CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-6-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculator is not allowed.

Section A (16 marks)

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

1. Williamson synthesis of preparing unsymmetrical ether is : [1 mark]

(A) S_N1 reaction

(B) S_N2 reaction

(C) Electrophilic addition reaction

(D) Elimination reaction

Correct Answer: (B) S_N2 reaction

Solution:

Concept:

- Williamson synthesis forms an ether by nucleophilic substitution of an alkyl halide by an alkoxide ion, RO^-.
- An S_N2 reaction occurs in one concerted step; primary alkyl halides minimise steric hindrance.

Step 1: Identify the reacting species The alkoxide is the nucleophile and the alkyl halide supplies the carbon bonded to the leaving group. For example,

$$CH_3ONa + C_2H_5Br \longrightarrow CH_3OC_2H_5 + NaBr.$$

This prepares an unsymmetrical ether because the two alkyl groups attached to oxygen differ.

Step 2: Check the mechanism and alternatives The alkoxide attacks the carbon from the side opposite the leaving group while the carbon–halogen bond breaks. This concerted displacement is S_N2, option (B). Option (A) involves a carbocation, whereas Williamson synthesis uses direct displacement. Option (C) adds across a multiple bond; no such addition occurs here. Option (D) removes groups to form an alkene, rather than replacing halogen with an alkoxy group.

Step 3: Conclusion Williamson synthesis proceeds by an S_N2 mechanism. Hence, the correct option is (B).

Quick Tip to Solve: For an unsymmetrical ether, choose the less hindered alkyl group as the alkyl halide to favour S_N2.

2. Which of the following compounds would be hydrolysed by aqueous KOH most easily ? [1 mark]

(A) CH_2=CH-Br

(B) CH_3-CH_2-Br

(C) CH_3-CHBr-CH_3

(D) CH_2=CH-CH_2-Br

Correct Answer: (D) CH_2=CH-CH_2-Br

Solution:

Concept:

- Aqueous KOH provides hydroxide ions, which replace halogen in a hydrolysis reaction to form an alcohol.
- Allylic halides are especially reactive because the neighbouring double bond stabilises the substitution transition state and an allylic carbocation, if formed.

Step 1: Locate the halogen-bearing carbon In option (D), $CH_2{=}CH{-}CH_2Br$, bromine is attached to an allylic carbon, immediately next to a double bond. The corresponding allylic carbocation has resonance forms $CH_2{=}CH{-}CH_2^+$ and $^+CH_2{-}CH{=}CH_2$. This stabilisation facilitates displacement of bromide.

Step 2: Compare all four options Option (A) is vinyl bromide: its carbon–bromine bond is on an sp^2 carbon and has partial double-bond character, making hydrolysis difficult. Options (B) and (C) are ordinary primary and secondary alkyl bromides; neither has allylic resonance stabilisation. Option (D) combines an accessible primary allylic carbon with activation by the adjacent double bond and is hydrolysed most readily to allyl alcohol:

$$CH_2{=}CHCH_2Br + KOH(aq) \longrightarrow CH_2{=}CHCH_2OH + KBr.$$

Step 3: Conclusion $CH_2{=}CH{-}CH_2Br$ is hydrolysed most easily. Hence, the correct option is (D).

Quick Tip to Solve: Locate the carbon bearing halogen: a halogen on an allylic carbon is reactive, whereas one directly on a double-bond carbon is resistant.

3. According to Werner's theory of coordination compounds : [1 mark]

(A) Primary valences are ionisable.

(B) Secondary valences are ionisable.

(C) Both primary and secondary valences are non-ionisable.

(D) Both primary and secondary valences are ionisable.

Correct Answer: (A) Primary valences are ionisable.

Solution:

Concept:

- In Werner's theory, primary valence corresponds to the oxidation state of the central metal and is ionisable.

Quick Tip to Solve: Remember primary valence as oxidation state and secondary valence as coordination number; the counter-ions are ionisable.

- Secondary valence corresponds to the coordination number; it is directional and non-ionisable.

Step 1: Distinguish the two valences Primary valences are normally satisfied by anions and can give ions in solution. Secondary valences are satisfied by ligands inside the coordination sphere. These ligands remain coordinated to the metal instead of dissociating as ordinary counter-ions.

Step 2: Test the statements For example, in $[Co(NH_3)_6]Cl_3$, cobalt has primary valence 3 and secondary valence 6. The three chloride counter-ions are ionisable, while the six ammonia ligands remain within the complex ion. Thus option (A) is correct. Options (B) and (D) incorrectly call secondary valences ionisable. Option (C) incorrectly calls primary valences non-ionisable.

Step 3: Conclusion Primary valences are ionisable. Hence, the correct option is (A).

Quick Tip to Solve: Remember primary valence as oxidation state and secondary valence as coordination number; the counter-ions are ionisable.

4. Which of the following complex ion is not optically active ? [1 mark]

(A) $[Co(ox)_3]^{3-}$

(B) cis-$[Co(en)_2Cl_2]^+$

(C) trans-$[Co(en)_2Cl_2]^+$

(D) $[Co(en)_3]^{3+}$

Correct Answer: (C) trans-$[Co(en)_2Cl_2]^+$

Solution:

Concept:

- Optical isomers are non-superimposable mirror images; an optically active complex must possess chirality.
- The ligands en (ethane-1,2-diamine) and ox^{2-} (oxalate) are bidentate and form chelate rings.

Step 1: Examine the trans arrangement In $\mathrm{trans}-[Co(en)_2Cl_2]^+$, the two chloride ligands occupy opposite positions in an octahedral arrangement. Its symmetrical arrangement has a plane of symmetry and is superimposable on its mirror image. It therefore does not form an optically active pair.

Step 2: Eliminate the other complexes $[Co(ox)_3]^{3-}$ and $[Co(en)_3]^{3+}$, options (A) and (D), have three chelate rings arranged with handedness and form Δ and Λ optical isomers. The cis complex in option (B) also forms non-superimposable mirror images. Thus among the listed complex configurations, only the trans complex in option (C) is optically inactive.

Step 3: Conclusion $\mathrm{trans}-[Co(en)_2Cl_2]^+$ is not optically active. Hence, the correct option is (C).

Quick Tip to Solve: For octahedral bis-chelate complexes with two identical monodentate ligands, compare cis and trans: the trans form has symmetry and is inactive.

5. Which of the following is the softest metal ? [1 mark]

(A) Zn

(B) Sc

(C) Cu

(D) Fe

Correct Answer: (A) Zn

Solution:

Concept:

- Metal hardness reflects the strength of metallic bonding, which depends on the electrons available for bonding.
- Zinc has the filled configuration $[\mathrm{Ar}]3\mathrm{d}^{10}4\mathrm{s}^{2}$, with no unpaired $3d$ electrons.

Step 1: Identify the distinctive configuration Zinc has a completely filled $3d$ subshell. Compared with the other listed metals, its filled d shell contributes less to the strong metallic bonding characteristic of metals with partially filled d subshells. Zinc is consequently relatively soft.

Step 2: Compare the given choices Scandium, copper and iron have stronger metallic cohesion than zinc in this comparison. Scandium and iron have partially occupied d subshells in their atomic configurations; copper, although also having a filled atomic $3d$ subshell, has appreciably stronger metallic bonding than zinc. Thus it would be incorrect to select solely by counting filled shells: among the actual metals listed, Zn is the softest.

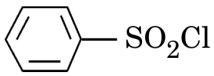
Step 3: Conclusion Zinc is the softest metal among these choices. Hence, the correct option is (A).

Quick Tip to Solve: In this comparison, recognise Zn as the filled-d-shell soft metal; do not confuse softness with ease of cutting an unrelated alkali metal.

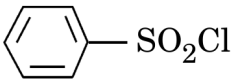
6. In the Hinsberg's method for separation of primary, secondary and tertiary amines, the reagent used is : [1 mark]

(A) Nitrous acid

(B) $CHCl_3$ + aq. NaOH

(C) 

(D) $HCl/ZnCl_2$

Correct Answer: (C) 

Solution:

Concept:

- Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$, used in aqueous alkali.
- The test separates amines through the different formation and alkali solubility of their sulphonamide products.

Step 1: Explain the separation principle A primary amine forms a sulphonamide with an N–H bond; this acidic hydrogen allows the product to dissolve in alkali as a salt. A secondary amine forms a

Quick Tip to Solve: For Hinsberg separation, check whether the sulphonamide retains an N–H bond: that determines its solubility in alkali.

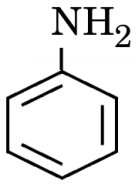
sulphonamide with no N–H hydrogen, so its product is insoluble in alkali. A tertiary amine does not form such a sulphonamide and can dissolve on treatment with dilute acid.

Step 2: Identify the correct reagent These distinctions require benzenesulphonyl chloride, shown in option (C). Nitrous acid, option (A), is used for nitrous-acid reactions of amines. Chloroform with alkali, option (B), is associated with the carbylamine test of primary amines. HCl with $ZnCl_2$, option (D), is Lucas reagent for classifying alcohols. None of these is Hinsberg's reagent.

Step 3: Conclusion The reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. Hence, the correct option is (C).

Quick Tip to Solve: For Hinsberg separation, check whether the sulphonamide retains an N–H bond: that determines its solubility in alkali.

7. Which one of the following amines gives an alcohol on reaction with HNO_2 ? [1 mark]

(A) 

(B) $C_2H_5NH_2$

(C) $(C_2H_5)_2NH$

(D) $(C_2H_5)_3N$

Correct Answer: (B) $C_2H_5NH_2$

Solution:

Concept:

- Primary aliphatic amines react with nitrous acid to form unstable diazonium intermediates that give alcohols and nitrogen gas.
- Aromatic primary amines form relatively stable diazonium salts at low temperature; secondary amines form N-nitroso compounds.

Step 1: Select the primary aliphatic amine Ethylamine, $C_2H_5NH_2$, in option (B) has one alkyl group attached to nitrogen and is a primary aliphatic amine. Its reaction is

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O.$$

The ethyldiazonium intermediate is unstable and loses nitrogen; replacement of the amino group by hydroxyl gives ethanol, a primary alcohol.

Step 2: Compare the remaining amines Aniline, option (A), is a primary aromatic amine and undergoes diazotisation at low temperature rather than this direct alcohol-forming reaction. Diethylamine, option (C), is secondary and gives an N-nitrosoamine. Triethylamine, option (D), is tertiary and does not undergo the primary-aliphatic-amine conversion to an alcohol. Therefore only ethylamine fits the stated reaction.

Step 3: Conclusion Ethylamine, $C_2H_5NH_2$, gives ethanol. Hence, the correct option is (B).

Quick Tip to Solve: Count the carbon groups on nitrogen and identify whether the group is aliphatic: a primary aliphatic amine gives alcohol with HNO_2.

8. The freezing point of one molal KCl solution, assuming KCl to be completely dissociated in water, is :

(K_f for water = 1.86 K kg mol^{-1}) [1 mark]

(A) -3.72°C

(B) +3.72°C

(C) -1.86°C

(D) +2.72°C

Correct Answer: (A) -3.72°C

Solution:

Concept:

- Freezing-point depression obeys $\Delta T_f = iK_f m$, where i is the number of solute particles per formula unit and m is molality.
- The freezing point of pure water is $0\,^\circ\mathrm{C}$; dissolving a non-volatile solute lowers this temperature.

Step 1: Count the dissolved particles Complete dissociation gives $\mathrm{KCl} \rightarrow \mathrm{K}^+ + \mathrm{Cl}^-$. Each formula unit produces two ions, so $i = 2$, and the given one-molal solution has $m = 1\,\mathrm{mol\,kg^{-1}}$.

Step 2: Calculate depression and temperature

$$\Delta T_f = 2 \times 1.86 \times 1 = 3.72\,\mathrm{K}.$$

Hence $T_f = 0 - 3.72 = -3.72\,^\circ\mathrm{C}$. Option (C) neglects dissociation. Options (B) and (D) give positive temperatures, whereas the freezing point must decrease.

Step 3: Conclusion The freezing point is $-3.72\,^\circ\mathrm{C}$. Hence, the correct option is (A).

Quick Tip to Solve: For fully dissociated KCl use $i = 2$, then subtract the depression from $0\,^\circ\mathrm{C}$.

9. A solution of acetone in ethanol : [1 mark]

(A) obeys Raoult's law.

(B) forms an ideal solution.

(C) shows a positive deviation from Raoult's law.

(D) shows a negative deviation from Raoult's law.

Correct Answer: (C) shows a positive deviation from Raoult's law.

Solution:

Concept:

- Raoult's law gives $p_j = x_j p_j^\circ$ for an ideal solution, where x_j is the mole fraction of component j.
- Positive deviation occurs when unlike-molecule attractions are weaker overall than the attractions in the pure liquids; molecules escape more readily.

