CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-2-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

(ii) This question paper is divided into **five** sections – **Section A, B, C, D and E**.

(iii) **Section A** – questions number **1 to 16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – questions number **17 to 21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – questions number **22 to 28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – questions number **29 and 30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – questions number **31 to 33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculators is not allowed.

Section A (16 marks)

Questions no. ***1 to 16*** *are Multiple Choice type Questions, carrying* ***1*** *mark each.*

1. The correct order for the increasing oxidizing power in 3d series of transition elements is : [1 mark]

(A) $MnO_4^- < Cr_2O_7^{2-} < VO_2^+$

(B) $Cr_2O_7^{2-} < VO_2^+ < MnO_4^-$

(C) $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

(D) $VO_2^+ < MnO_4^- < Cr_2O_7^-$

Correct Answer: (C) $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

Solution:

Concept:

- An oxidising agent accepts electrons and is itself reduced. A larger standard reduction potential, E°, indicates stronger oxidising power under the same standard conditions.
- For the familiar acidic-medium reductions, the order of reduction potentials is $VO_2^+/VO^{2+} < Cr_2O_7^{2-}/Cr^{3+} < MnO_4^-/Mn^{2+}$.

Step 1: Compare electron-accepting tendencies In acidic medium, the standard reduction potentials for the above vanadium, chromium and manganese couples are approximately $1.00\,V$, $1.33\,V$ and $1.51\,V$, respectively. Thus the vanadium species is the weakest oxidising agent among the three, while permanganate is the strongest.

Step 2: Check the printed orders Increasing oxidising power therefore requires vanadium first, dichromate second and permanganate last. Option (A) reverses this order; (B) places dichromate below vanadium; and (D) places permanganate below the chromium species. None gives the required sequence. Option (C) follows the increasing reduction potentials.

Step 3: Conclusion $\boxed{VO_2^+ < Cr_2O_7^{2-} < MnO_4^-}$. Hence, the correct option is (C).

Quick Tip to Solve: For these acidic-medium oxoanions, remember V < Cr < Mn in oxidising strength; compare reduction potentials, not oxidation states alone.

2. The type of isomerism shown by the complex $[CoCl_2(en)_2]^+$ is : [1 mark]

(A) Linkage isomerism

(B) Geometrical isomerism

(C) Coordination isomerism

(D) Ionization isomerism

Correct Answer: (B) Geometrical isomerism

Solution:

Concept:

- The ligand en is ethane-1,2-diamine, a bidentate ligand with two nitrogen donor atoms.

Quick Tip to Solve: For an octahedral complex with two identical monodentate ligands, check whether those ligands can be adjacent (cis) or opposite (trans).

- Two en ligands and two chloride ligands give coordination number six, so $[CoCl_2(en)_2]^+$ has an octahedral arrangement.

Step 1: Identify the possible spatial arrangements The two chloride ligands can occupy neighbouring positions in the octahedron, giving the cis isomer, or opposite positions, giving the trans isomer. These arrangements have the same composition and connectivity but differ in the relative positions of ligands.

Step 2: Distinguish the other forms of isomerism Linkage isomerism requires an ambidentate ligand capable of coordinating through different donor atoms; chloride and en do not provide that alternative here. Coordination isomerism involves exchange between complex cations and complex anions, while ionisation isomerism involves exchange of a coordinated ligand and a counter-ion. The cis/trans difference here is geometrical isomerism.

Step 3: Conclusion The complex exhibits cis-trans geometrical isomerism. Hence, the correct option is (B).

Quick Tip to Solve: For an octahedral complex with two identical monodentate ligands, check whether those ligands can be adjacent (cis) or opposite (trans).

3. Which one of the following hybrid states is associated with low spin complex ? [1 mark]

(A) sp^3d

(B) sp^3

(C) sp^3d^2

(D) d^2sp^3

Correct Answer: (D) d^2sp^3

Solution:

Concept:

- In an octahedral complex, strong-field ligands can cause pairing of metal d-electrons when the crystal-field splitting energy exceeds the pairing energy.
- In valence-bond terminology, an inner-orbital octahedral complex uses two $(n-1)d$, one ns and three np orbitals, giving d^2sp^3 hybridisation.

Step 1: Connect low spin with inner orbitals Pairing of electrons in the lower-energy metal orbitals can leave two inner d-orbitals available for hybridisation. Combining these with one s-orbital and three p-orbitals produces six equivalent hybrid orbitals. This is the usual inner-orbital, low-spin octahedral description in the CBSE valence-bond model.

Step 2: Check the alternatives sp^3d uses five orbitals and is associated with five-coordinate geometry; sp^3 uses four and gives tetrahedral geometry. sp^3d^2 uses the outer d-orbitals and describes the outer-orbital octahedral alternative generally associated with high spin. The listed hybrid state associated with low spin is therefore d^2sp^3.

Step 3: Conclusion $\boxed{d^2sp^3}$ is associated with a low-spin inner-orbital octahedral complex. Hence, the correct option is (D).

Quick Tip to Solve: For the usual octahedral low-spin question, locate the option with two inner d orbitals: d squared comes before sp cubed.

4. Butanenitrile may be prepared by heating : [1 mark]

(A) propyl chloride with KCN

(B) butyl chloride with KCN

(C) propyl alcohol with KCN

(D) butyl alcohol with KCN

Correct Answer: (A) propyl chloride with KCN

Solution:

Concept:

- With ionic KCN, the cyanide ion attacks an alkyl halide mainly through its carbon end, replacing the halogen and forming $\mathrm{R-C\equiv N}$.
- The nitrile carbon counts as part of the main carbon chain, so cyanide substitution increases the carbon count of the starting alkyl group by one.

Step 1: Count the carbons needed Butanenitrile has four carbon atoms: $\mathrm{CH_3CH_2CH_2C\equiv N}$. Since KCN supplies one carbon atom, the alkyl halide must supply three. Propyl chloride, $\mathrm{CH_3CH_2CH_2Cl}$, is the suitable starting compound.

Step 2: Write the substitution and test the options On heating with alcoholic KCN, the reaction is

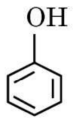
$$\mathrm{CH_3CH_2CH_2Cl + KCN \longrightarrow CH_3CH_2CH_2CN + KCl.}$$

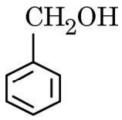
Butyl chloride would instead give pentanenitrile, with five carbons. Propyl alcohol and butyl alcohol do not undergo this direct substitution merely on heating with KCN because the hydroxyl group is not a suitable leaving group under these conditions.

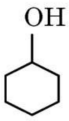
Step 3: Conclusion Butanenitrile is prepared by heating propyl chloride with KCN. Hence, the correct option is (A).

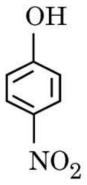
Quick Tip to Solve: Count the nitrile carbon in the product: a four-carbon nitrile requires a three-carbon alkyl halide when using KCN.

5. Which of the following is most acidic ? [1 mark]

(A) 

(B) 

(C) 

(D) 

(A) Phenol (C_6H_5OH)

(B) Benzyl alcohol ($C_6H_5CH_2OH$)

(C) Cyclohexanol ($C_6H_{11}OH$)

(D) p-Nitrophenol (p– $NO_2C_6H_4OH$)

Correct Answer: (D) p-Nitrophenol (p– $NO_2C_6H_4OH$)

Solution:

Concept:

- Acidity increases when the conjugate base formed by loss of H^+ is more stable.
- Phenoxide ions are resonance-stabilised. A para nitro group withdraws electrons by both inductive and resonance effects, further stabilising the conjugate base.

Step 1: Compare the two phenolic options Both phenol in (A) and para-nitrophenol in (D) form phenoxide-type ions. In para-nitrophenol, the electron-withdrawing NO_2 group permits additional delocalisation of negative charge through the aromatic ring toward the nitro group. Its conjugate base is more stabilised than unsubstituted phenoxide, making para-nitrophenol more acidic than phenol.

Step 2: Compare the alcohol options Option (B) is benzyl alcohol and option (C) is cyclohexanol. Their hydroxyl groups are bonded to saturated carbon atoms. The negative charge on the oxygen of their alkoxide conjugate bases does not receive the phenoxide-type resonance stabilisation; in benzyl alcohol the intervening CH_2 group interrupts conjugation with the ring. Both are much weaker acids than the phenolic options.

Step 3: Conclusion Para-nitrophenol is the most acidic compound shown. Hence, the correct option is (D).

Quick Tip to Solve: First locate OH directly on the aromatic ring, then look for a para electron-withdrawing nitro group that stabilises the phenoxide ion.

6. $(CH_3)_2CH-O-CH_3$ reacts with HI to give : [1 mark]

(A) $(CH_3)_2CH-OH + CH_3-OH$

(B) $(CH_3)_2CH-OH + CH_3-I$

(C) $(CH_3)_2CH-I + CH_3-OH$

(D) $(CH_3)_2CH-I + CH_3-I$

Correct Answer: (B) $(CH_3)_2CH-OH + CH_3-I$

Solution:

Concept:

- HI protonates the ether oxygen, making the carbon-oxygen bond susceptible to cleavage by iodide.
- For a methyl-secondary alkyl ether, iodide attacks the less hindered methyl carbon by the S_N2 mechanism, producing methyl iodide and the secondary alcohol.

Step 1: Identify the preferred site of attack The ether contains a methyl group and an isopropyl group on opposite sides of oxygen. Following oxygen protonation, the methyl carbon offers the least steric hindrance to backside attack by I^-. The methyl-oxygen bond therefore breaks preferentially, while oxygen remains attached to the isopropyl group.

Step 2: Write the primary cleavage products The reaction is

$$(CH_3)_2CH - O - CH_3 + HI \longrightarrow (CH_3)_2CH - OH + CH_3I.$$

This gives option (B). Option (A) gives two alcohols and omits iodide substitution. Option (C) requires attack at the more hindered secondary carbon. Option (D) represents further conversion of the alcohol with additional HI, rather than the initial ether-cleavage products asked for here.

Step 3: Conclusion The products are $(CH_3)_2CHOH$ and CH_3I. Hence, the correct option is (B).

Quick Tip to Solve: In an ether containing a methyl group, place iodine on that methyl group and retain oxygen as OH on the other group for the initial HI cleavage.

7. A compound (X) with the molecular formula C_3H_8O can be oxidized by strong oxidizing agents to another compound (Y) whose molecular formula is $C_3H_6O_2$. The compound (X) is : [1 mark]

(A) $CH_3-CH_2-O-CH_3$

(B) $CH_3-CH(OH)-CH_3$

(C) $CH_3-CH_2-CH_2-OH$

(D) None of the above

Correct Answer: (C) $CH_3-CH_2-CH_2-OH$

Solution:

Concept:

- A primary alcohol RCH_2OH is oxidised first to an aldehyde and then, with a strong oxidising agent, to a carboxylic acid.
- A secondary alcohol forms a ketone; an ether does not undergo this primary-alcohol oxidation.

Quick Tip to Solve: Look for a terminal $-CH_2OH$ group when oxidation gives a carboxylic acid with the same carbon count.

Step 1: Identify the required functional-group change The product $C_3H_6O_2$ is consistent with propanoic acid. Its formation while retaining all three carbon atoms requires the primary alcohol propan-1-ol, $CH_3CH_2CH_2OH$. The oxidation is

$$CH_3CH_2CH_2OH + 2[O] \longrightarrow CH_3CH_2COOH + H_2O.$$

Step 2: Check the other options Option (A) is methoxyethane, an ether. Option (B) is propan-2-ol, a secondary alcohol: its normal oxidation product is propanone, C_3H_6O, which has only one oxygen atom. Option (C) has a terminal $-CH_2OH$ group and gives the required acid; thus option (D) is unnecessary.

Step 3: Conclusion Compound (X) is $CH_3CH_2CH_2OH$, propan-1-ol. Hence, the correct option is (C).

