CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-6-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculator is not allowed.

Section A (16 marks)

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

1. During dehydration of alcohol to alkene by heating with conc. H_2SO_4, the initiation step is : [1 mark]

(A) Formation of an ester

(B) Formation of carbocation

(C) Protonation of alcohol

(D) Elimination of water

Correct Answer: (C) Protonation of alcohol

Solution:

Concept:

- Acid-catalysed dehydration converts an alcohol to an alkene by removal of water.
- The oxygen lone pair accepts a proton; protonation changes the poor leaving group OH into OH_2^+.

Step 1: Identify the first acid-base step The alcohol reacts first with the acid:

$$R{-}OH + H^+ \rightleftharpoons R{-}OH_2^+.$$

This proton transfer activates the alcohol for loss of water.

Step 2: Distinguish later steps Formation of a carbocation, where applicable, follows loss of water from the protonated alcohol. Elimination ultimately produces the alkene. Thus (B) and (D) describe subsequent events, while ester formation in (A) is not the initiation step of the standard dehydration mechanism.

Step 3: Conclusion The initiation step is protonation of alcohol. Hence, the correct option is (C).

Quick Tip to Solve: In acid-catalysed dehydration, first convert OH into the better leaving group, water.

2. Which reagents are required for one step conversion of Chlorobenzene to Diphenyl ? [1 mark]

(A) Chlorobenzene, Na, Dry ether

(B) Benzene, Anhydrous $AlCl_3$

(C) Chlorobenzene/Fe, Dark

(D) $NaNO_2$ + HCl

Correct Answer: (A) Chlorobenzene, Na, Dry ether

Solution:

Concept:

- Fittig reaction couples two aryl halide molecules using sodium in dry ether.
- Diphenyl (biphenyl) contains two phenyl groups joined directly by a carbon-carbon bond.

Quick Tip to Solve: Recognise aryl-halide plus sodium in dry ether as Fittig coupling to a biaryl.

Step 1: Apply aryl-halide coupling Two chlorobenzene molecules couple as follows:

$$2C_6H_5Cl + 2Na \xrightarrow{\text{dry ether}} C_6H_5{-}C_6H_5 + 2NaCl.$$

Sodium removes the halogen while the two aryl groups form the required bond.

Step 2: Check the alternatives Chlorobenzene, sodium and dry ether in (A) supply the Fittig conditions. Benzene with anhydrous aluminium chloride in (B) does not supply this coupling reaction. Chlorobenzene/iron in the dark in (C) does not produce biphenyl by the required coupling. Sodium nitrite and hydrochloric acid in (D) are diazotisation reagents, not Fittig reagents.

Step 3: Conclusion Use chlorobenzene with sodium in dry ether. Hence, the correct option is (A).

Quick Tip to Solve: Recognise aryl-halide plus sodium in dry ether as Fittig coupling to a biaryl.

3. Which of the following complexes show linkage isomerism ? [1 mark]

(A) $[Co(NH_3)_5Cl]^{2+}$

(B) $[Co(NH_3)_4Cl]Br_2$

(C) $[Co(H_2O)_6]^{3+}$

(D) $[Co(NH_3)_5(ONO)]^{2+}$

Correct Answer: (D) $[Co(NH_3)_5(ONO)]^{2+}$

Solution:

Concept:

- Linkage isomerism occurs when an ambidentate ligand binds through different donor atoms.
- NO_2^- can coordinate through N (nitro) or O (nitrito).

Step 1: Identify the ambidentate ligand In option (D), ONO denotes O-bonded nitrito. The same ligand can instead bond through nitrogen, giving $[Co(NH_3)_5(NO_2)]^{2+}$. The two species differ in the atom directly bonded to cobalt.

Step 2: Test the remaining complexes Option (A) contains ammonia and chloride, neither of which offers the required alternative donor atom. The ligands printed in (B) are also ammonia and chloride; the outside bromide does not create linkage isomerism. Option (C) contains only water ligands, which coordinate through oxygen. Therefore only (D) contains an ambidentate ligand.