Step 1: Compare intermolecular attractions Ethanol molecules form an extensive network of hydrogen bonds. Adding acetone disrupts this network. Although acetone can accept hydrogen bonds from

Quick Tip to Solve: For acetone mixed with ethanol, remember disruption of ethanol hydrogen bonding increases the vapour pressure.

ethanol, the resulting unlike interactions are weaker overall than those in the original ethanol network.

Step 2: Identify the vapour-pressure change The molecules escape more easily into the vapour, giving vapour pressures greater than those predicted by Raoult's law. Thus the mixture is non-ideal and shows positive deviation. Options (A) and (B) require ideal behaviour, while option (D) would require stronger unlike attractions and a lower vapour pressure.

Step 3: Conclusion The acetone–ethanol solution shows positive deviation from Raoult's law. Hence, the correct option is (C).

Quick Tip to Solve: For acetone mixed with ethanol, remember disruption of ethanol hydrogen bonding increases the vapour pressure.

10. Which of the following cell converts the energy of combustion of fuel into electrical energy ?

[1 mark]

(A) Mercury cell

(B) Fuel cell

(C) Dry cell

(D) Lead storage cell

Correct Answer: (B) Fuel cell

Solution:

Concept:

- A fuel cell converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy through electrode reactions.
- For a hydrogen–oxygen fuel cell the overall reaction is $2H_2 + O_2 \rightarrow 2H_2O$.

Step 1: Identify the energy conversion The overall reaction of a fuel cell is the same as combustion of the fuel. Oxidation of the fuel and reduction of the oxidant take place at separate electrodes, so electrons travel through an external circuit and supply electrical energy.

Step 2: Distinguish the other cells A mercury cell and a dry cell are primary cells with reactants held inside them. A lead storage cell is a rechargeable secondary cell. These descriptions do not identify the device operating on continuously supplied combustible fuel and oxidant. The required device is therefore the fuel cell, option (B).

Step 3: Conclusion A fuel cell converts the energy of combustion of fuel into electrical energy. Hence, the correct option is (B).

Quick Tip to Solve: Look for direct conversion of a continuously supplied fuel and oxidant into electricity: this identifies a fuel cell.

11. The unit of rate and rate constant are same for a : [1 mark]

(A) First order reaction

(B) Second order reaction

(C) Zero order reaction

(D) Third order reaction

Correct Answer: (C) Zero order reaction

Solution:

Concept:

- For an n-th order reaction, $r = k[A]^n$, where r is reaction rate, k the rate constant and $[A]$ concentration.
- Rate has units $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$, while k has units $(\text{mol}\,\text{L}^{-1})^{1-n}\text{s}^{-1}$.

Step 1: Require identical units From $k = r/[A]^n$, rate and rate constant have the same units only when the concentration factor is dimensionless. This occurs for $n = 0$, because $[A]^0 = 1$ and hence $r = k$.

Step 2: Check all the proposed orders For first order, k has units s^{-1}; for second order, $\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$; and for third order, $\text{L}^2\,\text{mol}^{-2}\,\text{s}^{-1}$. None matches the rate unit. For zero order, both are $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Step 3: Conclusion Rate and rate constant have the same units for a zero-order reaction. Hence, the correct option is (C).

Quick Tip to Solve: Write $r = k[A]^n$: if the units of r and k match, the concentration exponent must be zero.

12. Pyranose ring of glucose is formed due to the reaction between : [1 mark]

(A) C_1 and C_3

(B) C_1 and C_5

(C) C_1 and C_4

(D) C_1 and C_2

Correct Answer: (B) C_1 and C_5

Solution:

Concept:

- Glucose has an aldehyde group at C_1 and hydroxyl groups along its open chain.
- Intramolecular addition of a hydroxyl group to the aldehyde forms a cyclic hemiacetal; a pyranose has a six-membered ring with one oxygen.

Step 1: Identify the reacting groups The hydroxyl group attached to C_5 reacts with the aldehyde carbon at C_1. The hydroxyl oxygen becomes the ring oxygen, while C_1 becomes the anomeric carbon bearing a hydroxyl group.

Step 2: Count ring members and compare options The ring contains C_1, C_2, C_3, C_4, C_5 and one oxygen: six atoms in all. Reaction with C_4 would produce a five-membered furanose ring. The C_3

Quick Tip to Solve: Count five carbon atoms plus the hydroxyl oxygen for pyranose: glucose must close between C_1 and C_5.

and C_2 alternatives do not produce a six-membered pyranose ring. Thus the printed pair in option (B) is correct.

Step 3: Conclusion The pyranose ring forms by reaction between groups at C_1 and C_5. Hence, the correct option is (B).

Quick Tip to Solve: Count five carbon atoms plus the hydroxyl oxygen for pyranose: glucose must close between C_1 and C_5.

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

Reason (R) : Actinoids are radioactive in nature. [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:

- Actinoids have closely spaced $5f$, $6d$ and $7s$ orbital energies, allowing different numbers of electrons to participate in bonding.
- Radioactivity arises from instability of the atomic nucleus; oxidation state describes the electron accounting in chemical bonds.

Step 1: Judge the assertion The assertion is true. Actinoids exhibit a wide range of oxidation states because electrons in the $5f$, $6d$ and $7s$ orbitals can participate in bonding. For example, uranium commonly exhibits $+3$, $+4$, $+5$ and $+6$ oxidation states.

Step 2: Judge the reason The reason is also true. All actinoids are radioactive, since their nuclei are unstable and undergo spontaneous nuclear decay.

Step 3: Test the explanatory link Nuclear instability does not explain the availability of electrons for bonding. The wide oxidation-state range follows from the similar energies of the valence orbitals, whereas radioactivity is a nuclear property. Therefore both statements are true, but the reason does not explain the assertion; options (A), (C) and (D) fail this classification.

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

Quick Tip to Solve: Separate nuclear behaviour from electronic bonding: radioactivity cannot explain the actinoids' oxidation states.

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14. Assertion (A) : Hydrolysis of an ester follows first order kinetics.

Reason (R) : The concentration of water does not get altered much during the reaction. [1 mark]

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

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

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

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

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

Solution:

Concept:

- For ester hydrolysis in excess water, $r = k[\text{ester}][H_2O]$; any constant catalyst concentration is included in k.
- When one reactant remains effectively constant, it is absorbed into an observed rate constant, giving pseudo-first-order kinetics.

Step 1: Judge the assertion The assertion is true for ester hydrolysis in the usual excess-water conditions. The observed rate is proportional to ester concentration, so the reaction follows first-order kinetics with respect to the changing ester concentration.

Step 2: Judge the reason The reason is true. Water is present in a very large excess as solvent, and the amount consumed during hydrolysis is a very small fraction of the water initially present. Its concentration therefore changes negligibly.

Step 3: Establish the explanatory link Put $k_{obs} = k[H_2O]$, which is effectively constant. Then $r = k_{obs}[\text{ester}]$, the first-order rate law. Thus the nearly constant water concentration directly explains the observed first-order behaviour. Both statements are true and the explanation is correct, eliminating options (B), (C) and (D).

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

Quick Tip to Solve: When water is in large excess, absorb its constant concentration into k_{obs} to identify pseudo-first-order kinetics.

15. Assertion (A) : Boiling point of $(CH_3)_3N$ is higher than that of $CH_3CH_2CH_2NH_2$.
Reason (R) : Hydrogen bonding is more extensive in $CH_3CH_2CH_2NH_2$. [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:

- Intermolecular hydrogen bonding raises the boiling point by increasing the energy needed to separate molecules.
- Primary amines contain N–H bonds and can donate hydrogen bonds; tertiary amines have no N–H bond.

Step 1: Judge the assertion Trimethylamine, $(CH_3)_3N$, is a tertiary amine, whereas propan-1-amine, $CH_3CH_2CH_2NH_2$, is primary. They have the same molecular formula, but propan-1-amine forms intermolecular N–H hydrogen bonds. Consequently, its boiling point is higher. The asserted reverse order is false.

Step 2: Judge the reason Propan-1-amine has both N–H hydrogen-bond donors and a nitrogen lone pair that can accept a hydrogen bond. Pure trimethylamine has an acceptor lone pair but no N–H donor, so its molecules cannot form this intermolecular N–H hydrogen-bond network. The reason is true.

Step 3: Check the explanation and alternatives The reason supports a higher boiling point for the primary amine, opposite to the assertion. Options (A), (B) and (C) all require a true assertion and are therefore excluded.

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

Quick Tip to Solve: For isomeric amines, first check whether an N–H bond allows self hydrogen bonding.

16. Assertion (A) : Phenol is strongly acidic as compared to ethanol.

Reason (R) : Phenoxide ion is more stable than ethoxide ion. [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:

- Acid strength increases when the conjugate base formed after loss of H^+ is more stable.
- Resonance delocalises negative charge in phenoxide; the ethoxide charge is localised mainly on oxygen.

Step 1: Judge the assertion Phenol loses its O–H proton more readily than ethanol. Thus phenol is more acidic relative to ethanol, and the assertion is true. The wording is a comparison of acidity; phenol is still classified as a weak acid.

Step 2: Judge the reason In phenoxide, the oxygen lone pair conjugates with the aromatic ring, and resonance delocalises the negative charge over oxygen and the ortho and para positions. Ethoxide has no comparable resonance delocalisation; its ethyl group also has an electron-releasing inductive effect. Therefore phenoxide is more stable than ethoxide, making the reason true.

Step 3: Connect the reason to acidity The more stable phenoxide ion makes deprotonation of phenol more favourable than deprotonation of ethanol. This directly explains their relative acid strengths. Option (B) wrongly denies this explanatory link, while (C) and (D) incorrectly classify a true statement as false.

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

Quick Tip to Solve: Compare conjugate-base stability: resonance stabilisation makes phenol more acidic than ethanol.

Section B (10 marks)

17. State Henry's law. Why are aquatic species more comfortable in cold water as compared to warm water ? [2 marks]

Solution:

Concept:

- Henry's law relates a gas's partial pressure to its equilibrium mole fraction dissolved in a liquid at a fixed temperature.

Quick Tip to Solve: At fixed pressure use $x = p/K_H$: a larger Henry constant means less dissolved gas.

- In $p = K_H x$, p is the gas partial pressure, x its mole fraction in the solution, and K_H the Henry-law constant.

Step 1: State Henry's law At a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas above the liquid. In mole-fraction form,

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

The temperature must be specified because K_H depends on temperature.

Step 2: Explain the effect of water temperature For oxygen in water, the Henry-law constant increases as temperature rises. At a given oxygen partial pressure, $x = p/K_H$ therefore decreases on warming: cold water contains more dissolved oxygen than warm water. Aquatic organisms obtain oxygen for respiration from the dissolved oxygen in water, so its greater availability in cold water makes them more comfortable. It is the amount of dissolved oxygen, rather than a change in the oxygen fraction of air, that explains this comparison.

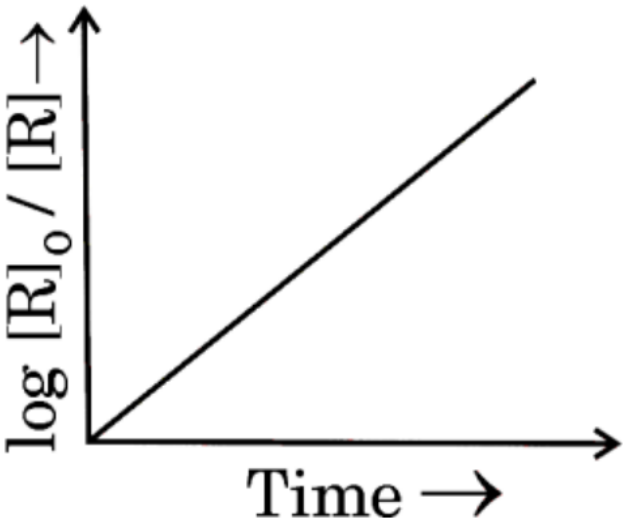
Step 3: Conclusion Henry's law is $p = K_H x$ at constant temperature. Cold water dissolves more oxygen than warm water, providing aquatic species with a better oxygen supply for respiration.

Quick Tip to Solve: At fixed pressure use $x = p/K_H$: a larger Henry constant means less dissolved gas.

18. Observe the graph in the given figure and answer the following questions :

(a) Predict the order of reaction.

(b) What is the slope of the curve ? [2 marks]



Solution:

Concept:

- For a first-order reaction, $-d[R]/dt = k[R]$, where $[R]$ is reactant concentration and k is the rate constant.

Quick Tip to Solve: Read the logarithm axis carefully: a common-log first-order plot has slope k/2.303, whereas a natural-log plot has slope k.

- The integrated first-order law is $\log_{10}([R]_0/[R]) = kt/2.303$, where $[R]_0$ is the initial concentration and t is time.