Quick Tip to Solve: Look for a terminal $-CH_2OH$ group when oxidation gives a carboxylic acid with the same carbon count.

8. On mixing 10 mL of acetone with 50 mL of chloroform, the total volume of the solution will be : [1 mark]

(A) $<$ 60 mL

(B) $>$ 60 mL

(C) = 60 mL

(D) = 100 mL

Correct Answer: (A) $<$ 60 mL

Solution:

Concept:

- Acetone and chloroform show stronger unlike-molecule attractions than their respective like-molecule attractions.
- Stronger interactions can produce contraction on mixing, so the final volume is less than the sum of the separate volumes.

Step 1: Identify the intermolecular attraction The carbonyl oxygen of acetone accepts a hydrogen bond from the hydrogen of chloroform, which is made relatively positive by its three chlorine atoms. These acetone–chloroform attractions bring the molecules closer together and account for negative deviation from Raoultś law.

Step 2: Compare the final volume with the additive value The separate volumes add to $10+50 = 60$ mL. Because mixing causes contraction, $\Delta V_{\text{mix}} < 0$, so

$$V_{\text{solution}} = 60\,\text{mL} + \Delta V_{\text{mix}} < 60\,\text{mL}.$$

An increase above 60 mL would indicate expansion, exact equality would assume additive volumes, and 100 mL is inconsistent with this contraction.

Step 3: Conclusion The total volume is less than 60 mL. Hence, the correct option is (A).

Quick Tip to Solve: For acetone and chloroform, recall hydrogen bonding between unlike molecules: stronger attraction implies contraction.

9. The unit of cell constant is : [1 mark]

(A) ohm cm^{-1}

(B) ohm^{-1}

(C) cm^{-1}

(D) $ohm^{-1}\ cm^2\ mol^{-1}$

Correct Answer: (C) cm^{-1}

Solution:

Concept:

- The cell constant is l/A, where l is the separation of the electrodes and A is their effective cross-sectional area.
- Conductivity and conductance are related by $\kappa = G(l/A)$.

Step 1: Determine the dimensions Using centimetres for electrode separation and square centimetres for electrode area gives

$$\left[\frac{l}{A}\right] = \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}.$$

Thus the cell constant has inverse-length units, independent of any electrical resistance unit.

Step 2: Distinguish the remaining units Option (A), ohm cm^{-1}, contains a resistance factor and is not an inverse length alone. Option (B), ohm^{-1}, is the unit of conductance. Option (D), $ohm^{-1}\ cm^2\ mol^{-1}$, is the unit of molar conductivity. Only option (C) matches the geometry ratio l/A.

Step 3: Conclusion The unit of cell constant is cm^{-1}. Hence, the correct option is (C).

Quick Tip to Solve: Derive the cell-constant unit directly from length divided by area; no ohm factor should appear.

10. For a certain reaction R $\rightarrow$ products, a plot of log[R] vs. time gives a straight line with a slope of $-1.25\ s^{-1}$. The order of the reaction is : [1 mark]

(A) One

(B) Zero

(C) Two

(D) Fractional

Correct Answer: (A) One

Solution:

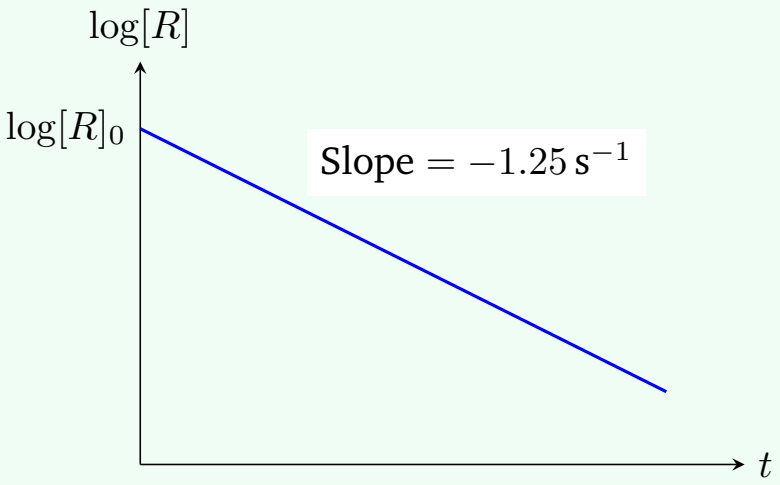
Concept:

- For a first-order reaction, $\log[R] = \log[R]_0 - kt/2.303$, where $[R]_0$ is the initial concentration and k is the rate constant.
- A straight line of $\log[R]$ against time has slope $-k/2.303$.

Step 1: Match the straight-line equation Comparing the given plot with $y = c + mt$, take $y = \log[R]$, $c = \log[R]_0$, and $m = -k/2.303$. Its negative slope therefore matches the integrated first-order law.

Quick Tip to Solve: Identify the ordinate first: $[R]$, $\log[R]$, and $1/[R]$ give straight lines for zero, first, and second order respectively.

The stated value gives $k = 2.303(1.25) = 2.87875\,\text{s}^{-1}$, which is positive as required.



Schematic first-order logarithmic concentration plot

Step 2: Check the alternatives A zero-order reaction gives a linear plot of $[R]$ against time, while a second-order reaction gives a linear plot of $1/[R]$ against time. Neither gives the stated logarithmic straight line. A fractional order does not satisfy this first-order integrated relation, so the supplied graph identifies order one.

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

Quick Tip to Solve: Identify the ordinate first: $[R]$, $\log[R]$, and $1/[R]$ give straight lines for zero, first, and second order respectively.

11. For a zero order reaction A → products, $t_{1/2}$ is :
where $[A]_0$ = initial concentration of the reactant, k = rate constant. [1 mark]

(A) $\dfrac{[A]_0}{k}$

(B) $\dfrac{2.303\log 2}{k}$

(C) $\dfrac{1}{k[A]_0}$

(D) $\dfrac{[A]_0}{2k}$

Correct Answer: (D) $\dfrac{[A]_0}{2k}$

Solution:

Concept:

- For a zero-order reaction, the integrated law is $[A] = [A]_0 - kt$, where $[A]_0$ is the initial reactant concentration and k is the rate constant.
- At the half-life $t_{1/2}$, half the initial reactant remains: $[A] = [A]_0/2$.

Quick Tip to Solve: For zero order, put the remaining concentration equal to half the initial concentration in $[A] = [A]_0 - kt$.

Step 1: Substitute the half-life condition Insert $[A] = [A]_0/2$ into the zero-order integrated law:

$$\frac{[A]_0}{2} = [A]_0 - kt_{1/2}.$$

Rearranging gives $kt_{1/2} = [A]_0/2$. Thus the time to consume half the reactant depends directly on its initial concentration.

Step 2: Check each printed expression Option (A), $[A]_0/k$, is the time for complete depletion in the ideal zero-order law, not half depletion. Option (B), $2.303 \log 2/k$, is the first-order half-life expression. Option (C), $1/(k[A]_0)$, is the second-order half-life expression. Option (D) contains the required factor of two in the denominator.

Step 3: Conclusion For the zero-order reaction, $t_{1/2} = \dfrac{[A]_0}{2k}$. Hence, the correct option is (D).

Quick Tip to Solve: For zero order, put the remaining concentration equal to half the initial concentration in $[A] = [A]_0 - kt$.

12. The relative lowering of vapour pressure of an aqueous solution containing non-volatile solute is 0.0225. The mole fraction of the non-volatile solute is : [1 mark]

(A) 0.80

(B) 0.725

(C) 0.15

(D) 0.0225

Correct Answer: (D) 0.0225

Solution:

Concept:

- Raoult's law for a solution with a non-volatile solute is $p_1 = x_1 p_1^\circ$, where p_1 is the solution's vapour pressure and p_1° is that of the pure solvent.
- The solvent and solute mole fractions satisfy $x_1 + x_2 = 1$; relative lowering is $(p_1^\circ - p_1)/p_1^\circ = x_2$.

Step 1: Express the lowering using Raoult's law Only the solvent contributes to the vapour pressure because the solute is non-volatile. Dividing Raoult's law by the pure-solvent pressure gives $p_1/p_1^\circ = x_1$. Therefore,

$$\frac{p_1^\circ - p_1}{p_1^\circ} = 1 - x_1 = x_2.$$

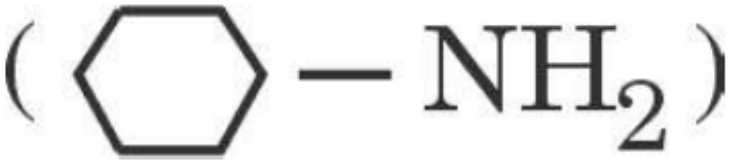
Step 2: Substitute the given relative lowering The stated relative lowering is 0.0225, so the solute mole fraction equals this number. No pressure unit or percentage conversion is needed. The solvent mole fraction would instead be $1 - 0.0225 = 0.9775$. Options (A), (B) and (C) do not equal the measured relative lowering and hence fail Raoult's-law relation.

Step 3: Conclusion The mole fraction of the non-volatile solute is $\boxed{x_2 = 0.0225}$. Hence, the correct option is (D).

Quick Tip to Solve: For a non-volatile solute, read its mole fraction directly from the relative lowering of vapour pressure; do not take the complement.

13. Assertion (A): Aniline is a weaker base than cyclohexylamine.

Reason (R): Aniline is resonance stabilized. [1 mark]



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

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

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

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

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

Solution:

Concept:

- An amine acts as a base by donating the nitrogen lone pair to a proton. Greater availability of this lone pair generally increases basicity.
- In aniline the lone pair is delocalised into the aromatic ring by resonance; in cyclohexylamine it remains localised on nitrogen.

Step 1: Evaluate the assertion Aniline accepts a proton less readily than cyclohexylamine because its nitrogen lone pair is less available. The cyclohexyl group also supplies electron density through its positive inductive effect. Thus aniline is the weaker base and Assertion (A) is true.

Step 2: Evaluate the reason The nitrogen lone pair in aniline overlaps with the benzene ring's delocalised electron system. Resonance contributors spread this electron density over the ring and stabilise the unprotonated amine. Reason (R), that aniline is resonance stabilised, is therefore true.

Step 3: Test the explanatory link Resonance makes the lone pair less available for protonation and accounts directly for aniline's lower basicity. Cyclohexylamine has no aromatic ring into which the lone pair can delocalise. Thus (B) incorrectly denies the explanation, while (C) and (D) incorrectly declare one of the true statements false.

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

Quick Tip to Solve: Compare where the nitrogen lone pair can go: delocalisation into benzene lowers basicity, while a saturated cyclohexyl ring leaves it available.

14. Assertion (A): Vitamin C cannot be stored in our body.

Reason (R): Vitamin C is water soluble and readily excreted in urine. [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:

- Vitamins are classified as water soluble or fat soluble. Water-soluble vitamins generally require regular dietary replenishment.
- Vitamin C, or ascorbic acid, is water soluble; excess vitamin C is readily removed through urine rather than stored as a reserve.

Step 1: Evaluate the assertion Vitamin C does not accumulate as a substantial stored reserve in the body in the way fat-soluble vitamins do. Consequently, a regular supply in food is needed. In the vitamin-storage classification used here, Assertion (A) is true.

Step 2: Evaluate the reason Vitamin C dissolves in water, and excess amounts are readily excreted in urine. This is the characteristic behaviour of this water-soluble vitamin. Therefore Reason (R) is true.

Step 3: Connect excretion with storage Ready loss of excess vitamin C through urine prevents it from being retained as a storage reserve. The reason therefore explains the assertion directly. Option (B) wrongly denies this link; (C) wrongly calls the reason false; and (D) wrongly calls the assertion false.

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

Quick Tip to Solve: For vitamin C, link water solubility to urinary excretion and the need for a regular dietary supply when judging the explanation.

15. Assertion (A): Ammonolysis of alkyl halides involves reaction between alkyl halide and ethanolic solution of ammonia.

