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

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. Which of the following ligands is an ambidentate ligand ? [1 mark]

(A) CO

(B) SCN^-

(C) NH_3

(D) H_2O

Correct Answer: (B) SCN^-

Solution:

Concept:

- An ambidentate ligand possesses two different possible donor atoms but coordinates through only one of them to a metal centre at a time.
- A monodentate ligand donates one lone pair to form one coordinate bond; ambidentate behaviour concerns alternative donor atoms, not simultaneous attachment.

Step 1: Identify the possible donor atoms Thiocyanate, SCN^-, can attach through its sulphur atom as $M-SCN$, or through its nitrogen atom as $M-NCS$. These alternative donor sites make linkage isomerism possible.

Step 2: Check the other ligands In the standard coordination compounds considered here, CO coordinates through carbon, NH_3 through nitrogen and H_2O through oxygen. Each is treated as having one donor site, so none has the alternative sulphur/nitrogen attachment of thiocyanate.

Step 3: Conclusion The ambidentate ligand is SCN^-. Hence, the correct option is (B).

Quick Tip to Solve: Look for two alternative donor atoms in the same ligand: SCN^- offers S or N, but binds through only one at a time.

2. On adding $AgNO_3$ solution to 1 mole of $CoCl_3 \cdot 4NH_3$, one mole of AgCl is precipitated. The secondary valency of Co is : [1 mark]

(A) 6

(B) 4

(C) 3

(D) 7

Correct Answer: (A) 6

Solution:

Concept:

- Werner's secondary valency is the coordination number: the number of donor atoms directly bonded to the metal.
- Only chloride ions outside the coordination sphere are ionisable and precipitate as $AgCl$ on adding

Quick Tip to Solve: Subtract the precipitated chloride count from the total chloride count, then add the coordinated chlorides to the ammonia donors.

$AgNO_3$.

Step 1: Locate the chloride ions One mole of the compound produces one mole of $AgCl$; hence one chloride ion per formula unit lies outside the coordination sphere. Of the three chloride ions in $CoCl_3 \cdot 4\,NH_3$, the remaining two are coordinated to cobalt.

Step 2: Count the coordinated donors The four NH_3 molecules and two coordinated chloride ions each supply one donor atom. Thus the formula is $[Co(NH_3)_4Cl_2]Cl$, and the coordination number is $4 + 2 = 6$. Counting only ammonia gives 4, while 3 is cobalt's oxidation state, not its secondary valency; 7 also does not match the donor count.

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

Quick Tip to Solve: Subtract the precipitated chloride count from the total chloride count, then add the coordinated chlorides to the ammonia donors.

3. Which of the following elements of 3d series of transition elements has the lowest $\Delta_a H^\circ$? [1 mark]

(A) Sc

(B) Cr

(C) Cu

(D) Zn

Correct Answer: (D) Zn

Solution:

Concept:

- Enthalpy of atomisation, $\Delta_a H^\circ$, is the enthalpy needed to form one mole of gaseous atoms from the element in its standard state.
- Stronger metallic bonding generally gives a larger atomisation enthalpy; participation of unpaired d electrons strengthens bonding in much of the 3d series.

Step 1: Examine the zinc configuration Zinc has the electronic configuration $[Ar]\,3d^{10}4s^2$. Its filled d subshell has no unpaired d electrons, and zinc has relatively weak metallic bonding compared with the other listed elements.

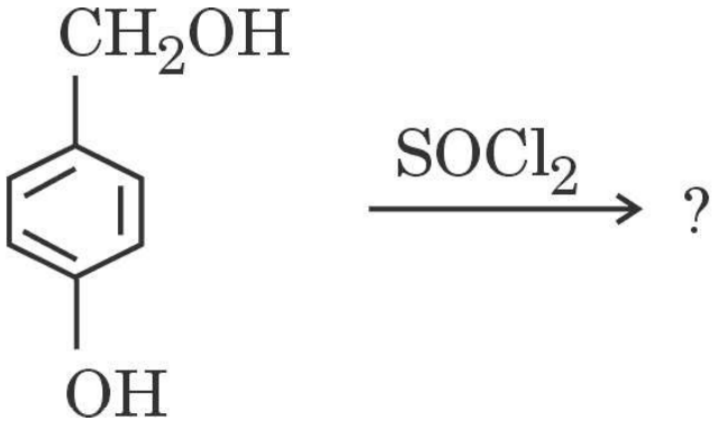
Step 2: Compare all listed elements For the choices in this question, the approximate atomisation enthalpies are 326 for Sc, 397 for Cr, 339 for Cu and $126\,kJ\,mol^{-1}$ for Zn. Thus Sc, Cr and Cu all require appreciably more energy to form gaseous atoms. Copper's filled atomic d subshell does not make its metallic bonding as weak as that of zinc.

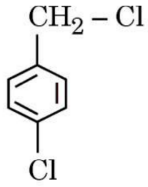
Step 3: Conclusion Zinc has the lowest $\Delta_a H^\circ$ among these elements. Hence, the correct option is (D).

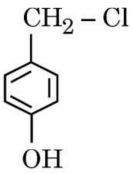
Quick Tip to Solve: In atomisation-enthalpy comparisons across the 3d series, check zinc first: its filled d subshell accompanies unusually weak metallic bonding.

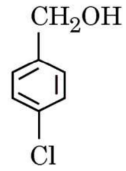
4. Consider the following reaction :

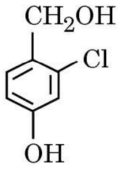
The major product obtained is : [1 mark]

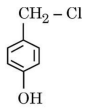


(A) 

(B) 

(C) 

(D) 

Correct Answer: (B) 

Solution:

Concept:

- Thionyl chloride, $SOCl_2$, converts an alcoholic hydroxyl group into chloride: $RCH_2OH + SOCl_2 \longrightarrow RCH_2Cl + SO_2 + HCl$.
- A phenolic $C-O$ bond has partial double-bond character through resonance and is not replaced like an alcoholic hydroxyl group under these conditions.

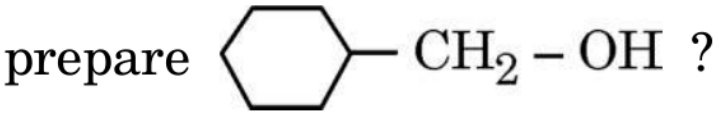
Step 1: Distinguish the two hydroxyl groups The starting compound has a $-CH_2OH$ group and a separate $-OH$ group directly bonded to the benzene ring, para to it. The first group is a benzylic alcohol; the second is phenolic. Their behaviour towards thionyl chloride therefore differs.

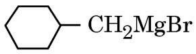
Step 2: Apply the selective substitution The benzylic $-CH_2OH$ becomes $-CH_2Cl$, while the phenolic hydroxyl remains. Option A wrongly replaces the phenolic group too; option C changes only the phenolic group; option D introduces chlorine on the ring, which is not the alcohol-to-chloride reaction of $SOCl_2$.

Step 3: Conclusion The major product is p-$HOC_6H_4CH_2Cl$, the structure with $-CH_2Cl$ and an unchanged para $-OH$. Hence, the correct option is (B).

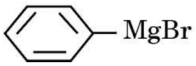
Quick Tip to Solve: Before using $SOCl_2$, distinguish $-CH_2OH$ from phenolic $Ar-OH$; replace only the alcoholic hydroxyl here.

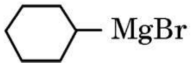
5. Which of the following Grignard reagent will be used with methanal to [1 mark]

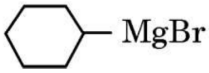


(A) 

(B) 

(C) 

(D) 

Correct Answer: (D) 

Solution:

Concept:

- A Grignard reagent RMgBr adds to methanal and, after hydrolysis, forms a primary alcohol $\mathrm{RCH_2OH}$.
- The carbon of methanal becomes the new $-\mathrm{CH_2OH}$ carbon, while the hydrocarbon group R comes unchanged from the Grignard reagent.

Step 1: Identify the group that must be transferred The printed target contains a saturated six-membered cyclohexane ring bonded to $-\mathrm{CH_2OH}$. Thus it is cyclohexylmethanol, $\mathrm{C_6H_{11}CH_2OH}$, and the group R needed for the addition is cyclohexyl, $\mathrm{C_6H_{11}}^{-}$.

Step 2: Match the reagent and exclude the alternatives The required sequence is

$$\mathrm{C_6H_{11}MgBr + HCHO \longrightarrow C_6H_{11}CH_2OMgBr}$$

followed by acidic hydrolysis to $\mathrm{C_6H_{11}CH_2OH}$. Option A has an extra methylene in R, and option B has two extra methylenes; both make a longer side chain. Option C is phenylmagnesium bromide, which produces benzyl alcohol with an aromatic ring rather than the printed saturated ring.

Step 3: Conclusion Use cyclohexylmagnesium bromide, $\mathrm{C_6H_{11}MgBr}$. Hence, the correct option is (D).

Quick Tip to Solve: Remove the terminal $-\mathrm{CH_2OH}$ of a methanal-derived alcohol and attach MgBr to the remaining group; preserve whether the ring is saturated or aromatic.

6. CH_3-O-CH_3 when treated with excess HI gives : [1 mark]

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

(B) $2\ CH_3-OH$

(C) $2\ CH_3-I$

(D) $CH_3-I + CH_4$

Correct Answer: (C) $2\ CH_3-I$

Solution:

Concept:

- HI cleaves an ether after protonation of its oxygen; iodide then attacks a methyl carbon to form an alkyl iodide and an alcohol.
- With excess HI, the alcohol formed in the first cleavage is also converted to alkyl iodide.

Step 1: Write the initial cleavage Protonation makes the ether oxygen a better leaving group. Iodide attacks one equivalent methyl group, giving

$$CH_3OCH_3 + HI \longrightarrow CH_3I + CH_3OH.$$

Option A describes this first stage but does not account for the excess reagent.

Step 2: Use the remaining HI The methanol reacts further:

$$CH_3OH + HI \longrightarrow CH_3I + H_2O.$$

Adding the equations gives

$$CH_3OCH_3 + 2\,HI \longrightarrow 2\,CH_3I + H_2O.$$

Option B incorrectly retains alcohol as the final product, and option D includes methane even though this reaction substitutes hydroxyl by iodide rather than reducing it to hydrogen.

Step 3: Conclusion The organic product is two equivalents of methyl iodide, $2\,CH_3I$. Hence, the correct option is (C).

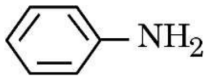
Quick Tip to Solve: The word excess means the alcohol from ether cleavage also reacts; for a symmetrical dimethyl ether, both methyl groups end as CH_3I.

7. Which of the following compounds will not react with benzene sulphonyl chloride ? [1 mark]

(A) $(C_2H_5)_3N$

(B) $C_2H_5-NH_2$

(C) $(C_2H_5)_2NH$

(D) 

Correct Answer: (A) $(C_2H_5)_3N$

Solution:

Concept:

- Benzene sulphonyl chloride, the Hinsberg reagent $C_6H_5SO_2Cl$, forms sulphonamides with primary and secondary amines.
- Sulphonamide formation replaces an N-bound hydrogen by $C_6H_5SO_2^-$; a tertiary amine has no N-H bond and does not undergo this reaction.

Step 1: Classify the amines $(C_2H_5)_3N$ has three ethyl groups attached to nitrogen and is tertiary. $C_2H_5NH_2$ and $C_6H_5NH_2$ are primary amines, while $(C_2H_5)_2NH$ is secondary. Only the first compound lacks a hydrogen directly bonded to nitrogen.

Step 2: Check their Hinsberg reactions Ethylamine and aniline each form an N-substituted benzene sulphonamide, retaining one N-H bond. Diethylamine forms an N,N-disubstituted sulphonamide. Triethylamine cannot form the corresponding sulphonamide because nitrogen already has three carbon substituents and no replaceable N-H hydrogen. The aromatic ring of aniline does not remove its primary-amine N-H bonds.