Step 1: (a) Identify the plotted variables and order The vertical axis in the printed graph is $\log([R]_0/[R])$, and the horizontal axis is time. The graph is a straight line passing through the origin. This agrees with the first-order integrated rate equation

$$\log_{10}\frac{[R]_0}{[R]} = \frac{k}{2.303}t.$$

Hence the reaction is first order. At $t = 0$, $[R] = [R]_0$, so the logarithm is zero, consistent with the shown intercept.

Step 2: (b) Determine the slope Compare the equation with $y = mt + c$, taking $y = \log_{10}([R]_0/[R])$ and $c = 0$. Thus

$$m = \frac{\Delta \log_{10}([R]_0/[R])}{\Delta t} = \frac{k}{2.303}.$$

The slope is positive because the reactant concentration decreases with time, increasing the ratio $[R]_0/[R]$. Its unit is inverse time. No numerical value can be obtained because the figure gives no numerical scale.

Step 3: Conclusion (a) The reaction is first order. (b) The slope of the given common-logarithm plot is $k/2.303$.

Quick Tip to Solve: Read the logarithm axis carefully: a common-log first-order plot has slope k/2.303, whereas a natural-log plot has slope k.

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

$[CoCl_2(en)_2]SO_4$ [1 mark]

Solution:

Concept:

- For a coordination compound, name the complex cation before the counter-anion, and list ligand names alphabetically.
- Ethane-1,2-diamine, abbreviated en, is a neutral bidentate ligand; chlorido has charge -1, and sulphate has charge -2.

Step 1: Find the metal oxidation state The sulphate ion outside the brackets is SO_4^{2-}, so the complex cation must have charge $+2$. Let the cobalt oxidation state be z. The two chlorido ligands contribute -2, while both en ligands are neutral. Hence

$$z + 2(-1) + 2(0) = +2 \quad \Longrightarrow \quad z = +4.$$

The oxidation state follows from the printed formula, so the metal is cobalt(IV).

Step 2: Assemble the systematic name Two chlorido ligands are named dichlorido. Two ligands with the compound name ethane-1,2-diamine are named bis(ethane-1,2-diamine). Alphabetical order

Quick Tip to Solve: Use the sulphate charge first: the bracket has charge +2, forcing cobalt to be +4 in this printed formula.

places chlorido before ethane-1,2-diamine; multiplicative prefixes do not affect that order. Since the complex is cationic, the metal retains the name cobalt, followed by its oxidation state in Roman numerals. Finally name the counter-ion sulphate.

Step 3: Conclusion The IUPAC name is dichloridobis(ethane-1,2-diamine)cobalt(IV) sulphate.

Quick Tip to Solve: Use the sulphate charge first: the bracket has charge $+2$, forcing cobalt to be $+4$ in this printed formula.

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

$K_3[Fe(C_2O_4)_3]$ [1 mark]

Solution:

Concept:

- Oxalato, $C_2O_4^{2-}$, is a bidentate ligand with charge -2.
- An anionic iron complex uses the metal name ferrate; complex ligand names use tris for three ligands.

Step 1: Find the oxidation state of iron Three potassium ions contribute $+3$, so the complex ion is $[Fe(C_2O_4)_3]^{3-}$. If iron has oxidation state z, charge balance gives

$$z + 3(-2) = -3 \quad \Longrightarrow \quad z = +3.$$

Therefore iron is in oxidation state III. The three oxalato ligands are each counted with their full charge, independently of their denticity.

Step 2: Name the cation and complex anion Name potassium first because it is the cation outside the coordination sphere. Three oxalato ligands are designated tris(oxalato). The coordination sphere is anionic, so iron is named ferrate, followed by (III) for its oxidation state. Combining these parts gives the complete salt name; the three potassium ions do not require a numerical prefix in the name.

Step 3: Conclusion The IUPAC name is potassium tris(oxalato)ferrate(III).

Quick Tip to Solve: For an anionic iron coordination sphere use ferrate, and balance ligand charges before assigning the Roman numeral.

OR

19(b)(i). Differentiate between :

Double salt and Complex compound [1 mark]

Solution:

Concept:

- Both double salts and complex compounds can contain more than one kind of ion, but their behaviour in aqueous solution differs.
- A complex ion retains its coordination sphere in solution; a double salt dissociates into its constituent simple ions.

Step 1: Describe a double salt A double salt loses its identity on dissolving in water and dissociates completely into the ions of its constituent salts. For example, Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O$, gives $NH_4{}^+$, Fe^{2+} and $SO_4{}^{2-}$ ions. Its aqueous solution therefore shows the characteristic tests of these simple ions.

Step 2: Describe a complex compound A complex compound gives a complex ion which retains its identity in aqueous solution. For example, $K_4[Fe(CN)_6]$ gives $4\,K^+$ and $[Fe(CN)_6]^{4-}$; it does not dissociate into free Fe^{2+} and CN^- ions. The ligands remain coordinated to the central metal ion.

Step 3: Conclusion A double salt produces its constituent simple ions in water, whereas a complex compound retains its complex ion in solution.

Quick Tip to Solve: Compare the ions present after dissolution: simple constituent ions indicate a double salt; an intact coordination sphere indicates a complex compound.

19(b)(ii). Differentiate between :

Didentate ligand and Ambidentate ligand [1 mark]

Solution:

Concept:

- A donor atom supplies a lone pair to form a coordinate bond with a central metal ion.
- Denticity counts the donor atoms of one ligand bonded simultaneously to the same metal centre; ambidentate behaviour describes alternative donor atoms.

Step 1: Explain a didentate ligand A didentate (bidentate) ligand coordinates to the same metal ion through two donor atoms simultaneously. For example, ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$ (en), bonds through both nitrogen atoms. The two coordinate bonds commonly form a chelate ring with the metal centre.

Step 2: Explain an ambidentate ligand An ambidentate ligand has two different possible donor atoms, but attaches through only one of them at a time. For example, $NO_2{}^-$ can coordinate through nitrogen (nitro) or oxygen (nitrito). Likewise, SCN^- can coordinate through sulfur or nitrogen. Such alternative attachment can give linkage isomerism.

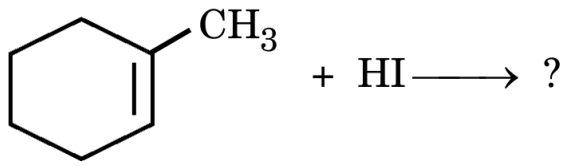
Step 3: Conclusion A didentate ligand binds through two donor atoms simultaneously; an ambidentate

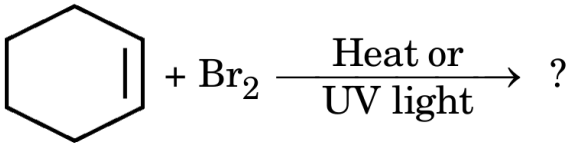
Quick Tip to Solve: Ask whether both donor atoms bond at once: both means didentate; either one means ambidentate.

ligand binds through either of two alternative donor atoms, one at a time.

Quick Tip to Solve: Ask whether both donor atoms bond at once: both means didentate; either one means ambidentate.

20. Draw the structures of major monohalo products in each of the following reactions : [2 marks]

(a) 

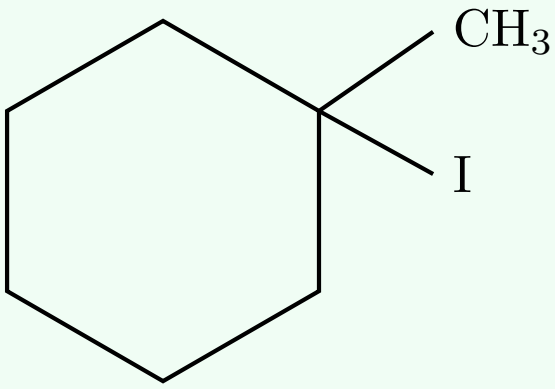
(b) 

Solution:

Concept:

- Addition of HI to an unsymmetrical alkene follows Markovnikov's rule: hydrogen attaches to the double-bond carbon bearing more hydrogen atoms.
- Bromination under heat or UV light proceeds by a radical pathway and replaces an allylic hydrogen; the carbon-carbon double bond remains in the monobromo product.

Step 1: Add HI to 1-methylcyclohexene In reaction (a), one carbon of the double bond carries a methyl group and no hydrogen, whereas the other carries one hydrogen. Addition of a proton to the latter carbon gives the more stable tertiary carbocation at the methyl-bearing carbon. Attack by I^- then places iodine on that same carbon. Thus both the methyl group and iodine are attached to carbon 1 of the saturated cyclohexane ring, as drawn below.

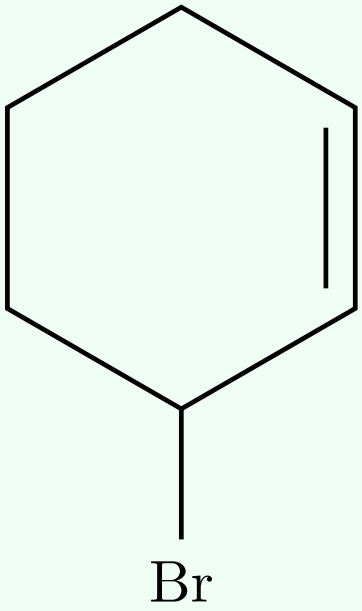


(a) 1-Iodo-1-methylcyclohexane

Step 2: Brominate an allylic position of cyclohexene In reaction (b), the printed reagent is Br_2 with

Quick Tip to Solve: For (a), put iodine on the methyl-bearing alkene carbon. For (b), heat or UV signals allylic substitution: retain the double bond and place bromine beside it.

heat or UV light. These conditions initiate free-radical substitution. Removal of an allylic hydrogen produces a resonance-stabilised allylic radical; its reaction with bromine substitutes one hydrogen by bromine and releases HBr. The equivalent allylic positions give the same constitutional monobromo product, with bromine at carbon 3 of cyclohex-1-ene. A vicinal dibromide would correspond to addition across the double bond and would not be the requested monohalo product under these conditions.



(b) 3-Bromocyclohex-1-ene

Step 3: Conclusion The major monohalo products are (a) 1-iodo-1-methylcyclohexane and (b) 3-bromocyclohex-1-ene, with the structures shown in the diagrams.

Quick Tip to Solve: For (a), put iodine on the methyl-bearing alkene carbon. For (b), heat or UV signals allylic substitution: retain the double bond and place bromine beside it.

21. How do you explain the following ?

(a) Presence of an aldehydic group in glucose.

(b) Presence of five -OH groups in glucose. [2 marks]

Solution:

Concept:

- Mild oxidation by bromine water converts an aldehyde group into a carboxylic acid without oxidising the alcohol groups of glucose.
- Acetylation converts each free hydroxyl group into an acetate ester; the number of acetyl groups introduced identifies the number of hydroxyl groups.

Step 1: Establish the aldehydic group (a) Glucose reacts with hydroxylamine to form an oxime, indicating a carbonyl group. More specifically, bromine water oxidises glucose to gluconic acid,

Quick Tip to Solve: Associate bromine water with conversion of the aldehyde into an acid, and count five acetyl groups in the pentaacetate to identify five hydroxyl groups.

a monocarboxylic acid. This mild oxidation of the terminal carbonyl group establishes that it is aldehydic rather than ketonic:

$$\mathrm{CHO{-}(CHOH)_4{-}CH_2OH + Br_2 + H_2O \longrightarrow}$$

$$\mathrm{COOH{-}(CHOH)_4{-}CH_2OH + 2\,HBr.}$$

The terminal $-\mathrm{CHO}$ group becomes $-\mathrm{COOH}$, while the remaining carbon chain is retained.

Step 2: Count the hydroxyl groups by acetylation (b) Glucose reacts with acetic anhydride to form glucose pentaacetate. Each free $-\mathrm{OH}$ group incorporates one acetyl group on esterification. Formation of a pentaacetate therefore establishes the presence of five hydroxyl groups in one glucose molecule. Since glucose is a stable compound, these hydroxyl groups are attached to five different carbon atoms; in its open-chain structure there are four $-\mathrm{CHOH}-$ groups and one terminal $-\mathrm{CH_2OH}$ group.

Step 3: Conclusion Oxidation by bromine water to gluconic acid establishes an aldehydic group; formation of glucose pentaacetate with acetic anhydride establishes five hydroxyl groups.

Quick Tip to Solve: Associate bromine water with conversion of the aldehyde into an acid, and count five acetyl groups in the pentaacetate to identify five hydroxyl groups.

Section C (21 marks)

22. Vapour pressure of pure water at 298 K is 24.8 mm Hg. Calculate the lowering in vapour pressure of an aqueous solution which freezes at -0.3°C. (K_f of water = 1.86 K kg mol^{-1}) [3 marks]

Solution:

Concept:

- Depression in freezing point obeys $\Delta T_f = K_f m$, where m is the effective solute-particle molality and K_f is the cryoscopic constant of water.
- For a dilute solution of a nonvolatile solute, Raoult's law gives $\Delta p = p^0 x_s$, where p^0 is the vapour pressure of pure solvent and x_s is the solute mole fraction.

