity counts reacting particles in a single elementary step.

Step 1: Write the rate law in part (a) Step I is slow:



It involves one hydrogen peroxide molecule and one iodide ion. Because this is an elementary step, its rate is proportional to each reactant concentration:

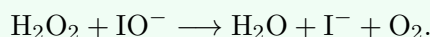
$$r = k[\text{H}_2\text{O}_2][\text{I}^-].$$

Step II is fast and consumes the intermediate IO^- as soon as it is formed, so it does not determine the overall rate. Adding the two steps cancels IO^- and regenerates I^- , giving the printed net equation. Iodide is a catalyst, but its concentration can still appear in the rate law.

Step 2: Determine the orders in part (b) Compare the derived law with $r = k[\text{H}_2\text{O}_2]^a[\text{I}^-]^b$. The exponent of $[\text{H}_2\text{O}_2]$ is $a = 1$, so the reaction is first order with respect to hydrogen peroxide. The exponent of $[\text{I}^-]$ is $b = 1$, so it is first order with respect to iodide. The overall order is $a + b = 1 + 1 = 2$. These orders follow from the given elementary slow step, not from the coefficient 2 in the net equation.

Quick Tip to Solve: Read the slow step for the rate law, but count the reactants in Step II when asked for its molecularity.

Step 3: Find molecularity of Step II in part (c) The fast elementary step is



Its reacting entities are one H_2O_2 molecule and one IO^- ion. Thus two reactant particles participate, making Step II bimolecular. Product particles are not counted in molecularity; molecularity is assigned to this elementary step rather than to the multistep overall reaction.

Step 4: Conclusion (a) $r = k[\text{H}_2\text{O}_2][\text{I}^-]$. (b) First order in each reactant; overall second order. (c) Step II is bimolecular (molecularity 2).

Quick Tip to Solve: Read the slow step for the rate law, but count the reactants in Step II when asked for its molecularity.

28. Answer the following:

- (a) Which isomer of $\text{C}_4\text{H}_9\text{Br}$ is most reactive towards $\text{S}_{\text{N}}1$ reaction?
(b) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.
(c) Although chlorine shows strong $-I$ effect, yet it is ortho- and para-directing in electrophilic aromatic substitution reactions. Why?

[3 marks]

Solution:

Concept:

- In an $\text{S}_{\text{N}}1$ reaction, ionisation of the carbon-halogen bond produces a carbocation in the slow step. Greater carbocation stability gives faster reaction.
- Dehydrohalogenation removes a halogen and a hydrogen from adjacent carbon atoms. According to Saytzeff's rule, the more substituted alkene is usually the major product.
- Chlorine withdraws electrons by its $-I$ effect, but donates a lone pair to the aromatic ring by resonance; the two effects control reactivity and orientation differently.

Step 1: (a) Compare the carbocations The isomer is 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$. Its ionisation gives the tertiary tert-butyl carbocation, $(\text{CH}_3)_3\text{C}^+$, stabilised by the electron-releasing effects and hyperconjugation of three methyl groups. The other butyl bromide isomers give primary or secondary carbocations, so they react more slowly by this mechanism.

Step 2: (b) Identify the major elimination product In 1-bromo-1-methylcyclohexane, bromine is attached to carbon 1. Removal of a hydrogen from the adjacent ring carbon, carbon 2 or the equivalent carbon 6, gives a double bond within the ring. The product is 1-methylcyclohex-1-ene. It has a trisubstituted double bond and is favoured over the less substituted exocyclic alkene, methylenecyclohexane, obtained by removing hydrogen from the methyl group.

Step 3: (c) Separate activation from orientation Chlorine's strong $-I$ effect reduces the overall electron density of the ring and makes chlorobenzene less reactive than benzene. However, donation of a chlorine lone pair by resonance increases electron density preferentially at the ortho and para positions. The intermediates formed by attack at these positions receive additional resonance stabilisation involving chlorine, whereas the meta intermediate does not. Hence chlorine deactivates

Quick Tip to Solve: For halogens on benzene, use induction to judge overall reactivity and resonance to judge the position of substitution.

the ring but directs electrophiles to ortho and para positions.

Step 4: Conclusion (a) 2-Bromo-2-methylpropane; (b) 1-methylcyclohex-1-ene; (c) chlorine's resonance donation favours ortho and para substitution despite its deactivating $-I$ effect.

Quick Tip to Solve: For halogens on benzene, use induction to judge overall reactivity and resonance to judge the position of substitution.

Section D (8 marks)

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

29(a). Case Study (Alcohols and Phenols): Alcohols and Phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron releasing groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents, while secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation. The presence of $-OH$ group in phenols activates the aromatic ring towards electrophilic substitution and directs the incoming group to ortho and para positions due to resonance effect.

(a) Write the mechanism of acid dehydration of ethanol to yield ethene.

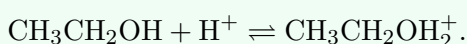
[2 marks]

Solution:

Concept:

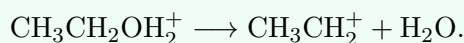
- Concentrated H_2SO_4 at about 443 K converts ethanol into ethene by acid-catalysed dehydration.
- Protonation converts the poor leaving group $-OH$ into water; elimination then forms the carbon-carbon double bond and regenerates the acid.