Reason (R): Ammonolysis of alkyl halides mainly produces secondary amines. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Ammonolysis is cleavage of the carbon-halogen bond by ammonia, which acts as a nucleophile. Alkyl halides react with ethanolic ammonia to form amines.
- A primary amine is the first amine formed. Further alkylation can give secondary and tertiary amines and a quaternary ammonium salt; excess ammonia favours the primary amine.

Step 1: Evaluate the assertion In ammonolysis, an alkyl halide reacts with ammonia dissolved in ethanol. Ammonia attacks the alkyl carbon and replaces the halogen, leading initially to a primary amine after deprotonation. The overall equation can be written as

$$\mathrm{R{-}X} + 2\,\mathrm{NH_3} \longrightarrow \mathrm{R{-}NH_2} + \mathrm{NH_4X}.$$

Here R denotes an alkyl group and X a halogen. Assertion (A) is true.

Step 2: Evaluate the reason The primary amine formed can itself react with more alkyl halide, so ammonolysis may produce a mixture. Secondary amines are not its characteristic main product. Using excess ammonia suppresses further alkylation and favours primary amines. Hence Reason (R) is false.

Step 3: Apply the assertion-reason code A false reason cannot explain a true assertion. Options (A) and (B) incorrectly require a true reason, while (D) incorrectly requires a false assertion. The combination true assertion and false reason matches the remaining code.

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

Quick Tip to Solve: In ammonolysis, identify the first product as a primary amine and remember that excess ammonia favours it over further alkylation products.

16. Assertion (A): Aniline does not undergo Friedel-Crafts reaction.

Reason (R): Friedel-Crafts reaction is a nucleophilic substitution reaction. [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:

- Friedel-Crafts alkylation and acylation are electrophilic aromatic substitution reactions, usually catalysed by the Lewis acid $AlCl_3$.
- Aniline's nitrogen lone pair interacts strongly with $AlCl_3$, forming a Lewis acid-base complex or salt that deactivates the ring toward the usual Friedel-Crafts reaction.

Step 1: Evaluate the assertion Aniline does not undergo the normal Friedel-Crafts reaction because its amino group reacts with the Lewis acid catalyst $AlCl_3$. The resulting complex or salt withdraws electron density and strongly deactivates the ring. Thus Assertion (A) is true, even though free aniline is otherwise reactive toward many electrophiles.

Step 2: Evaluate the reason In Friedel-Crafts reactions an electrophile attacks the aromatic ring and replaces a ring hydrogen. This is electrophilic aromatic substitution, not nucleophilic substitution. Therefore Reason (R) is false.

Step 3: Test whether the reason explains the assertion The stated reaction classification is false and cannot explain the assertion. The actual cause is reaction of the amino group with the Lewis acid catalyst. Options (A) and (B) wrongly treat the reason as true, and (D) wrongly treats the assertion as false.

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

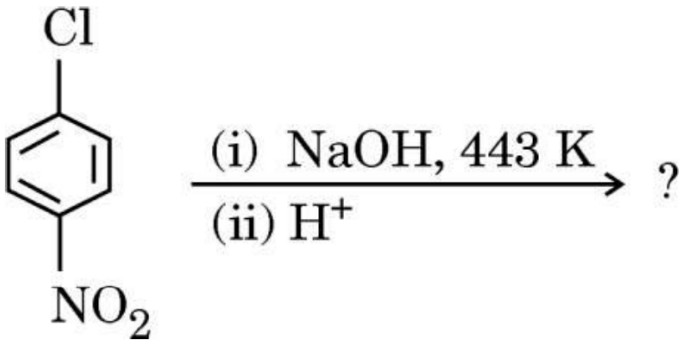
Quick Tip to Solve: For aniline and Friedel-Crafts reactions, check amino-group binding to the Lewis acid catalyst; the reaction itself is electrophilic substitution.

Section B (10 marks)

17. (a) Which one of the following pairs of substances undergoes S_N1 reaction faster and why?

$CH_3-CH_2-CH_2-Cl$ **OR** $CH_2=CH-CH_2-Cl$

(b) Write the major product in the following: [2 marks]



Solution:

Concept:

- The slow step of an S_N1 reaction is carbon-halogen bond ionisation to give a carbocation. Greater carbocation stability favours faster ionisation.
- A nitro group para to a halogen activates an aryl halide toward nucleophilic aromatic substitution by stabilising the negatively charged addition intermediate.

Step 1: Compare the carbocations in part (a) Propyl chloride would generate the unstable primary propyl carbocation $CH_3-CH_2-CH_2^+$. Allyl chloride instead generates an allylic carbocation whose positive charge is delocalised over two carbon atoms:

$$CH_2=CH-CH_2^+ \longleftrightarrow CH_2^+-CH=CH_2.$$

The double bond stabilises the allylic carbocation by resonance. Therefore the energy needed for ionisation is lower for allyl chloride, making $CH_2=CH-CH_2-Cl$ react faster by the S_N1 mechanism than $CH_3-CH_2-CH_2-Cl$.

Step 2: Identify the substitution product in part (b) The starting aryl halide is para-chloronitrobenzene. At $443\,K$, hydroxide replaces chlorine because the para nitro group stabilises the anionic intermediate. The product under alkaline conditions is sodium para-nitrophenoxide. The subsequent acid treatment protonates its phenoxide oxygen:

$$\text{p-}NO_2-C_6H_4-ONa + H^+ \longrightarrow \text{p-}NO_2-C_6H_4-OH + Na^+.$$

Thus chlorine is replaced by hydroxyl, while the nitro group remains at the para position. The acid-workup product is the neutral phenol rather than its sodium salt.

Step 3: Conclusion (a) Allyl chloride, $CH_2=CH-CH_2-Cl$, reacts faster because its carbocation is resonance stabilised. (b) The major final product is $\boxed{\text{4-nitrophenol (para-nitrophenol)}}$, $\text{p-}NO_2-C_6H_4-OH$.

Quick Tip to Solve: For S_N1, compare carbocation stability first; for the nitroaryl chloride, replace chlorine by hydroxyl and retain the para nitro group after acid workup.

18(a). What is lanthanoid contraction ? Actinoid contraction is greater from element to element than lanthanoid contraction. Why ? [2 marks]

Solution:

Concept:

- Across an f-block series, increasing nuclear charge attracts the electron cloud more strongly, while the added f electrons shield this charge poorly.
- Lanthanoids involve filling of the $4f$ subshell; actinoids involve filling of the $5f$ subshell. Shielding means reduction of nuclear attraction by intervening electrons.

Step 1: Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in the atomic and ionic radii of lanthanoids as atomic number increases from lanthanum to lutetium. In a comparison of ions, the same oxidation state, usually Ln^{3+}, is considered. Each successive element has a higher nuclear charge, but the extra $4f$ electron does not adequately screen that increase; the electron cloud is therefore pulled inward.

Step 2: Explain the greater actinoid contraction In the actinoid series, successive electrons enter the $5f$ subshell. The $5f$ electrons shield the increasing nuclear charge even less effectively than the $4f$ electrons of lanthanoids. Consequently, the effective nuclear attraction increases more strongly from one actinoid to the next, leading to a greater element-to-element contraction.

Step 3: Conclusion Lanthanoid contraction is the progressive decrease in lanthanoid atomic and ionic radii with increasing atomic number. Actinoid contraction is greater because $5f$ electrons have poorer shielding effectiveness than $4f$ electrons.

Quick Tip to Solve: Compare the shielding of the subshell being filled: poorer f-electron shielding produces a greater contraction.

OR

18(b). Why do transition metals have high enthalpy of atomization ? Which element of 3d-series has lowest enthalpy of atomization? [2 marks]

Solution:

Concept:

- Enthalpy of atomization is the enthalpy required to convert one mole of an element into separate gaseous atoms; stronger metallic bonding requires more energy.
- Transition-metal bonding involves valence s and d electrons. Several unpaired d electrons can contribute to strong bonding between metal atoms.

Step 1: Explain the high enthalpy of atomization Transition metals generally contain several unpaired electrons in their $(n-1)d$ orbitals, along with outer ns electrons. These electrons participate in strong interatomic metallic bonding. Considerable energy is needed to break this bonding and separate the solid metal into individual gaseous atoms, so transition metals have high enthalpies of atomization. The trend reflects bond strength, rather than merely the atomic mass of the metal.

Quick Tip to Solve: For the lowest atomization enthalpy in the 3d series, look for the filled 3d subshell: zinc is 3d10 4s2.

Step 2: Identify the lowest value in the 3d series Zinc has the electronic configuration $[\mathrm{Ar}]\,3d^{10}4s^2$. Its $3d$ subshell is completely filled, so there are no unpaired d electrons to contribute to the strong d-electron bonding characteristic of the other metals in the series. Its metallic bonding is relatively weak, and zinc therefore has the lowest enthalpy of atomization in the $3d$ series.

Step 3: Conclusion Transition metals have high enthalpies of atomization because of strong metallic bonding involving their valence s and d electrons. Zinc, Zn, has the lowest enthalpy of atomization in the $3d$ series.

Quick Tip to Solve: For the lowest atomization enthalpy in the 3d series, look for the filled 3d subshell: zinc is 3d10 4s2.

19. Define the following terms :

(a) Peptide linkage

(b) Essential amino acids [2 marks]

Solution:

Concept:

- Amino acids contain amino and carboxyl functional groups. Joining these groups between two amino acids produces an amide bond.
- Essentiality refers to the body's inability to synthesize enough of a required amino acid; such amino acids must be obtained from food.

Step 1: (a) Define peptide linkage A peptide linkage is the amide linkage $-\mathrm{CO}-\mathrm{NH}-$ formed when the carboxyl group $-\mathrm{COOH}$ of one amino acid reacts with the amino group $-\mathrm{NH_2}$ of another amino acid, eliminating one molecule of water. The resulting covalent linkage joins the two amino-acid residues in a peptide. Repetition of this condensation forms the backbone of polypeptides and proteins.

Step 2: (b) Define essential amino acids Essential amino acids are amino acids that the human body cannot synthesize in adequate amounts and therefore must obtain through the diet. They are required for protein synthesis and normal growth and maintenance, just as other amino acids are. Valine and lysine are examples. The word essential describes their dietary requirement, rather than suggesting that other amino acids are unimportant.

Step 3: Conclusion (a) A peptide linkage is the $-\mathrm{CO}-\mathrm{NH}-$ bond formed between two amino acids with loss of water. (b) Essential amino acids must be supplied in the diet because the body cannot synthesize them adequately.

Quick Tip to Solve: Remember peptide as the linking amide bond; remember essential as an amino acid that must come from the diet.

20. A first order reaction has a rate constant 1.25×10^{-3} s^{-1}. How long will 5 g of this reactant take to reduce to 2.5 g ?

[log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021] [2 marks]

Solution:

Concept:

- For a first-order reaction, $kt = \ln([A]_0/[A]_t) = 2.303 \log_{10}([A]_0/[A]_t)$, where k is the rate constant and t is time.
- For the same reactant at constant volume, the concentration ratio equals the mass ratio. Reduction to half the initial mass corresponds to one half-life.

Step 1: Identify the fraction remaining The initial reactant mass is $m_0 = 5\,\text{g}$, and the remaining mass is $m_t = 2.5\,\text{g}$. Thus $m_0/m_t = 5/2.5 = 2$, so exactly half of the reactant remains. The given rate constant is $k = 1.25 \times 10^{-3}\,\text{s}^{-1}$. Since mass is proportional to the amount of this same reactant, its ratio can be used in the integrated first-order equation.

Step 2: Substitute into the first-order equation Using the supplied value $\log_{10} 2 = 0.301$,

$$\begin{aligned} t &= \frac{2.303}{k} \log_{10} \frac{m_0}{m_t} \\ &= \frac{2.303 \times 0.301}{1.25 \times 10^{-3}} \\ &= 554.56\,\text{s} \approx 555\,\text{s}. \end{aligned}$$

This also agrees with the half-life relation $t_{1/2} = 0.693/k$. Because k is in inverse seconds, the resulting time is in seconds; multiplying by 60 here would be incorrect.