Step 3: Conclusion Triethylamine, $(C_2H_5)_3N$, does not react with benzene sulphonyl chloride in the Hinsberg test. Hence, the correct option is (A).

Quick Tip to Solve: Count N-H bonds rather than carbon-chain length: primary and secondary amines react with Hinsberg reagent, but a tertiary amine has none.

8. 'Scurvy' is caused by the deficiency of vitamin : [1 mark]

(A) E

(B) A

(C) C

(D) D

Correct Answer: (C) C

Solution:

Concept:

- Vitamins are organic nutrients required in small amounts for normal metabolism; their deficiency causes characteristic diseases.
- Vitamin C (ascorbic acid) supports collagen formation and is a water-soluble vitamin.

Step 1: Identify the deficiency disease Scurvy is the characteristic disease caused by a deficiency of vitamin C. Inadequate collagen formation leads to symptoms such as bleeding gums and poor wound healing, so the disease identifies the vitamin directly.

Quick Tip to Solve: Link scurvy and bleeding gums to vitamin C; link night blindness to A and rickets to D.

Step 2: Check the other vitamins Vitamin A deficiency is associated with night blindness, and vitamin D deficiency causes rickets in children. Vitamin E is an antioxidant and is not the vitamin whose deficiency characteristically causes scurvy. Thus only vitamin C matches the disease named in the question.

Step 3: Conclusion Scurvy is caused by deficiency of vitamin C. Hence, the correct option is (C).

Quick Tip to Solve: Link scurvy and bleeding gums to vitamin C; link night blindness to A and rickets to D.

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9. A 1% solution of solute 'X' is isotonic with a 6% solution of sucrose (molar mass = 342 g mol^{-1}). The molar mass of solute 'X' is : [1 mark]

(A) 34.2 g mol^{-1}

(B) 57 g mol^{-1}

(C) 114 g mol^{-1}

(D) 3.42 g mol^{-1}

Correct Answer: (B) 57 g mol^{-1}

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.

Step 1: Use equal osmotic pressures Treat the stated percentage concentrations on the same mass-per-volume basis: in 100 mL there are 1 g of X and 6 g of sucrose. Since both solutions are at the same temperature, equal osmotic pressures imply equal molarities and hence equal numbers of moles in equal volumes.

Step 2: Calculate and compare the molar mass Let M_X be the molar mass of X. Then

$$\frac{1}{M_X} = \frac{6}{342}, \qquad M_X = \frac{342}{6} = 57\ \text{g mol}^{-1}.$$

At 34.2, 114 and 3.42 g mol^{-1}, the moles in the 1% solution would not equal $6/342$; therefore options (A), (C) and (D) fail the isotonic condition.

Step 3: Conclusion The molar mass of X is 57 g mol^{-1}. Hence, the correct option is (B).

Quick Tip to Solve: For isotonic non-electrolytes, use concentration divided by molar mass: $1/M_X = 6/342$.

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10. The half life of a first order reaction with rate constant (k) of 3 min^{-1} is : [1 mark]

(A) 0.693 min

(B) 2.31 min

(C) 6.93 min

(D) 0.231 min

Correct Answer: (D) 0.231 min

Solution:

Concept:

- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant.
- The half-life is independent of initial concentration; its time unit is the reciprocal of the unit of k.

Step 1: Apply the first-order half-life relation At half-life, the reactant concentration falls from $[A]_0$ to $[A]_0/2$. The integrated first-order law gives $kt_{1/2} = \ln([A]_0/([A]_0/2)) = \ln 2$. Therefore divide 0.693 by the given rate constant, rather than multiplying by it.

Step 2: Substitute the rate constant Using $k = 3\,\text{min}^{-1}$,

$$t_{1/2} = \frac{0.693}{3\,\text{min}^{-1}} = 0.231\,\text{min}.$$

The value 0.693 min would apply to $k = 1\,\text{min}^{-1}$, not 3. The values 2.31 and 6.93 min likewise do not satisfy $kt_{1/2} = 0.693$.

Step 3: Conclusion The half-life is 0.231 min. Hence, the correct option is (D).

Quick Tip to Solve: Keep the unit of time from k: with k in min^{-1}, divide 0.693 by 3 to obtain minutes.

11. Which of the following cells is used in hearing aids ? [1 mark]

(A) Dry cell

(B) Mercury cell

(C) Nickel-cadmium cell

(D) Fuel cell

Correct Answer: (B) Mercury cell

Solution:

Concept:

- A mercury cell is a compact primary cell suited to low-current devices such as hearing aids and watches.
- Its anode is zinc amalgam and its cathode contains mercury(II) oxide; the cell gives an approximately constant potential of $1.35\,\text{V}$.

Step 1: Identify the textbook application Among the listed cells, the mercury cell is the cell associated with hearing aids. Its small size and nearly constant output potential during use make it suitable for

Quick Tip to Solve: For the textbook hearing-aid application, recall the compact mercury cell and its nearly constant voltage.

operating such low-current electronic devices.

Step 2: Distinguish the alternatives A dry cell is the common zinc-carbon cell used in devices such as torches. A nickel-cadmium cell is a rechargeable secondary cell. A fuel cell produces electricity while fuel and oxidant are continuously supplied. These descriptions do not match the standard CBSE identification of the hearing-aid cell. The mercury cell has the overall reaction $Zn + HgO \longrightarrow ZnO + Hg$.

Step 3: Conclusion The cell used in hearing aids is the mercury cell. Hence, the correct option is (B).

Quick Tip to Solve: For the textbook hearing-aid application, recall the compact mercury cell and its nearly constant voltage.

12. Aniline on reaction with Bromine water gives : [1 mark]

(A) o-bromoaniline

(B) 2,4,6-tribromoaniline

(C) m-bromoaniline

(D) p-bromoaniline

Correct Answer: (B) 2,4,6-tribromoaniline

Solution:

Concept:

- The $-NH_2$ group strongly activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- In bromine water, unprotected aniline undergoes substitution at both ortho positions and the para position.

Step 1: Apply the directing effect The lone pair on nitrogen participates in resonance with the aromatic ring. This increases electron density especially at positions 2, 4 and 6 relative to the amino group. As a result, bromination of aniline occurs readily without a Lewis-acid catalyst.

Step 2: Identify the product under the stated conditions Bromine water gives a white precipitate of 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr.$$

The ortho- and para-monobromo products listed in (A) and (D) do not represent the product with bromine water. The meta product in (C) contradicts the directing effect of $-NH_2$.

Step 3: Conclusion Aniline reacts with bromine water to form 2,4,6-tribromoaniline. Hence, the correct option is (B).

Quick Tip to Solve: When unprotected aniline meets bromine water, put bromine at 2, 4 and 6 rather than stopping at one substitution.

13. Assertion (A): $\Delta_{mix}H$ and $\Delta_{mix}V$ are zero for an ideal solution.

Reason (R): The solution which obeys Raoult's law over the entire range of concentration is called an ideal solution. [1 mark]

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

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

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

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

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

Solution:

Concept:

- An ideal solution obeys Raoult's law, $p_i = x_i p_i^0$, over the entire composition range.
- For ideal mixing, $\Delta_{\text{mix}} H = 0$ and $\Delta_{\text{mix}} V = 0$; unlike and like intermolecular interactions have comparable strengths.

Step 1: Judge the Assertion The Assertion is true. In an ideal solution, replacing A–A and B–B contacts by A–B contacts involves no net enthalpy change. Mixing also causes no expansion or contraction. Thus both $\Delta_{\text{mix}} H$ and $\Delta_{\text{mix}} V$ are zero.

Step 2: Judge the Reason The Reason is true: obeying Raoult's law throughout the concentration range is the defining behaviour of an ideal solution. Here p_i is the partial vapour pressure of component i, x_i its mole fraction and p_i^0 its pure-liquid vapour pressure.

Step 3: Check the explanatory link The Reason states the definition of an ideal solution, but does not explain why mixing causes neither an enthalpy change nor a volume change. The explanation rests on the comparable intermolecular interactions. Therefore both statements are true, while the given Reason is not the correct explanation of the Assertion. Options (C) and (D) wrongly classify a statement as false, and (A) assigns the explanatory link incorrectly.

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

Quick Tip to Solve: Judge truth and explanation separately: a definition of ideality does not itself explain the absence of mixing changes.

14. Assertion (A): Rate of reaction decreases with increase in temperature.

Reason (R): Number of effective collisions increases with increase in temperature. [1 mark]

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

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

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

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

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

Solution:

Concept:

- For a typical reaction with positive activation energy, $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, T absolute temperature and A the pre-exponential factor.
- Effective collisions require sufficient energy and a suitable molecular orientation; raising temperature increases the fraction of molecules with sufficient energy.

Step 1: Judge the Assertion The Assertion is false. Under the usual comparison at the same reactant concentrations, the rate of reaction increases with an increase in temperature. More molecules can cross the activation-energy barrier, so the rate constant increases rather than decreases.

Step 2: Judge the Reason The Reason is true. Increasing temperature increases the proportion of collisions with energy at least equal to the activation energy. This increases the number of effective collisions and therefore the reaction rate.

Step 3: Select the correct code The required combination is a false Assertion and a true Reason. Option (D) states precisely this combination. Options (A) and (B) incorrectly treat the Assertion as true, while option (C) incorrectly treats the Reason as false. Since the Assertion is false, the question of the Reason explaining a true Assertion does not arise.

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

Quick Tip to Solve: For this temperature statement, test the direction first: heating usually increases effective collisions and rate.

15. Assertion (A): Phenol on reaction with aqueous NaOH gives sodium phenoxide.
Reason (R): This reaction supports the acidic nature of phenol. [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:

- Phenol is a weak acid: it can donate the proton of its $-\mathrm{OH}$ group to a sufficiently strong base.
- The phenoxide ion, $\mathrm{C_6H_5O^-}$, is stabilised by resonance; sodium hydroxide supplies $\mathrm{OH^-}$, which accepts the proton.

Step 1: Evaluate the assertion Phenol reacts with aqueous sodium hydroxide by an acid-base reaction:

$$\mathrm{C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O.}$$

Sodium phenoxide is formed, so Assertion (A) is true. This is removal of the hydroxyl proton, not replacement of the hydroxyl group by sodium.

Step 2: Evaluate the reason Formation of a salt with a base supports the acidic nature of phenol. The phenol molecule donates $\mathrm{H^+}$, while hydroxide forms water. Hence Reason (R) is also true.

Step 3: Check the explanatory connection The acid-base character identified in the reason accounts for why phenol reacts with NaOH to give sodium phenoxide. The reaction is the characteristic neutralisation of an acid by a base, so R correctly explains A. Option (B) would deny this connection, and (C) and (D) incorrectly label one of the true statements false.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is $\boxed{\text{(A)}}$.

Quick Tip to Solve: Recognise phenoxide formation as loss of the O–H proton: salt formation with NaOH demonstrates phenol's acidity.

16. Assertion (A): Boiling point of butan-1-ol is higher than that of butan-1-amine.

Reason (R): Being more polar, butan-1-ol forms stronger intermolecular hydrogen bonds as compared to butan-1-amine. [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:

- Boiling requires overcoming intermolecular attractions. Stronger attractions generally raise the boiling point of comparable molecules.
- Oxygen is more electronegative than nitrogen, so an $O-H$ bond is more polar than an $N-H$ bond; alcohols form stronger hydrogen bonds than analogous amines.

Step 1: Evaluate the assertion Butan-1-ol and butan-1-amine both have unbranched chains of four carbon atoms, so their carbon skeletons are comparable. Butan-1-ol has the higher boiling point because its molecules are more strongly associated. Thus Assertion (A) is true.