Step 1: Find the freezing-point depression Pure water freezes at 0°C, whereas the solution freezes at -0.3°C. Thus the positive depression is

$$\Delta T_f = 0 - (-0.3) = 0.3\,\mathrm{K}.$$

The temperature interval has the same numerical value in kelvin and degrees Celsius; the negative freezing temperature does not make the depression negative.

Step 2: Determine the solute mole fraction Use the freezing-point measurement to determine the concentration:

$$m = \frac{\Delta T_f}{K_f} = \frac{0.3}{1.86} = 0.16129\,\mathrm{mol\ kg^{-1}}.$$

Choose 1 kg of water as the basis. The amount of dissolved solute particles is $n_s = 0.16129$ mol, while

Quick Tip to Solve: Use 1 kg of water: freezing depression gives solute moles directly, and dividing by 1000/18 converts them to a dilute mole fraction.

the solvent amount is

$$n_w = \frac{1000}{18} = 55.5556\,\text{mol}.$$

The molar mass of water, H_2O, is $18\,\text{g mol}^{-1}$. Hence

$$x_s = \frac{n_s}{n_s + n_w} = \frac{0.16129}{0.16129 + 55.5556} = 0.0028948.$$

Step 3: Apply Raoult's law at the stated temperature The pure-water vapour pressure at $298\,\text{K}$ is $24.8\,\text{mm Hg}$. Since adding nonvolatile solute reduces the solvent mole fraction, the lowering is positive:

$$\Delta p = p^0 x_s = 24.8(0.0028948) = 0.07179\,\text{mm Hg}.$$

In the usual dilute-solution approximation, $x_s \simeq n_s/n_w$, this becomes $24.8(0.16129/55.5556) = 0.072\,\text{mm Hg}$; both give the same rounded result.

Step 4: Conclusion The lowering in vapour pressure is approximately $\boxed{0.072\,\text{mm Hg}}$.

Quick Tip to Solve: Use 1 kg of water: freezing depression gives solute moles directly, and dividing by 1000/18 converts them to a dilute mole fraction.

23. The rate of a reaction :

A + B $\rightarrow$ product

is given below as a function of different initial concentrations of A and B.

Experiment	[A] / mol L^{-1}	[B] / mol L^{-1}	Initial Rate / mol L^{-1} min^{-1}
1	0.01	0.01	5×10^{-3}
2	0.02	0.01	1×10^{-2}
3	0.01	0.02	5×10^{-3}

Calculate the order of the reaction with respect to A and B. Determine the rate constant of the reaction. [3 marks]

Solution:

Concept:

- Write the initial-rate law as $r = k[A]^a[B]^b$, where a and b are the experimentally determined partial orders and k is the rate constant.
- Compare experiments changing only one reactant concentration; the total order is $a + b$, and the units of k follow from the rate law.

Step 1: Compare experiments 1 and 2 The concentration of B stays fixed at $0.01\,\text{mol L}^{-1}$. Doubling A from 0.01 to $0.02\,\text{mol L}^{-1}$ doubles the initial rate from 5×10^{-3} to $1 \times 10^{-2}\,\text{mol L}^{-1}\text{min}^{-1}$. Thus

$$\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^a, \qquad 2 = 2^a.$$

Therefore $a = 1$. The rate is directly proportional to A when B is held constant.

Quick Tip to Solve: Compare 1 with 2 for A and 1 with 3 for B. After finding the orders, divide rate by [A]; retain minutes in the rate constant.

Step 2: Compare experiments 1 and 3 Here A stays fixed at $0.01\,\text{mol L}^{-1}$, whereas B doubles from 0.01 to $0.02\,\text{mol L}^{-1}$. The rate remains $5 \times 10^{-3}\,\text{mol L}^{-1}\text{min}^{-1}$. Hence

$$\frac{r_3}{r_1} = \left(\frac{[B]_3}{[B]_1}\right)^b, \qquad 1 = 2^b.$$

Thus $b = 0$: over these experimental concentrations, changing B does not change the rate. Stoichiometric coefficients cannot be used to assign reaction orders.

Step 3: Calculate and check the rate constant The resulting rate law is $r = k[A]$, and the overall order is $1 + 0 = 1$. Using experiment 1,

$$k = \frac{r_1}{[A]_1} = \frac{5 \times 10^{-3}}{0.01} = 0.5\,\text{min}^{-1}.$$

The concentration units cancel, leaving inverse time. Experiment 2 independently gives $(1 \times 10^{-2})/0.02 = 0.5\,\text{min}^{-1}$, and experiment 3 gives the same value. This verifies that one rate constant describes all three observations.

Step 4: Conclusion The order with respect to A is $\boxed{1}$, with respect to B is $\boxed{0}$, and the total order is 1. The rate constant is $\boxed{k = 0.5\,\text{min}^{-1}}$.

Quick Tip to Solve: Compare 1 with 2 for A and 1 with 3 for B. After finding the orders, divide rate by [A]; retain minutes in the rate constant.

24. Give reasons for the following :

(a) The pH of aqueous NaCl increases when it is electrolysed.

(b) Unlike dry cell, mercury cell has a constant cell potential through its lifetime.

(c) Conductivity of solution decreases with dilution. [3 marks]

Solution:

Concept:

- The pH increases when electrolysis produces hydroxide ions in the aqueous solution; reduction takes place at the cathode.
- Cell potential depends on the reaction quotient through the Nernst equation. Pure solids and liquids have unit activity.
- Conductivity κ measures conductance for a unit length and unit cross-sectional area; it depends on the number of charge carriers per unit volume.

Step 1: Explain the rise in pH during NaCl electrolysis In aqueous NaCl, water is reduced more readily than Na^+ at the cathode:

$$2\,\text{H}_2\text{O} + 2\,\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\,\text{OH}^-.$$

Hydroxide ions accumulate and make the cathodic solution alkaline. The Na^+ ions remain in solution with OH^-, forming NaOH; chloride is oxidised to chlorine at the anode. Thus the hydroxide

Quick Tip to Solve: For pH write the water-reduction half-reaction; for mercury-cell voltage add the half-reactions; for conductivity count ions per unit volume.

concentration increases and the pH rises.

Step 2: Explain the constant potential of a mercury cell The net reaction in an alkaline mercury cell is

$$\mathrm{Zn(Hg) + HgO\,(s) \longrightarrow ZnO\,(s) + Hg\,(l)}.$$

Hydroxide ions consumed at the zinc-amalgam anode are regenerated at the mercury-oxide cathode, so they cancel from the overall reaction. No electrolyte ion appears in this net equation and its concentration remains constant during discharge. With the electrode phases present, the reaction quotient stays essentially constant, maintaining an approximately constant potential of $1.35\,\mathrm{V}$ throughout its useful life. In a dry cell, the concentrations of species involved in the reaction change, so the potential falls during use.

Step 3: Explain the decrease in conductivity on dilution Dilution increases the solution volume and decreases the number of ions per unit volume. Therefore fewer charge carriers are available in a given volume to transport current, and conductivity κ decreases. Although ion mobility may increase as interionic attractions weaken, the decrease in carrier concentration determines the decrease in conductivity. Molar conductivity is a different quantity: $\Lambda_m = \kappa(1000/c)$ for c in $\mathrm{mol\,L^{-1}}$, and it increases on dilution.

Step 4: Conclusion (a) Electrolysis forms $\mathrm{OH^-}$, raising pH. (b) A mercury cell maintains its electrolyte concentration because ions cancel from the overall reaction. (c) Dilution reduces the number of ions per unit volume, decreasing conductivity.

Quick Tip to Solve: For pH write the water-reduction half-reaction; for mercury-cell voltage add the half-reactions; for conductivity count ions per unit volume.

25(a)(i). Answer the following about the complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{4-}$:
Write the hybridization involved in each case.
[Atomic number : Fe = 26] [1 mark]

Solution:

Concept:

- Find the metal oxidation state before counting its d electrons. Neutral iron has configuration $[\mathrm{Ar}]\,3d^6 4s^2$.
- In valence-bond theory, weak-field ligands allow outer-orbital sp^3d^2 hybridisation, whereas strong-field ligands can pair electrons to provide inner d^2sp^3 orbitals.

Step 1: Determine the iron ion in each complex In $[\mathrm{FeF_6}]^{3-}$, each fluoride ligand has charge -1, so $x - 6 = -3$ gives iron in the $+3$ state, with configuration $3d^5$. In $[\mathrm{Fe(CN)_6}]^{4-}$, each cyanide ligand also has charge -1; $x - 6 = -4$ gives iron in the $+2$ state, with configuration $3d^6$. Remove the $4s$ electrons before the $3d$ electrons when forming these ions.

Step 2: Identify the hybrid orbitals Fluoride is a weak-field ligand and does not pair the five $3d$ electrons of $\mathrm{Fe^{3+}}$. Two vacant $3d$ orbitals are therefore unavailable, so the octahedral complex uses $4s$, three $4p$, and two $4d$ orbitals: sp^3d^2. Cyanide is a strong-field ligand and pairs the six $3d$ electrons of

Quick Tip to Solve: Determine Fe(III) versus Fe(II) first, then use weak-field fluoride and strong-field cyanide to decide whether inner 3d orbitals are available.

Fe^{2+} into three orbitals. The remaining two vacant $3d$ orbitals combine with $4s$ and three $4p$ orbitals, giving d^2sp^3.

Step 3: Conclusion $[FeF_6]^{3-}$: $\boxed{sp^3d^2}$. $[Fe(CN)_6]^{4-}$: $\boxed{d^2sp^3}$.

Quick Tip to Solve: Determine Fe(III) versus Fe(II) first, then use weak-field fluoride and strong-field cyanide to decide whether inner 3d orbitals are available.

25(a)(ii). Answer the following about the complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{4-}$:

Which of them is the outer orbital complex and which one is the inner orbital complex ?

[Atomic number : Fe = 26] [1 mark]

Solution:

Concept:

- An octahedral inner orbital complex uses two inner $3d$ orbitals in d^2sp^3 hybridisation; an outer orbital complex uses two outer $4d$ orbitals in sp^3d^2 hybridisation.
- The ligand field controls pairing: F^- is weak field, whereas CN^- is strong field.

Step 1: Identify the weak-field complex In $[FeF_6]^{3-}$, iron is Fe^{3+}, with configuration $3d^5$. Fluoride does not force pairing of the five $3d$ electrons. Consequently, two vacant inner $3d$ orbitals are unavailable, and the complex uses outer $4d$ orbitals along with $4s$ and $4p$.

Step 2: Identify the strong-field complex In $[Fe(CN)_6]^{4-}$, iron is Fe^{2+}, with configuration $3d^6$. Cyanide promotes pairing of the six electrons in three $3d$ orbitals, leaving two inner $3d$ orbitals empty for bonding.

Step 3: Conclusion $[FeF_6]^{3-}$ is an outer orbital complex (sp^3d^2); $[Fe(CN)_6]^{4-}$ is an inner orbital complex (d^2sp^3).

Quick Tip to Solve: First obtain the metal oxidation state; then use ligand strength to decide whether two inner d orbitals become vacant.

25(a)(iii). Answer the following about the complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{4-}$:

Compare their magnetic behaviour.

[Atomic number : Fe = 26] [1 mark]

Solution:

Concept:

- Unpaired electrons cause paramagnetism; a complex with all electrons paired is diamagnetic.
- For an octahedral field, weak-field ligands favour high spin and strong-field ligands favour low spin.

Step 1: Count unpaired electrons in the fluoride complex In $[FeF_6]^{3-}$, the six fluoride ions contribute charge -6, so iron is Fe^{3+}, a d^5 ion. As F^- is weak field, the configuration is $t_{2g}^3e_g^2$, with one electron

Quick Tip to Solve: Do not compare only the ligand names: calculate Fe(III) as d5 and Fe(II) as d6 before counting unpaired electrons.

in each of the five d orbitals. There are five unpaired electrons.

Step 2: Count unpaired electrons in the cyanide complex In $[Fe(CN)_6]^{4-}$, iron is Fe^{2+}, a d^6 ion. Strong-field CN^- produces the low-spin configuration $t_{2g}^6 e_g^0$. The three lower-energy orbitals each contain an electron pair, so no unpaired electron remains.

Step 3: Conclusion $[FeF_6]^{3-}$ is strongly paramagnetic (five unpaired electrons), whereas $[Fe(CN)_6]^{4-}$ is diamagnetic (no unpaired electrons).

Quick Tip to Solve: Do not compare only the ligand names: calculate Fe(III) as d5 and Fe(II) as d6 before counting unpaired electrons.

OR

25(b)(i). What happens to the colour of complex $[Ti(H_2O)_6]^{3+}$ when heated gradually ? [1 mark]

Solution:

Concept:

- In $[Ti(H_2O)_6]^{3+}$, titanium is Ti^{3+}, a d^1 ion.
- The violet colour arises from absorption of visible light for a d–d transition between the crystal-field-split d orbitals.