Step 3: Conclusion $[Co(NH_3)_5(ONO)]^{2+}$ shows linkage isomerism. Hence, the correct option is (D).

Quick Tip to Solve: Look inside the coordination sphere for an ambidentate ligand such as NO2, SCN or CN.

4. Which of the following transition metals has the highest melting point ? [1 mark]

(A) Sc

(B) Cr

(C) Mn

(D) Zn

Correct Answer: (B) Cr

Solution:

Concept:

- Melting points reflect the strength of metallic bonding in the crystal.
- In the 3d series, chromium has a much higher melting point than Sc, Mn and Zn.

Step 1: Use the 3d-series trend Chromium exhibits strong metallic bonding involving its valence electrons. Its melting point is about $1907\,^{\circ}\mathrm{C}$, higher than scandium (about $1541\,^{\circ}\mathrm{C}$) and manganese (about $1246\,^{\circ}\mathrm{C}$). These values establish the required comparison.

Step 2: Exclude zinc and compare all choices Zinc has a filled $3d^{10}$ subshell and a comparatively low melting point, about $420\,^{\circ}\mathrm{C}$. Thus neither (A), (C) nor (D) exceeds chromium. The unusually low melting point of manganese also warns against assuming a perfectly smooth trend across the series.

Step 3: Conclusion Chromium has the highest melting point among the listed metals. Hence, the correct option is (B).

Quick Tip to Solve: For the listed 3d metals, remember the high chromium value and the manganese dip.

5. 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 is $\Delta T_f = iK_f m$, where i is the van't Hoff factor and m is molality.
- Complete dissociation of KCl gives two ions per formula unit, so $i = 2$.

Step 1: Find the depression $\mathrm{KCl} \rightarrow \mathrm{K^+} + \mathrm{Cl^-}$. With $m = 1\,\mathrm{mol\,kg^{-1}}$,

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

The factor two counts the independently dissolved ions.

Quick Tip to Solve: Count ions first, then subtract iKfm from the freezing point of pure water.

Step 2: Calculate the actual freezing point Pure water freezes at $0\,^\circ\mathrm{C}$, so

$$T_f = 0 - 3.72 = -3.72\,^\circ\mathrm{C}.$$

The positive values in (B) and (D) contradict freezing-point depression. Option (C) omits the dissociation factor and would apply to a non-electrolyte at this molality.

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

Quick Tip to Solve: Count ions first, then subtract iKfm from the freezing point of pure water.

6. The reagent that can be used to convert benzenediazonium chloride to benzonitrile is : [1 mark]

(A) Cu/HCl

(B) CH_3CN

(C) CuCN

(D) AgCN

Correct Answer: (C) CuCN

Solution:

Concept:

- Sandmeyer reaction replaces an aromatic diazonium group using a suitable cuprous salt.
- Cuprous cyanide supplies the cyanide group to form an aromatic nitrile.

Step 1: Write the required substitution Benzonitrile contains $C_6H_5{-}CN$. The required conversion is

$$C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5CN + N_2.$$

Evolution of nitrogen accompanies replacement of the diazonium group by CN.

Step 2: Check the reagent choices CuCN in (C) is the standard Sandmeyer cyanation reagent. Cu/HCl in (A) supplies conditions for replacing the diazonium group by chlorine instead. Acetonitrile in (B) is not the required cuprous cyanide reagent. AgCN in (D) is not the standard reagent for this diazonium-to-benzonitrile conversion.

Step 3: Conclusion The required reagent is CuCN. Hence, the correct option is (C).

Quick Tip to Solve: Match the group replacing N2+ with the cuprous salt: CN requires CuCN.