Step 2: Evaluate the reason Both substances form intermolecular hydrogen bonds. However, the greater electronegativity of oxygen makes the $O-H$ group more polar, and the $O-H\cdots O$ hydrogen bonds in the alcohol are stronger than the $N-H\cdots N$ bonds in the amine. Reason (R) is true; the presence of two N–H bonds does not make each hydrogen bond stronger.

Step 3: Relate the reason to the boiling point Stronger hydrogen bonding in butan-1-ol means more energy is needed to separate its molecules into the vapour phase. This directly explains the higher boiling point. Option (B) incorrectly denies this explanation; options (C) and (D) wrongly call one of the statements false.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is $\boxed{\text{(A)}}$.

Quick Tip to Solve: For comparable alcohol and amine carbon chains, compare O–H with N–H bond polarity before comparing boiling points.

Section B (10 marks)

17. Write the reactions of glucose with :

(a) HI

(b) $(CH_3CO)_2O$ [2 marks]

Solution:

Concept:

- Prolonged heating of glucose with excess HI completely reduces its oxygen-containing groups and gives n-hexane, revealing a straight chain of six carbon atoms.
- Acetic anhydride acetylates each free hydroxyl group: $-OH$ becomes $-OCOCH_3$. Glucose has five such hydroxyl groups and gives glucose pentaacetate.

Step 1: (a) Reaction with HI On prolonged heating with hydroiodic acid, glucose is reduced to n-hexane:

$$CHO(CHOH)_4CH_2OH \xrightarrow{\text{excess HI, prolonged heating}} CH_3(CH_2)_4CH_3.$$

The product has all six carbon atoms in one unbranched chain. The balanced overall equation is

$$C_6H_{12}O_6 + 14HI \longrightarrow C_6H_{14} + 6H_2O + 7I_2.$$

Step 2: (b) Reaction with acetic anhydride Acetic anhydride reacts with the five hydroxyl groups of glucose to form glucose pentaacetate:

$$\text{Glucose} + 5(CH_3CO)_2O \longrightarrow \text{Glucose pentaacetate} + 5CH_3COOH.$$

Each of the five hydroxyl hydrogens is replaced by an acetyl group, CH_3CO-, forming five ester groups. The remaining oxygen is not a sixth free hydroxyl group; therefore the product is a pentaacetate. Formation of the pentaacetate establishes the presence of five hydroxyl groups in glucose.

Step 3: Conclusion Glucose gives $\boxed{n\text{-hexane}}$ with HI on prolonged heating and $\boxed{\text{glucose pentaacetate}}$ with acetic anhydride.

Quick Tip to Solve: Link HI reduction to the six-carbon chain, and count only the five free hydroxyl groups for acetylation.

18(a). Define molal depression constant. How is it related to enthalpy of fusion ? [2 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property. For a dilute solution of a non-volatile, non-electrolyte solute, $\Delta T_f = K_f m$, where m is the molality.
- The molal depression constant K_f, also called the cryoscopic constant, depends on the solvent and

Quick Tip to Solve: Use the solvent's freezing point in kelvin, and insert the factor 1000 only if molar mass is given in grams per mole.

is related to its freezing temperature, molar mass and molar enthalpy of fusion.

Step 1: Define molal depression constant The molal depression constant is the depression in the freezing point of a solvent when one mole of a non-volatile, non-electrolyte solute is dissolved in one kilogram of the solvent. Equivalently, it is the freezing-point depression for a solution of unit molality in the dilute-solution relation

$$K_f = \frac{\Delta T_f}{m}.$$

Its SI-compatible unit is $\mathrm{K\,kg\,mol^{-1}}$. A temperature difference of one kelvin equals a difference of one degree Celsius.

Step 2: State the relation with enthalpy of fusion The required relation is

$$\boxed{K_f = \frac{R(T_f^0)^2 M_1}{\Delta H_{\text{fus}}}}.$$

Here R is the gas constant, T_f^0 is the freezing point of the pure solvent in kelvin, M_1 is its molar mass in $\mathrm{kg\,mol^{-1}}$, and ΔH_{fus} is the molar enthalpy of fusion in $\mathrm{J\,mol^{-1}}$. If molar mass is entered in $\mathrm{g\,mol^{-1}}$, the denominator includes an additional factor of 1000. This relation follows from the solid-liquid equilibrium for an ideal dilute solution.

Step 3: Conclusion K_f is the freezing-point depression per unit molality. Its relation to fusion enthalpy is

$$\boxed{K_f = \frac{R(T_f^0)^2 M_1}{\Delta H_{\text{fus}}}},$$

with M_1 expressed in $\mathrm{kg\,mol^{-1}}$.

Quick Tip to Solve: Use the solvent's freezing point in kelvin, and insert the factor 1000 only if molar mass is given in grams per mole.

OR

18(b). What type of deviation is shown by ethanol and acetone mixture ? Give reason. What type of azeotropic mixture is formed by that deviation ? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal solution gives $p_i = x_i p_i^0$, where x_i is the liquid mole fraction and p_i^0 is the vapour pressure of the pure component.
- Positive deviation occurs when unlike-molecule attractions are weaker than the relevant attractions in the pure liquids. The components then escape more readily into the vapour phase.
- A minimum-boiling azeotrope has a maximum in total vapour pressure and a boiling point below those of both pure components at the same external pressure.

Step 1: Identify the deviation The ethanol-acetone mixture shows positive deviation from Raoult's

Quick Tip to Solve: Weaker attractions mean higher vapour pressure; higher vapour pressure reaches atmospheric pressure at a lower boiling temperature.

law. Its observed vapour pressure exceeds the ideal value predicted from the mole fractions and pure-component vapour pressures.

Step 2: Explain the molecular reason Pure ethanol molecules are associated through strong intermolecular hydrogen bonds. On adding acetone, some acetone molecules enter between ethanol molecules and disrupt these ethanol-ethanol associations. Although ethanol and acetone can also interact, the resulting unlike-molecule attractions are weaker overall than the attractions that have been disrupted. Consequently, molecules escape more easily from the liquid, and the vapour pressure rises above the Raoult's-law prediction.

Step 3: Identify the azeotrope A sufficiently large positive deviation gives a maximum in vapour pressure and therefore a minimum in boiling temperature. The resulting constant-boiling mixture is a minimum-boiling azeotrope. At its azeotropic composition, liquid and vapour have the same composition, so ordinary fractional distillation cannot separate that mixture further.

Step 4: Conclusion Ethanol-acetone shows $\boxed{\text{positive deviation}}$ because mixing weakens the effective intermolecular attractions; this type of deviation forms a $\boxed{\text{minimum-boiling azeotrope}}$.

Quick Tip to Solve: Weaker attractions mean higher vapour pressure; higher vapour pressure reaches atmospheric pressure at a lower boiling temperature.

19. (a) In a reaction, if the concentration of reactant 'X' is tripled, the rate of reaction becomes twenty-seven times. What is the order of the reaction ?

(b) State a condition under which a bimolecular reaction is kinetically a first-order reaction. Give an example of such a reaction. [2 marks]

Solution:

Concept:

- The rate law is $r = k[X]^n$, where r is the reaction rate, k the rate constant and n the order with respect to reactant X.
- For a reaction involving two reactants, keeping one in large excess makes its concentration effectively constant and can produce pseudo-first-order kinetics.

Step 1: (a) Compare the two rates At the same temperature, k remains unchanged. If the initial concentration is $[X]$, the new concentration is $3[X]$. Thus

$$\frac{r_2}{r_1} = \frac{k(3[X])^n}{k[X]^n} = 3^n = 27 = 3^3.$$

Equating the exponents gives $n = 3$. The rate therefore depends on the cube of the concentration of X.

Step 2: (b) Keep one reactant in large excess In a bimolecular reaction with rate $r = k[A][B]$, if B is present in large excess, its concentration changes negligibly during the reaction. Writing $k' = k[B]$ gives $r = k'[A]$, which is first order in the measured reactant. An example is acid-catalysed hydrolysis

Quick Tip to Solve: Write the rate ratio as $3^n = 27$ before finding the order; for pseudo-first order, identify the reactant whose concentration stays effectively constant.

of ethyl acetate in excess water:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH.$$

At fixed acid concentration, the almost constant water concentration is included in the observed rate constant, so the rate depends on ester concentration alone.

Step 3: Conclusion (a) The order is $\boxed{3}$. (b) A bimolecular reaction is pseudo-first order when one reactant is in large excess; hydrolysis of ethyl acetate in excess water is an example.

Quick Tip to Solve: Write the rate ratio as $3^n = 27$ before finding the order; for pseudo-first order, identify the reactant whose concentration stays effectively constant.

20. Complete and balance the following chemical equations :

(a) $3\,MnO_4^{2-} + 4\,H^+ \longrightarrow$ **?**

(b) $Cr_2O_7^{2-} + 14\,H^+ + 6\,Fe^{2+} \longrightarrow$ **?** [2 marks]

Solution:

Concept:

- Disproportionation means that the same species undergoes oxidation and reduction. In MnO_4^{2-}, manganese has oxidation state $+6$.
- In acidic medium, dichromate is reduced to Cr^{3+}, while Fe^{2+} is oxidised to Fe^{3+}. A balanced ionic equation conserves both atoms and charge.

Step 1: (a) Balance the disproportionation of manganate On acidification, manganese in two manganate ions is oxidised from $+6$ to $+7$, forming permanganate. Manganese in the third ion is reduced from $+6$ to $+4$, forming manganese dioxide. The two electrons lost equal the two gained. Balancing oxygen and hydrogen gives

$$3\,MnO_4^{2-} + 4\,H^+ \longrightarrow 2\,MnO_4^- + MnO_2 + 2\,H_2O.$$

There are three Mn atoms, twelve O atoms and four H atoms on each side. The total charge is -2 on each side, confirming the balance.

Step 2: (b) Balance dichromate reduction by iron(II) Each of the two chromium atoms changes from $+6$ to $+3$, requiring six electrons altogether. Each iron(II) ion loses one electron, so six such ions are needed. The balanced equation is

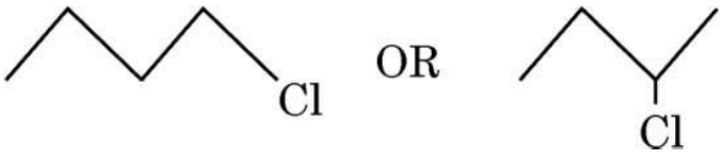
$$Cr_2O_7^{2-} + 14\,H^+ + 6\,Fe^{2+} \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O.$$

Seven water molecules balance the oxygen atoms and fourteen hydrogen ions balance hydrogen. The total charge on the left is $-2 + 14 + 12 = 24$, matching $6 + 18 = 24$ on the right.

Step 3: Conclusion (a) The products are $2\,MnO_4^- + MnO_2 + 2\,H_2O$. (b) The products are $2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$, with the balanced equations shown above.

Quick Tip to Solve: Check the starting ion's charge: manganate has $2-$ and disproportionates on acidification. After balancing atoms, always compare the total charges.

21. (a) Which halogen compound in the following pair will react faster in S_N2 reaction and why ?
(b) Why does the presence of nitro groups at ortho- and para- positions in haloarenes increase their reactivity towards nucleophilic substitution reaction ? [2 marks]



Solution:

Concept:

- An S_N2 reaction is a single-step substitution in which a nucleophile attacks from the side opposite the leaving group. Lower steric hindrance permits faster attack.
- An electron-withdrawing nitro group at an ortho or para position stabilises the negatively charged intermediate in nucleophilic aromatic substitution through resonance.

Step 1: (a) Compare the carbon atoms bonded to chlorine The left-hand skeletal structure is 1-chlorobutane, $CH_3CH_2CH_2CH_2Cl$, a primary alkyl chloride. The right-hand structure is 2-chlorobutane, $CH_3CH_2CH(Cl)CH_3$, a secondary alkyl chloride. The carbon bearing chlorine has one alkyl group in the first compound and two in the second. The nucleophile can approach the primary carbon more easily from the back because fewer alkyl groups obstruct its path. Hence, the left-hand compound, 1-chlorobutane, reacts faster by the S_N2 mechanism. Both compounds have the same leaving group, so the difference is due to steric hindrance.