Step 3: Conclusion The reactant takes approximately 5.55×10^2 s, or 9.24 min, to decrease from 5 g to 2.5 g.

Quick Tip to Solve: When the mass halves in a first-order reaction, use t = 0.693/k directly and keep the time unit consistent with k.

21. A 3% solution of glucose (molar mass = 180 g mol^{-1}) is isotonic with 2.5% solution of an unknown organic substance. Calculate the molecular weight of the unknown organic substance. [2 marks]

Solution:

Concept:

- Isotonic solutions have equal osmotic pressure at the same temperature. For a dilute non-electrolyte solution, $\pi = CRT$, where C is molarity, R is the gas constant and T is absolute temperature.
- A percentage mass-by-volume concentration gives solute mass per 100 mL of solution. Moles are $n = w/M$, where w is solute mass and M is molar mass.

Step 1: Express the isotonic condition Glucose and the unknown organic solute are treated as

Quick Tip to Solve: For isotonic non-electrolytes at the same temperature, equate percentage concentration divided by molar mass: $3/180 = 2.5/M$.

non-electrolytes. At the same temperature,

$$C_{\text{glucose}}RT = C_{\text{unknown}}RT \quad \Rightarrow \quad C_{\text{glucose}} = C_{\text{unknown}}.$$

Take $100\,\text{mL}$ of each solution. This contains $3\,\text{g}$ of glucose and $2.5\,\text{g}$ of the unknown substance. Since the solution volumes and molarities are equal, their amounts of solute in moles are equal too.

Step 2: Calculate the unknown molar mass Let the unknown molar mass be M. Using the glucose molar mass $180\,\text{g mol}^{-1}$,

$$\frac{3}{180} = \frac{2.5}{M} \quad \Rightarrow \quad M = \frac{2.5 \times 180}{3} = 150\,\text{g mol}^{-1}.$$

The unknown solution has a smaller mass concentration. An equal number of solute particles therefore requires a smaller molar mass than glucose, which agrees with this calculation.

Step 3: Conclusion The molecular weight of the unknown substance is $\boxed{150}$, corresponding to a molar mass of $\boxed{150\,\text{g mol}^{-1}}$.

Quick Tip to Solve: For isotonic non-electrolytes at the same temperature, equate percentage concentration divided by molar mass: $3/180 = 2.5/M$.

Section C (21 marks)

22. Give the equations of reactions for the preparation of : (any three)

(a) Phenol from chlorobenzene

(b) Salicylaldehyde from phenol

(c) 2-Methoxyacetophenone from anisole

(d) Picric acid from phenol [3 marks]

Solution:

Concept:

- Chlorobenzene undergoes substitution with aqueous sodium hydroxide at high temperature and pressure to give sodium phenoxide; acidification then gives phenol.
- Phenol undergoes Reimer–Tiemann formylation with chloroform and alkali. Anisole undergoes Friedel–Crafts acylation, and phenol undergoes nitration readily because its hydroxyl group activates the ring.

Step 1: (a) Phenol from chlorobenzene Heat chlorobenzene with aqueous NaOH at $623\,\text{K}$ and about $300\,\text{atm}$. Acidify the sodium phenoxide formed:

$$\text{C}_6\text{H}_5\text{Cl} + 2\text{NaOH} \xrightarrow[300\,\text{atm}]{623\,\text{K}} \text{C}_6\text{H}_5\text{ONa} + \text{NaCl} + \text{H}_2\text{O},$$
$$\text{C}_6\text{H}_5\text{ONa} + \text{HCl} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{NaCl}.$$

Acidification converts the phenoxide salt to free phenol.

Quick Tip to Solve: Match the new group to its reagent: $-\text{CHO}$ requires $\text{CHCl}_3/\text{NaOH}$, $-\text{COCH}_3$ requires $\text{CH}_3\text{COCl}/\text{AlCl}_3$, and picric acid requires concentrated HNO_3.

Step 2: (b) Salicylaldehyde from phenol Treat phenol with chloroform and aqueous sodium hydroxide on heating, followed by acidic work-up. In the Reimer–Tiemann reaction, a formyl group ($-CHO$) is introduced mainly at the ortho position. The net equation after work-up is

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow[\text{then } H^+]{\Delta} \text{o–}\ HOC_6H_4CHO + 3NaCl + 2H_2O.$$

The ortho product is salicylaldehyde, or 2-hydroxybenzaldehyde.

Step 3: (c) 2-Methoxyacetophenone from anisole Acylate anisole using acetyl chloride and anhydrous aluminium chloride:

$$C_6H_5OCH_3 + CH_3COCl \xrightarrow{\text{anhydrous } AlCl_3} \text{o–}\ CH_3OC_6H_4COCH_3 + HCl.$$

The methoxy group directs substitution ortho and para. Separate the desired ortho product, 2-methoxyacetophenone, from the mixture; the para isomer is normally the major product.

Step 4: (d) Picric acid from phenol Treat phenol with concentrated nitric acid. Strong activation by the hydroxyl group allows nitration at both ortho positions and the para position:

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{concentrated } HNO_3} C_6H_2(NO_2)_3OH + 3H_2O.$$

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

Step 5: Conclusion Any three of these four preparations answer the question; the products are phenol, salicylaldehyde, 2-methoxyacetophenone and picric acid, respectively.

Quick Tip to Solve: Match the new group to its reagent: $-CHO$ requires $CHCl_3/NaOH$, $-COCH_3$ requires $CH_3COCl/AlCl_3$, and picric acid requires concentrated HNO_3.

23. Give reasons for the following :

(a) Chlorine is ortho/para directing in electrophilic aromatic substitution reactions, though chlorine is an electron withdrawing group.

(b) Racemic mixture is optically inactive.

(c) Allyl chloride is hydrolysed more readily than n-propyl chloride. [3 marks]

Solution:

Concept:

- An inductive effect acts through sigma bonds, whereas a resonance effect delocalises electrons through overlapping orbitals. In chlorobenzene, chlorine withdraws inductively but donates a lone pair by resonance.
- Enantiomers rotate plane-polarised light by equal magnitudes in opposite directions under identical conditions. A racemic mixture contains equal amounts of the two enantiomers.
- Resonance stabilisation of an allylic carbocation or substitution transition state lowers the activation barrier for hydrolysis of an allylic halide.

Step 1: (a) Explain chlorine's directing effect Chlorine is electronegative and withdraws electron

Quick Tip to Solve: Separate overall reactivity from direction for chlorine: $-I$ deactivates the ring, while lone-pair resonance donation favours ortho and para attack.

density from the benzene ring by its $-I$ effect. Thus chlorobenzene is less reactive towards electrophilic substitution than benzene. However, a chlorine lone pair can overlap with the ring's π system and donate electron density by its $+R$ effect, especially at the ortho and para positions. Electrophilic attack at these positions produces intermediates with additional resonance stabilisation through chlorine's lone-pair donation. The corresponding stabilisation is unavailable for meta attack. Consequently chlorine is deactivating overall, yet directs the incoming electrophile to the ortho and para positions.

Step 2: (b) Explain optical inactivity of a racemate A racemic mixture has a 1:1 ratio of dextrorotatory and laevorotatory enantiomers. Each rotates plane-polarised light through an equal angle in an opposite direction, so their contributions cancel:

$$\alpha_{\text{net}} = (+\alpha) + (-\alpha) = 0.$$

This is external compensation: each enantiomer remains optically active individually, but the mixture shows no net optical rotation.

Step 3: (c) Compare allyl chloride and n-propyl chloride In allyl chloride, $CH_2 = CH - CH_2Cl$, the carbon bonded to chlorine is adjacent to a double bond. If the carbon–chlorine bond ionises, the allylic carbocation is stabilised by resonance:

$$CH_2 = CH - CH_2^+ \longleftrightarrow {}^+CH_2 - CH = CH_2.$$

Charge is delocalised over the terminal carbon atoms. The primary carbocation corresponding to $CH_3CH_2CH_2Cl$ lacks this stabilisation. Allylic resonance also stabilises the transition state for direct nucleophilic substitution. Both effects facilitate hydrolysis of allyl chloride compared with n-propyl chloride.

Step 4: Conclusion (a) Chlorine's resonance donation accounts for ortho/para direction despite its electron-withdrawing inductive effect. (b) Equal and opposite rotations cancel in a racemate. (c) Allylic resonance stabilisation facilitates hydrolysis of allyl chloride.

Quick Tip to Solve: Separate overall reactivity from direction for chlorine: $-I$ deactivates the ring, while lone-pair resonance donation favours ortho and para attack.

24. The vapour pressure of a solvent at 283 K is 100 mm Hg. Calculate the vapour pressure of a dilute solution containing 1 mole of a strong electrolyte AB in 50 moles of the solvent at 283 K (assuming complete dissociation of solute AB). [3 marks]

Solution:

Concept:

- Raoult's law for a non-volatile solute is $p = p^\circ x_1$, where p° is the pure solvent's vapour pressure and x_1 is its mole fraction in the solution.
- Complete dissociation of an electrolyte increases the number of dissolved particles. The van't Hoff factor i is the number of particles produced per formula unit; the solvent mole fraction is $x_1 = n_1/(n_1 + in_2)$.

Quick Tip to Solve: Replace one mole of fully dissociated AB by two moles of particles before calculating the solvent mole fraction; include those particles in the total-mole denominator.

Step 1: Count the particles after dissociation The strong electrolyte dissociates completely according to

$$\mathrm{AB} \longrightarrow \mathrm{A}^{+} + \mathrm{B}^{-}.$$

Thus one mole of AB produces one mole of each ion, or two moles of dissolved particles. Hence $i = 2$, $n_2 = 1\,\text{mol}$, and the effective solute-particle amount is $in_2 = 2\,\text{mol}$. The solvent amount remains $n_1 = 50\,\text{mol}$; dissociation changes the number of solute particles, not the amount of solvent.

Step 2: Evaluate the solvent mole fraction The denominator must include both the solvent molecules and all solute particles. Therefore,

$$x_1 = \frac{50}{50+2} = \frac{50}{52} = 0.96154.$$

The two ions are counted separately because vapour-pressure lowering is a colligative property and depends on the number of dissolved particles.

Step 3: Apply Raoult's law at the given temperature At $283\,\text{K}$, the pure solvent has $p^\circ = 100\,\text{mm Hg}$. Substituting the mole fraction gives

$$p = 100 \times \frac{50}{52} = 96.15\,\text{mm Hg}.$$

The lowering is $100 - 96.15 = 3.85\,\text{mm Hg}$, so the solution pressure is below the pure-solvent pressure, as required. If the dilute-solution approximation $n_1 + in_2 \simeq n_1$ is used in relative lowering, it gives $(p^\circ - p)/p^\circ \simeq 2/50$ and $p \simeq 96\,\text{mm Hg}$.

Step 4: Conclusion The vapour pressure is $\boxed{96.15\,\text{mm Hg}}$ using the full solvent mole fraction, or approximately $96\,\text{mm Hg}$ with the dilute-solution approximation.

Quick Tip to Solve: Replace one mole of fully dissociated AB by two moles of particles before calculating the solvent mole fraction; include those particles in the total-mole denominator.

25. The rate of a gaseous reaction triples when temperature is increased from 17°C to 27°C. Calculate the energy of activation for this reaction.

[Given : 2.303 R = 19.15 JK^{-1} mol^{-1}, log 3 = 0.48] [3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For two temperatures, $\log(k_2/k_1) = \dfrac{E_a}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$. Under the same concentration conditions, a threefold increase in reaction rate gives $k_2/k_1 = 3$.