Step 1: Relate the initial colour to coordinated water The six water ligands create an octahedral crystal field around Ti^{3+}. Its single d electron occupies the lower t_{2g} level and can absorb visible radiation to reach the higher e_g level. The transmitted light gives the complex its violet appearance.

Step 2: Consider gradual heating On gradual heating, coordinated water molecules are lost from the complex. The original hydrated octahedral species, whose splitting gives the characteristic violet absorption, is consequently destroyed. Thus the violet colour progressively fades as the water ligands are removed.

Step 3: Conclusion The violet colour of $[Ti(H_2O)_6]^{3+}$ fades and ultimately disappears on gradual heating because the coordinated water is lost.

Quick Tip to Solve: For this hydrated titanium complex, connect heating with loss of water ligands and disappearance of its violet colour.

25(b)(ii). Write the electronic configuration for d^5 ion if $\Delta_o < P$. [1 mark]

Solution:

Concept:

- In an octahedral field, the five d orbitals split into three lower-energy t_{2g} orbitals and two higher-energy e_g orbitals.
- Δ_o is the octahedral splitting energy and P is the electron-pairing energy. If $\Delta_o < P$, occupying a higher orbital costs less than pairing.

Quick Tip to Solve: When splitting is smaller than pairing energy, fill all five d orbitals singly before pairing any electrons.

Step 1: Fill the lower-energy orbitals singly A d^5 ion contains five d electrons. Following Hund's rule, the first three electrons occupy the three t_{2g} orbitals singly, with parallel spins. This gives t_{2g}^3 before the remaining two electrons are placed.

Step 2: Use the energy inequality Since $\Delta_o < P$, the fourth and fifth electrons enter the two vacant e_g orbitals rather than pairing in t_{2g}. Each e_g orbital receives one electron, giving the high-spin arrangement with five unpaired electrons. The low-spin alternative t_{2g}^5 would instead require pairing and is inappropriate for this inequality.

Step 3: Conclusion The electronic configuration is $\boxed{t_{2g}^3 e_g^2}$, the high-spin configuration of a d^5 ion.

Quick Tip to Solve: When splitting is smaller than pairing energy, fill all five d orbitals singly before pairing any electrons.

25(b)(iii). Write the hybridization and magnetic behaviour of the complex [Ni(CO)$_4$].
[Atomic number : Ni = 28] [1 mark]

Solution:

Concept:

- CO is a neutral strong-field ligand, so the oxidation state of nickel in $\mathrm{Ni(CO)_4}$ is zero.
- A tetrahedral complex uses sp^3 hybridisation. Magnetic behaviour is determined by the presence or absence of unpaired electrons.

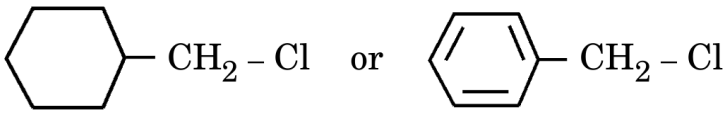
Step 1: Obtain the nickel electron arrangement Nickel (atomic number 28) has ground-state configuration $[\mathrm{Ar}]3d^8 4s^2$. Under the influence of strong-field CO, the two $4s$ electrons enter the $3d$ subshell, giving the filled $3d^{10}$ arrangement. Thus every d electron is paired.

Step 2: Identify the bonding orbitals The now-vacant $4s$ orbital and three vacant $4p$ orbitals hybridise to form four equivalent sp^3 orbitals. These accept lone pairs from four carbon monoxide ligands, producing the tetrahedral geometry. No unpaired electron remains to produce paramagnetism.

Step 3: Conclusion $\mathrm{Ni(CO)_4}$ has $\boxed{sp^3}$ hybridisation and is $\boxed{\text{diamagnetic}}$.

Quick Tip to Solve: For nickel carbonyl, remember neutral CO gives Ni(0), a paired d10 arrangement and tetrahedral sp3 bonding.

26. Write any two differences between S_N1 and S_N2 reactions. Which of the following compounds would undergo S_N1 reaction faster and why ? [3 marks]



Solution:

Concept:

- An S_N1 reaction proceeds through a carbocation; the slow ionisation step determines its rate.
- An S_N2 reaction is concerted: nucleophile attack and leaving-group departure occur in one step.
- A carbocation stabilised by resonance is formed more readily than a comparable carbocation lacking resonance.

Step 1: Compare the mechanisms First difference: S_N1 is a two-step mechanism. The leaving group departs to form a carbocation, and the nucleophile then attacks it. In S_N2, nucleophile attack and leaving-group departure occur simultaneously through a single transition state; no carbocation intermediate is formed.

Step 2: Compare the rate laws Second difference: the S_N1 rate depends only on the substrate concentration, whereas the S_N2 rate depends on both substrate and nucleophile concentrations. Writing RCl for the substrate and Nu^- for the nucleophile,

$$\text{Rate}(S_N1) = k_1[\mathrm{RCl}],$$
$$\text{Rate}(S_N2) = k_2[\mathrm{RCl}][\mathrm{Nu}^-].$$

Thus the former is first order overall, and the latter is second order overall.

Step 3: Compare the carbocations formed The right-hand compound is benzyl chloride, $\mathrm{C_6H_5CH_2Cl}$; the left-hand compound is cyclohexylmethyl chloride, $\mathrm{C_6H_{11}CH_2Cl}$. Ionisation gives $\mathrm{C_6H_5CH_2}^+$ and $\mathrm{C_6H_{11}CH_2}^+$, respectively. In the benzyl carbocation, the vacant p orbital on the benzylic carbon overlaps with the aromatic π system. Its positive charge is delocalised by resonance over the benzylic carbon and the ortho and para ring positions. The saturated cyclohexyl ring has no conjugated π system for this delocalisation. Therefore formation of the benzyl carbocation in the rate-determining step is more favourable.

Step 4: Conclusion S_N1 and S_N2 differ in their mechanisms and rate laws as stated above. Benzyl chloride (the right-hand compound) undergoes S_N1 faster because its carbocation is resonance-stabilised.

Quick Tip to Solve: For an SN1 comparison, draw the carbocation after Cl leaves: an aromatic ring adjacent to the charged carbon stabilises it by resonance.

27. A compound (A) with molecular formula C_4H_5N on reduction with DIBAL-H followed by hydrolysis, gives a compound (B). Compound (B) gives positive Tollens' test but does not give iodoform test. Compound (B) can also be obtained when ethanal is treated with dilute NaOH followed by heating. Identify (A) and (B). Write the reactions of (A) with DIBAL-H followed by hydrolysis. [3 marks]

Solution:

Concept:

- DIBAL-H selectively reduces a nitrile group to an aldehyde on subsequent hydrolysis: $\mathrm{R-CN} \xrightarrow[2.\,H_2O]{1.\,\mathrm{DIBAL-H}} \mathrm{R-CHO}$.
- Ethanal has alpha-hydrogen atoms and undergoes aldol addition with dilute base; heating the aldol removes water to form an alpha,beta-unsaturated aldehyde.
- Aldehydes reduce Tollens' reagent. The iodoform test requires a suitable methyl carbonyl group $\mathrm{CH_3-CO-}$, or a group that can be oxidised to it.

Step 1: Identify the aldehyde from the ethanal reaction First, two molecules of ethanal form 3-hydroxybutanal in dilute sodium hydroxide. Heating gives but-2-enal (crotonaldehyde):

$$2\,\mathrm{CH_3CHO} \xrightarrow{\mathrm{dil\cdot NaOH}} \mathrm{CH_3CH(OH)CH_2CHO}$$

$$\mathrm{CH_3CH(OH)CH_2CHO} \xrightarrow{\Delta} \mathrm{CH_3CH{=}CHCHO} + \mathrm{H_2O}$$

Thus the four-carbon aldehyde obtained after heating is the candidate for compound (B), rather than the initial beta-hydroxy aldehyde.

Step 2: Check the tests and identify the nitrile $\mathrm{CH_3CH{=}CHCHO}$ contains an aldehyde group, so it gives a positive Tollens' test. It has no $\mathrm{CH_3-CO-}$ group and is not ethanal, so it gives no iodoform test. Replace its terminal $-\mathrm{CHO}$ group by $-\mathrm{CN}$ to find its nitrile precursor, $\mathrm{CH_3CH{=}CHCN}$. This contains four carbon atoms, five hydrogen atoms and one nitrogen atom, exactly agreeing with C_4H_5N.

Step 3: Write the selective reduction and hydrolysis The nitrile carbon is retained as the aldehyde carbon. Controlled DIBAL-H reduction followed by aqueous hydrolysis gives the aldehyde while retaining the carbon-carbon double bond:

$$\mathrm{CH_3CH{=}CHCN} \xrightarrow[2.\,H_2O]{1.\,\mathrm{DIBAL-H}} \mathrm{CH_3CH{=}CHCHO}$$

The product is not a primary amine, which would result from a different, more complete nitrile reduction.

Step 4: Conclusion (A) is $\mathrm{CH_3CH{=}CHCN}$, but-2-enenitrile (crotononitrile); (B) is $\mathrm{CH_3CH{=}CHCHO}$, but-2-enal (crotonaldehyde).

Quick Tip to Solve: Identify the heated ethanal aldol product first; then replace its terminal aldehyde group by a nitrile group without changing the carbon count.

28. How will you obtain the following from aniline ? Give chemical equations only.

(a) Sulphanilic acid

(b) Phenylisocyanide

(c) Acetanilide [3 marks]

Solution:

Concept:

- Sulphonation of aniline proceeds through anilinium hydrogen sulphate; heating gives the para sulphonic acid, sulphanilic acid. Its acid and amino groups permit internal proton transfer to form a zwitterion.
- The carbylamine reaction converts a primary amine into an isocyanide using chloroform and alcoholic potassium hydroxide on heating. The phenyl group is bonded to nitrogen in C_6H_5NC, not to the carbon of a nitrile group.
- Acetylation replaces one hydrogen on the amino nitrogen by an acetyl group. Acetic anhydride or acetyl chloride gives acetanilide; base removes hydrogen chloride when acetyl chloride is used.

Step 1: (a) Sulphanilic acid

$$C_6H_5NH_2 + H_2SO_4 \xrightarrow{\text{conc.}} [C_6H_5NH_3]^+ HSO_4^-$$

$$[C_6H_5NH_3]^+ HSO_4^- \xrightarrow{\text{453-473 K}} \text{p-}H_2NC_6H_4SO_3H + H_2O$$

$$\text{p-}H_2NC_6H_4SO_3H \rightleftharpoons \text{p-}H_3N^+C_6H_4SO_3^-$$

Step 2: (b) Phenylisocyanide

$$C_6H_5NH_2 + CHCl_3 + 3\,KOH \xrightarrow[\Delta]{\text{alcoholic KOH}} C_6H_5NC + 3\,KCl + 3\,H_2O$$

Step 3: (c) Acetanilide

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

$$C_6H_5NH_2 + CH_3COCl + NaOH \longrightarrow C_6H_5NHCOCH_3 + NaCl + H_2O$$

Step 4: Conclusion

$$C_6H_5NH_2 \xrightarrow[\text{453-473 K}]{\text{conc. H2SO4}} \text{p-}H_2NC_6H_4SO_3H$$

$$C_6H_5NH_2 \xrightarrow[\Delta]{\text{CHCl3, alcoholic KOH}} C_6H_5NC$$

$$C_6H_5NH_2 \xrightarrow{\text{acetic anhydride}} C_6H_5NHCOCH_3$$

Quick Tip to Solve: For phenylisocyanide write phenyl-NC, retaining the nitrogen attached to the ring; for acetanilide attach the acetyl group to that same nitrogen.

Section D (8 marks)

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

29(a). Case-based: Alcohols undergo a number of reactions involving the cleavage of C - OH bond. However, phenols do not undergo reactions involving the cleavage of C - OH bond. Alcohols are weaker acids than water. Alcohols react with halogen acids to form the corresponding haloalkanes. Phenols are stronger acids than alcohols. A characteristic feature of phenols is that they undergo electrophilic substitution reactions such as halogenation, nitration, etc. Since -OH group is a strong activating group, phenol gives trisubstituted products during halogenation, nitration, etc.

What happens when phenol is treated with the following ? [2]

(i) Br_2 water (ii) Conc. HNO_3 [2 marks]

Solution:

Concept:

- The hydroxyl group activates the aromatic ring of phenol through resonance and directs an incoming electrophile to the ortho and para positions.
- With bromine water or concentrated nitric acid, substitution occurs at both ortho positions and the para position, giving a 2,4,6-trisubstituted phenol.

Step 1: Treat phenol with bromine water Phenol reacts readily with bromine water without a Lewis-acid catalyst. Bromine water is decolourised and a white precipitate of 2,4,6-tribromophenol is formed:

$$C_6H_5OH + 3\,Br_2 \xrightarrow{\text{water}} C_6H_2Br_3OH + 3\,HBr$$

The three bromine atoms replace ring hydrogens at positions 2, 4 and 6; the hydroxyl group remains attached to the ring.