Step 2: (b) Explain activation by ortho and para nitro groups The $-NO_2$ group withdraws electron density by both inductive and resonance effects. It makes the carbon bonded to halogen more susceptible to attack by a nucleophile. During attack, a negatively charged intermediate forms; its negative charge is delocalised to the ortho and para positions of the ring. A nitro group at either of these positions allows further delocalisation of this charge onto its oxygen atoms. This stabilises the intermediate and lowers the activation barrier, increasing the rate of substitution. A meta nitro group cannot provide this direct resonance stabilisation of the intermediate.

Step 3: Conclusion (a) Left-hand 1-chlorobutane reacts faster because it is less sterically hindered. (b) Ortho and para nitro groups increase reactivity by withdrawing electron density and stabilising the anionic intermediate through resonance.

Quick Tip to Solve: For S_N2, first count alkyl groups on the carbon bearing halogen. For activated haloarenes, check whether the nitro group can stabilise the intermediate by resonance.

Section C (21 marks)

22. (a) What type of nucleophilic substitution (S_N1 or S_N2) occurs in the hydrolysis of 2-Bromobutane to form ($\pm$)-Butan-2-ol ? Give reason.

(b) What happens when chlorobenzene and methyl chloride are treated with sodium metal in dry ether ? [3 marks]

Solution:

Concept:

- The S_N1 mechanism involves formation of a carbocation followed by nucleophilic attack. The carbocation carbon is sp^2-hybridised and planar, so attack can occur from either face.
- Racemisation produces a mixture of the two enantiomers. An S_N2 substitution instead proceeds by a single backside attack and gives inversion of configuration.
- The Wurtz–Fittig reaction couples an aryl halide and an alkyl halide using sodium metal in dry ether, forming a carbon–carbon bond.

Step 1: (a) Identify the mechanism from the product The formation of ($\pm$)-butan-2-ol indicates racemisation at carbon 2. It is explained by the S_N1 mechanism: the carbon–bromine bond first breaks heterolytically, releasing bromide and producing a secondary carbocation.

$$CH_3CH(Br)CH_2CH_3 \longrightarrow CH_3CH^+CH_2CH_3 + Br^-.$$

Carbocation formation is the slow, rate-determining step. The positively charged carbon has a planar arrangement of its three attached groups.

Step 2: Explain attack on the planar intermediate Water attacks the carbocation from either face of its plane, followed by loss of a proton from the oxonium ion to form the alcohol:

$$CH_3CH^+CH_2CH_3 + H_2O \longrightarrow CH_3CH(OH_2{}^+)CH_2CH_3$$

$$CH_3CH(OH_2{}^+)CH_2CH_3 \longrightarrow CH_3CH(OH)CH_2CH_3 + H^+.$$

Attack from opposite faces produces opposite configurations at carbon 2, giving the two enantiomers denoted by ($\pm$). A single backside S_N2 attack would give inversion rather than this racemised product, so it does not explain the stated outcome.

Step 3: (b) Write the coupling reaction Chlorobenzene and methyl chloride react with sodium metal in dry ether by the Wurtz–Fittig reaction. The phenyl group is joined to the methyl group, forming toluene (methylbenzene):

$$C_6H_5Cl + CH_3Cl + 2\,Na \xrightarrow{\text{dry ether}} C_6H_5CH_3 + 2\,NaCl.$$

Two sodium atoms remove the two chlorine atoms as sodium chloride. Dry ether provides an anhydrous medium; water would consume the reactive sodium.

Step 4: Conclusion (a) The hydrolysis proceeds by S_N1, because a planar carbocation permits attack from both faces and leads to racemisation. (b) Toluene, $C_6H_5CH_3$, is formed by Wurtz–Fittig coupling.

Quick Tip to Solve: Use the ($\pm$) product as the clue to a planar S_N1 intermediate; for Wurtz–Fittig coupling, join the aryl and alkyl groups and add $2\,NaCl$.

23. A first-order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% complete ?

[Given : log 2 = 0.30, log 3 = 0.48, log 4 = 0.60, log 5 = 0.69] [3 marks]

Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are the initial and remaining reactant concentrations, and t is elapsed time.
- If $x\%$ has reacted, $(100-x)\%$ remains. The concentration ratio is $100/(100-x)$; the rate constant has units of inverse time.

Step 1: Calculate the rate constant from the remaining reactant At $t = 40\,\text{min}$, completion is 25%, so the unreacted fraction is 75%, not 25%. Thus,

$$\begin{aligned} k &= \frac{2.303}{40}\log\frac{100}{75} = \frac{2.303}{40}\log\frac{4}{3} \\ &= \frac{2.303}{40}(\log 4 - \log 3) = \frac{2.303}{40}(0.60 - 0.48) \\ &= 0.006909\,\text{min}^{-1}. \end{aligned}$$

The given logarithms have been used consistently rather than replacing them with more precise calculator values.

Step 2: Find the total time for 80 percent completion For 80% completion, 20% of the original reactant remains. The rate constant is unchanged at the same temperature, so

$$\begin{aligned} t_{80} &= \frac{2.303}{k}\log\frac{100}{20} = \frac{2.303 \times 0.69}{0.006909} \\ &= 230\,\text{min}. \end{aligned}$$

Equivalently, $t_{80}/40 = \log 5/\log(4/3) = 0.69/0.12$. This is measured from the start. The further time after the first 40 minutes would be $230 - 40 = 190\,\text{min}$.

Step 3: Conclusion The rate constant is $\boxed{k = 6.909 \times 10^{-3}\,\text{min}^{-1}}$, and 80% completion occurs in a total time of $\boxed{230\,\text{min}}$.

Quick Tip to Solve: Convert percent completion into percent remaining first; divide logarithmic concentration ratios to find the time ratio without rounding k.

24. (a) Write the reactions involved in the following :

(i) Reimer-Tiemann reaction

(ii) Kolbe's reaction

(b) Name the reagent used in the bromination of phenol to form 2,4,6-Tribromophenol. [3 marks]

Solution:

Concept:

- Phenol undergoes electrophilic substitution readily because its hydroxyl group activates the benzene ring and directs substitution mainly to the ortho and para positions.
- The Reimer–Tiemann reaction introduces an ortho formyl group $(-CHO)$, whereas Kolbe's reaction introduces an ortho carboxyl group $(-COOH)$ after acidification.

Step 1: (a)(i) Reimer–Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify the reaction mixture. The major product is 2-hydroxybenzaldehyde (salicylaldehyde), with the formyl group ortho to the hydroxyl group. The net reaction after work-up is

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

Chloroform in alkali generates the reactive dichlorocarbene species; subsequent hydrolysis gives the aldehyde group.

Step 2: (a)(ii) Kolbe's reaction First convert phenol to sodium phenoxide. Treat sodium phenoxide with carbon dioxide at approximately $400\,K$ under pressure, then acidify the sodium salicylate formed:

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O,$$

$$C_6H_5ONa + CO_2 \xrightarrow[\text{pressure}]{400\,K} o\text{-}HOC_6H_4COONa,$$

$$o\text{-}HOC_6H_4COONa + HCl \longrightarrow o\text{-}HOC_6H_4COOH + NaCl.$$

The product is 2-hydroxybenzoic acid (salicylic acid); the carboxyl group is ortho to the hydroxyl group.

Step 3: (b) Reagent for tribromination Use bromine water, $Br_2(aq)$. Phenol reacts with it at room temperature to form a white precipitate of 2,4,6-tribromophenol:

$$C_6H_5OH + 3Br_2 \longrightarrow 2,4,6\text{-}C_6H_2Br_3OH + 3HBr.$$

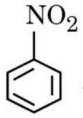
The aqueous reagent promotes substitution at all three activated positions. Bromine in a non-polar solvent under controlled conditions instead favours monobromination.

Step 4: Conclusion Reimer–Tiemann gives o-HOC_6H_4CHO; Kolbe's reaction gives o-HOC_6H_4COOH after acidification. The reagent for 2,4,6-tribromophenol is $\boxed{\text{bromine water}}$.

Quick Tip to Solve: Associate chloroform/alkali with ortho-CHO, carbon dioxide/phenoxide with ortho-COOH, and bromine water with three bromine substitutions.

25. Give the structures of A, B and C in the following reactions: [3 marks]

(a) $CH_3CH_2Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(b)  $\xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{C_6H_5OH} C$

Solution:

Concept:

- Potassium cyanide substitutes an alkyl halide through the carbon end of CN^-, forming a nitrile with one additional carbon. $LiAlH_4$ reduces the nitrile group to $-CH_2NH_2$.
- Primary aliphatic amines react with nitrous acid to give alcohols with nitrogen evolution. Aromatic primary amines instead form diazonium salts at 273–278 K.
- Benzenediazonium salts undergo azo coupling with phenol in alkaline medium, mainly at the para position relative to $-OH$, giving an azo linkage $-N=N-$.

Step 1: (a) Identify the nitrile and the primary aliphatic amine Ethyl chloride reacts with KCN to form propanenitrile, since the carbon atom of the cyanide group joins the two-carbon ethyl group:

$$CH_3CH_2Cl \xrightarrow{KCN} \underbrace{CH_3CH_2C \equiv N}_{A}.$$

Reduction converts the nitrile carbon into a methylene group without removing it:

$$CH_3CH_2C \equiv N \xrightarrow{LiAlH_4} \underbrace{CH_3CH_2CH_2NH_2}_{B}.$$

Therefore A is propanenitrile and B is propan-1-amine; both contain three carbon atoms.

Step 2: (a) Identify the product with nitrous acid The primary aliphatic amine reacts with nitrous acid at the printed $0°C$. Its aliphatic diazonium intermediate is unstable even at this temperature and loses nitrogen, giving the corresponding alcohol:

$$CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow \underbrace{CH_3CH_2CH_2OH}_{C} + N_2 + H_2O.$$

Thus C is propan-1-ol. The low temperature does not make an aliphatic diazonium salt an isolable final product.

Step 3: (b) Reduce nitrobenzene and diazotise aniline Iron and hydrochloric acid reduce the nitro group of nitrobenzene to an amino group. A is aniline, $C_6H_5NH_2$, obtained as the free amine after

Quick Tip to Solve: Count the cyanide carbon in part (a); in part (b), keep the diazonium group at low temperature and put the azo linkage para to phenol's OH.

work-up. At 273 K, sodium nitrite and hydrochloric acid generate nitrous acid for diazotisation:

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} \underbrace{C_6H_5NH_2}_{A},$$

$$C_6H_5NH_2 \xrightarrow[273\,K]{NaNO_2+HCl} \underbrace{[C_6H_5N \equiv N]^+Cl^-}_{B}.$$

B is benzenediazonium chloride, retaining the diazonium group bonded to the benzene ring.

Step 4: (b) Couple the diazonium salt with phenol Coupling with phenol in alkaline medium introduces the azo group mainly para to its hydroxyl group:

$$C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{\text{alkaline medium}} \underbrace{p\text{-}HOC_6H_4 - N = N - C_6H_5}_{C} + HCl.$$

This is 4-(phenylazo)phenol, also called p-hydroxyazobenzene, an orange azo dye. The structure contains two benzene rings joined by $-N = N-$, with OH para to that linkage on one ring.

Step 5: Conclusion (a) $A = CH_3CH_2C \equiv N$, $B = CH_3CH_2CH_2NH_2$, $C = CH_3CH_2CH_2OH$. (b) $A = C_6H_5NH_2$, $B = [C_6H_5N \equiv N]^+Cl^-$, $C = p\text{-}HOC_6H_4 - N = N - C_6H_5$.