7. The strongest base in aqueous solution among the following amines is : [1 mark]

(A) $(C_2H_5)_2NH$

(B) $(C_2H_5)_3N$

(C) $C_2H_5NH_2$

(D) $C_6H_5NH_2$

Correct Answer: (A) $(C_2H_5)_2NH$

Solution:

Concept:

- Aqueous basicity depends on electron donation, hydration of the conjugate acid and steric effects.
- For the ethylamines in water, the order is secondary greater than tertiary greater than primary; aniline is much weaker.

Step 1: Compare the alkylamines in water Two ethyl groups increase electron density on nitrogen in diethylamine, while its protonated form is effectively hydrated. The combined inductive and solvation effects favour $(C_2H_5)_2NH$ over triethylamine and ethylamine. Counting alkyl groups alone would incorrectly favour the tertiary amine.

Step 2: Compare with aniline In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance and is less available for accepting a proton. Thus (D) is weaker than the aliphatic amines. Options (B) and (C) are also weaker than (A) in aqueous solution, making diethylamine the strongest base among all four.

Step 3: Conclusion Diethylamine, $(C_2H_5)_2NH$, is the strongest base. Hence, the correct option is (A).

Quick Tip to Solve: For aqueous ethylamines, balance hydration with the inductive effect: the secondary amine wins.

8. On mixing 30 mL of acetone with 20 mL of chloroform, the total volume of solution is : [1 mark]

(A) equal to 10 mL

(B) less than 50 mL

(C) greater than 50 mL

(D) equal to 50 mL

Correct Answer: (B) less than 50 mL

Solution:

Concept:

- Mixing volumes are additive only when intermolecular interactions remain essentially unchanged.
- Acetone and chloroform form stronger unlike-molecule attractions, producing contraction and negative deviation from Raoult's law.

Step 1: Identify the interaction The oxygen atom of the carbonyl group in acetone accepts a hydrogen bond from the hydrogen of chloroform. This intermolecular attraction is stronger than the average attractions present in the separate liquids, allowing molecules to pack more closely after mixing.

Quick Tip to Solve: Recognise acetone-chloroform as a hydrogen-bonding pair: stronger attraction means contraction.

Step 2: Compare the volumes The sum before mixing is $30 + 20 = 50$ mL. Stronger unlike-molecule attractions cause a decrease in volume on mixing. Thus the volume is below this sum; equality would neglect contraction and a larger volume would indicate expansion. The value 10 mL is merely the difference of the initial volumes and has no basis here.

Step 3: Conclusion The total volume is less than 50 mL. Hence, the correct option is (B).

Quick Tip to Solve: Recognise acetone-chloroform as a hydrogen-bonding pair: stronger attraction means contraction.

---

9. We cannot measure the resistance of an ionic solution using DC because : [1 mark]

(A) it changes the composition of the solution.

(B) it can cause sparks and shocks.

(C) it does not affect the composition of the solution.

(D) it converts electrolytic cell to galvanic cell.

Correct Answer: (A) it changes the composition of the solution.

Solution:

Concept:

- The resistance of an electrolyte depends on its ionic composition and concentration.
- Direct current can cause electrolysis at the electrodes; alternating current avoids sustained electrode reactions during the measurement.

Step 1: Trace the effect of direct current With direct current, ions move continuously towards fixed electrodes and can undergo oxidation or reduction there. This produces electrolysis and changes the concentrations or identities of ions near the electrodes, so the solution being measured no longer retains its original composition.

Step 2: Assess the alternatives A resistance measurement should characterise the original solution. The composition change caused by direct current prevents a reliable measurement, which is why alternating current is used. Sparks or shocks are not the chemical reason; saying composition is unaffected contradicts electrolysis. Applying DC does not convert an electrolytic cell into a galvanic cell.

Step 3: Conclusion DC changes the composition of the ionic solution. Hence, the correct option is (A).

Quick Tip to Solve: For electrolyte resistance measurements, link DC to electrolysis and AC to avoiding composition changes.