Step 2: Treat phenol with concentrated nitric acid Concentrated nitric acid gives 2,4,6-trinitrophenol, commonly called picric acid, a yellow compound:

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

The nitro groups occupy positions 2, 4 and 6. In contrast, dilute nitric acid gives mainly mononitrated ortho and para products, so the stated acid concentration determines the product required here.

Step 3: Conclusion (i) Bromine water gives a white precipitate of 2,4,6-tribromophenol. (ii) Concentrated HNO_3 gives 2,4,6-trinitrophenol (picric acid).

Quick Tip to Solve: Mark positions 2, 4 and 6 relative to the phenolic hydroxyl group, then place Br or the nitro group at all three positions for these reagents.

29(b). Write the mechanism of alcohol reacting as nucleophile in a reaction with $CH_3{}^+$. [1] [1 mark]

Solution:

Concept:

- An alcohol, ROH, acts as a nucleophile through a lone pair on its oxygen atom; $CH_3{}^+$ is the electron-deficient electrophile.
- Formation of an oxygen-carbon bond first produces an oxonium ion; loss of a proton then gives a neutral ether. Here R denotes the alcohol's alkyl group.

Step 1: Donate the oxygen lone pair to the methyl cation The electron pair moves from oxygen to the positively charged carbon, creating the new bond:

$$\mathrm{R{-}OH + CH_3{}^+ \longrightarrow R{-}O^+(H){-}CH_3}$$

Oxygen now has three bonds and carries the positive formal charge. The oxygen acts as the electron-pair donor, so the alcohol is the nucleophile in this step.

Step 2: Remove a proton from the oxonium ion Another alcohol molecule can accept the proton; the oxygen-hydrogen bond pair remains on the ether oxygen:

$$\mathrm{R{-}O^+(H){-}CH_3 + ROH \longrightarrow R{-}O{-}CH_3 + ROH_2{}^+}$$

This restores the neutral two-bonded oxygen in the ether. The carbon-oxygen bond newly formed in the first step remains intact.

Step 3: Conclusion Alcohol attacks $CH_3{}^+$ through oxygen to form an oxonium ion, which loses a proton to yield the methyl alkyl ether $\mathrm{R{-}O{-}CH_3}$.

Quick Tip to Solve: Follow the electron pair from oxygen to the methyl cation, then remove H from oxygen to neutralise the three-bonded oxonium intermediate.

OR

29(b). Why do phenols not undergo reactions involving cleavage of C - OH bond ? [1] [1 mark]

Solution:

Concept:

- In phenol, an oxygen lone pair overlaps with the aromatic ring; resonance gives the aryl $\mathrm{C{-}O}$ bond partial double-bond character.
- The carbon bonded to oxygen is sp^2-hybridised, making this bond shorter and stronger than the $\mathrm{C{-}O}$ bond of an alcohol.

Step 1: Examine the bond in phenol Resonance delocalises an oxygen lone pair into the benzene ring. Consequently, the bond joining the ring carbon and oxygen cannot be treated as an ordinary single bond.

Step 2: Explain resistance to cleavage The strengthened aryl $\mathrm{C{-}O}$ bond is difficult to break. Thus

Quick Tip to Solve: When asked about cleavage in phenol, identify the aryl C-O bond and cite its resonance-induced partial double-bond character.

the usual substitution reactions of alcohols that replace $-OH$ do not occur readily with phenol.

Step 3: Conclusion Phenols resist cleavage of the $C-OH$ bond because resonance gives it partial double-bond character, making it shorter and stronger.

Quick Tip to Solve: When asked about cleavage in phenol, identify the aryl C-O bond and cite its resonance-induced partial double-bond character.

29(c). How can you distinguish between Butan-1-ol and 2-Methylpropan-2-ol by using HCl in the presence of anhydrous $ZnCl_2$? [1] [1 mark]

Solution:

Concept:

- Lucas reagent is concentrated HCl with anhydrous $ZnCl_2$.
- Alkyl chlorides are insoluble in the aqueous reagent, so their formation produces turbidity; tertiary alcohols react much faster than primary alcohols.

Step 1: Carry out the Lucas test Add Lucas reagent separately to samples of butan-1-ol and 2-methylpropan-2-ol at room temperature, shake, and compare the appearance immediately.

Step 2: Compare the observations 2-Methylpropan-2-ol is a tertiary alcohol and gives immediate turbidity as 2-chloro-2-methylpropane forms. Butan-1-ol is a primary alcohol and gives no turbidity at room temperature during the test.

Step 3: Conclusion Immediate turbidity identifies 2-methylpropan-2-ol; absence of turbidity at room temperature identifies butan-1-ol.

Quick Tip to Solve: Classify the carbon carrying OH first: tertiary gives immediate Lucas turbidity, while primary stays clear at room temperature.

30(a). Case-based: The α-amino acids are the building blocks of proteins. All α-amino acids exist as zwitter ion due to which they show amphoteric behaviour. All amino acids are joined through peptide bond. Proteins are broadly classified as globular proteins and fibrous proteins. Globular proteins are water soluble, whereas fibrous proteins are not. The complete structure of protein is discussed at four different levels i.e. primary, secondary, tertiary and quaternary structures. Protein loses its biological activity in denatured form.

Define the following : [2]

(i) Peptide linkage (ii) Denatured protein [2 marks]

Solution:

Concept:

- A peptide bond is an amide linkage, $-CO-NH-$, between amino-acid residues.
- The biological activity of a protein depends on its native folded structure; denaturation disrupts that structure without normally breaking peptide bonds.

Quick Tip to Solve: For denaturation, distinguish loss of folding and activity from hydrolysis: peptide-bond cleavage is not the defining change.

Step 1: Define peptide linkage A peptide linkage is the $-CO-NH-$ bond formed when the carboxyl group of one amino acid reacts with the amino group of another, eliminating a molecule of water. For example,

$$H_2N-CH(R)-COOH + H_2N-CH(R')-COOH \longrightarrow H_2N-CH(R)-CO-NH-CH(R')-COOH + H_2O.$$

Here R and R' denote the amino-acid side chains.

Step 2: Define a denatured protein A denatured protein is a protein that has lost its native conformation and biological activity because of factors such as heating or a change in pH. Its secondary and tertiary structures are disrupted, while its primary structure, the sequence of amino acids joined by peptide bonds, generally remains intact. Coagulation of egg white on heating is an example.

Step 3: Conclusion (i) Peptide linkage: the amide bond $-CO-NH-$ joining amino-acid residues. (ii) Denatured protein: a protein whose native structure is disrupted and which consequently loses biological activity.

Quick Tip to Solve: For denaturation, distinguish loss of folding and activity from hydrolysis: peptide-bond cleavage is not the defining change.

30(b). Why do amino acids show amphoteric behaviour ? [1] [1 mark]

Solution:

Concept:

- Amphoteric substances can react with both acids and bases.
- An amino acid contains an acidic carboxyl group, $-COOH$, and a basic amino group, $-NH_2$; it can exist as a zwitterion.

Step 1: Identify the two functional groups The carboxyl group can donate a proton, whereas the amino group can accept a proton. Internal proton transfer produces the zwitterion $H_3N^+-CH(R)-COO^-$, where R is the side chain.

Step 2: Explain reaction with acid and base With an acid, the carboxylate group of the zwitterion accepts a proton. With a base, its ammonium group donates a proton. Thus amino acids behave as bases towards acids and as acids towards bases.

Step 3: Conclusion Amino acids show amphoteric behaviour because their acidic carboxyl and basic amino groups enable them to react with both bases and acids.

Quick Tip to Solve: Link amphoteric behaviour to both COOH and NH2 groups; use the zwitterion to identify proton acceptance and donation.

30(c). How can you differentiate between Fibrous protein and Globular protein ? [1] [1 mark]

Solution:

Concept:

- Fibrous and globular proteins differ in molecular shape and their usual solubility in water.
- Protein shape arises from the arrangement and folding of polypeptide chains.

Step 1: Describe fibrous proteins Fibrous proteins have long, fibre-like structures in which polypeptide chains run largely parallel. They are generally insoluble in water and often provide structural support; keratin is an example.

Step 2: Describe globular proteins Globular proteins have polypeptide chains folded into compact, approximately spherical structures. They are generally soluble in water and often perform metabolic functions; insulin is an example.

Step 3: Conclusion Fibrous proteins are elongated and generally water-insoluble, whereas globular proteins are compact and generally water-soluble.

Quick Tip to Solve: Use two paired contrasts in this comparison: elongated versus compact shape, and insoluble versus soluble in water.

OR

30(c). (ii) Write the names of two different secondary structures of proteins. [1] [1 mark]

Solution:

Concept:

- Secondary structure describes the regular local folding of a polypeptide backbone.
- Hydrogen bonds involving peptide carbonyl and NH groups stabilise the common secondary structures.

Step 1: Identify the helical structure In an α-helix, the polypeptide backbone coils into a helix stabilised by hydrogen bonds within the same chain. This is one common type of secondary structure.

Step 2: Identify the sheet structure In a β-pleated sheet, extended polypeptide strands lie side by side and are joined by hydrogen bonds between neighbouring strands. The resulting folded sheet is the other common type.

Step 3: Conclusion The two secondary structures are the α-helix and the β-pleated sheet.

Quick Tip to Solve: Remember secondary structure by its two shapes: alpha is a helix, while beta is a pleated sheet; write both complete names.

Section E (15 marks)

31(a)(i). Calculate E_{cell} of a galvanic cell in which the following reaction takes place at 25°C :
$Zn(s) + Pb^{2+}(0.02\ M) \rightarrow Zn^{2+}(0.1\ M) + Pb(s)$
[Given : $E^{\circ}_{Zn^{2+}/Zn}$ = -0.76 V, $E^{\circ}_{Pb^{2+}/Pb}$ = -0.13 V; log 2 = 0.3010, log 4 = 0.6021, log 5 = 0.6990]

[3 marks]

Solution:

Concept:

- For a galvanic cell, $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$, with both electrode potentials written as reduction potentials.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify the electrodes and electron transfer In the given direction, zinc is oxidised at the anode and lead ions are reduced at the cathode. The half-reactions are

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-},$$
$$\mathrm{Pb^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Pb(s)}.$$

Thus, two electrons are transferred per reaction as written, so $n = 2$. The solid metal terms do not enter the concentration quotient.

Step 2: Calculate the standard cell potential and quotient Subtract the zinc reduction potential from the lead reduction potential:

$$E^{\circ}_{\text{cell}} = (-0.13) - (-0.76) = 0.63\,\mathrm{V}.$$

Using concentrations relative to the standard concentration, the reaction quotient is

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Pb^{2+}}]} = \frac{0.1}{0.02} = 5.$$

Zinc ions are products and lead ions are reactants, so their concentrations must appear in that order.

Step 3: Apply the Nernst equation Substitute $n = 2$, $Q = 5$, and the supplied $\log 5 = 0.6990$:

$$E_{\text{cell}} = 0.63 - \frac{0.0591}{2}(0.6990)$$
$$= 0.63 - 0.02066\,\mathrm{V}.$$

Because $Q > 1$, the concentration correction decreases the potential from its standard value; this checks the sign of the subtraction.

Step 4: Conclusion The cell potential is $\boxed{E_{\text{cell}} = 0.6093\,\mathrm{V} \approx 0.61\,\mathrm{V}}$.

Quick Tip to Solve: Write products over reactants in Q, omit solid metals, and count the two electrons before substituting into the Nernst equation.

31(a)(ii). State Faraday's first law of electrolysis. How much electricity, in terms of Faraday, is required to reduce one mol of MnO_4^- to Mn^{2+} ion ? [2 marks]

Solution:

Concept:

- Faraday's first law states that the mass m deposited or liberated at an electrode is directly proportional to the charge Q passed through the electrolyte: $m = ZQ = ZIt$, where Z is the electrochemical equivalent, I is current and t is time.
- One Faraday, F, is the charge carried by one mole of electrons. A change of n in oxidation number requires nF for one mole of the species.

Step 1: Determine the change in oxidation number In MnO_4^-, oxygen has oxidation number -2. If manganese has oxidation number x, then

$$x + 4(-2) = -1, \qquad x = +7.$$

In Mn^{2+}, manganese is in oxidation state $+2$. Reduction from $+7$ to $+2$ therefore requires five electrons for each manganese atom.

Step 2: Convert the electron requirement to charge The balanced reduction half-reaction in acidic medium confirms the electron count:

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

Both atoms and total charge balance. Hence, one mole of permanganate ions consumes five moles of electrons. Since one mole of electrons carries one Faraday, the required charge is $5F$, irrespective of the current chosen; changing current changes the time needed.