Step 1: Protonate the hydroxyl group Ethanol accepts a proton on the oxygen atom. The resulting ethyloxonium ion has water as a good leaving group:



The acid therefore facilitates removal of the hydroxyl group without requiring direct departure of the poorly leaving hydroxide ion.

Step 2: Lose water in the slow step In the simplified NCERT mechanism, the protonated alcohol loses a water molecule in the slow, rate-determining step to give the ethyl carbocation:



Protonation makes this departure possible because neutral water is a much better leaving group than hydroxide. This step is represented separately in the prescribed acid-dehydration mechanism.

Step 3: Remove a proton to form ethene The carbocation loses a proton from the adjacent carbon.

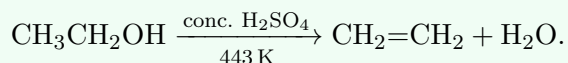
Quick Tip to Solve: First turn the hydroxyl group into water by protonation; then show removal of an adjacent hydrogen and regeneration of the acid.

The electrons of that carbon-hydrogen bond form the carbon-carbon double bond:



Water present in the reaction mixture can accept this proton. The acid catalyst is regenerated, while the net change is elimination of water from ethanol. Heating ethanol with concentrated sulphuric acid at about 443 K favours alkene formation.

Step 4: Conclusion



Acid-catalysed protonation followed by elimination yields ethene.

Quick Tip to Solve: First turn the hydroxyl group into water by protonation; then show removal of an adjacent hydrogen and regeneration of the acid.

29(b). Why are tertiary alcohols resistant to oxidation?

[1 mark]

Solution:

Concept:

- Usual oxidation of an alcohol to a carbonyl compound requires a hydrogen on the carbon bearing the hydroxyl group.
- A tertiary alcohol has the general structure $\text{R}_3\text{C}-\text{OH}$; that carbon is bonded to three carbon groups and has no hydrogen.

Step 1: Inspect the hydroxyl-bearing carbon In a tertiary alcohol, all three non-oxygen bonds of the hydroxyl-bearing carbon are carbon-carbon bonds. Therefore there is no hydrogen on this carbon that can be removed during the normal alcohol-to-carbonyl oxidation.

Step 2: Explain the resistance Formation of a carbonyl compound would require cleavage of a carbon-carbon bond. Ordinary mild oxidising agents do not readily carry out this cleavage, so tertiary alcohols resist oxidation under the usual conditions. Severe oxidation can break the carbon skeleton, so the resistance is not absolute under all conditions.

Step 3: Conclusion Tertiary alcohols resist ordinary oxidation because they lack a hydrogen on the carbon bearing $-\text{OH}$; oxidation would require carbon-carbon bond cleavage.

Quick Tip to Solve: Look for a hydrogen on the carbon attached to oxygen, rather than counting hydrogens elsewhere in the molecule.

29(b). Write the structure of the major product expected from the dinitration of 3-methylphenol.

[1 mark]

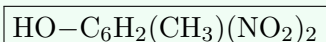
Solution:

Concept:

- The $-\text{OH}$ group strongly activates a benzene ring and directs incoming electrophiles to its ortho and para positions.
- In 3-methylphenol, number the hydroxyl-bearing carbon as 1 and the methyl-bearing carbon as 3; the jointly directed positions are 2, 4 and 6.

Step 1: Locate the favoured sites Both the hydroxyl group at carbon 1 and the methyl group at carbon 3 favour substitution at carbons 2, 4 and 6. Carbon 2 lies between the two existing groups and is more sterically crowded. Nitration therefore preferentially occupies the less crowded positions 4 and 6.

Step 2: Write the disubstituted product The major product retains the hydroxyl group at carbon 1 and the methyl group at carbon 3, and has $-\text{NO}_2$ groups at carbons 4 and 6. Its condensed structural formula is



with the ring substituent positions specified as 1-OH, 3-CH₃, 4-NO₂, 6-NO₂. These locants specify the complete constitutional structure.

Step 3: Conclusion The major product is 3-methyl-4,6-dinitrophenol: $-\text{OH}$ at carbon 1, $-\text{CH}_3$ at carbon 3, and $-\text{NO}_2$ at carbons 4 and 6.

Quick Tip to Solve: Number from the phenolic hydroxyl group and avoid the crowded position between hydroxyl and methyl when placing the two nitro groups.

29(c). Why is ortho-nitrophenol more acidic than ortho-methoxyphenol?

[1 mark]

Solution:

Concept:

- Phenol acidity depends on the stability of the phenoxide ion formed after loss of H^+ .
- An electron-withdrawing group stabilises the conjugate base, whereas resonance donation by an electron-releasing group generally destabilises it.

Step 1: Examine the nitro substituent The ortho nitro group withdraws electron density through both its $-I$ and $-R$ effects. It stabilises the negative charge of the corresponding phenoxide ion by induction and resonance, making loss of the phenolic proton more favourable.

Step 2: Compare the methoxy substituent The ortho methoxy group donates a lone pair into the aromatic ring through its $+R$ effect. Although oxygen also has an inductive withdrawing effect, resonance donation increases electron density and makes the phenoxide ion less stabilised than in the nitro-substituted compound. The difference in conjugate-base stability explains the acidity order.

Step 3: Conclusion Ortho-nitrophenol is more acidic because $-\text{NO}_2$ stabilises its phenoxide ion by

Quick Tip to Solve: Compare the conjugate bases: a group that disperses or withdraws their negative charge increases phenol acidity.

electron withdrawal, while the $+R$ effect of $-OCH_3$ opposes this stabilisation.