Step 1: Express the temperatures in kelvin The reciprocal-temperature terms in the Arrhenius relation

Quick Tip to Solve: Convert both Celsius temperatures to kelvin first, and use $T_1T_2/(T_2 - T_1)$ to simplify the reciprocal-temperature difference without rounding early.

require the absolute temperature scale. Using the usual board-examination conversion,

$$T_1 = 17 + 273 = 290\,\text{K}, \qquad T_2 = 27 + 273 = 300\,\text{K}.$$

The temperature difference is $10\,\text{K}$, and the given rate ratio implies $\log(k_2/k_1) = \log 3 = 0.48$.

Step 2: Rearrange the two-temperature equation Since $T_2 > T_1$, the difference $1/T_1 - 1/T_2$ is positive. It can be written as $(T_2 - T_1)/(T_1T_2)$. Therefore,

$$E_a = 2.303R \log\left(\frac{k_2}{k_1}\right) \frac{T_1T_2}{T_2 - T_1}.$$

This expression determines the activation barrier directly; the unknown frequency factor cancels when the two Arrhenius equations are divided.

Step 3: Substitute and convert the energy unit With the supplied value $2.303R = 19.15\,\text{J K}^{-1}\text{mol}^{-1}$,

$$\begin{aligned} E_a &= 19.15 \times 0.48 \times \frac{290 \times 300}{10} \\ &= 19.15 \times 0.48 \times 8700 \\ &= 79970.4\,\text{J mol}^{-1} \\ &= 79.97\,\text{kJ mol}^{-1}. \end{aligned}$$

The kelvin factor from $T_1T_2/(T_2 - T_1)$ cancels the inverse-kelvin unit in R, leaving energy per mole.

Step 4: Conclusion The activation energy is $\boxed{E_a \simeq 80.0\,\text{kJ mol}^{-1}}$, using the given logarithm and gas-constant values.

Quick Tip to Solve: Convert both Celsius temperatures to kelvin first, and use $T_1T_2/(T_2 - T_1)$ to simplify the reciprocal-temperature difference without rounding early.

26. Calculate emf of the following cell:

$$\text{Zn(s)}\,|\,\text{Zn}^{2+}(0.1\,\text{M})\,||\,\text{Sn}^{2+}(0.001\,\text{M})\,|\,\text{Sn(s)}$$

Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\,\text{V}$, $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14\,\text{V}$.
[$\log 10 = 1$**]** [3 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using the tabulated standard reduction potentials for both electrodes.
- For the standard textbook temperature $298\,\text{K}$, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log Q$. Here n is the number of electrons transferred, and Q is the reaction quotient; pure solids have unit activity.

Step 1: Identify the electrode reactions Tin has the more positive reduction potential, so Sn^{2+} is

Quick Tip to Solve: Write the balanced cell reaction before forming Q: product zinc ions go above reactant tin ions, and two transferred electrons give the denominator $n = 2$.

reduced at the right-hand cathode. Zinc is oxidised at the left-hand anode:

$$\text{Anode: } \mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-},$$
$$\text{Cathode: } \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Sn(s)}.$$

Adding gives $\mathrm{Zn(s)} + \mathrm{Sn^{2+}(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Sn(s)}$. Thus $n = 2$; the zinc-ion concentration belongs in the numerator of Q, because it is a reaction product.

Step 2: Calculate the standard cell potential and reaction quotient Both given electrode values are reduction potentials. Hence,

$$E^\circ_{\text{cell}} = -0.14 - (-0.76) = 0.62\,\text{V}.$$

Omitting the solid electrodes from the quotient and using the given molar concentrations,

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Sn^{2+}}]} = \frac{0.1}{0.001} = 100.$$

Consequently $\log Q = \log 100 = 2\log 10 = 2$. The concentrations are used as the dilute-solution approximation to activities.

Step 3: Apply the Nernst correction Using the conventional 298 K Nernst coefficient,

$$\begin{aligned} E_{\text{cell}} &= 0.62 - \frac{0.0591}{2}\log 100 \\ &= 0.62 - \frac{0.0591}{2} \times 2 \\ &= 0.5609\,\text{V}. \end{aligned}$$

Since $Q > 1$, the correction lowers the potential relative to its standard value. This agrees with the excess product-ion concentration relative to the reactant-ion concentration.

Step 4: Conclusion The cell emf is $\boxed{E_{\text{cell}} \simeq 0.561\,\text{V}}$ at the conventional Nernst-equation temperature of 298 K.

Quick Tip to Solve: Write the balanced cell reaction before forming Q: product zinc ions go above reactant tin ions, and two transferred electrons give the denominator $n = 2$.

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

(a) $\mathrm{CH_3CH_2Br} \xrightarrow{\mathrm{KCN}} A \xrightarrow[\textbf{Partial hydrolysis}]{\mathrm{OH^-}} B \xrightarrow{\mathrm{NaOH + Br_2}} C$

(b) $\mathrm{C_6H_5NO_2} \xrightarrow{\mathrm{Fe + HCl}} A \xrightarrow[273-278\,\mathrm{K}]{\mathrm{NaNO_2 + HCl}} B \xrightarrow{\mathrm{C_2H_5OH}} C$ [3 marks]

Solution:

Concept:

- Cyanide ion replaces bromide in a primary alkyl halide. Its carbon becomes part of the nitrile chain, increasing the carbon count by one.
- Partial hydrolysis converts a nitrile, $\mathrm{R-CN}$, into an amide, $\mathrm{R-CONH_2}$. Hofmann bromamide

Quick Tip to Solve: Track carbons: KCN adds one, partial hydrolysis retains it, and Hofmann degradation removes the carbonyl carbon.

degradation converts that amide into $R - NH_2$, removing its carbonyl carbon.

- Reduction of nitrobenzene gives aniline. Diazotisation at $273 - 278\,K$ gives benzenediazonium chloride; ethanol replaces its diazonium group by hydrogen.

Step 1: (a) Identify the nitrile and amide With KCN, ethyl bromide undergoes substitution through the carbon end of cyanide:

$$CH_3CH_2Br + KCN \longrightarrow CH_3CH_2C \equiv N + KBr.$$

Thus A is propanenitrile, $CH_3CH_2C \equiv N$. Partial hydrolysis stops at the amide rather than proceeding to the carboxylate. Hence B is propanamide, $CH_3CH_2CONH_2$.

Step 2: (a) Apply Hofmann bromamide degradation Bromine and aqueous NaOH remove the amide carbonyl carbon:

$$CH_3CH_2CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3CH_2NH_2 + Na_2CO_3 + 2NaBr + 2H_2O.$$

Therefore C is ethanamine, $CH_3CH_2NH_2$.

Step 3: (b) Reduce and diazotise nitrobenzene Iron and hydrochloric acid reduce the nitro group to an amino group. The product A is aniline, $C_6H_5NH_2$. Aniline undergoes diazotisation at $273 - 278\,K$:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

Thus B is benzenediazonium chloride, $C_6H_5 - N \equiv N^+\,Cl^-$.

Step 4: (b) React the diazonium salt with ethanol Ethanol reduces the diazonium salt, replacing the diazonium group by hydrogen and liberating nitrogen. Ethanol forms ethanal:

$$C_6H_5N_2^+Cl^- + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

The product C is therefore benzene, C_6H_6.

Step 5: Conclusion (a) A: $CH_3CH_2C \equiv N$; B: $CH_3CH_2CONH_2$; C: $CH_3CH_2NH_2$.
(b) A: $C_6H_5NH_2$; B: $C_6H_5 - N \equiv N^+\,Cl^-$; C: benzene, C_6H_6.

Quick Tip to Solve: Track carbons: KCN adds one, partial hydrolysis retains it, and Hofmann degradation removes the carbonyl carbon.

28. Write the reaction involved in the following :

(a) Wolff-Kishner reduction

(b) Decarboxylation reaction

(c) Cannizzaro reaction [3 marks]

Solution:

Concept:

- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine and a strong base on heating.
- Decarboxylation of a sodium carboxylate with soda lime removes its carboxyl carbon, producing an alkane containing one carbon fewer.
- In the Cannizzaro reaction, an aldehyde lacking an α-hydrogen undergoes disproportionation in concentrated alkali: one molecule is reduced and another is oxidised.

Step 1: (a) Wolff-Kishner reduction An aldehyde or ketone is heated with hydrazine, NH_2NH_2, and potassium hydroxide in a high-boiling solvent such as ethylene glycol. The initially formed hydrazone loses nitrogen and the carbonyl oxygen is ultimately removed as water. For acetone:

$$CH_3COCH_3 + NH_2NH_2 \xrightarrow[\Delta]{\text{KOH, glycol}} CH_3CH_2CH_3 + N_2 + H_2O.$$

The carbon skeleton is retained: the three-carbon ketone gives three-carbon propane.

Step 2: (b) Decarboxylation reaction Heat the sodium salt of a carboxylic acid with soda lime, a mixture of sodium hydroxide and calcium oxide:

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3.$$

For example, sodium ethanoate gives methane:

$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3.$$

The carboxyl carbon becomes part of sodium carbonate. Consequently, the alkane has one carbon atom fewer than the starting carboxylate.

Step 3: (c) Cannizzaro reaction Treat an aldehyde without an α-hydrogen with concentrated sodium hydroxide. For benzaldehyde:

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa.$$

Here the NaOH solution is concentrated. One benzaldehyde molecule is reduced to benzyl alcohol while the other is oxidised to sodium benzoate. The acid is obtained only after acidifying the carboxylate; under the alkaline reaction conditions the product is its sodium salt.

Step 4: Conclusion Wolff-Kishner reduction: acetone gives propane with hydrazine and KOH on heating. Decarboxylation: sodium ethanoate gives methane with soda lime on heating. Cannizzaro reaction: benzaldehyde gives benzyl alcohol and sodium benzoate with concentrated NaOH.

Quick Tip to Solve: In the Cannizzaro equation use two aldehyde molecules and write the carboxylate salt, since the reaction medium is strongly alkaline.

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: Carbohydrates are essential for life in both plants and animals. Carbohydrates are used as storage molecules as starch in plants and glycogen in animals. Chemically they are polyhydroxy aldehydes or ketones. On the basis of their behaviour on hydrolysis, carbohydrates are classified as monosaccharides, oligosaccharides and polysaccharides. All monosaccharides are reducing sugars, i.e., they are oxidized by Tollens' reagent and Fehling's solution. A monosaccharide like glucose is aldohexose and its molecular formula was found to be $C_6H_{12}O_6$. After reacting with different reagents like HI, H_2N-OH, Bromine water, $(CH_3CO)_2O$, etc. its structure was found to contain one aldehyde group, one primary alcoholic group ($-CH_2OH$) and four secondary alcoholic groups ($>CHOH$). Despite having the aldehyde group, glucose does not give some of the reactions of aldehyde group like Schiff's test, $NaHSO_3$ addition. This explains the existence of glucose in two cyclic hemiacetal forms which differ only in the configuration of the hydroxyl group at C-1.

(a) What are reducing sugars ? [1 mark]

Solution:

Concept:

- A reducing sugar reduces Tollens' reagent or Fehling's solution and is itself oxidised during the reaction.
- A free anomeric group permits the cyclic sugar to open to a carbonyl form. Examples include glucose and lactose.

Step 1: Identify the characteristic test Reducing sugars give a positive test with Tollens' reagent or Fehling's solution. They reduce silver ions to metallic silver in the former, or copper(II) ions to copper(I) oxide in the latter. The sugar acts as the reducing agent.

Step 2: Connect the test to the sugar's structure Such sugars can provide a reactive carbonyl form under the test conditions. For example, glucose has a free hemiacetal group and its ring can open to an aldehyde form. Fructose also gives these tests because it rearranges to aldoses in the alkaline medium. Therefore reducing sugars need not all be aldehydes in their predominant form.

Step 3: Conclusion Reducing sugars are carbohydrates that reduce Tollens' reagent or Fehling's solution and are themselves oxidised; glucose is an example.

Quick Tip to Solve: Define the sugar by its ability to reduce the named reagents; saying only that it contains hydroxyl groups is insufficient.