Step 3: Conclusion Faraday's first law is $m \propto Q$, or $m = ZIt$. Reducing one mole of MnO_4^- to Mn^{2+} requires $\boxed{5 \text{ Faradays}}$.

Quick Tip to Solve: Calculate manganese's oxidation state first; the decrease from $+7$ to $+2$ directly gives five Faradays per mole of permanganate.

OR

31(b)(i). The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1000 ohm. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.125×10^{-3} S cm^{-1} ? [2 marks]

Solution:

Concept:

- Conductance G is the reciprocal of resistance R: $G = 1/R$. Its unit is siemens, S.
- Conductivity κ and conductance are related by $\kappa = G(l/A)$, where l is the separation of the electrodes and A is their effective area. The ratio l/A is the cell constant, so $l/A = \kappa R$.

Quick Tip to Solve: Use cell constant $= \kappa R$, and keep the conductivity in S cm^{-1} to obtain the answer directly in cm^{-1}.

Step 1: Express the measured conductance For the cell containing the given solution at $298\,\text{K}$, the resistance is $R = 1000\,\Omega$. Therefore,

$$G = \frac{1}{1000\,\Omega} = 1.0 \times 10^{-3}\,\text{S}.$$

Conductance describes this particular cell, whereas conductivity is a property of the solution at the stated temperature. The cell constant relates these two quantities through the cell geometry.

Step 2: Substitute the conductivity into the cell-constant relation The stated conductivity is $\kappa = 0.125 \times 10^{-3}\,\text{S cm}^{-1}$. Hence,

$$\begin{aligned}\frac{l}{A} &= \frac{\kappa}{G} = \kappa R \\ &= (0.125 \times 10^{-3})(1000)\,\text{cm}^{-1} \\ &= 0.125\,\text{cm}^{-1}.\end{aligned}$$

The factor 10^{-3} cancels 10^{3}. Also, $\text{S} \times \Omega = 1$, leaving inverse length as required for l/A. The concentration identifies the calibration solution; it is not an additional factor in this calculation.

Step 3: Conclusion The conductivity cell has cell constant $\boxed{l/A = 0.125\,\text{cm}^{-1}}$.

Quick Tip to Solve: Use cell constant $= \kappa R$, and keep the conductivity in S cm^{-1} to obtain the answer directly in cm^{-1}.

31(b)(ii). Calculate the $E_{Mg^{2+}/Mg}$ potential for the following half cell at 25°C :
$Mg/Mg^{2+}(1 \times 10^{-4}\,M)$; $E^{\circ}_{Mg^{2+}/Mg} = +2.36\,V$
[Given : log 10 = 1] [2 marks]

Solution:

Concept:

- For the reduction half-reaction $\text{Mg}^{2+}(\text{aq}) + 2\,\text{e}^- \longrightarrow \text{Mg}\,(\text{s})$, the number of electrons transferred is $n = 2$.
- The Nernst equation at 25°C is $E = E^\circ - (0.0591/n)\log Q$. Since pure solid magnesium has unit activity, $Q = 1/[\text{Mg}^{2+}]$, with concentration measured relative to its standard value.

Step 1: Form the quotient for the reduction reaction The requested electrode potential is $E_{\text{Mg}^{2+}/\text{Mg}}$, so use the reduction direction even though the half-cell notation lists the metal first. With $[\text{Mg}^{2+}] = 1 \times 10^{-4}\,\text{mol L}^{-1}$,

$$Q = \frac{1}{1 \times 10^{-4}} = 10^{4}, \qquad \log Q = 4 \log 10 = 4.$$

Magnesium metal is omitted from the concentration expression because its activity is unity.

Step 2: Substitute the given standard potential Using the value $E^{\circ}_{\text{Mg}^{2+}/\text{Mg}} = +2.36\,\text{V}$ supplied in the question gives

$$\begin{aligned}E_{\text{Mg}^{2+}/\text{Mg}} &= 2.36 - \frac{0.0591}{2}(4) \\ &= 2.36 - 0.1182\,\text{V}.\end{aligned}$$

Quick Tip to Solve: For a metal-ion reduction, use $E = E^\circ + (0.0591/n)\log[\text{metal ion}]$; here $\log 10^{-4} = -4$ and $n = 2$.

Equivalently, one may use $E = E^\circ + (0.0591/2)\log[Mg^{2+}]$; the negative logarithm then gives the same decrease in potential. Diluting the metal-ion solution makes reduction less favourable and lowers the reduction potential relative to its standard value.

Step 3: Conclusion With the supplied standard potential, $\boxed{E_{Mg^{2+}/Mg} = +2.2418\,V \approx +2.24\,V}$.

Quick Tip to Solve: For a metal-ion reduction, use $E = E^\circ + (0.0591/n)\log[\text{metal ion}]$; here $\log 10^{-4} = -4$ and $n = 2$.

31(b)(iii). What is the effect of temperature on the electrical conductance of metallic conductor ?

[1 mark]

Solution:

Concept:

- Electrical conductance is the reciprocal of resistance: $G = 1/R$. In a metallic conductor, mobile electrons carry the current.
- Increasing temperature increases lattice vibrations and the scattering of conduction electrons.

Step 1: Examine the effect on electron motion On heating a metal, its lattice ions vibrate more vigorously. Conduction electrons suffer more frequent collisions with these vibrating ions, so their mobility decreases.

Step 2: Relate resistance to conductance For an ordinary metallic conductor, resistance increases with temperature. Since $G = 1/R$, an increase in R corresponds to a decrease in electrical conductance.

Step 3: Conclusion The electrical conductance of a metallic conductor decreases as its temperature increases.

Quick Tip to Solve: For metals, remember: hotter lattice, more electron scattering, higher resistance and lower conductance.

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

(I) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali.

(II) Zn, Cd and Hg are non-transition elements.

(III) E° value for Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}. [3 marks]

Solution:

Concept:

- Dichromate and chromate ions interconvert through an acid-base equilibrium; $Cr_2O_7^{2-}$ is orange and CrO_4^{2-} is yellow.
- A transition element has an incompletely filled d subshell in its atom or in at least one of its commonly formed ions.
- Stable electronic configurations favour reduction products. A half-filled d^5 configuration and the stable d^3 configuration help explain the relative reduction tendencies of manganese and chromium

Quick Tip to Solve: For a reduction couple, compare the d configurations on both sides: Mn gains d5 stability, whereas Cr loses d3 stability.

ions.

Step 1: (I) Explain the orange-to-yellow colour change Addition of alkali converts orange dichromate ions into yellow chromate ions:

$$\mathrm{Cr_2O_7^{2-}} + 2\mathrm{OH^-} \rightleftharpoons 2\mathrm{CrO_4^{2-}} + \mathrm{H_2O}.$$

Hydroxide removes acidity and favours the chromate side of the equilibrium. Chromium remains in oxidation state $+6$; the colour change is caused by conversion between these two oxoanions, not by reduction of chromium.

Step 2: (II) Examine the d subshells of Zn, Cd and Hg The atoms have outer configurations $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$, respectively. Their usual divalent ions retain fully filled d^{10} subshells after losing the two outer s electrons. Thus neither their atoms nor their usual ions possess a partially filled d subshell, so Zn, Cd and Hg are not transition elements.

Step 3: (III) Compare the manganese and chromium couples Reduction of $\mathrm{Mn^{3+}}$, with configuration $3d^4$, produces $\mathrm{Mn^{2+}}$, with the particularly stable half-filled $3d^5$ configuration:

$$\mathrm{Mn^{3+}} + \mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}.$$

This strongly favoured reduction accounts for the highly positive $E^\circ = +1.57\,\mathrm{V}$. In contrast, $\mathrm{Cr^{3+}}$ already has a stable $3d^3$ configuration; its reduction produces $\mathrm{Cr^{2+}}$, which is $3d^4$, sacrificing that stability. The chromium reduction is therefore less favourable and its standard reduction potential is much lower.

Step 4: Conclusion (I) Alkali forms yellow chromate from orange dichromate. (II) Zn, Cd and Hg have filled d subshells in their atoms and usual ions. (III) Reduction to stable d^5 $\mathrm{Mn^{2+}}$ is favoured, whereas reduction of stable d^3 $\mathrm{Cr^{3+}}$ is not.

Quick Tip to Solve: For a reduction couple, compare the d configurations on both sides: Mn gains d5 stability, whereas Cr loses d3 stability.

32(a)(ii). What happens when :

(I) Manganate ion undergoes disproportionation reaction in acidic medium ?

(II) $KMnO_4$ is heated ? [2 marks]

Solution:

Concept:

- In disproportionation, the same element in one oxidation state undergoes both oxidation and reduction. Manganese is in oxidation state $+6$ in $\mathrm{MnO_4^{2-}}$.
- On heating, potassium permanganate decomposes into potassium manganate, manganese dioxide and oxygen.

Step 1: (I) Disproportionation of manganate in acid Green manganate ions form purple permanganate

Quick Tip to Solve: Track manganese states: acidic manganate splits +6 into +7 and +4; heated permanganate releases O2.

ions and brown manganese dioxide in acidic medium:

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

Two manganese atoms are oxidised from $+6$ to $+7$, each losing an electron, while the third is reduced from $+6$ to $+4$, gaining two electrons. Thus the internal electron transfer is balanced.

Step 2: (II) Thermal decomposition of permanganate Heating solid potassium permanganate liberates oxygen and leaves potassium manganate and manganese dioxide:

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2.$$

The products contain two potassium atoms, two manganese atoms and eight oxygen atoms in total, matching the reactants.

Step 3: Conclusion (I) Acidic manganate disproportionates into permanganate and MnO_2. (II) Heated $KMnO_4$ gives K_2MnO_4, MnO_2 and oxygen, as shown by the balanced equations above.

Quick Tip to Solve: Track manganese states: acidic manganate splits $+6$ into $+7$ and $+4$; heated permanganate releases O2.

OR

32(b)(i). What is 'Misch metal' ? Give its one use. [1 mark]

Solution:

Concept:

- Misch metal is an alloy containing approximately 95% lanthanoid metals and 5% iron, together with traces of carbon, sulphur, calcium and aluminium.
- An alloy combines metallic constituents to obtain useful properties; misch metal is used in magnesium-based alloys.

Step 1: State the composition Misch metal consists mainly of lanthanoid metals, especially cerium and lanthanum, with approximately 5% iron and small amounts of other elements. Its name denotes this mixed-metal alloy rather than a single element.

Step 2: Give one application Misch metal is used in magnesium-based alloys employed in making bullets and shells. This gives a specific practical use of the alloy.

Step 3: Conclusion Misch metal is an alloy of about 95% lanthanoid metals and 5% iron with traces of other elements. One use is in magnesium-based alloys for making bullets and shells.

Quick Tip to Solve: Remember the composition as about 95 percent lanthanoids plus 5 percent iron, then give the magnesium-alloy application.

32(b)(ii). Write the formula of an oxoanion of chromium in which it shows the oxidation state equal to its group number. [1 mark]

Solution:

Concept:

- Chromium belongs to group 6 of the periodic table, so the required oxidation state is $+6$.
- In an ordinary oxoanion, oxygen has oxidation state -2, and the sum of all oxidation states equals the charge on the ion.

Step 1: Choose a chromium oxoanion The chromate ion has formula CrO_4^{2-}. It contains one chromium atom bonded to four oxygen atoms and carries an overall charge of -2.

Step 2: Verify chromium's oxidation state Let the oxidation state of chromium be x. Then

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

This is numerically equal to chromium's group number, 6, so chromate satisfies the printed condition.

Step 3: Conclusion A suitable oxoanion is $\boxed{CrO_4^{2-}}$, the chromate ion, in which chromium has oxidation state $+6$.

Quick Tip to Solve: Use the ion's total charge when checking oxidation states: four O atoms contribute -8, so chromate's Cr must be $+6$.

32(b)(iii). Why does Vanadium pentoxide (V_2O_5) act as a catalyst ? [1 mark]

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with lower activation energy and is regenerated at the end of the catalytic cycle.
- Vanadium exhibits variable oxidation states, allowing reversible electron transfer between reactants and the catalyst.

Step 1: Identify the redox property Vanadium in V_2O_5 has oxidation state $+5$. It can accept electrons and be reduced to a lower oxidation state, then be oxidised back to $+5$. This ability makes it an effective redox catalyst.

Step 2: Explain the catalytic cycle For example, in the contact process, V_2O_5 transfers oxygen to SO_2, forming SO_3 and V_2O_4. Oxygen then regenerates the pentoxide:

$$V_2O_5 + SO_2 \longrightarrow V_2O_4 + SO_3,$$
$$V_2O_4 + \tfrac{1}{2}O_2 \longrightarrow V_2O_5.$$

Thus the catalyst takes part in intermediate steps but is restored, providing an easier route for the overall oxidation.

Step 3: Conclusion V_2O_5 acts as a catalyst because vanadium can change its oxidation state reversibly, facilitating electron or oxygen transfer through a lower-activation-energy pathway.