---

10. The primary and secondary valences of Co in $[Co(en)_3]Cl_3$ respectively are : [1 mark]

(A) 3, 3

(B) 0, 3

(C) 6, 3

(D) 3, 6

Correct Answer: (D) 3, 6

Solution:

Concept:

- Werner's primary valence equals the oxidation state of the metal; secondary valence equals its coordination number.
- Ethylenediamine, en, is a neutral bidentate ligand: each molecule supplies two donor atoms.

Step 1: Find primary valence The three chloride ions outside the coordination sphere each carry charge -1. The complex ion therefore has charge $+3$. Since all three ethylenediamine ligands are neutral, cobalt has oxidation state $+3$, and its primary valence is 3.

Step 2: Count donor atoms for secondary valence There are three coordinated ethylenediamine molecules, each bonding through two nitrogen atoms. The coordination number is therefore $3 \times 2 = 6$. Counting ligand molecules alone would give 3, but secondary valence counts donor atoms. Zero ignores the complex charge, while the pair 6, 3 reverses the two valences.

Step 3: Conclusion The primary and secondary valences are 3 and 6 respectively. Hence, the correct option is (D).

Quick Tip to Solve: Count donor atoms, not ligand molecules: three bidentate en ligands provide six coordination sites.

11. In the Arrhenius equation $k = Ae^{-E_a/RT}$, 'A' represents : [1 mark]

(A) effective collisions

(B) frequency factor

(C) fraction of collisions

(D) threshold energy

Correct Answer: (B) frequency factor

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, E_a activation energy, R gas constant and T absolute temperature.
- A is the frequency or pre-exponential factor; the exponential factor describes the energy-dependent fraction.

Step 1: Identify the factors In the equation, A multiplies the exponential term and is called the frequency factor. In a collision interpretation it incorporates collision-frequency and appropriate

Quick Tip to Solve: Separate the Arrhenius factors: A is frequency factor, while the exponential term gives the energy fraction.

orientation effects; it is not itself the fraction of collisions having sufficient energy.

Step 2: Distinguish the other choices The exponential factor $e^{-E_a/(RT)}$ is associated with the fraction of collisions able to overcome the activation-energy barrier. Effective collisions require sufficient energy and suitable orientation together, so that phrase is not the name of A. Threshold energy is an energy quantity, whereas A has the same units as the rate constant.

Step 3: Conclusion A represents the frequency factor. Hence, the correct option is (B).

Quick Tip to Solve: Separate the Arrhenius factors: A is frequency factor, while the exponential term gives the energy fraction.

12. α-D-glucose and β-D-glucose differ from each other with respect to the : [1 mark]

(A) size of the hemiacetal ring

(B) configuration at the C_2 carbon

(C) number of -OH groups

(D) configuration at the C_1 carbon

Correct Answer: (D) configuration at the C_1 carbon

Solution:

Concept:

- Anomers are cyclic sugar stereoisomers differing only at the anomeric carbon.
- For glucose, the aldehyde carbon C_1 becomes the anomeric carbon on hemiacetal formation.

Step 1: Locate the new stereocentre When open-chain D-glucose forms its cyclic hemiacetal, the carbonyl carbon at C_1 acquires a hydroxyl group and becomes a new stereogenic centre. Two possible configurations at this carbon give the alpha and beta forms.

Step 2: Compare the two forms In the usual Haworth representation of D-glucopyranose, the anomeric hydroxyl group is opposite to the terminal CH_2OH group in the alpha form and on the same side in the beta form. Both have the same ring size and number of hydroxyl groups; their configuration at C_2 is unchanged. Their sole anomeric difference is at C_1.

Step 3: Conclusion They differ in configuration at the C_1 carbon. Hence, the correct option is (D).

Quick Tip to Solve: For an aldose such as glucose, find the former aldehyde carbon: C1 is the anomeric centre.