Quick Tip to Solve: Compare the conjugate bases: a group that disperses or withdraws their negative charge increases phenol acidity.

30(a). Case Study (Carbohydrates): Carbohydrates are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. They have been broadly classified into three groups — monosaccharides, oligosaccharides and polysaccharides. The carbohydrates may also be classified as either reducing or non-reducing sugars. An important monosaccharide glucose is an aldohexose and is correctly named as D(+)-glucose. It was assigned the open structure on the basis of its reactions with HI, NH_2OH , Br_2 water, $(CH_3CO)_2O$ and nitric acid. Despite having the $-CHO$ group, glucose does not give Schiff's test and hydrogen sulphite addition product with $NaHSO_3$. It was found that glucose forms a six-membered ring in which one of the $-OH$ groups add to the $-CHO$ group and form a cyclic hemiacetal structure.

(a) How do you explain the following?

(i) Presence of a carbonyl group in glucose

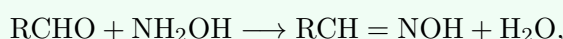
(ii) Presence of five $-OH$ groups in glucose which are attached to different carbon atoms. [2 marks]

Solution:

Concept:

- Hydroxylamine, NH_2OH , reacts with a carbonyl group to form an oxime; this reaction identifies the $>C=O$ functional group.
- Acetic anhydride acetylates free hydroxyl groups. The number of acetyl groups introduced equals the number of reactive $-OH$ groups.

Step 1: (i) Identify the carbonyl group Glucose reacts with hydroxylamine to form glucose oxime. In its open-chain form, the terminal aldehyde group undergoes the condensation reaction



where R represents the remaining glucose chain. Formation of the oxime establishes the presence of a carbonyl group in glucose.

Step 2: (ii) Count the hydroxyl groups Glucose reacts with acetic anhydride to give glucose pentaacetate. Five hydroxyl hydrogens are replaced by five acetyl groups, so glucose contains five $-OH$ groups. The pentaacetate is stable; this supports the assignment of these hydroxyl groups to different carbon atoms, since two hydroxyl groups on the same carbon generally give an unstable geminal diol. In the open-chain structure, the hydroxyl groups occur at C2, C3, C4, C5 and C6.

Step 3: Conclusion Oxime formation proves the carbonyl group; formation of stable glucose pentaacetate establishes five hydroxyl groups attached to different carbon atoms.

Quick Tip to Solve: Link hydroxylamine to the carbonyl group and stable pentaacetate to five hydroxyl groups on different carbons.

30(b). What type of carbohydrates are called reducing sugars?

[1 mark]

Solution:

Concept:

- Reducing sugars are carbohydrates that reduce mild oxidising reagents such as Fehling's solution or Tollens' reagent.
- A free anomeric group can open to a carbonyl form, enabling the sugar to undergo oxidation.

Step 1: Identify the chemical behaviour A carbohydrate is called a reducing sugar when it reduces Fehling's solution or Tollens' reagent. During this reaction the sugar is oxidised, while the reagent is reduced.

Step 2: Relate the behaviour to structure Sugars with an available aldehydic group, or a ketonic group that can rearrange under the test conditions, show this behaviour. Glucose and fructose are examples; fructose can rearrange to aldoses in the alkaline test medium.

Step 3: Conclusion Reducing sugars are carbohydrates that reduce Fehling's solution or Tollens' reagent.

Quick Tip to Solve: Identify reducing sugars by the Fehling or Tollens test; remember that fructose also gives a positive test.

30(c). In D(+)-glucose, what do the letter 'D' and sign '(+)' represent?

[1 mark]

Solution:

Concept:

- The D/L notation specifies relative configuration by comparison with glyceraldehyde.
- The signs (+) and (−) describe the experimentally observed direction of optical rotation; they are independent of D/L configuration.

Step 1: Interpret the letter D In the Fischer projection of D-glucose with the aldehyde group at the top, the hydroxyl group on the penultimate carbon, C5, lies on the right. Its configuration corresponds to that of D-glyceraldehyde.

Step 2: Interpret the sign (+) The sign (+) means that glucose is dextrorotatory: it rotates the plane of plane-polarised light to the right under the stated measurement conditions. The letter D alone does not imply positive optical rotation.

Step 3: Conclusion D denotes configuration relative to D-glyceraldehyde, while (+) denotes dextrorotatory optical rotation.

Quick Tip to Solve: Check C5 for the D configuration; use the (+) sign separately to identify the direction of optical rotation.

30(c). Draw the six-membered ring structure of α -D(+)-glucose.

[1 mark]

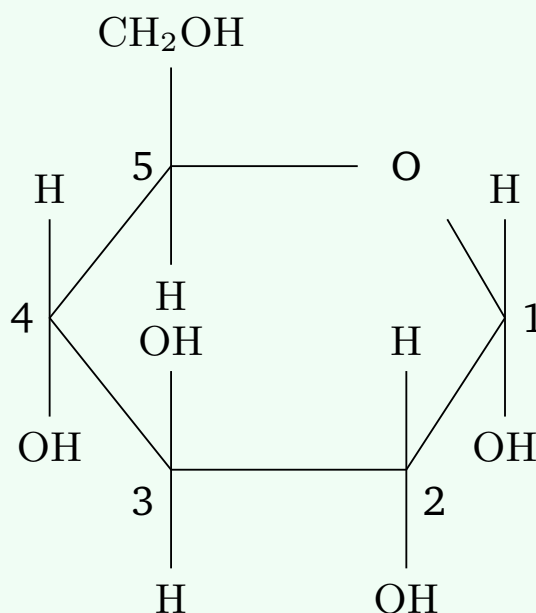
Solution:

Concept:

- D-glucose forms a six-membered cyclic hemiacetal when its C5 hydroxyl group reacts with its C1 aldehyde group.
- In the Haworth projection of α -D-glucose, the C5 CH_2OH group is above the ring and the anomeric C1 hydroxyl group is below it.