Quick Tip to Solve: For a transition-metal oxide catalyst, connect variable oxidation states with a cycle that regenerates the catalyst.

32(b)(iv). Why do transition elements have high enthalpies of atomisation ? [1 mark]

Solution:

Concept:

- Enthalpy of atomisation is the enthalpy needed to form one mole of isolated gaseous atoms from an element in its standard state.
- Strong metallic bonding requires a large energy input to separate atoms; both $(n-1)d$ and ns electrons can participate in transition-metal bonding.

Step 1: Relate atomisation to metallic bond strength Atomisation separates the atoms of the metal completely. It therefore requires the metallic bonds holding the solid together to be overcome. Stronger metal-metal bonding gives a greater positive enthalpy of atomisation.

Step 2: Explain why the bonding is strong Transition elements generally possess several unpaired electrons in their partially filled d orbitals. Their d electrons, together with the outer s electrons, contribute to strong interatomic metallic bonding. The participation of a relatively large number of electrons produces high cohesive strength, so considerable energy is needed to form isolated gaseous atoms.

Step 3: Conclusion Transition elements have high enthalpies of atomisation because participation of several d and s electrons, especially unpaired d electrons, produces strong metallic bonds.

Quick Tip to Solve: Link high atomisation enthalpy directly to strong metal-metal bonding and the participation of unpaired d electrons.

32(b)(v). How do you prepare $Na_2Cr_2O_7$ from Na_2CrO_4 ? [1 mark]

Solution:

Concept:

- Chromate and dichromate ions are interconverted by changing the acidity of their aqueous solution.
- Acidification favours dichromate formation: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$.

Step 1: Acidify sodium chromate solution Treat an aqueous solution of sodium chromate, Na_2CrO_4, with dilute sulphuric acid. Hydrogen ions shift the chromate-dichromate equilibrium towards the dichromate ion. The yellow chromate solution consequently becomes orange.

Step 2: Write the preparation equation The balanced reaction is

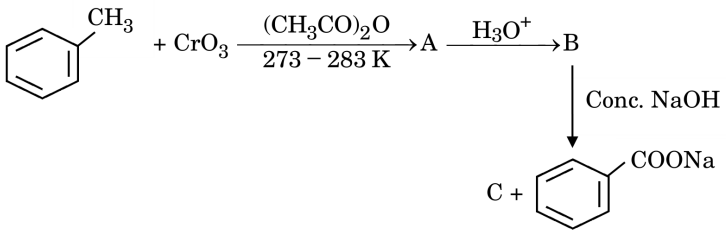
$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

Two chromate units combine to give one dichromate unit. Chromium remains in oxidation state $+6$; this conversion is an acid-dependent equilibrium change rather than a redox reaction.

Step 3: Conclusion Prepare $Na_2Cr_2O_7$ by acidifying aqueous Na_2CrO_4 with dilute sulphuric acid according to the balanced equation above.

Quick Tip to Solve: Remember yellow chromate changes to orange dichromate on acidification; use two chromate units in the balanced equation.

33(a)(i). Identify A, B and C in the following reactions : [3 marks]



Solution:

Concept:

- Oxidation of toluene with CrO_3 in acetic anhydride at 273–283 K traps the aldehyde as benzylidene diacetate, a geminal diacetate.
- Acidic hydrolysis of a geminal diacetate releases the corresponding carbonyl compound; here it produces benzaldehyde.
- Aldehydes without an α-hydrogen undergo the Cannizzaro reaction in concentrated alkali: one molecule is reduced to an alcohol while another is oxidised to a carboxylate salt.

Step 1: Identify intermediate A The starting compound in the printed sequence is toluene, $C_6H_5CH_3$. Chromium trioxide in acetic anhydride at the given low temperature converts its methyl group to a protected aldehyde form:

$$C_6H_5CH_3 \xrightarrow[273\text{–}283\,K]{CrO_3,\,(CH_3CO)_2O} C_6H_5CH(OCOCH_3)_2.$$

Thus A is benzylidene diacetate. Trapping the carbonyl in this form prevents further oxidation.

Step 2: Hydrolyse A to identify B The next reagent is H_3O^+, which hydrolyses benzylidene diacetate to benzaldehyde:

$$C_6H_5CH(OCOCH_3)_2 + H_2O \xrightarrow{H^+} C_6H_5CHO + 2CH_3COOH.$$

Hence B is benzaldehyde, C_6H_5CHO.

Step 3: Use the Cannizzaro reaction to identify C Benzaldehyde has no α-hydrogen because the carbon next to its aldehyde group belongs to the aromatic ring. It therefore undergoes disproportionation with concentrated sodium hydroxide:

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

The sodium benzoate is already drawn in the question, so the remaining product C is benzyl alcohol.

Step 4: Conclusion $A = C_6H_5CH(OCOCH_3)_2$, benzylidene diacetate; $B = C_6H_5CHO$, benzaldehyde; $C = C_6H_5CH_2OH$, benzyl alcohol.

Quick Tip to Solve: Recognise the protected aldehyde after CrO3/acetic anhydride, then hydrolyse it before applying Cannizzaro to benzaldehyde.

33(a)(ii). Give reasons for the following :

(I) Carboxylic acids do not give the characteristic reactions of carbonyl group.

(II) Ethanoic acid is a stronger acid than ethanol. [2 marks]

Solution:

Concept:

- Resonance donation from the hydroxyl oxygen to the carbonyl group reduces the electrophilic character of the carbonyl carbon in a carboxylic acid.
- Acid strength increases when the conjugate base formed by loss of H^+ is more stable.
- The ethanoate ion has two equivalent resonance contributors, whereas the ethoxide ion has a localised negative charge on oxygen.

Step 1: Explain the absence of characteristic carbonyl addition reactions In a carboxylic acid, the lone pair on the hydroxyl oxygen participates in resonance with the carbonyl group:

$$\mathrm{R-C(=O)-OH} \longleftrightarrow \mathrm{R-C(-O^-)=O^+H}.$$

This electron donation decreases the positive character of the carbonyl carbon. Consequently, nucleophiles do not attack it as readily as they attack the carbonyl carbon of aldehydes and ketones. Carboxylic acids therefore do not give the characteristic nucleophilic addition reactions of aldehydes and ketones, such as ordinary oxime or hydrazone formation.

Step 2: Compare the conjugate bases of ethanoic acid and ethanol Loss of a proton from ethanoic acid forms ethanoate, CH_3COO^-. Its negative charge is delocalised equally over two oxygen atoms through two equivalent resonance contributors:

$$\mathrm{CH_3-C(=O)-O^-} \longleftrightarrow \mathrm{CH_3-C(-O^-)=O}.$$

Ethanol instead forms ethoxide, $CH_3CH_2O^-$, whose charge is localised on one oxygen and cannot be stabilised by such resonance. The ethyl group's electron-releasing inductive effect also increases electron density at this negatively charged oxygen. The more stable ethanoate ion makes proton loss from ethanoic acid much more favourable.

Step 3: Conclusion (I) Resonance reduces the electrophilicity of the carboxyl carbon, suppressing the characteristic carbonyl addition reactions. (II) Ethanoic acid is stronger than ethanol because its conjugate base, ethanoate, is resonance-stabilised, while ethoxide is not.

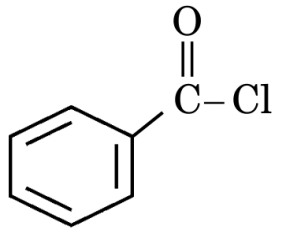
Quick Tip to Solve: For the first reason compare electrophilicity; for the acidity comparison compare the stability of the two conjugate bases.

OR

33(b)(i). Write the product(s) in the following reactions :

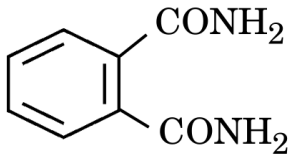
(I) $2\,CH_3COOH \xrightarrow[\text{heat}]{P_4O_{10}}$ [3 marks]

(II)



$+\ (CH_3)_2Cd \rightarrow$

(III)



strong heating $\longrightarrow$

Solution:

Concept:

- A strong dehydrating agent such as P_4O_{10} removes water from two molecules of a carboxylic acid, forming the corresponding acid anhydride.
- Acid chlorides react with dialkylcadmium reagents to form ketones. One alkyl group replaces the chloride of the acyl chloride without further addition to the ketone.
- On strong heating, an aromatic compound bearing two adjacent amide groups can eliminate ammonia and form a stable five-membered cyclic imide.

Step 1: Dehydrate ethanoic acid in reaction (I) Both reactant molecules are ethanoic acid, so the acyl groups on either side of the anhydride oxygen are identical. The net condensation is

$$2\,CH_3COOH \xrightarrow[\text{heat}]{P_4O_{10}} (CH_3CO)_2O + H_2O.$$

The organic product is ethanoic anhydride, also called acetic anhydride. Water is eliminated in the condensation and taken up by the dehydrating agent. Thus the reagent favours formation of the anhydride rather than retaining the acid.

Step 2: Replace chloride with methyl in reaction (II) The structure is benzoyl chloride, C_6H_5COCl. Dimethylcadmium supplies methyl groups, giving the ketone acetophenone, $C_6H_5COCH_3$. A balanced equation using both methyl groups is

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

The carbonyl group remains intact: the chlorine is replaced by CH_3. Dialkylcadmium is sufficiently selective to stop at the ketone, so a tertiary alcohol is not the expected product.

Step 3: Cyclise the adjacent amide groups in reaction (III) The benzene ring bears two $CONH_2$ groups in adjacent positions; the reactant is phthalamide. Strong heating allows the two groups to

Quick Tip to Solve: Identify the reagent first: dehydration gives an anhydride, dialkylcadmium gives a ketone, and adjacent amides on heating give a cyclic imide.

form a cyclic imide with loss of one molecule of ammonia:

$$\text{o-}C_6H_4(CONH_2)_2 \xrightarrow{\text{strong heating}} C_6H_4(CO)_2NH + NH_3.$$

The product $C_6H_4(CO)_2NH$ is phthalimide. In its five-membered ring the same NH nitrogen is bonded to both carbonyl carbons. The two carbonyl groups remain attached to the adjacent benzene carbons, so the transformation preserves the original ortho arrangement.

Step 4: Conclusion (I) Ethanoic anhydride, $(CH_3CO)_2O$; (II) acetophenone, $C_6H_5COCH_3$; (III) phthalimide, $C_6H_4(CO)_2NH$, with ammonia eliminated.

Quick Tip to Solve: Identify the reagent first: dehydration gives an anhydride, dialkylcadmium gives a ketone, and adjacent amides on heating give a cyclic imide.

33(b)(ii). Write the reaction involved in the following reactions :

(I) Wolff-Kishner Reduction

(II) Decarboxylation Reaction [2 marks]

Solution:

Concept:

- Wolff–Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group by using hydrazine and a strong base on heating.
- Decarboxylation removes the carboxyl carbon. Heating a sodium carboxylate with soda lime, a mixture of NaOH and CaO, gives an alkane with one fewer carbon atom.

Step 1: Write the Wolff–Kishner reduction First, the carbonyl compound reacts with hydrazine to form a hydrazone. On heating with KOH in a high-boiling solvent such as ethylene glycol, the hydrazone gives the hydrocarbon and nitrogen:

$$R^1{-}CO{-}R^2 + H_2NNH_2 \longrightarrow R^1{-}C(=NNH_2){-}R^2 + H_2O,$$

$$R^1{-}C(=NNH_2){-}R^2 \xrightarrow[\text{heat}]{KOH} R^1{-}CH_2{-}R^2 + N_2.$$

Here R^1 and R^2 represent organic groups; taking $R^2 = H$ includes aldehydes. The carbonyl oxygen is removed while the carbon skeleton is retained. For example, acetone gives propane:

$$CH_3COCH_3 + H_2NNH_2 \xrightarrow[\text{heat}]{KOH} CH_3CH_2CH_3 + N_2 + H_2O.$$

Step 2: Write the soda-lime decarboxylation Heat the sodium salt of a carboxylic acid with soda lime. The general reaction is

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

The carboxyl carbon becomes part of sodium carbonate, while the organic group receives hydrogen. Thus the alkane contains one carbon atom fewer than the original acid. For sodium ethanoate, the

Quick Tip to Solve: Check the carbon count: Wolff–Kishner reduction retains it, whereas soda-lime decarboxylation removes the carboxyl carbon.

reaction is

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

This equation shows explicitly that the two-carbon acid derivative gives one-carbon methane; CaO is part of the soda-lime mixture and is written as a reaction condition.

Step 3: Conclusion Wolff–Kishner reduction replaces a carbonyl oxygen with two hydrogens using hydrazine, base and heat. Soda-lime decarboxylation converts $RCOONa$ into RH, with Na_2CO_3 as the inorganic product.

Quick Tip to Solve: Check the carbon count: Wolff–Kishner reduction retains it, whereas soda-lime decarboxylation removes the carboxyl carbon.