29(b). Classify the following into monosaccharide and disaccharide : Fructose, Sucrose, Lactose, Galactose [1 mark]

Solution:

Concept:

- Monosaccharides cannot be hydrolysed into simpler carbohydrate units.

Quick Tip to Solve: Classify by hydrolysis: a single sugar unit is a monosaccharide, while a sugar yielding two such units is a disaccharide.

- A disaccharide yields two monosaccharide units on hydrolysis of its glycosidic linkage.

Step 1: Identify the single sugar units Fructose and galactose are monosaccharides. Each is a single hexose unit and cannot be hydrolysed to simpler carbohydrates. Fructose is a ketohexose, whereas galactose is an aldohexose; this difference does not change their classification by hydrolysis.

Step 2: Identify sugars formed from two units Sucrose and lactose are disaccharides. Hydrolysis of sucrose gives glucose and fructose; hydrolysis of lactose gives glucose and galactose. Each contains two monosaccharide units joined by a glycosidic bond. Whether a sugar is reducing is a separate classification, so both sucrose and lactose belong here despite their different reducing behaviour.

Step 3: Conclusion Monosaccharides: fructose and galactose. Disaccharides: sucrose and lactose.

Quick Tip to Solve: Classify by hydrolysis: a single sugar unit is a monosaccharide, while a sugar yielding two such units is a disaccharide.

29(c). Name the polysaccharide which is known as 'animal starch'. Why is it called 'animal starch' ?

[2 marks]

Solution:

Concept:

- Polysaccharides are carbohydrates whose hydrolysis yields many monosaccharide units; glycogen is a polymer of α-D-glucose.
- Storage polysaccharides act as reserves of glucose: starch serves this function in plants, while glycogen serves it in animals.

Step 1: Identify the polysaccharide The polysaccharide known as animal starch is **glycogen**. Its glucose units form a highly branched structure, principally with $\alpha(1 \rightarrow 4)$ links along chains and $\alpha(1 \rightarrow 6)$ links at branch points.

Step 2: Explain the name Glycogen is stored mainly in the liver and muscles of animals as a reserve carbohydrate. When energy is required, it can be broken down to make glucose available. It therefore performs in animals the same storage function that starch performs in plants. The name refers to this similarity of function and to its starch-like glucose-polymer structure; glycogen is more highly branched than starch.

Step 3: Conclusion **Glycogen** is called **animal starch** because it is the storage polysaccharide of animals, analogous to starch in plants.

Quick Tip to Solve: Connect the word animal to the storage sites liver and muscles; connect starch to the reserve-carbohydrate function.

OR

29(c). (i) Name the isomers of glucose which in the cyclic form differ only in the configuration of the $-$OH group at C-1.

(ii) Presence of which functional group was detected when glucose reacted with Br_2 water ? [2 marks]

Solution:

Concept:

- Anomers are cyclic sugar stereoisomers that differ only at the anomeric carbon; in glucose this is C-1.
- Bromine water is a mild oxidising agent: it oxidises an aldehyde group, $-\mathrm{CHO}$, to a carboxylic acid group, $-\mathrm{COOH}$.

Step 1: (i) Name the cyclic isomers The isomers are **α-D-glucose and β-D-glucose**, called **anomers**. Their cyclic hemiacetal structures differ only in the configuration of the hydroxyl group at C-1. In the usual Haworth representation of D-glucose, the anomeric OH is below the ring in the α form and above it in the β form.

Step 2: (ii) Identify the functional group The reaction of glucose with bromine water detects an **aldehyde group**, $-\mathrm{CHO}$. Glucose is oxidised to gluconic acid, while bromine is reduced to hydrogen bromide:

$$\mathrm{CHO(CHOH)_4CH_2OH + Br_2 + H_2O \longrightarrow COOH(CHOH)_4CH_2OH + 2HBr.}$$

The terminal aldehyde is converted into a carboxyl group; the alcohol groups are retained under this mild oxidation.

Step 3: Conclusion (i) **α-D-glucose and β-D-glucose (anomers).** (ii) **Aldehyde group, $-\mathrm{CHO}$.**

Quick Tip to Solve: For glucose, a difference only at C-1 means anomers; mild oxidation by bromine water identifies the aldehyde group.

30(a). Case study: Transition metals have incomplete d-subshell either in neutral atom or in their ions. The presence of partly filled d-orbitals in their atoms makes transition elements different from that of the non-transition elements. With partly filled d-orbitals, these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands. The transition metals and their compounds also exhibit catalytic properties and paramagnetic behaviour. The transition metals are very hard and have low volatility. An examination of the $E^{\circ}_{M^{2+}/M}$ values shows the varying trends :

(a) On what basis can we say that Cu is a transition element but Zn is not ? (Atomic number : Cu = 29, Zn = 30) [1 mark]

	$E^{o}_{M^{2+}/M}$
V	– 1·18
Cr	– 0·91
Mn	– 1·18
Fe	– 0·44
Co	– 0·28
Ni	– 0·25
Cu	+ 0·34
Zn	– 0·76

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its common ions.
- Electrons are removed from the $4s$ orbital before the $3d$ orbitals when first-row d-block metal cations form.

Step 1: Check copper and its ion Copper has configuration $[Ar]3d^{10}4s^{1}$, but Cu^{2+} has $[Ar]3d^{9}$. Its divalent ion therefore has an incomplete d subshell, so copper meets the definition.

Step 2: Check zinc and its ion Zinc has configuration $[Ar]3d^{10}4s^{2}$, and its usual ion Zn^{2+} has $[Ar]3d^{10}$. The d subshell is completely filled in both, so zinc does not meet the transition-element criterion.

Step 3: Conclusion **Cu is a transition element because Cu^{2+} is $3d^{9}$; Zn is not because Zn and Zn^{2+} both have a filled $3d^{10}$ subshell.**

Quick Tip to Solve: Check the common ion as well as the neutral atom: the filled d shell of neutral Cu does not exclude it.

30(b). Why do transition elements show variety of oxidation states ? [1 mark]

Solution:

Concept:

- The valence orbitals of transition metals include both ns and $(n-1)d$ orbitals.
- The relatively small energy difference between these orbitals permits their electrons to participate in bonding or ion formation.

Step 1: Compare the orbital energies The ns and $(n-1)d$ orbitals in transition elements have similar energies. After the outer ns electrons participate, some d electrons can also be involved without an exceptionally large additional energy cost.

Step 2: Relate this to oxidation states Different numbers of these s and d electrons can participate in bonding or be removed under different chemical conditions. This gives several oxidation states; for example, iron commonly forms Fe^{2+} and Fe^{3+}.

Step 3: Conclusion Transition elements show variable oxidation states because **both ns and $(n-1)d$ electrons can participate, owing to their similar energies**.

Quick Tip to Solve: For variable oxidation states, state both participating subshells and the small energy gap that makes this possible.

30(c). (i) Why do $E^{\circ}_{M^{2+}/M}$ values show irregular trend from Vanadium to Zinc ?
(ii) How is the variability in oxidation states of transition metals different from that of the non-transition elements ?

[2 marks]

Solution:

Concept:

- The standard reduction potential $E^{\circ}_{M^{2+}/M}$ refers to $M^{2+}(aq) + 2e^- \rightarrow M(s)$.
- The energetics of forming an aqueous metal ion depend on atomisation, ionisation and hydration; their combined effect determines the potential.
- Transition metals commonly exhibit successive oxidation states differing by one, whereas non-transition elements commonly show states differing by two.

Step 1: (i) Explain the irregular potential trend The $E^{\circ}_{M^{2+}/M}$ values depend on the combined effects of enthalpy of atomisation of the metal, its first and second ionisation enthalpies, and the hydration enthalpy of M^{2+}. These contributions do not vary smoothly or compensate uniformly from V to Zn. Their resultant therefore shows an irregular trend. The extra stability associated with particular d-electron configurations also affects the ionisation and ion-stabilisation contributions.

Step 2: (ii) Compare the oxidation-state variability Transition elements commonly show oxidation states differing by **one unit**, since both s and d electrons can participate individually: manganese, for example, shows $+2, +3, +4, +5, +6, +7$. Non-transition elements commonly show oxidation states differing by **two units**; for example, tin shows $+2$ and $+4$, while phosphorus shows $+3$ and $+5$. These are characteristic patterns rather than a claim that every element has every such state.

Quick Tip to Solve: For an electrode-potential trend, combine atomisation, ionisation and hydration; a single factor does not determine the trend.

Step 3: Conclusion (i) The irregular trend results from the non-uniform combined effects of **atomisation, ionisation and hydration enthalpies**. (ii) Transition-metal states commonly differ by **one unit**; non-transition-element states commonly differ by **two units**.

Quick Tip to Solve: For an electrode-potential trend, combine atomisation, ionisation and hydration; a single factor does not determine the trend.

OR

30(c). (i) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing. Why ? (Atomic number : Cr = 24, Mn = 25)

(ii) Complete the following ionic equation : $2MnO_4^- + H_2O + I^- \rightarrow$ [2 marks]

Solution:

Concept:

- A reducing species loses electrons, whereas an oxidizing species accepts electrons. The stability of the product ion helps determine the preferred change in oxidation state.
- Chromium(III) has a stable $3d^3$ configuration, while manganese(II) has the particularly stable half-filled $3d^5$ configuration.

Step 1: (i) Explain the opposite redox behaviour Both Cr^{2+} and Mn^{3+} have the configuration $[Ar]3d^4$. Chromium(II) readily loses an electron to form the more stable chromium(III) ion:

$$Cr^{2+} \longrightarrow Cr^{3+} + e^-, \qquad 3d^4 \longrightarrow 3d^3.$$

This loss of an electron reduces another species, so Cr^{2+} is strongly reducing. In contrast, manganese(III) readily gains an electron to form the stable half-filled manganese(II) ion:

$$Mn^{3+} + e^- \longrightarrow Mn^{2+}, \qquad 3d^4 \longrightarrow 3d^5.$$

Its acceptance of an electron oxidizes another species, explaining its strongly oxidizing nature.

Step 2: (ii) Balance the permanganate-iodide reaction In the neutral or alkaline reaction indicated by water as a reactant, permanganate is reduced to manganese dioxide and iodide is oxidized to iodate. The half-reactions are

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-,$$
$$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-.$$

Multiply the first equation by two, add, and cancel electrons, water and hydroxide ions common to both sides. The resulting equation conserves each atom and has charge -3 on each side.

Step 3: Conclusion (i) Cr^{2+} is reducing because it forms stable Cr^{3+} ($3d^3$); Mn^{3+} is oxidizing because it forms stable Mn^{2+} ($3d^5$). (ii) The completed equation is

$$\boxed{2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-}.$$

Quick Tip to Solve: For the given water-containing permanganate equation, pair manganese dioxide with iodate and check oxygen atoms and total charge last.

Section E (15 marks)

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

(1) Oxidation of aldehydes is easier as compared to ketones.

(2) The alpha (α) hydrogen atoms of aldehydes are acidic in nature.

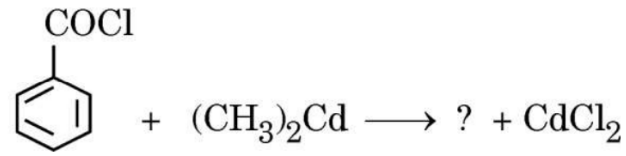
(ii) Write the products in the following reactions :

(1) $C_6H_5COCH_3 \xrightarrow{NaOH/I_2} ?+?$

(2) $C_6H_5COCl + (CH_3)_2Cd \longrightarrow ? + CdCl_2$

(iii) Give a simple chemical test to distinguish between ethanoic acid and ethanal. [5 marks]

(1) 

(2) 

Solution:

Concept:

- An aldehyde has a hydrogen attached directly to its carbonyl carbon; its oxidation to a carboxylic acid retains the carbon skeleton. Oxidation of a ketone generally requires cleavage of a carbon-carbon bond.
- The α-carbon is the carbon adjacent to the carbonyl group. Loss of an α-hydrogen as a proton produces a resonance-stabilized enolate ion.
- A methyl ketone $RCOCH_3$ undergoes the iodoform reaction with iodine and sodium hydroxide, yielding $RCOONa$ and CHI_3. An acyl chloride reacts with a dialkylcadmium reagent to give a ketone.
- Carboxylic acids liberate carbon dioxide from sodium hydrogen carbonate; aldehydes do not show this acid-base reaction.