Step 1: Construct the pyranose ring The ring contains five carbon atoms, C1 to C5, and one oxygen atom from the C5 hydroxyl group. C6 remains outside the ring as the CH_2OH group attached to C5.

Step 2: Place the substituents For D-glucose, place CH_2OH above C5. The C2 and C4 hydroxyl groups point down and the C3 hydroxyl group points up. For the α anomer, put the C1 hydroxyl group below the ring, opposite the C5 CH_2OH group. Each hydrogen lies opposite its hydroxyl substituent.



Haworth projection of α -D-glucopyranose

Step 3: Conclusion The diagram represents the six-membered ring of α -D(+)-glucose, called α -D-glucopyranose.

Quick Tip to Solve: For alpha-D-glucose, draw C1-OH down and C5- CH_2OH up; the C2, C3, C4 OH pattern is down, up, down.

Section E (15 marks)

31(a). (i) Account for the following:

(I) MnO is basic while Mn_2O_7 is acidic.

(II) Iron has higher enthalpy of atomization than that of copper.

(III) Mn^{3+} is a stronger oxidising agent than Cr^{3+} .

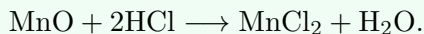
(ii) How do you prepare potassium dichromate from sodium chromate? Write balanced chemical equation for each step. [5 marks]

Solution:

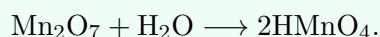
Concept:

- The acid-base character of a metal oxide changes with the oxidation state: lower oxidation states generally give basic ionic oxides, while higher oxidation states give acidic covalent oxides.
- Enthalpy of atomization measures the energy needed to form gaseous atoms from a metal. Stronger metallic bonding gives a higher value.
- An oxidising agent accepts electrons. The relative stability of the original ion and its reduction product helps explain its oxidising strength.
- Acidification converts chromate into dichromate. Potassium dichromate is isolated because it is less soluble than sodium dichromate.

Step 1: (i)(I) Compare the two manganese oxides In MnO , manganese is in the low oxidation state +2. The oxide has predominantly ionic character and is basic: it reacts with acids to form a manganese(II) salt and water. For example,



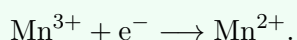
In Mn_2O_7 , manganese has the high oxidation state +7. The oxide is predominantly covalent and is the acid anhydride of permanganic acid:



Thus, increasing the oxidation state from +2 to +7 changes the oxide from basic to acidic.

Step 2: (i)(II) Compare metallic bonding in iron and copper Iron has the atomic configuration $[\text{Ar}]3d^64s^2$, with more unpaired d electrons than copper, whose configuration is $[\text{Ar}]3d^{10}4s^1$. The greater participation of unpaired electrons in metallic bonding makes the interatomic bonding in iron stronger. Therefore, more energy is needed to separate iron into individual gaseous atoms, and iron has a higher enthalpy of atomization than copper.

Step 3: (i)(III) Compare the reduction of the trivalent ions Mn^{3+} has configuration $3d^4$. By accepting an electron it forms Mn^{2+} , with the particularly stable half-filled configuration $3d^5$:

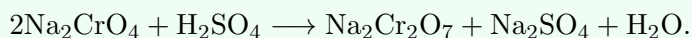


In contrast, Cr^{3+} already has a stable $3d^3$ configuration; its reduction gives Cr^{2+} , with configuration $3d^4$, losing that stability. Hence electron acceptance is much more favourable for Mn^{3+} , making it the

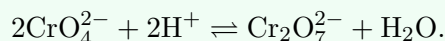
Quick Tip to Solve: For dichromate preparation, remember the order: acidify chromate first, then add KCl and cool to isolate the less soluble potassium salt.

stronger oxidising agent.

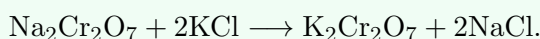
Step 4: (ii) Convert sodium chromate into sodium dichromate Acidify an aqueous solution of sodium chromate with sulphuric acid. Two chromate ions combine in acidic medium to form a dichromate ion. The balanced molecular equation is



The corresponding ionic equilibrium is



Step 5: (ii) Obtain and crystallise potassium dichromate Treat the sodium dichromate solution with potassium chloride:



Concentrate the solution and cool it. Potassium dichromate, being less soluble than sodium dichromate, crystallises out as orange crystals and is separated from the mother liquor.

Step 6: Conclusion MnO is basic because Mn is in the low +2 state, while Mn_2O_7 is acidic because Mn is in the high +7 state. Stronger metallic bonding explains the higher atomization enthalpy of iron, and formation of stable $3d^5$ Mn^{2+} explains the greater oxidising strength of Mn^{3+} . Acidification followed by treatment with KCl and crystallisation yields $\text{K}_2\text{Cr}_2\text{O}_7$.