13. Assertion (A) : Actinoid contraction is greater from element to element than lanthanoid contraction.

Reason (R) : Actinoids show wide range of oxidation states. [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:

- Actinoid contraction is the progressive decrease in size across the actinoid series as nuclear charge increases.
- Poor shielding by $5f$ electrons produces greater contraction than the corresponding $4f$ shielding in lanthanoids.

Step 1: Judge the assertion The assertion is true. Increasing nuclear charge attracts the electrons more strongly across the actinoid series, while added $5f$ electrons shield inefficiently. The poorer shielding of $5f$ electrons compared with $4f$ electrons makes actinoid contraction greater from element to element.

Step 2: Judge the reason The reason is also true: actinoids exhibit a wide range of oxidation states. The comparable energies of their $5f$, $6d$ and $7s$ orbitals allow different numbers of electrons to participate in bonding.

Step 3: Test the explanatory connection Variable oxidation states describe how many electrons can participate in bonding; they do not explain the comparative contraction. The relevant cause is the shielding efficiency of the f electrons. Therefore neither the option claiming an explanatory link nor either option declaring a statement false is appropriate.

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

Quick Tip to Solve: For contraction, test shielding and nuclear attraction; variable oxidation states address a different property.

14. Assertion (A) : Molecularity of reaction is determined experimentally.

Reason (R) : Molecularity is applicable only for an elementary reaction and not for a complex 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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- Molecularity is the number of reacting species participating in one elementary step and is a positive integer.
- Reaction order is obtained experimentally from the rate law; it must not be confused with molecularity.

Step 1: Judge the assertion The assertion is false. Molecularity is assigned from the elementary reaction step by counting the reacting species that participate in it. It is the order of a reaction that is determined experimentally by studying how the rate depends on reactant concentrations.

Step 2: Judge the reason The reason is true. Molecularity applies to an elementary reaction, because such a step specifies a single molecular event. A complex reaction consists of several elementary steps, each of which may have its own molecularity; the overall equation does not specify one such event.

Step 3: Select the logical combination The two statements must first be judged separately: A is false and R is true. Options stating that both are true therefore fail, and the option saying R is false reverses its validity. No explanatory link can make the false assertion correct.

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

Quick Tip to Solve: Keep the distinction explicit: experiment gives order; an elementary step gives molecularity.

15. Assertion (A) : Boiling point of $(C_2H_5)_2NH$ is lower than that of n-$C_4H_9NH_2$.

Reason (R) : Hydrogen bonding is much more extensive in $(C_2H_5)_2NH$ as compared to n-$C_4H_9NH_2$.

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

Solution:

Concept:

- Intermolecular hydrogen bonding increases the attraction between amine molecules and generally raises their boiling point.
- A primary amine has two N–H bonds, whereas a secondary amine has one N–H bond; their capacity to donate hydrogen bonds therefore differs.

Step 1: Judge the assertion Both compounds are isomeric amines with molecular formula $C_4H_{11}N$. The primary amine n-$C_4H_9NH_2$ forms more extensive intermolecular hydrogen bonding than the secondary amine $(C_2H_5)_2NH$. Consequently, diethylamine has the lower boiling point. Assertion (A) is true.

Step 2: Judge the reason The reason reverses the hydrogen-bonding comparison. Butan-1-amine has two N–H hydrogen-bond donors per molecule; diethylamine has only one and greater crowding around nitrogen. Hydrogen bonding is more extensive in the primary amine, so Reason (R) is false.

Step 3: Check the explanation and options A false reason cannot explain the true assertion. Options (A) and (B) require a true reason and are eliminated; option (D) incorrectly calls the assertion false.

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

Quick Tip to Solve: For isomeric primary and secondary amines, first count N–H bonds before comparing intermolecular hydrogen bonding.

16. Assertion (A) : The bond angle C - O - C in ethers is slightly greater than tetrahedral angle.
Reason (R) : This is because of the repulsive interaction between the two bulky alkyl groups. [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:

- The oxygen atom of an ether has two bond pairs and two lone pairs, giving an approximately tetrahedral electron-pair arrangement.
- Repulsion between the two alkyl groups can widen the C–O–C angle slightly beyond the ideal tetrahedral angle of 109.5°.