Step 1: (i)(1) Explain why aldehydes oxidize more easily In an aldehyde, $RCHO$, the carbonyl carbon bears a hydrogen atom. Oxidation can convert the aldehydic group directly into a carboxyl group without breaking a carbon-carbon bond:

$$RCHO + [O] \longrightarrow RCOOH.$$

Ketones, $RCOR'$, do not have a hydrogen attached to the carbonyl carbon. Their oxidation to smaller carboxylic acids requires carbon-carbon bond cleavage, which needs stronger oxidizing agents and more vigorous conditions. Hence aldehydes oxidize more readily than ketones.

Step 2: (i)(2) Explain the acidity of alpha hydrogen The carbonyl group withdraws electron density through its electron-withdrawing inductive effect. More decisively, removal of an α-hydrogen as H^+

Quick Tip to Solve: In the iodoform reaction, retain the part attached to CO as its carboxylate and convert the methyl group into yellow CHI3; alkaline medium gives a salt.

gives a conjugate base whose negative charge is delocalized between the α-carbon and oxygen. For ethanal, the two resonance contributors are

$$CH_2^- - CH{=}O \longleftrightarrow CH_2{=}CH{-}O^-.$$

This resonance stabilization of the enolate ion favours proton removal and accounts for the acidic nature of the α-hydrogens. The term α-hydrogen refers to a hydrogen on the adjacent carbon, rather than the hydrogen attached to the carbonyl carbon itself.

Step 3: (ii)(1) Obtain the iodoform-reaction products The printed reactant is acetophenone, $C_6H_5COCH_3$, which contains the methyl-ketone group. Iodine in aqueous sodium hydroxide replaces the three methyl hydrogens by iodine, followed by cleavage to give sodium benzoate and iodoform, a yellow precipitate. The balanced overall reaction is

$$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3 + 3NaI + 3H_2O.$$

The carboxylic product remains its sodium salt in the alkaline medium; no acidification step is specified.

Step 4: (ii)(2) Obtain the organocadmium-reaction product Dimethylcadmium transfers methyl groups to benzoyl chloride and gives the ketone acetophenone. The balanced equation, showing the use of both methyl groups, is

$$2C_6H_5COCl + (CH_3)_2Cd \longrightarrow 2C_6H_5COCH_3 + CdCl_2.$$

Thus the organic product replacing the question mark is $C_6H_5COCH_3$. Dialkylcadmium reagents permit ketone formation without the further addition characteristic of a Grignard reagent.

Step 5: (iii) Distinguish ethanoic acid from ethanal Add a small quantity of aqueous sodium hydrogen carbonate separately to the two samples. Ethanoic acid produces brisk effervescence of carbon dioxide:

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 \uparrow + H_2O.$$

The evolved gas turns limewater milky. Ethanal does not liberate carbon dioxide with sodium hydrogen carbonate and hence shows no such effervescence. This gives a simple visible distinction between the two compounds.

Step 6: Conclusion (i) Aldehydes oxidize without carbon-carbon cleavage, and their α-hydrogens are acidic because the resulting enolate ion is resonance-stabilized. (ii)(1) The products are sodium benzoate, C_6H_5COONa, and iodoform, CHI_3. (ii)(2) The organic product is acetophenone, $C_6H_5COCH_3$. (iii) Sodium hydrogen carbonate gives carbon dioxide effervescence with ethanoic acid, but not with ethanal.

Quick Tip to Solve: In the iodoform reaction, retain the part attached to CO as its carboxylate and convert the methyl group into yellow CHI3; alkaline medium gives a salt.

OR

31(b). (i) Draw structure of the 2,4-dinitrophenylhydrazone of benzaldehyde.

(ii) Arrange the following in increasing order of their reactivity towards HCN: CH_3COCH_3, $(CH_3)_3C-COCH_3$, CH_3CHO.

(iii) How can you convert phenyl magnesium bromide to benzoic acid?

(iv) Give a simple chemical test to distinguish between benzaldehyde and ethanal.

(v) Write the main product in the following reaction:

$$CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4} \quad ?$$

[5 marks]

Solution:

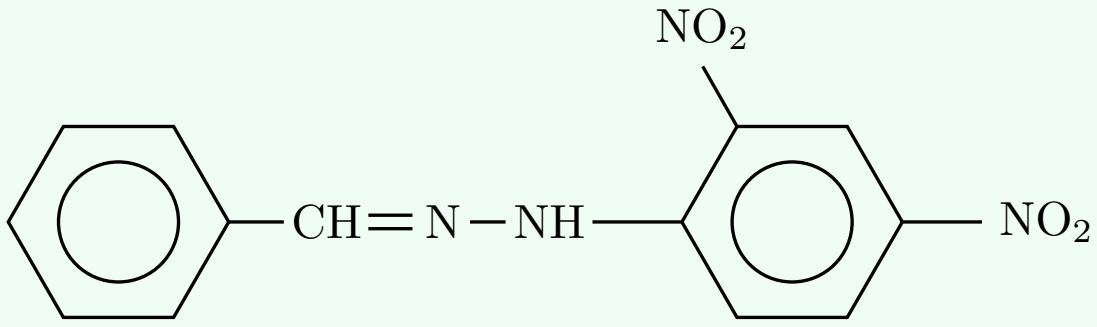
Concept:

- Aldehydes and ketones condense with 2,4-dinitrophenylhydrazine by replacing the carbonyl oxygen with $=N-NH-C_6H_3(NO_2)_2$, eliminating water.
- HCN adds to a carbonyl group by nucleophilic attack of CN^-. Electron donation by alkyl groups and steric crowding decrease the reactivity of the carbonyl carbon.
- Grignard reagents react with CO_2 to give magnesium carboxylates; acidification gives carboxylic acids. Sodium borohydride reduces aldehydes and ketones while leaving ordinary esters unchanged.

Step 1: (i) Form the 2,4-dinitrophenylhydrazone Benzaldehyde reacts with the terminal $-NH_2$ group of 2,4-dinitrophenylhydrazine in acidic medium. Condensation eliminates one molecule of water, forming a carbon-nitrogen double bond:

$$C_6H_5CHO + H_2N-NH-C_6H_3(NO_2)_2 \longrightarrow C_6H_5CH=N-NH-C_6H_3(NO_2)_2 + H_2O.$$

The nitro groups occupy positions 2 and 4 relative to the ring carbon bonded to $-NH-N=CH-C_6H_5$. The labelled structure below shows the product explicitly; the hydrogen on the original aldehyde carbon remains attached to that carbon.



Benzaldehyde 2,4-dinitrophenylhydrazone, with nitro groups ortho and para to the hydrazone linkage.

Step 2: (ii) Compare nucleophilic addition of HCN The tert-butyl group in $(CH_3)_3C-COCH_3$ causes greater steric hindrance than the methyl groups of acetone and donates electron density to the carbonyl carbon. This reduces both access of CN^- and the electrophilicity of that carbon. Ethanal has

Quick Tip to Solve: In a molecule containing both a ketone and an ester, apply sodium borohydride only to the ketone carbonyl; keep the ester intact when writing the product.

only one alkyl group and one small hydrogen attached to the carbonyl carbon, so it is more reactive than either ketone. Thus the increasing order is

$$(CH_3)_3C - COCH_3 < CH_3COCH_3 < CH_3CHO.$$

Step 3: (iii) Carboxylate the Grignard reagent Treat phenylmagnesium bromide with dry carbon dioxide in dry ether. The phenyl group attacks the carbon of CO_2, forming magnesium benzoate. Hydrolysis with dilute acid then gives benzoic acid:

$$C_6H_5MgBr + CO_2 \xrightarrow{\text{dry ether}} C_6H_5COOMgBr,$$
$$C_6H_5COOMgBr + HCl \longrightarrow C_6H_5COOH + MgBrCl.$$

Moisture must be excluded during the first stage because it would destroy the Grignard reagent. The carbon of carbon dioxide becomes the carboxyl carbon, extending the carbon framework by one carbon.

Step 4: (iv) Use Fehling's solution to distinguish the aldehydes Warm separate samples with freshly mixed Fehling's solution. Ethanal gives a brick-red precipitate of Cu_2O, whereas benzaldehyde gives no brick-red precipitate under the usual test conditions. Ethanal is an aliphatic aldehyde and reduces the copper(II) complex; benzaldehyde is an aromatic aldehyde and does not give this test. For ethanal the net reaction is

$$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3COO^- + Cu_2O \downarrow + 3H_2O.$$

Tollens' reagent would give a positive result with both aldehydes, so it would not distinguish this pair.

Step 5: (v) Reduce the ketone group selectively The starting compound, ethyl acetoacetate, contains a ketone carbonyl and an ester group. $NaBH_4$ reduces the ketone carbonyl to a secondary alcohol; subsequent acidic work-up protonates the alkoxide. The ester group remains unchanged:

$$CH_3COCH_2COOC_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) } NaBH_4} CH_3CH(OH)CH_2COOC_2H_5.$$

The product is ethyl 3-hydroxybutanoate. Its newly formed stereogenic carbon gives a racemic mixture in the absence of a chiral reagent.

Step 6: Conclusion (i) $C_6H_5CH = N - NH - C_6H_3(NO_2)_2$, with nitro groups at positions 2 and 4; (ii) $(CH_3)_3CCOCH_3 < CH_3COCH_3 < CH_3CHO$; (iii) dry CO_2, then acidic hydrolysis; (iv) Fehling's test: ethanal gives brick-red Cu_2O, benzaldehyde does not; (v) $CH_3CH(OH)CH_2COOC_2H_5$.

Quick Tip to Solve: In a molecule containing both a ketone and an ester, apply sodium borohydride only to the ketone carbonyl; keep the ester intact when writing the product.

32(a). (i) The resistance of 0.05 M CH_3COOH solution is found to be 100 ohm. If the cell constant is 0.0354 cm^{-1}, calculate the molar conductivity of the acetic acid solution.

(ii) State Faraday's first law of electrolysis. How much charge in Faraday is required for the reduction of 1 mol of MnO_4^- to Mn^{2+} ? [5 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$. Conductivity is $\kappa = G(l/A)$, where l/A is the cell constant.
- For concentration C in mol L^{-1}, molar conductivity is $\Lambda_m = 1000\kappa/C$ when κ is in S cm^{-1}.
- Faraday's first law relates the mass of substance deposited or liberated at an electrode to the charge passed: $m = ZQ = ZIt$, where Z is its electrochemical equivalent.
- One faraday, F, is the charge of one mole of electrons, approximately $96485\,\text{C mol}^{-1}$. The electron requirement follows from the change in oxidation number.

Step 1: (i) Obtain conductance and conductivity The measured resistance is $R = 100\,\Omega$, and the cell constant is $l/A = 0.0354\,\text{cm}^{-1}$. Therefore,

$$G = \frac{1}{100} = 0.0100\,\text{S}.$$

Multiplying conductance by the cell constant gives

$$\kappa = 0.0100 \times 0.0354 = 3.54 \times 10^{-4}\,\text{S cm}^{-1}.$$

Conductance describes this particular cell, whereas conductivity accounts for its geometry. Thus the cell constant must multiply the reciprocal of resistance, rather than resistance itself.

Step 2: (i) Calculate the molar conductivity The concentration is $C = 0.05\,\text{mol L}^{-1}$. Since the conductivity uses centimetres, the factor 1000 converts the volume of solution per mole from litres to cubic centimetres. Substitution gives

$$\Lambda_m = \frac{1000\kappa}{C} = \frac{1000 \times 3.54 \times 10^{-4}}{0.05} = 7.08\,\text{S cm}^2\,\text{mol}^{-1}.$$

This is the molar conductivity at the stated concentration; the limiting molar conductivity is not needed for this calculation.