Quick Tip to Solve: Count the cyanide carbon in part (a); in part (b), keep the diazonium group at low temperature and put the azo linkage para to phenol's OH.

26. How will you bring about the following conversions ? (any three)

(a) Benzoic acid to Benzaldehyde

(b) Ethanal to Propanone

(c) Acetophenone to Benzoic acid

(d) Bromobenzene to 1-Phenylethanol [3 marks]

Solution:

Concept:

- A carboxylic acid is converted into its acid chloride, which gives an aldehyde on controlled Rosenmund reduction using hydrogen and poisoned palladium on barium sulphate.
- Grignard reagents add a carbon group to a carbonyl carbon. Addition to ethanal followed by acidic hydrolysis gives a secondary alcohol, which can be oxidised to a ketone.
- A methyl ketone undergoes the haloform reaction with iodine and alkali, forming a carboxylate salt and iodoform. Acidification releases the carboxylic acid.

Step 1: (a) Benzoic acid to benzaldehyde First treat benzoic acid with thionyl chloride to obtain benzoyl chloride. Then carry out Rosenmund reduction:

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl,$$

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl.$$

Quick Tip to Solve: Count carbons first: a Grignard addition supplies the extra carbon group, whereas the haloform reaction removes the methyl carbon of a methyl ketone.

The poisoned catalyst controls the reduction at the aldehyde stage, preventing further reduction to benzyl alcohol.

Step 2: (b) Ethanal to propanone Add methylmagnesium bromide to ethanal in dry ether, then hydrolyse with dilute acid to obtain propan-2-ol. Oxidise this secondary alcohol with acidified potassium dichromate:

$$\begin{aligned} \mathrm{CH_3CHO} + \mathrm{CH_3MgBr} &\xrightarrow{\text{dry ether}} \mathrm{CH_3CH(OMgBr)CH_3}, \\ \mathrm{CH_3CH(OMgBr)CH_3} &\xrightarrow{\mathrm{H_3O^+}} \mathrm{CH_3CH(OH)CH_3}, \\ \mathrm{CH_3CH(OH)CH_3} + [\mathrm{O}] &\xrightarrow{\mathrm{K_2Cr_2O_7/H^+}} \mathrm{CH_3COCH_3} + \mathrm{H_2O}. \end{aligned}$$

The Grignard step adds the required third carbon; oxidation then forms the ketone without changing the carbon skeleton.

Step 3: (c) Acetophenone to benzoic acid Acetophenone contains the $-\mathrm{COCH_3}$ group. Treat it with iodine and aqueous sodium hydroxide, then acidify the sodium benzoate obtained:

$$\begin{aligned} \mathrm{C_6H_5COCH_3} + 3\mathrm{I_2} + 4\mathrm{NaOH} &\longrightarrow \\ &\mathrm{C_6H_5COONa} + \mathrm{CHI_3} + 3\mathrm{NaI} + 3\mathrm{H_2O}, \\ \mathrm{C_6H_5COONa} + \mathrm{HCl} &\longrightarrow \mathrm{C_6H_5COOH} + \mathrm{NaCl}. \end{aligned}$$

The methyl carbon is removed as yellow iodoform, while the carbonyl carbon remains in benzoic acid.

Step 4: (d) Bromobenzene to 1-phenylethanol Prepare phenylmagnesium bromide using magnesium in dry ether. React it with ethanal and then hydrolyse the magnesium alkoxide:

$$\begin{aligned} \mathrm{C_6H_5Br} + \mathrm{Mg} &\xrightarrow{\text{dry ether}} \mathrm{C_6H_5MgBr}, \\ \mathrm{C_6H_5MgBr} + \mathrm{CH_3CHO} &\longrightarrow \mathrm{C_6H_5CH(OMgBr)CH_3}, \\ \mathrm{C_6H_5CH(OMgBr)CH_3} &\xrightarrow{\mathrm{H_3O^+}} \mathrm{C_6H_5CH(OH)CH_3}. \end{aligned}$$

Anhydrous conditions are essential during Grignard formation and addition because moisture destroys the reagent. The final alcohol is 1-phenylethanol.

Step 5: Conclusion The conversions use, respectively, acid-chloride formation followed by Rosenmund reduction; methyl Grignard addition followed by oxidation; haloform reaction followed by acidification; and phenyl Grignard addition to ethanal followed by hydrolysis. Any three of these routes answer the question.

Quick Tip to Solve: Count carbons first: a Grignard addition supplies the extra carbon group, whereas the haloform reaction removes the methyl carbon of a methyl ketone.

27. A solution is prepared by dissolving 5 g of a non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 300 K. Calculate the molar mass of the solute. (Vapour pressure of pure water at 300 K = 32 mm Hg) [3 marks]

Solution:

Concept:

- For a solution of a non-volatile solute, Raoult's law gives $p = x_1 p^0$. Here p^0 is the vapour pressure of pure solvent, p is that of the solution, and x_1 is the solvent mole fraction.
- The relative lowering of vapour pressure is $(p^0 - p)/p^0 = x_2 = n_2/(n_1 + n_2)$, where n_1 and n_2 are solvent and solute amounts in moles. For a dilute solution, $n_2 \ll n_1$, so this is approximately n_2/n_1.
- The amount of a substance is $n = w/M$, where w is its mass and M its molar mass. Water has molar mass $18\,\text{g mol}^{-1}$.

Step 1: Calculate the relative lowering of vapour pressure The pure water and solution are both at $300\,\text{K}$, so their vapour pressures can be directly compared. The vapour-pressure lowering is

$$\Delta p = 32 - 31.84 = 0.16\,\text{mm Hg}.$$

Therefore,

$$\frac{\Delta p}{p^0} = \frac{0.16}{32} = 0.005.$$

The pressure units cancel. This small dimensionless value also supports using the dilute-solution approximation.

Step 2: Use the dilute-solution relation to find the molar mass Let the solute molar mass be M_2. With $w_2 = 5\,\text{g}$, $w_1 = 200\,\text{g}$ and $M_1 = 18\,\text{g mol}^{-1}$,

$$\frac{\Delta p}{p^0} \simeq \frac{w_2/M_2}{w_1/M_1},$$

$$M_2 \simeq \frac{w_2 M_1}{w_1(\Delta p/p^0)}$$

$$= \frac{5 \times 18}{200 \times 0.005} = 90\,\text{g mol}^{-1}.$$

The solvent mass must be kept as $200\,\text{g}$; using the total solution mass would incorrectly change the mole ratio.

Step 3: Check against the exact mole-fraction expression Without neglecting solute moles, $n_1 = 200/18$ and

$$0.005 = \frac{n_2}{200/18 + n_2},$$

$$n_2 = \frac{0.005}{0.995}\frac{200}{18},$$

$$M_2 = \frac{5}{n_2} = 89.55\,\text{g mol}^{-1}.$$

This differs from the dilute result by only 0.5%, so both give approximately $90\,\text{g mol}^{-1}$ at the precision appropriate to the data.

Quick Tip to Solve: Calculate the dimensionless relative lowering first; then use solvent mass, rather than solution mass, in the dilute mole-ratio formula.

Step 4: Conclusion The molar mass of the non-volatile solute is approximately $\boxed{90\,\text{g mol}^{-1}}$ by the standard dilute-solution relation. The exact Raoult-law mole-fraction calculation gives $89.55\,\text{g mol}^{-1}$.

Quick Tip to Solve: Calculate the dimensionless relative lowering first; then use solvent mass, rather than solution mass, in the dilute mole-ratio formula.

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28. The conductivity of 0.2 M solution of KCl is 2.48 $\times$ 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given : $\lambda^0_{K+} = 73.5\,\textbf{S cm}^2\,\textbf{mol}^{-1}$, $\lambda^0_{Cl-} = 76.5\,\textbf{S cm}^2\,\textbf{mol}^{-1}$ [3 marks]

Solution:

Concept:

- Molar conductivity is the conductivity contributed by the solution volume containing one mole of electrolyte. When conductivity κ is in S cm^{-1} and concentration C is in mol L^{-1}, $\Lambda_m = 1000\kappa/C$, in S cm^2 mol^{-1}.
- Kohlrausch's law gives the limiting molar conductivity as the sum of limiting ionic contributions. For KCl, $\Lambda^0_m = \lambda^0_{\text{K+}} + \lambda^0_{\text{Cl}-}$, since each formula unit gives one ion of each kind.
- The conductivity-ratio estimate requested here is $\alpha = \Lambda_m/\Lambda^0_m$. For a strong electrolyte such as KCl, this ratio is an apparent degree of dissociation: finite-concentration ionic interactions reduce mobility even though the electrolyte is essentially dissociated.

Step 1: Substitute into the molar-conductivity formula The given values are $\kappa = 2.48 \times 10^{-2}$ S cm^{-1} and $C = 0.2$ mol L^{-1}. Since $1\,\text{L} = 1000\,\text{cm}^3$, the concentration in centimetre units is $0.2/1000$ mol cm^{-3}. Hence,

$$\begin{aligned}\Lambda_m &= \frac{1000\kappa}{C}\\ &= \frac{1000 \times 2.48 \times 10^{-2}}{0.2}\\ &= 124\,\text{S cm}^2\,\text{mol}^{-1}.\end{aligned}$$

The factor of 1000 converts litres to cubic centimetres; omitting it would make the answer too small by that factor.

Step 2: Calculate the limiting molar conductivity Add the supplied limiting conductivities of the two ions:

$$\begin{aligned}\Lambda^0_m &= \lambda^0_{\text{K+}} + \lambda^0_{\text{Cl}-}\\ &= 73.5 + 76.5\\ &= 150.0\,\text{S cm}^2\,\text{mol}^{-1}.\end{aligned}$$

No extra stoichiometric factors are needed because KCl contains one potassium ion and one chloride ion per formula unit.

Step 3: Obtain the requested conductivity ratio Using the relation intended by the question,

$$\alpha = \frac{\Lambda_m}{\Lambda^0_m} = \frac{124}{150} = 0.8267 \simeq 0.827.$$

Quick Tip to Solve: With conductivity in S per centimetre and molarity in moles per litre, include the factor 1000 before dividing by concentration; then add both ionic limiting values.

As a percentage, this is 82.67%. The units cancel, so α is dimensionless. This ratio must not be interpreted as proof that 17.33% of KCl remains as neutral molecules: KCl is a strong electrolyte and its lower molar conductivity at finite concentration also reflects interionic effects on ion motion.

Step 4: Conclusion $\boxed{\Lambda_m = 124\,\text{S cm}^2\,\text{mol}^{-1}}$, and the requested conductivity-based value is $\boxed{\alpha \simeq 0.827}$, or 82.67% (an apparent degree of dissociation for KCl).

Quick Tip to Solve: With conductivity in S per centimetre and molarity in moles per litre, include the factor 1000 before dividing by concentration; then add both ionic limiting values.

Section D (8 marks)

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

29. The involvement of $(n-1)d$ electrons in the behaviour of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions. The transition metals react with a number of non-metals like oxygen, nitrogen and halogens. $KMnO_4$ and $K_2Cr_2O_7$ are common examples.

The two series of inner transition elements, lanthanoids and actinoids, constitute the f-block of the periodic table. In the lanthanoids, there is regular decrease in atomic size with increase in atomic number due to the imperfect shielding effect of 4f-orbital electrons which causes contraction.

Answer the following questions: [4 marks]

29(a). Why do transition metals and their compounds act as good catalysts ? [1 mark]

Solution:

Concept:

- A catalyst increases the reaction rate by providing an alternative pathway with a lower activation energy.
- Transition metals can exhibit variable oxidation states and can form intermediate complexes with reactants.

Step 1: Use variable oxidation states A transition-metal ion can change its oxidation state during a reaction. It can therefore accept electrons in one step and donate them in a later step, providing an alternative sequence of reactions and returning to its original state at the end.