Quick Tip to Solve: For dichromate preparation, remember the order: acidify chromate first, then add KCl and cool to isolate the less soluble potassium salt.

OR

31(b). Answer the following questions:

(i) Why is chemistry of actinoids more complicated as compared to lanthanoids?

(ii) $E_{\text{M}^{2+}/\text{M}}^\circ$ values are not regular for first row transition elements (3d series). Why?

(iii) Identify the following:

(I) Oxoanion of chromium which is stable in acidic medium.

(II) The lanthanoid element that exhibits +4 oxidation state.

(iv) Write the products obtained on heating KMnO_4 .

(v) Predict which of the following ions will be coloured in aqueous solution:

Cu^+ , Sc^{3+} , Fe^{2+} , Ti^{3+} , Zn^{2+}

[5 marks]

Solution:

Concept:

- Comparable energies of valence orbitals allow electrons from several subshells to participate in bonding, giving a wider range of oxidation states.
- The standard potential $E_{\text{M}^{2+}/\text{M}}^\circ$ reflects the combined effects of atomization, ionization and

Quick Tip to Solve: To predict colour, first remove 4s electrons and count the remaining 3d electrons: d0 and d10 ions are colourless, while the d6 and d1 ions here are coloured.

hydration energies, rather than one atomic property alone.

- Acidic medium favours dichromate, and transition-metal ions with partially filled d subshells can absorb visible light through electronic transitions.

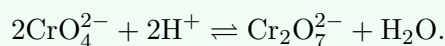
Step 1: (i) Explain the greater complexity of actinoid chemistry The $5f$, $6d$ and $7s$ subshells of actinoids have comparable energies. Consequently, different numbers of electrons from these subshells can participate in bonding, and actinoids exhibit a wider variety of oxidation states than lanthanoids. In lanthanoids the deeply buried $4f$ electrons participate less readily, so the $+3$ oxidation state predominates. The wider range of oxidation states and bonding behaviour makes actinoid chemistry more complicated; their radioactivity adds further difficulty to their study.

Step 2: (ii) Explain the irregular standard electrode potentials Formation of aqueous M^{2+} from solid metal involves atomization, removal of two electrons and hydration of the resulting ion:



The energies of these stages vary differently across the $3d$ series. In particular, ionization energies reflect the extra stability of half-filled and completely filled d configurations, while atomization and hydration enthalpies also vary. Their combined contribution to the overall free-energy change is therefore irregular, producing irregular $E_{M^{2+}/M}^\circ$ values.

Step 3: (iii) Identify the chromium oxoanion and lanthanoid (I) The oxoanion stable in acidic medium is the dichromate ion, $Cr_2O_7^{2-}$. Acidification shifts the chromate-dichromate equilibrium towards dichromate:



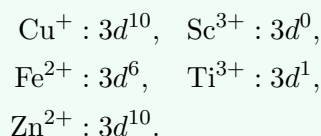
(II) Cerium, Ce, exhibits the $+4$ oxidation state. The ion Ce^{4+} has the stable noble-gas configuration [Xe].

Step 4: (iv) Write the products of heating potassium permanganate On heating, potassium permanganate decomposes into potassium manganate, manganese dioxide and oxygen. The balanced equation is



There are two K atoms, two Mn atoms and eight O atoms on each side, so the stoichiometric coefficients also satisfy atom balance.

Step 5: (v) Determine which aqueous ions are coloured Use the d -electron configurations after removing the outer s electrons:



Fe^{2+} and Ti^{3+} have partially filled d subshells and show colour in aqueous solution owing to electronic transitions between split d levels. The aqueous Fe^{2+} ion is pale green and Ti^{3+} is violet. The d^0 or d^{10} ions Sc^{3+} , Cu^+ and Zn^{2+} have no such $d-d$ transitions and are colourless.

Step 6: Conclusion Actinoids show greater chemical variety because their $5f$, $6d$ and $7s$ energies are close. Irregular atomization, ionization and hydration contributions give irregular electrode potentials.

Quick Tip to Solve: To predict colour, first remove $4s$ electrons and count the remaining $3d$ electrons: d^0 and d^{10} ions are colourless, while the d^6 and d^1 ions here are coloured.

The required species are $\text{Cr}_2\text{O}_7^{2-}$ and cerium; heated KMnO_4 gives K_2MnO_4 , MnO_2 and O_2 . The coloured ions in the printed list are Fe^{2+} and Ti^{3+} .

Quick Tip to Solve: To predict colour, first remove 4s electrons and count the remaining 3d electrons: d0 and d10 ions are colourless, while the d6 and d1 ions here are coloured.

32(a). (i) How will you bring about the following conversions:

(I) Bromobenzene to 1-phenylethanol

(II) Benzene to m-nitroacetophenone

(ii) An organic compound with the molecular formula $\text{C}_8\text{H}_8\text{O}$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation with acidic or alkaline KMnO_4 it gives Benzene-1,2-dicarboxylic acid. Identify the compound and write the products when it undergoes Cannizzaro reaction.