Step 3: (ii) State Faraday's first law of electrolysis The mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electric charge passed through the electrolyte. For a fixed substance,

$$m \propto Q, \qquad m = ZQ = ZIt,$$

where m is the deposited or liberated mass, I is the current, t is the time, and Z is the electrochemical equivalent. When Q is measured in coulombs and m in grams, Z has units g C^{-1}.

Step 4: (ii) Determine the electron requirement for permanganate reduction Let the oxidation number

Quick Tip to Solve: Use $\Lambda_m = 1000(l/A)/(RC)$ directly when the cell constant is in cm^{-1}; count the oxidation-number drop per manganese atom to find the faradays required.

of manganese in MnO_4^- be x. Oxygen has oxidation number -2, so

$$x + 4(-2) = -1 \quad \Rightarrow \quad x = +7.$$

In Mn^{2+}, manganese is in the $+2$ state. Its oxidation number decreases by five, so each manganese centre gains five electrons. The balanced reduction half-reaction in acidic medium is

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O.$$

Hence reduction of one mole of permanganate ions consumes five moles of electrons. Since each mole of electrons carries one faraday of charge, $Q = 5F$, equivalent to approximately 4.82×10^5 C.

Step 5: Conclusion (i) The molar conductivity of the acetic acid solution is $\boxed{7.08\ \text{S cm}^2\ \text{mol}^{-1}}$. (ii) Faraday's first law is $m = ZIt$; reduction of 1 mol of MnO_4^- to Mn^{2+} requires $\boxed{5F}$ of charge.

Quick Tip to Solve: Use $\Lambda_m = 1000(l/A)/(RC)$ directly when the cell constant is in cm^{-1}; count the oxidation-number drop per manganese atom to find the faradays required.

OR

32(b). (i) The conductivity of 0.0025 mol L^{-1} acetic acid is 5.25×10^{-5} S cm^{-1}. Calculate its degree of dissociation if Λ_m^0 for acetic acid is 390 S cm^2 mol^{-1}.

(ii) Write anode, cathode and overall reaction of lead storage battery. [5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = \kappa \times 1000/c$, where conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1}. The factor 1000 converts litres to cubic centimetres.
- For a weak electrolyte such as acetic acid, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^0$. Here Λ_m^0 is the limiting molar conductivity, corresponding to complete dissociation at infinite dilution.
- During discharge of a lead storage battery, lead is oxidised at the negative anode and lead dioxide is reduced at the positive cathode. Sulphuric acid supplies hydrogen and sulphate ions; both electrodes form lead sulphate.

Step 1: (i) Calculate the molar conductivity The given concentration and conductivity are

$$c = 0.0025\ \text{mol L}^{-1}, \qquad \kappa = 5.25 \times 10^{-5}\ \text{S cm}^{-1}.$$

Hence,

$$\Lambda_m = \frac{5.25 \times 10^{-5} \times 1000}{0.0025} = 21\ \text{S cm}^2\ \text{mol}^{-1}.$$

Conductivity and molar conductivity are different quantities: the latter refers to the volume of solution containing one mole of electrolyte. Thus the concentration conversion must be included before calculating dissociation.

Quick Tip to Solve: First convert conductivity to molar conductivity using the factor 1000; then divide by 390. For the battery, check that both electrodes form lead sulphate and that two electrons cancel.

Step 2: (i) Obtain the degree and percentage of dissociation Acetic acid dissociates according to

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^- + H^+}.$$

Using the ratio of its molar conductivity at the given concentration to its limiting value,

$$\alpha = \frac{21}{390} = 0.05385, \qquad 100\alpha = 5.385\%.$$

The degree of dissociation is dimensionless because the two conductivities have identical units. Its small value agrees with the weak-electrolyte nature of acetic acid.

Step 3: (ii) Write the electrode reactions during discharge At the anode, lead loses two electrons and combines with sulphate ions:

$$\mathrm{Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-}.$$

At the cathode, lead dioxide accepts those two electrons in acidic solution:

$$\mathrm{PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)}.$$

Lead changes from oxidation state 0 to +2 at the anode; lead in lead dioxide changes from +4 to +2 at the cathode. Each half-reaction therefore involves two electrons.

Step 4: (ii) Add the half-reactions to obtain the overall reaction On adding the electrode reactions, the two electrons cancel. The two sulphate ions and four hydrogen ions correspond to two molecules of sulphuric acid, giving

$$\mathrm{Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)}.$$

Both electrodes become coated with lead sulphate while sulphuric acid is consumed. Consequently the acid concentration decreases during discharge. Since this is a rechargeable secondary cell, the overall reaction runs in the reverse direction when the battery is charged using an external source.

Step 5: Conclusion (i) The degree of dissociation is $\boxed{\alpha = 0.05385}$, or approximately $\boxed{5.38\%}$. (ii) During discharge, the anode oxidises Pb to $\mathrm{PbSO_4}$, the cathode reduces $\mathrm{PbO_2}$ to $\mathrm{PbSO_4}$, and the overall reaction is $\mathrm{Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O}$.

Quick Tip to Solve: First convert conductivity to molar conductivity using the factor 1000; then divide by 390. For the battery, check that both electrodes form lead sulphate and that two electrons cancel.

33. Answer any five of the following :

(a) How is the crystal field splitting energy for octahedral complex (Δ_o) related to that of tetrahedral complex (Δ_t) ?

(b) Write the IUPAC name of the following complex : $[PtCl_2(en)_2](NO_3)_2$

(c) Write the geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ on the basis of Valency Bond Theory (VBT).

(d) What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?

(e) For the coordination compound on the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$. Is the coordination compound a high spin or low spin complex ?

(f) Out of $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_4Cl_2]^+$, which complex is heteroleptic and why ?

(g) Draw the structures of optical isomers of $[PtCl_2(en)_2]^{2+}$. [5 marks]

Solution:

Concept:

- In crystal field theory, Δ_o and Δ_t denote the splitting energies in octahedral and tetrahedral fields; P is the electron-pairing energy. For the same metal ion and ligands, $\Delta_t = \frac{4}{9}\Delta_o$.
- The neutral bidentate ligand ethane-1,2-diamine, en, coordinates through its two nitrogen atoms. Oxidation states follow from the total charge and ligand charges.
- A heteroleptic complex has more than one kind of ligand. Coordination isomerism involves interchange of ligands between complex cations and complex anions; optical isomers are non-superimposable mirror images.

Step 1: (a) Relate the two splitting energies Tetrahedral splitting is smaller than octahedral splitting for the same metal ion and ligands. The relation is

$$\Delta_t = \frac{4}{9}\Delta_o, \qquad \Delta_o = \frac{9}{4}\Delta_t.$$

Step 2: (b) Name the platinum complex Two nitrate ions make the complex cation's charge $+2$. Since each chlorido ligand has charge -1 and en is neutral, the platinum oxidation state x satisfies $x - 2 = +2$, giving $x = +4$. Name the ligands alphabetically, with chlorido before ethane-1,2-diamine; use bis for the two bidentate ligands. The name is dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate.

Step 3: (c) Apply VBT to nickel tetracarbonyl Carbon monoxide is neutral, so nickel has oxidation state zero. In the VBT description, its electrons pair to give the $3d^{10}$ arrangement, leaving the $4s$ and three $4p$ orbitals available for sp^3 hybridisation. The four CO ligands donate electron pairs into these four hybrid orbitals. Thus $[Ni(CO)_4]$ has tetrahedral geometry and is diamagnetic because all electrons are paired.

Step 4: (d) Identify the isomerism Both the cation and the anion are coordination entities. Interchanging their ligands produces the coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$ of $[Co(NH_3)_6][Cr(CN)_6]$. Therefore the compound shows coordination isomerism.

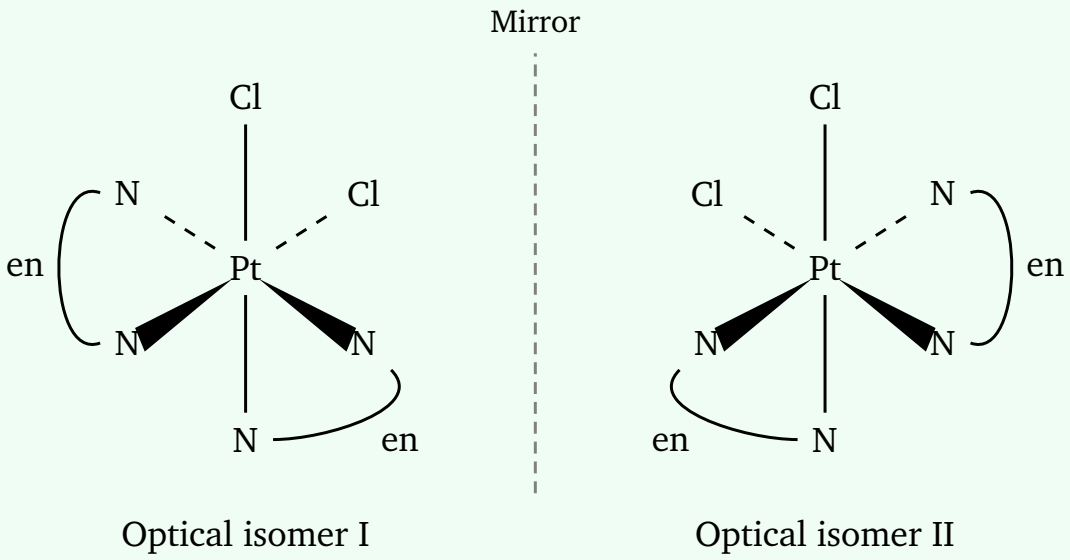
Step 5: (e) Fill the octahedral levels for the given condition Since $\Delta_o < P$, occupying an upper e_g

Quick Tip to Solve: For the platinum name, first use the two nitrate ions to find the cation charge, then subtract the two chlorido charges. For optical isomers, check the cis arrangement and trace each en chelate separately.

orbital costs less energy than pairing two electrons in a lower t_{2g} orbital. The first three electrons occupy the three t_{2g} orbitals singly; the fourth occupies an e_g orbital. Therefore the configuration is $t_{2g}^3 e_g^1$, with four unpaired electrons, and the complex is high spin.

Step 6: (f) Compare the ligand types $[Co(NH_3)_4Cl_2]^+$ is heteroleptic because it contains two types of ligands: ammine, NH_3, and chlorido, Cl^-. In contrast, $[Co(NH_3)_6]^{3+}$ contains only ammine ligands and is homoleptic.

Step 7: (g) Draw the optical isomers The two optical isomers belong to the cis form of the octahedral complex $[PtCl_2(en)_2]^{2+}$: its chlorido ligands occupy adjacent coordination positions. Each curved connection labelled en joins the two nitrogen donors of one ethane-1,2-diamine ligand. Solid wedges project towards the viewer and dashed bonds project away. Reflection reverses the arrangement of the two chelate rings, producing the non-superimposable mirror images shown below. The trans form does not give this optical pair.



Non-superimposable mirror images of cis-$[PtCl_2(en)_2]^{2+}$; N denotes a donor nitrogen of en.

Step 8: Conclusion (a) $\Delta_t = \frac{4}{9}\Delta_o$. (b) Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate. (c) sp^3, tetrahedral and diamagnetic. (d) Coordination isomerism. (e) $t_{2g}^3 e_g^1$, high spin. (f) $[Co(NH_3)_4Cl_2]^+$ is heteroleptic. (g) The cis complex gives the mirror-image optical pair illustrated. All seven alternatives are supplied; the question requires any five.

Quick Tip to Solve: For the platinum name, first use the two nitrate ions to find the cation charge, then subtract the two chlorido charges. For optical isomers, check the cis arrangement and trace each en chelate separately.