Step 2: Explain intermediate formation Transition metals and their compounds can form intermediate complexes with reactants. Metal surfaces can also adsorb reactants, bringing them together and weakening bonds. These processes lower the activation energy and increase the rate of the reaction.

Step 3: Conclusion Transition metals and their compounds are good catalysts because of their variable oxidation states and their ability to form intermediates or adsorb reactants, giving a lower-activation-energy pathway.

Quick Tip to Solve: Link catalytic activity to variable oxidation states and intermediate formation; merely saying that d electrons are present does not explain the faster reaction.

29(b). What is the cause of contraction in the atomic size of lanthanoids ? [1 mark]

Solution:

Concept:

- Shielding is the reduction in nuclear attraction experienced by outer electrons due to other electrons.
- The $4f$ electrons shield the increasing nuclear charge poorly across the lanthanoid series.

Step 1: Compare nuclear charge and shielding From one lanthanoid to the next, the atomic number and hence nuclear charge increase by one. The additional electron enters the inner $4f$ subshell, whose electrons have a poor shielding effect.

Step 2: Relate effective nuclear charge to size The increased nuclear charge is not fully offset by shielding from the newly added $4f$ electron. The effective nuclear attraction on the outer electrons therefore increases, drawing the electron cloud closer to the nucleus and causing the atomic size to decrease gradually.

Step 3: Conclusion Lanthanoid contraction is caused by the poor shielding of the increasing nuclear charge by $4f$ electrons, which increases effective nuclear attraction and decreases atomic size.

Quick Tip to Solve: State both parts of the cause: nuclear charge increases, while the added 4f electrons shield it poorly.

29(c). Define lanthanoid contraction. How does it affect the atomic radii of the third transition series and the second transition series ? [2 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series with increasing atomic number.
- Poor shielding by $4f$ electrons increases the effective nuclear attraction and influences the sizes of elements that follow the lanthanoids.

Step 1: Define the contraction Lanthanoid contraction is the regular, gradual decrease in the atomic and ionic radii of the lanthanoids from lanthanum to lutetium as atomic number increases. The added $4f$ electrons shield the increasing nuclear charge imperfectly, so the outer electrons experience greater effective nuclear attraction.

Step 2: Compare the second and third transition series The third transition series, the $5d$ series, follows the filling of the $4f$ subshell. An additional principal shell would ordinarily make its atoms larger than those of the corresponding $4d$, or second-series, elements. However, lanthanoid contraction largely offsets this expected increase. Consequently, corresponding elements of the two series have nearly equal atomic radii; for example, zirconium and hafnium have very similar sizes.

Step 3: Conclusion Lanthanoid contraction is the progressive decrease in lanthanoid atomic and ionic radii with increasing atomic number. It makes corresponding third-series $(5d)$ and second-series $(4d)$ transition elements nearly equal in atomic radius, as illustrated by Zr and Hf.

Quick Tip to Solve: For the radius comparison, write that 4f contraction offsets the extra shell in the 5d series; use Zr and Hf as the example.

OR

29(c). In aqueous media, which is a stronger reducing agent — Cr^{2+} or Fe^{2+} and why ? [2 marks]

Solution:

Concept:

- A reducing agent donates electrons and is itself oxidised. A more negative standard reduction potential for the corresponding couple indicates a stronger reducing agent in its reduced form.
- The Cr^{3+} ion has the stable $3d^3$ configuration, while Fe^{3+} has the half-filled $3d^5$ configuration.

Step 1: Examine oxidation of the two ions The relevant oxidation changes in aqueous solution are

$$Cr^{2+} \longrightarrow Cr^{3+} + e^- \quad (3d^4 \longrightarrow 3d^3),$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad (3d^6 \longrightarrow 3d^5).$$

Chromium(II) readily loses an electron to form chromium(III), whose $3d^3$ configuration is stabilised in the aqueous octahedral environment. Both ions can donate an electron, so the comparison must concern their relative tendency to do so.

Step 2: Compare their aqueous electrode potentials The standard reduction potentials are approximately

$$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41\,V, \qquad E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\,V.$$

The substantially more negative reduction potential of the chromium couple means that Cr^{2+} has the greater tendency to undergo the reverse process, oxidation, and donate an electron. Thus, the stability of half-filled Fe^{3+} does not make Fe^{2+} the stronger reducing agent in water.

Step 3: Conclusion Cr^{2+} is the stronger reducing agent in aqueous media. It is readily oxidised to the stable $3d^3$ Cr^{3+} ion, and its couple has a more negative reduction potential than the Fe^{3+}/Fe^{2+} couple.

Quick Tip to Solve: Compare the reduction potentials of the $3+/2+$ couples: the ion belonging to the more negative potential is the stronger electron donor.

30. Proteins are the most abundant biomolecules of the living system. Proteins are the polymers of about twenty different α-amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

On the basis of their molecular shape, proteins are classified into two types: Fibrous and Globular proteins. Structure and shape of proteins can be studied at four different levels i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one. The secondary or tertiary structure of proteins get disturbed on change of pH or temperature and they are not able to perform their functions. This is called denaturation of proteins.

Answer the following questions: [4 marks]

30(a). What are essential amino acids ? [1 mark]

Solution:

Concept:

- Amino acids are the building units of proteins; the body needs a supply of these units for protein synthesis.
- The term essential refers to dietary necessity: the body cannot synthesise these amino acids adequately to meet its needs.

Step 1: Identify the body's limitation Some amino acids cannot be synthesised by the human body. Consequently, the body cannot obtain all the amino acids required for making proteins solely by its own metabolic reactions.

Step 2: State the required source Such amino acids must be supplied through the diet and are therefore called essential amino acids. For example, valine and lysine are essential amino acids. Essential does not mean that other amino acids are unimportant; it specifies the need to obtain these particular amino acids in food.

Step 3: Conclusion Essential amino acids are those which the body cannot synthesise and which must therefore be obtained through the diet.

Quick Tip to Solve: Link the word essential to an essential dietary supply, rather than merely to an amino acid's role in proteins.

30(b). What is meant by zwitter ionic form of amino acids ? [1 mark]

Solution:

Concept:

- An amino acid contains a basic amino group and an acidic carboxyl group in the same molecule.
- A zwitterion has both a positive charge and a negative charge, but its net charge is zero.

Step 1: Explain the internal proton transfer In aqueous solution, the carboxyl group donates a proton to the amino group. The amino group becomes $-NH_3{}^+$, while the carboxyl group becomes $-COO-$. Both charged groups belong to the same amino acid molecule.

Step 2: Write the dipolar form For an α-amino acid with side chain R, the zwitterionic form is

Quick Tip to Solve: Show both charges in the same molecule: an uncharged amino group plus an uncharged carboxyl group is not the zwitterion.

$H_3N^+-CH(R)-COO^-$. The equal and opposite charges cancel overall; nevertheless, the molecule retains distinct positive and negative centres and can react with both acids and bases.

Step 3: Conclusion The zwitterionic form of an amino acid is its dipolar form containing $-NH_3{}^+$ and $-COO-$ groups simultaneously, with zero net charge.

Quick Tip to Solve: Show both charges in the same molecule: an uncharged amino group plus an uncharged carboxyl group is not the zwitterion.

30(c). (i) Give one example each for Fibrous protein and Globular protein.
(ii) What type of linkages hold monomers of proteins together ? [2 marks]

Solution:

Concept:

- Fibrous proteins have extended, fibre-like structures, whereas globular proteins have folded, compact structures.
- The monomers of proteins are α-amino acids. A peptide linkage joins the carboxyl group of one amino acid to the amino group of another.

Step 1: Give the examples in part (i) Keratin, found in hair and nails, is an example of a fibrous protein. Its long protein chains form a fibre-like structure suited to a structural role. Insulin is an example of a globular protein: its chains are folded into a compact structure. Thus the examples are classified by molecular shape, as required by the question.

Step 2: Identify the linkage in part (ii) Amino acid monomers are held together by peptide linkages, $-CO-NH-$. Each linkage forms by condensation between the carboxyl group of one amino acid and the amino group of the next, with loss of a water molecule. The peptide bond is therefore a covalent amide linkage in the protein backbone. Hydrogen bonds help stabilise folded protein structures but are not the bonds joining successive amino acid monomers.

Step 3: Conclusion (i) Fibrous protein: keratin; globular protein: insulin. (ii) Amino acid monomers are joined by peptide linkages, $-CO-NH-$.

Quick Tip to Solve: Pair keratin with the fibre-like structure of hair, and distinguish the backbone peptide bond from hydrogen bonds involved in folding.

OR

30(c). (i) What is the structural feature which characterises a reducing sugar ?

(ii) What is the structural difference between nucleoside and nucleotide ? [2 marks]

Solution:

Concept:

- A reducing sugar has a free aldehydic or ketonic group, or a free anomeric centre that can open to give the corresponding carbonyl form.
- A nucleoside contains a nitrogenous base linked to a pentose sugar. A nucleotide additionally contains a phosphate group.

Step 1: Identify the structural feature in part (i) A reducing sugar possesses a free aldehydic or ketonic group. In a cyclic sugar, this corresponds to a free anomeric hydroxyl group, allowing the ring to open and produce the carbonyl form. This available group enables reduction of reagents such as Fehling's solution or Tollens' reagent. Merely having several hydroxyl groups does not establish reducing behaviour: when the relevant anomeric centres are locked in a glycosidic linkage, as in sucrose, the sugar is non-reducing.

Step 2: Compare the components in part (ii) A nucleoside consists of a nitrogenous base and a pentose sugar. A nucleotide is formed when a phosphate group is attached to the sugar of a nucleoside, usually at its 5-prime carbon. Therefore, nucleoside = base + sugar, whereas nucleotide = base + sugar + phosphate. For example, adenosine is a nucleoside and adenosine monophosphate is a nucleotide.

Step 3: Conclusion (i) A free aldehydic or ketonic group, available through ring opening when the sugar is cyclic, characterises a reducing sugar. (ii) A nucleotide has a phosphate group in addition to the base and pentose sugar of a nucleoside.

Quick Tip to Solve: Check whether the anomeric centre can open to a carbonyl form; for the second part, remember that adding phosphate converts a nucleoside into a nucleotide.

Section E (15 marks)

31(a). (i) Write the major product(s) in the following reactions :

(1) $C_6H_5-CH_2CH_3 \xrightarrow[\text{b) } H^+]{\text{a) } KMnO_4, KOH}$ **?**

(2) $C_6H_5-CHO + CH_3-CO-CH_3 \xrightarrow{\text{dil. NaOH}}$ **?**

(3) Benzoic acid $C_6H_5COOH \xrightarrow{Br_2/FeBr_3}$ **?**

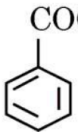
(ii) Give simple chemical tests to distinguish between the following pairs of compounds :

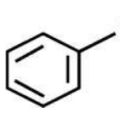
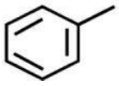
(1) $C_6H_5COCH_3$ **and** $C_6H_5COCH_2CH_3$

(2) Pentanal and Pentan-3-one [5 marks]

(1)  $\xrightarrow[\text{b) } H^+]{\text{a) } KMnO_4\text{ , KOH}}$?

(2)  $+ CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 \xrightarrow{\text{dil NaOH}}$?

(3)  $\xrightarrow{Br_2\,/\,FeBr_3}$?

 and 

Solution:

Concept:

- Alkaline permanganate oxidises an alkylbenzene with a benzylic hydrogen to a benzoate salt; acidification gives benzoic acid.
- Crossed aldol condensation occurs between benzaldehyde, which has no alpha hydrogen, and acetone, which has alpha hydrogens. Dehydration gives an alpha,beta-unsaturated ketone.
- The $-COOH$ group deactivates an aromatic ring and directs electrophilic substitution mainly to the meta position.
- The iodoform test detects a methyl ketone group, $-COCH_3$. Tollens' reagent is reduced by an aldehyde to metallic silver, but an ordinary ketone gives no silver mirror.