(iii) Arrange the following compounds in increasing order of their acid strength:

$\text{C}_6\text{H}_5\text{COOH}$, $\text{O}_2\text{N} - \text{CH}_2 - \text{COOH}$, $\text{CF}_3 - \text{COOH}$, HCOOH

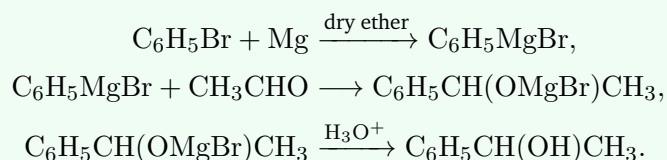
[5 marks]

Solution:

Concept:

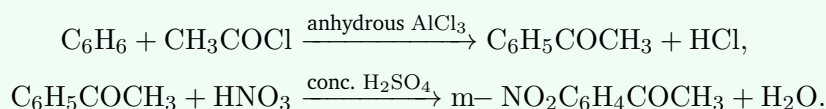
- A Grignard reagent RMgBr , prepared in dry ether, adds to an aldehyde; acidic hydrolysis gives an alcohol. With ethanal it gives a secondary alcohol.
- The acetyl group $-\text{COCH}_3$ deactivates benzene and directs nitration mainly to the meta position. Install it before nitration.
- Aldehydes without an alpha-hydrogen undergo Cannizzaro disproportionation in concentrated alkali. Electron-withdrawing groups stabilise carboxylate ions and increase acid strength.

Step 1: (i)(I) Convert bromobenzene to 1-phenylethanol Treat bromobenzene with magnesium in strictly dry ether to form phenylmagnesium bromide. Add ethanal and then hydrolyse with dilute acid:



The phenyl group adds to the carbonyl carbon of ethanal, producing the required two-carbon side chain. Water must be excluded until hydrolysis because it destroys the Grignard reagent.

Step 2: (i)(II) Convert benzene to m-nitroacetophenone First carry out Friedel-Crafts acylation with acetyl chloride and anhydrous aluminium chloride. Nitrate the resulting acetophenone using concentrated nitric and sulphuric acids:



The acetyl group directs the incoming nitro group to the meta position. Reversing the order is

Quick Tip to Solve: For the benzene conversion, install the meta-directing acetyl group first; for Cannizzaro identification, distinguish a ring methyl group from an alpha-hydrogen.

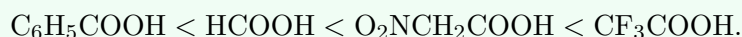
unsuitable because nitrobenzene does not undergo Friedel-Crafts acylation.

Step 3: (ii) Identify the compound and its Cannizzaro products Formation of a 2,4-DNP derivative indicates a carbonyl group; reduction of Tollens' reagent identifies an aldehyde. Cannizzaro reaction indicates absence of an α -hydrogen. Oxidation to benzene-1,2-dicarboxylic acid shows two oxidisable side chains in adjacent positions. Together with C_8H_8O , these facts identify $o-CH_3C_6H_4CHO$, 2-methylbenzaldehyde (o-tolualdehyde). The methyl group is attached to the ring, not to the carbon adjacent to the aldehyde carbonyl, so it does not supply an α -hydrogen.



Concentrated NaOH gives 2-methylbenzyl alcohol and sodium 2-methylbenzoate; acidification of the salt gives 2-methylbenzoic acid. One aldehyde molecule is reduced and the other oxidised.

Step 4: (iii) Compare acid strengths Formic acid is stronger than benzoic acid. The strongly electron-withdrawing nitro group makes nitroacetic acid stronger than formic acid by stabilising its carboxylate through the inductive effect. Three fluorine atoms in trifluoroacetic acid exert an even stronger electron-withdrawing effect. Thus increasing acid strength is



Step 5: Conclusion Use phenylmagnesium bromide followed by ethanal and acidic hydrolysis for 1-phenylethanol; acetylate benzene before nitration for the meta product. The unknown is 2-methylbenzaldehyde, giving 2-methylbenzyl alcohol and sodium 2-methylbenzoate in concentrated NaOH. Acid strength increases as $C_6H_5COOH < HCOOH < O_2NCH_2COOH < CF_3COOH$.

Quick Tip to Solve: For the benzene conversion, install the meta-directing acetyl group first; for Cannizzaro identification, distinguish a ring methyl group from an α -hydrogen.

OR

32(b). (i) Write the products formed when benzaldehyde reacts with the following reagents:

(I) 2,4-Dinitrophenylhydrazine

(II) Acetophenone in the presence of dilute NaOH followed by heating

(ii) Give reasons for the following:

(I) Benzoic acid does not undergo Friedel-Crafts reaction.

(II) Carboxylic acids have higher boiling point than alcohols of comparable molecular mass.

(iii) Write simple chemical test to distinguish between propanal and propanone.

[5 marks]

Solution:

Concept:

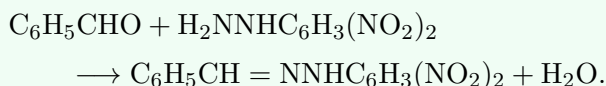
- Aldehydes condense with 2,4-dinitrophenylhydrazine to form a hydrazone, eliminating water. The carbonyl oxygen is replaced by $=NNHC_6H_3(NO_2)_2$.
- A carbonyl compound with α -hydrogens forms an enolate in dilute alkali. It can add to

Quick Tip to Solve: In the crossed aldol product retain acetophenone's carbonyl and place the new double bond between its α carbon and benzaldehyde's former carbonyl carbon.

benzaldehyde; heating dehydrates the aldol addition product to a conjugated enone.

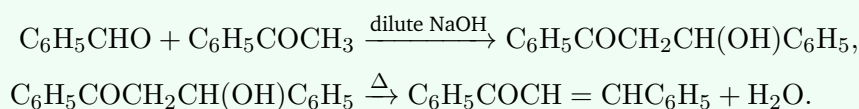
- Carboxyl groups deactivate aromatic rings, and carboxylic acids form hydrogen-bonded dimers. Tollens' reagent oxidises aldehydes while ordinary ketones do not reduce it.

Step 1: (i)(I) Reaction with 2,4-dinitrophenylhydrazine Benzaldehyde forms benzaldehyde 2,4-dinitrophenylhydrazone, an orange or yellow-orange precipitate. The condensation eliminates one molecule of water:



The two nitro substituents retain their 2,4 positions on the reagent's aromatic ring. This reaction detects the carbonyl group but by itself does not distinguish aldehydes from ketones.

Step 2: (i)(II) Reaction with acetophenone Acetophenone has alpha-hydrogens and produces an enolate in dilute NaOH. Benzaldehyde has no alpha-hydrogen and acts as the carbonyl electrophile in the crossed aldol condensation. The initial beta-hydroxy ketone loses water on heating:

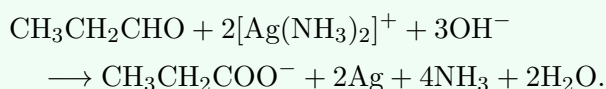


The final product is benzalacetophenone (chalcone), or 1,3-diphenylprop-2-en-1-one, chiefly the trans isomer. The ketone carbonyl remains in the product.

Step 3: (ii)(I) Why benzoic acid fails in Friedel-Crafts reactions The $-\text{COOH}$ group withdraws electron density from the benzene ring by both inductive and resonance effects. The ring is consequently strongly deactivated towards electrophilic substitution and does not undergo Friedel-Crafts alkylation or acylation. The carboxyl group also coordinates with the Lewis-acid catalyst AlCl_3 , further hindering the reaction. Its meta-directing character does not imply that a Friedel-Crafts reaction will occur.

Step 4: (ii)(II) Why carboxylic acids boil at higher temperatures Carboxylic acids associate as cyclic dimers in which two molecules are joined by two intermolecular hydrogen bonds: each acid supplies an O-H donor and a carbonyl-oxygen acceptor. This strong association increases intermolecular attraction and the energy needed to separate molecules during vaporisation. Alcohols also hydrogen-bond, but acids form particularly stable double hydrogen-bonded dimers. Hence acids generally have higher boiling points than alcohols of comparable molecular mass.

Step 5: (iii) Distinguish propanal from propanone Warm separate samples gently with freshly prepared Tollens' reagent. Propanal gives a silver mirror (or a grey silver deposit), whereas propanone does not. Propanal is oxidised to propanoate while silver(I) is reduced to metallic silver:



This contrast identifies the aldehyde and ketone. The 2,4-DNP test would be unsuitable for distinguishing them because both compounds give derivatives.

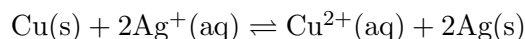
Step 6: Conclusion Benzaldehyde gives its 2,4-dinitrophenylhydrazone with 2,4-DNP and chalcone with acetophenone in dilute NaOH followed by heating. Benzoic acid is too strongly deactivated for Friedel-Crafts reaction; acid dimers explain the higher boiling points. A silver mirror with Tollens'

Quick Tip to Solve: In the crossed aldol product retain acetophenone's carbonyl and place the new double bond between its alpha carbon and benzaldehyde's former carbonyl carbon.

reagent identifies propanal, while propanone gives no silver mirror.

Quick Tip to Solve: In the crossed aldol product retain acetophenone's carbonyl and place the new double bond between its alpha carbon and benzaldehyde's former carbonyl carbon.

33(a). (i) Calculate E_{cell}° for the following reaction which is at equilibrium:



Equilibrium constant (K_c) for the cell is 10^{15} . [Given: $\log 10 = 1$]

(ii) Write anode, cathode and overall reaction of lead storage battery when it is in use.

(iii) How much electricity is required in coulombs for the oxidation of 1 mol of FeO to Fe_2O_3 ? [5 marks]

Solution:

Concept:

- At equilibrium the actual cell potential is zero, but the standard cell potential is related to the equilibrium constant by $E_{\text{cell}}^{\circ} = (0.0591/n) \log K_c$ at 298 K; n is the number of electrons transferred.
- A lead storage battery discharges by oxidation of lead at its anode and reduction of lead dioxide at its cathode, in sulphuric acid electrolyte.
- Faraday's law gives $Q = n_e F$, where n_e is the amount of electrons in moles and $F = 96500 \text{ C mol}^{-1}$.

Step 1: (i) Identify electron transfer and use the equilibrium constant The copper half-reaction is $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$, so one mole of the written reaction transfers $n = 2$ moles of electrons. The Nernst equation is

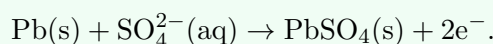
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log Q_r.$$

At equilibrium, $Q_r = K_c$ and $E_{\text{cell}} = 0$. Therefore, for the standard potential asked in the question,

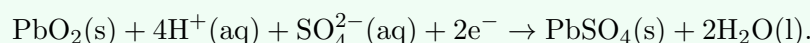
$$E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log(10^{15}) = \frac{0.0591}{2} \times 15 = 0.44325 \text{ V}.$$

A large equilibrium constant is thus consistent with a positive standard potential; the zero equilibrium potential must not be substituted as the standard potential.