Step 1: (i)(1) Oxidise the ethyl side chain Ethylbenzene, $C_6H_5CH_2CH_3$, has benzylic hydrogens on the carbon directly attached to the benzene ring. Treatment with alkaline $KMnO_4$ oxidises the entire side chain to the carboxylate group, irrespective of its original length. Acidification converts potassium benzoate into benzoic acid. The product sequence is

$$C_6H_5CH_2CH_3 \xrightarrow{KMnO_4/KOH} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH.$$

Quick Tip to Solve: For these reactions, check the benzylic hydrogen, the alpha hydrogen, and the meta-directing carboxyl group. For the tests, first identify the specific methyl ketone group or aldehyde group rather than just a carbonyl group.

The aromatic ring remains intact; the final organic product is benzoic acid, rather than benzaldehyde or a two-carbon side-chain alcohol.

Step 2: (i)(2) Carry out crossed aldol condensation Dilute $NaOH$ removes an alpha hydrogen from acetone to generate its enolate. This attacks the carbonyl carbon of benzaldehyde. Protonation first gives the beta-hydroxy ketone $C_6H_5CH(OH)CH_2COCH_3$. Loss of water yields the conjugated condensation product:

$$C_6H_5CHO + CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} C_6H_5CH{=}CHCOCH_3 + H_2O.$$

Thus the product is benzylideneacetone (4-phenylbut-3-en-2-one). Benzaldehyde cannot form its own enolate because it has no alpha hydrogen. If two equivalents of benzaldehyde are supplied, the other methyl group of acetone can also condense, giving $C_6H_5CH{=}CHCOCH{=}CHC_6H_5$, dibenzalacetone; this is the further condensation product.

Step 3: (i)(3) Brominate benzoic acid at the meta position $FeBr_3$ activates bromine for electrophilic aromatic substitution. The electron-withdrawing $-COOH$ group is meta directing, so bromine replaces a ring hydrogen at the meta position relative to this group:

$$C_6H_5COOH + Br_2 \xrightarrow{FeBr_3} \text{m-}BrC_6H_4COOH + HBr.$$

The major product is 3-bromobenzoic acid. The carboxyl group remains attached to the ring.

Step 4: (ii)(1) Use the iodoform test Warm each compound separately with iodine and aqueous sodium hydroxide. Acetophenone, $C_6H_5COCH_3$, contains the methyl ketone group and gives a yellow precipitate of iodoform, CHI_3:

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

Propiophenone, $C_6H_5COCH_2CH_3$, has an ethyl group next to the carbonyl rather than $-COCH_3$; it gives no yellow iodoform precipitate. This visible difference distinguishes the two ketones.

Step 5: (ii)(2) Use Tollens' reagent Warm the samples separately with freshly prepared Tollens' reagent (ammoniacal silver nitrate) in a water bath. Pentanal is an aldehyde and is oxidised to pentanoate while silver(I) is reduced to metallic silver, producing a silver mirror on the test tube:

$$CH_3CH_2CH_2CH_2CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow$$

$$CH_3CH_2CH_2CH_2COO^- + 2\,Ag\downarrow + 4\,NH_3 + 2\,H_2O.$$

Pentan-3-one is an ordinary ketone and does not reduce Tollens' reagent, so it gives no silver mirror.

Step 6: Conclusion (i) The products are benzoic acid, benzylideneacetone (with dibenzalacetone on further condensation), and 3-bromobenzoic acid, respectively. (ii) Acetophenone gives yellow iodoform while propiophenone does not; pentanal gives a Tollens' silver mirror while pentan-3-one does not.

Quick Tip to Solve: For these reactions, check the benzylic hydrogen, the alpha hydrogen, and the meta-directing carboxyl group. For the tests, first identify the specific methyl ketone group or aldehyde group rather than just a carbonyl group.

OR

31(b). (i) Give reasons for the following :

(1) In semicarbazide, only one –NH_2 group is involved in the formation of semicarbazone.

(2) Acetaldehyde is more reactive than acetone towards addition of HCN.

(ii) (1) Arrange the following in decreasing order of their acidic strength : CH_3COOH, $O_2N–CH_2–COOH$, HCOOH

(2) Name the reagent in the following reaction : $CH_3–CH=CH–CH_2–CN \rightarrow CH_3–CH=CH–CH_2–CHO$

(iii) Write the reaction involved in Hell-Volhard-Zelinsky reaction. [5 marks]

Solution:

Concept:

- A nitrogen lone pair available for nucleophilic attack can react with a carbonyl compound; conjugation with a neighbouring carbonyl group reduces its availability.
- Nucleophilic addition to a carbonyl carbon depends on its positive character and on steric accessibility. Alkyl groups donate electron density by the $+I$ effect.
- A carboxylic acid is stronger when its conjugate carboxylate ion is stabilised. Electron-withdrawing groups stabilise this ion, whereas electron-donating groups destabilise it.
- Controlled reduction converts a nitrile group into an aldehyde after hydrolysis. The Hell–Volhard–Zelinsky reaction replaces an α-hydrogen of a carboxylic acid with a halogen.

Step 1: (i)(1) Identify the reactive amino group in semicarbazide Semicarbazide has the structure $H_2N-NH-C(=O)-NH_2$. The lone pair on the nitrogen of the $-C(=O)-NH_2$ group is delocalised into the adjoining carbonyl group by resonance. This amide amino group is therefore much less nucleophilic and does not participate in semicarbazone formation. The terminal hydrazino H_2N-NH- group has an available lone pair and attacks the carbonyl carbon. Subsequent elimination of water forms the semicarbazone:

$$R_2C=O + H_2N-NH-CONH_2 \longrightarrow R_2C=N-NH-CONH_2 + H_2O.$$

Thus only the terminal amino group forms the new carbon–nitrogen double bond; the amide amino group remains unchanged.

Step 2: (i)(2) Compare acetaldehyde and acetone towards HCN Cyanide ion acts as the nucleophile and attacks the electrophilic carbonyl carbon. Acetaldehyde, CH_3CHO, has only one electron-donating methyl group, whereas acetone, CH_3COCH_3, has two. The two methyl groups reduce the positive character of acetone's carbonyl carbon more strongly through their $+I$ effect. In addition, acetone's two methyl groups cause greater steric hindrance to the incoming cyanide ion than the methyl group and hydrogen in acetaldehyde. Both the electronic and steric effects therefore favour faster addition of HCN to acetaldehyde.

Step 3: (ii)(1) Arrange the acids by conjugate-base stability The $-NO_2$ group in nitroacetic acid withdraws electron density strongly through the $-I$ effect and stabilises the negative charge in its carboxylate ion. Formic acid has no electron-donating alkyl group. The methyl group of acetic acid has a $+I$ effect and destabilises its carboxylate ion relative to formate. Consequently, the decreasing

Quick Tip to Solve: For these comparisons, check lone-pair resonance, count alkyl groups at the carbonyl carbon, and compare the inductive effects on the carboxylate ion.

order of acidic strength is

$$O_2N{-}CH_2{-}COOH > HCOOH > CH_3COOH.$$

Step 4: (ii)(2) Select a reagent for partial reduction of the nitrile Use diisobutylaluminium hydride (DIBAL-H), followed by hydrolysis with water. Controlled reduction of the nitrile produces an intermediate that yields the aldehyde on hydrolysis, while retaining the carbon–carbon double bond:

$$CH_3{-}CH{=}CH{-}CH_2{-}CN \xrightarrow[\text{(2) water}]{\text{(1) DIBAL-H}} CH_3{-}CH{=}CH{-}CH_2{-}CHO.$$

The nitrile carbon becomes the aldehyde carbon; no carbon atom is lost. A complete reduction to a primary amine would not give the required product.

Step 5: (iii) Write the Hell–Volhard–Zelinsky reaction A carboxylic acid containing at least one α-hydrogen reacts with bromine in the presence of a small amount of red phosphorus to give an α-bromocarboxylic acid. The general reaction, with R representing an alkyl group or hydrogen, is

$$R{-}CH_2{-}COOH + Br_2 \xrightarrow{\text{red P}} R{-}CHBr{-}COOH + HBr.$$

For example, acetic acid gives bromoacetic acid:

$$CH_3COOH + Br_2 \xrightarrow{\text{red P}} BrCH_2COOH + HBr.$$

Chlorine can similarly be used for α-chlorination. The replacement occurs on the carbon adjacent to the carboxyl group.

Step 6: Conclusion (i) The terminal amino group of semicarbazide reacts because the amide nitrogen lone pair is delocalised; acetaldehyde is more reactive because it has less electron donation and steric hindrance. (ii) $O_2NCH_2COOH > HCOOH > CH_3COOH$; use DIBAL-H followed by hydrolysis. (iii) RCH_2COOH gives $RCHBrCOOH$ with Br_2/red phosphorus.

Quick Tip to Solve: For these comparisons, check lone-pair resonance, count alkyl groups at the carbonyl carbon, and compare the inductive effects on the carboxylate ion.

32. Attempt any five of the following :

(a) Write the IUPAC name of the complex : $[Co(H_2O)(CN)(en)_2]^{2+}$

(b) Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

(c) Arrange the following complex ions in increasing order of their crystal field splitting energy (Δ_o) : $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$

(d) Write the hybridization and magnetic character of the complex $[Ni(CO)_4]$ on the basis of valence bond theory. [Atomic No. : Ni = 28]

(e) Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is : (i) more stable ? (ii) the high spin complex ?

(f) What is the difference between an ambidentate ligand and bidentate ligand ?

(g) Write the electronic configuration of d^5 in terms of t_{2g} and e_g in an octahedral field when : (i) $\Delta_o > P$, and (ii) $\Delta_o < P$ [5 marks]

Solution:

Concept:

- In coordination nomenclature, name ligands alphabetically before the metal, then state its oxidation number. Neutral ligands do not contribute to the charge balance.
- In a tetrahedron all four coordination positions are equivalent. In an octahedron the five d orbitals split into the lower-energy t_{2g} set and higher-energy e_g set.
- The splitting energy Δ_o, compared with pairing energy P, determines whether electrons pair in t_{2g} or occupy e_g. Unpaired electrons produce paramagnetism.
- A chelating ligand coordinates through two or more donor atoms to form rings; chelation generally enhances complex stability compared with comparable unidentate ligands.

Step 1: (a) Determine the oxidation state and name the complex Water and ethane-1,2-diamine (en) are neutral ligands, whereas cyanido has charge -1. If cobalt has oxidation number x, then $x-1=+2$, so $x=+3$. The ligand names in alphabetical order are aqua, cyanido and ethane-1,2-diamine. The two en ligands are indicated by bis, and cobalt retains its usual name because the coordination entity is cationic. Thus $[Co(H_2O)(CN)(en)_2]^{2+}$ is **aquacyanidobis(ethane-1,2-diamine)cobalt(III)**.

Step 2: (b) Compare the positions in a tetrahedral complex All four vertices of a tetrahedron are equivalent, and the angle between any two metal–ligand bonds is approximately $109.5°$. For a complex containing two kinds of unidentate ligand, exchanging their positions does not create distinct adjacent and opposite arrangements: rotation superimposes the proposed arrangements. Therefore tetrahedral complexes of this kind do not exhibit geometrical isomerism; there are no separate cis and trans forms.

Step 3: (c) Apply the spectrochemical series Each complex contains cobalt in oxidation state $+3$ and has six ligands. Thus compare ligand field strengths: F^- is weaker than NH_3, which is weaker than CN^-. A stronger ligand field gives a larger octahedral splitting. The increasing order is

$$[CoF_6]^{3-} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}.$$

Quick Tip to Solve: First calculate the metal oxidation state. Then separately check ligand field strength, number of donor atoms used at once, and whether pairing or promotion costs less energy; these answer different parts of this question.