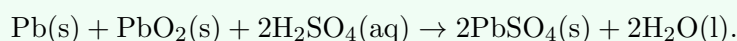
Step 2: (ii) Write the discharge reactions of the lead storage battery At the anode, lead is oxidised and insoluble lead sulphate forms:



At the cathode, lead dioxide is reduced:



Adding the half-reactions cancels the two electrons. Expressing the acid as sulphuric acid gives the overall reaction:



Both plates acquire lead sulphate during use, and sulphuric acid is consumed. The reverse reactions

Quick Tip to Solve: Distinguish equilibrium cell potential from standard potential; for FeO count electrons per iron atom, not the two iron atoms in the product formula.

describe charging and are not the reactions requested here.

Step 3: (iii) Determine the amount of electricity for oxidising FeO Oxygen has oxidation number -2 , so iron is $+2$ in FeO and $+3$ in Fe_2O_3 . Each iron atom loses one electron. One mole of FeO contains one mole of iron atoms; hence its oxidation removes one mole of electrons, even though the product has two iron atoms per formula unit.

$$Q = n_e F = 1 \text{ mol} \times 96500 \text{ C mol}^{-1} = 96500 \text{ C}.$$

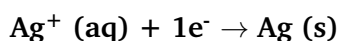
Step 4: Conclusion (i) $E^\circ_{\text{cell}} \approx +0.443 \text{ V}$. (ii) During discharge, Pb is oxidised at the anode and PbO_2 is reduced at the cathode; overall, $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$. (iii) The electricity required is $9.65 \times 10^4 \text{ C}$.

Quick Tip to Solve: Distinguish equilibrium cell potential from standard potential; for FeO count electrons per iron atom, not the two iron atoms in the product formula.

OR

33(b). (i) Conductivity of 0.0024 M acetic acid is $7.2 \times 10^{-5} \text{ S cm}^{-1}$. If Λ°_m for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, then calculate the degree of dissociation (α) of acetic acid.

(ii) Calculate the cell potential for the following half cell reaction at 25°C :



Given that: $[\text{Ag}^+] = 0.01 \text{ M}$ and $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$ [$\log 10 = 1$]

(iii) Write the name of the electrolyte used in:

(I) Dry cell

(II) Fuel cell ($\text{H}_2\text{-O}_2$)

[5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} . Its unit is $\text{S cm}^2 \text{ mol}^{-1}$.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda^\circ_m$, where Λ°_m is the limiting molar conductivity at infinite dilution.
- At 25°C , the Nernst equation is $E = E^\circ - (0.0591/n) \log Q_r$, with n the electrons transferred; the activity of a pure solid is one.

Step 1: (i) Calculate molar conductivity and degree of dissociation Given $\kappa = 7.2 \times 10^{-5} \text{ S cm}^{-1}$ and $c = 0.0024 \text{ mol L}^{-1}$, the factor 1000 converts the molar concentration to the volume convention used with centimetres:

$$\Lambda_m = \frac{1000 \times 7.2 \times 10^{-5}}{0.0024} = 30 \text{ S cm}^2 \text{ mol}^{-1}.$$

Acetic acid is a weak electrolyte. At this concentration only a fraction of its molecules dissociate into

Quick Tip to Solve: Use the factor 1000 in molar conductivity, and for silver reduction use the plus sign before log of silver-ion concentration.

ions, so its molar conductivity is much less than its limiting value. Using $\Lambda_m^\circ = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$,

$$\alpha = \frac{30}{390.5} = 0.07682, \quad 100\alpha = 7.682\%.$$

The degree of dissociation is dimensionless; its percentage form is obtained by multiplying by 100.

Step 2: (ii) Apply the Nernst equation to the silver half-cell The reduction $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ transfers one electron, so $n = 1$. Since silver is a pure solid, its activity is unity and the reaction quotient is $Q_r = 1/[\text{Ag}^+]$, taking the stated dilute concentration as the ion activity relative to the standard state.

$$E = E^\circ - 0.0591 \log \frac{1}{[\text{Ag}^+]} = E^\circ + 0.0591 \log [\text{Ag}^+].$$

Substitution of $[\text{Ag}^+] = 0.01 = 10^{-2}$ and $E^\circ = +0.80 \text{ V}$ gives

$$E = 0.80 + 0.0591(-2) = 0.80 - 0.1182 = +0.6818 \text{ V}.$$

Lower silver-ion concentration lowers this reduction potential below its standard value, providing a check on the sign.

Step 3: (iii) State the electrolytes in the two cells (I) A dry cell uses a moist paste of ammonium chloride, NH_4Cl , and zinc chloride, ZnCl_2 , as its electrolyte. The paste permits ionic conduction while avoiding a freely flowing liquid.

(II) The hydrogen-oxygen fuel cell uses concentrated aqueous potassium hydroxide, KOH , as the alkaline electrolyte. Hydrogen and oxygen are the reactant gases, not the electrolyte; the electrolyte supports transport of hydroxide ions between the electrodes.

Step 4: Conclusion (i) $\alpha = 0.0768$, corresponding to about 7.68% dissociation. (ii) The silver half-cell potential is +0.682 V. (iii) The dry-cell electrolyte is a moist NH_4Cl - ZnCl_2 paste; the hydrogen-oxygen fuel-cell electrolyte is concentrated aqueous KOH .

Quick Tip to Solve: Use the factor 1000 in molar conductivity, and for silver reduction use the plus sign before log of silver-ion concentration.