Step 4: (d) Find the hybridisation and magnetism of nickel carbonyl Carbon monoxide is neutral, so nickel has oxidation state zero in $\mathrm{Ni(CO)_4}$. Free nickel has configuration $[\mathrm{Ar}]3d^8 4s^2$. In the valence-bond description of complex formation, the electrons pair to give a filled $3d^{10}$ set, leaving the $4s$ and three $4p$ orbitals available for hybridisation. These four orbitals form four sp^3 hybrids which accept ligand electron pairs, producing a tetrahedral complex. All electrons are paired, so $\mathrm{Ni(CO)_4}$ is **diamagnetic**; its hybridisation is $\boldsymbol{sp^3}$.

Step 5: (e) Identify the more stable and high-spin complexes Both complexes have cobalt in the $+3$ oxidation state. Oxalato, $\mathrm{C_2O_4}^{2-}$, is bidentate: its two donor oxygen atoms bind to the same cobalt ion, forming chelate rings. Fluorido is unidentate. Owing to the chelate effect, $[\mathrm{Co(C_2O_4)_3}]^{3-}$ is the **more stable** complex. Fluorido is a weak-field ligand, so in $[\mathrm{CoF_6}]^{3-}$, the splitting is small relative to pairing energy. Cobalt(III) is d^6, and its high-spin distribution is $t_{2g}^4 e_g^2$, with four unpaired electrons. Hence $[\mathrm{CoF_6}]^{3-}$ is the **high-spin** complex asked for.

Step 6: (f) Distinguish ambidentate from bidentate coordination An **ambidentate ligand** possesses two alternative donor atoms but coordinates through **only one at a time**. For example, $\mathrm{NO_2}^-$ can bind through nitrogen or oxygen, giving different linkage modes. A **bidentate ligand** coordinates through **two donor atoms simultaneously** to the same metal ion. For example, ethane-1,2-diamine binds through both nitrogen atoms, or oxalato binds through two oxygen atoms, usually forming a chelate ring. Thus the distinction is alternative single-site attachment versus simultaneous two-site attachment.

Step 7: (g) Fill the octahedral levels for five d electrons When $\Delta_o > P$, occupying an upper e_g orbital costs more energy than pairing in the lower t_{2g} orbitals. The five electrons therefore remain in t_{2g}:

$$\Delta_o > P: \qquad t_{2g}^5 e_g^0 \quad \text{(low spin; one unpaired electron).}$$

When $\Delta_o < P$, it costs less energy to occupy e_g than to pair electrons. By Hund's rule, the electrons occupy all five d orbitals singly:

$$\Delta_o < P: \qquad t_{2g}^3 e_g^2 \quad \text{(high spin; five unpaired electrons).}$$

Step 8: Conclusion (a) Aquacyanidobis(ethane-1,2-diamine)cobalt(III). (b) Equivalent tetrahedral positions prevent geometrical isomerism. (c) Splitting increases as fluorido $<$ ammine $<$ cyanido. (d) sp^3, diamagnetic. (e) Oxalato complex: more stable; fluorido complex: high spin. (f) One alternative donor versus two simultaneous donors. (g) $t_{2g}^5 e_g^0$ for $\Delta_o > P$; $t_{2g}^3 e_g^2$ for $\Delta_o < P$. These give all seven answers, from which any five may be selected.

Quick Tip to Solve: First calculate the metal oxidation state. Then separately check ligand field strength, number of donor atoms used at once, and whether pairing or promotion costs less energy; these answer different parts of this question.

33(a). (i) Calculate emf of the following cell at 25°C :

Zn (s) | Zn^{2+} (0.001 M) || Cd^{2+} (0.1 M) | Cd (s)

Given : $E^{\circ}_{Zn^{2+}/Zn} = -0.76\,V$, $E^{\circ}_{Cd^{2+}/Cd} = -0.40\,V$ **[log 10 = 1]**

(ii) State Faraday's second law of electrolysis. How will the pH of aqueous NaCl solution be affected when it is electrolysed ? [5 marks]

Solution:

Concept:

- The standard emf is the cathode reduction potential minus the anode reduction potential: $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$. The electrode with the more positive reduction potential undergoes reduction.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- For the same electric charge, deposited or liberated masses are proportional to their equivalent masses, M/z, where M is molar mass and z is the number of electrons involved per formula unit.

Step 1: (i) Identify the electrodes and cell reaction Since $-0.40\,\text{V} > -0.76\,\text{V}$, cadmium ions are reduced at the cathode and zinc is oxidised at the anode:

$$\begin{aligned} \text{Anode:} \quad & \text{Zn(s)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{e}^{-}, \\ \text{Cathode:} \quad & \text{Cd}^{2+}\text{(aq)} + 2\text{e}^{-} \rightarrow \text{Cd(s)}. \end{aligned}$$

Adding the half-reactions gives $\text{Zn(s)} + \text{Cd}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cd(s)}$, so $n = 2$. The standard emf is

$$E^{\circ}_{\text{cell}} = (-0.40) - (-0.76) = 0.36\,\text{V}.$$

Step 2: (i) Substitute the concentrations into the Nernst equation Using the given molar concentrations for the aqueous-ion activities, the reaction quotient is

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} = \frac{0.001}{0.1} = 0.01 = 10^{-2}.$$

Since $\log 10 = 1$, $\log Q = -2$. Therefore,

$$\begin{aligned} E_{\text{cell}} &= 0.36 - \frac{0.0591}{2}(-2) \\ &= 0.36 + 0.0591 = 0.4191\,\text{V}. \end{aligned}$$

Here $Q < 1$, so the non-standard emf is greater than the standard emf, providing a check on the sign of the correction.

Step 3: (ii) State Faraday's second law of electrolysis When the same quantity of electricity is passed through different electrolytes, the masses of substances deposited or liberated at their respective electrodes are proportional to their chemical equivalent masses:

$$\frac{m_1}{m_2} = \frac{M_1/z_1}{M_2/z_2}.$$

Quick Tip to Solve: Write the balanced cell reaction before forming Q: metal solids are omitted, and the zinc-ion concentration belongs in the numerator.

Here m_1, m_2 are the deposited or liberated masses and M_i/z_i are the corresponding equivalent masses. This follows from $m = (M/z)(q/F)$, with charge q and Faraday constant F the same for both electrolytes.

Step 4: (ii) Explain the change in pH during electrolysis of aqueous NaCl At the cathode, water is reduced in preference to sodium ions:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq).$$

Chloride ions are oxidised at the anode in the usual electrolysis of aqueous sodium chloride:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-.$$

Sodium ions remain in solution with the hydroxide ions, producing sodium hydroxide. The overall process is

$$2NaCl(aq) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + Cl_2(g).$$

The concentration of OH^- increases; hence the solution becomes alkaline and its pH increases.

Step 5: Conclusion (i) The cell emf is $\boxed{0.4191\,\text{V} \approx 0.42\,\text{V}}$. (ii) For equal electric charge, deposited or liberated masses are proportional to equivalent masses. Electrolysis of aqueous NaCl produces hydroxide ions, so the pH increases.

Quick Tip to Solve: Write the balanced cell reaction before forming Q: metal solids are omitted, and the zinc-ion concentration belongs in the numerator.

OR

33(b). (i) Calculate the $\Delta_r G^\circ$ and $\log K_c$ for the following cell reaction:

$$Fe(s) + Ag^+(aq) \rightleftharpoons Fe^{2+}(aq) + Ag(s)$$

Given: $E^\circ_{Fe^{2+}/Fe} = -0.44\,\text{V}$, $E^\circ_{Ag^+/Ag} = +0.80\,\text{V}$, $1\,\text{F} = 96500\,\text{C mol}^{-1}$.
(ii) Write any two advantages of the fuel cells over primary and secondary batteries?
(iii) How many Faradays are required for the oxidation of 1 mole of H_2O to O_2? [5 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$, using reduction potentials for both electrodes. Iron is oxidised and silver ions are reduced.
- For a balanced reaction transferring n moles of electrons, $\Delta_r G^\circ = -nFE^\circ_{cell}$, where F is the Faraday constant. Also $\Delta_r G^\circ = -RT \ln K_c$.
- At $298\,\text{K}$, $E^\circ_{cell} = (0.0591/n) \log K_c$. One Faraday is the charge associated with one mole of electrons, approximately $96500\,\text{C}$.

Step 1: (i) Balance the cell reaction and obtain the electron transfer The printed reaction is a skeletal

Quick Tip to Solve: Balance the iron–silver reaction first: Fe loses two electrons, so use n = 2. For water, four electrons come from two water molecules, giving 2 F per mole of water.

equation. Balance its atoms and charge before using the thermodynamic relations:

$$\mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2e^-$$
$$\mathrm{2Ag^+(aq)} + 2e^- \longrightarrow \mathrm{2Ag(s)}.$$

Thus the balanced cell reaction is

$$\mathrm{Fe(s)} + \mathrm{2Ag^+(aq)} \rightleftharpoons \mathrm{Fe^{2+}(aq)} + \mathrm{2Ag(s)}, \qquad n = 2.$$

Multiplying the silver half-reaction by two balances electrons; it does not multiply its electrode potential, since electrode potential is an intensive quantity.

Step 2: (i) Calculate the standard cell potential and Gibbs energy The silver electrode is the cathode, since its reduction potential is higher. Therefore,

$$E^\circ_{\text{cell}} = 0.80 - (-0.44) = 1.24\,\text{V}.$$

The Gibbs energy change for one mole of the balanced reaction is

$$\begin{aligned}\Delta_r G^\circ &= -2 \times 96500 \times 1.24 \\ &= -239320\,\text{J mol}^{-1} \\ &= -239.32\,\text{kJ mol}^{-1}.\end{aligned}$$

The negative sign is consistent with the positive standard cell potential: the forward reaction is spontaneous under standard conditions.

Step 3: (i) Find the equilibrium constant Using the usual standard temperature $298\,\text{K}$,

$$\log K_c = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{2 \times 1.24}{0.0591} \approx 41.96.$$

Here $\log$ means the logarithm to base ten. Consequently $K_c \approx 9.2 \times 10^{41}$, so equilibrium strongly favours products. The value refers to the balanced reaction with two silver ions, not the unbalanced skeletal equation.

Step 4: (ii) Give two advantages of fuel cells First, fuel cells convert the chemical energy of continuously supplied fuel directly into electrical energy with high efficiency; the hydrogen–oxygen fuel cell has an efficiency of about 70%. Second, they can deliver electricity continuously as long as fuel and oxidant are supplied. Unlike primary batteries, they need not be discarded after their stored reactants are exhausted; unlike secondary batteries, they do not require interruption for recharging. These advantages follow from continuous reactant supply rather than a finite charge stored in the cell.

Step 5: (iii) Calculate the Faradays needed for oxidation of water The oxidation half-reaction is

$$\mathrm{2H_2O(l)} \longrightarrow \mathrm{O_2(g)} + \mathrm{4H^+(aq)} + 4e^-.$$

Two moles of water release four moles of electrons. Therefore, one mole of water releases $4/2 = 2$ moles of electrons. Since one mole of electrons corresponds to one Faraday, the required charge is $2\,\text{F}$, or $193000\,\text{C}$.

Quick Tip to Solve: Balance the iron–silver reaction first: Fe loses two electrons, so use n = 2. For water, four electrons come from two water molecules, giving 2 F per mole of water.

Step 6: Conclusion (i) $\Delta_r G^\circ = -239.32\,\text{kJ mol}^{-1}$ and $\log K_c \approx 41.96$ at $298\,\text{K}$, for the balanced cell reaction. (ii) Fuel cells have high conversion efficiency and provide continuous power while fuel and oxidant are supplied. (iii) Oxidation of one mole of water requires $2\,\text{F}$.

Quick Tip to Solve: Balance the iron–silver reaction first: Fe loses two electrons, so use n = 2. For water, four electrons come from two water molecules, giving 2 F per mole of water.