Step 1: Judge the assertion In the usual structural description of ethers, the C–O–C bond angle is slightly greater than the tetrahedral angle. Although oxygen has two lone pairs, the two attached alkyl groups occupy space and repel each other. Assertion (A) is therefore true.

Step 2: Judge the reason The two bulky alkyl groups on oxygen exert repulsive interactions. Increasing their separation by opening the C–O–C angle reduces this crowding. Thus Reason (R) is true.

Step 3: Check the explanatory link The repulsion stated in the reason directly accounts for the widened angle in the assertion. Option (B) wrongly denies this link, while (C) and (D) wrongly classify one of the two statements 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: For an ether bond-angle assertion, connect the widening of C–O–C directly to repulsion between the attached alkyl groups.

Section B (10 marks)

17. Define osmotic pressure. Why is measurement of osmotic pressure method preferred for the determination of molar masses of macromolecules such as proteins and polymers ? [2 marks]

Solution:

Concept:

- Osmosis is the movement of solvent through a semipermeable membrane from pure solvent or a dilute solution towards a more concentrated solution.

Quick Tip to Solve: When explaining this choice, mention both accurate measurement in dilute solutions and protection of heat-sensitive macromolecules.

- For a dilute solution, osmotic pressure follows $\pi = CRT = \frac{wRT}{MV}$, where w is solute mass, M its molar mass, V solution volume, R the gas constant and T absolute temperature.

Step 1: Define osmotic pressure Osmotic pressure is the minimum excess pressure that must be applied to a solution to prevent the entry of solvent into it through a semipermeable membrane. At this pressure, the net osmotic flow of solvent into the solution stops.

Step 2: Explain why this method is preferred Proteins and polymers have very high molar masses, so even a measurable mass gives only a small number of solute particles. Their dilute solutions therefore show very small boiling-point elevations and freezing-point depressions. Osmotic pressure, however, remains appreciable and can be measured accurately in such dilute solutions. The measurement can also be made at room temperature, avoiding heating that could denature proteins or decompose sensitive macromolecules. Rearranging the osmotic-pressure equation gives

$$M = \frac{wRT}{\pi V}.$$

This permits the molar mass to be calculated from the measured pressure.

Step 3: Conclusion Osmotic pressure is the pressure required to stop osmosis. Its appreciable value in dilute solutions and its measurement at room temperature make it preferable for determining macromolecular molar masses.

Quick Tip to Solve: When explaining this choice, mention both accurate measurement in dilute solutions and protection of heat-sensitive macromolecules.

18. 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:

- A mild oxidising agent such as bromine water oxidises an aldehyde group to a carboxylic acid group without cleaving the carbon chain.
- Acetylation converts each free hydroxyl group into an acetate ester; the number of acetyl groups introduced reveals the number of hydroxyl groups.

Step 1: (a) Establish the aldehydic group Glucose is oxidised by bromine water to gluconic acid, a monocarboxylic acid with the same six-carbon chain. Bromine water is a mild oxidising agent and oxidises the terminal aldehydic group to a carboxyl group. The reaction can be represented as

$$\mathrm{CHO(CHOH)_4CH_2OH + Br_2 + H_2O}$$

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

This oxidation is evidence for the presence of a $-\mathrm{CHO}$ group in the open-chain form of glucose.

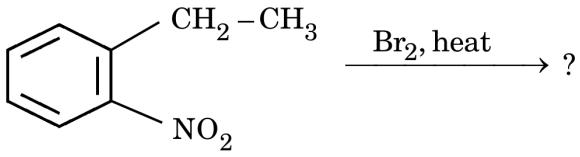
Quick Tip to Solve: Use bromine-water oxidation for the aldehyde evidence and pentaacetate formation to count the five hydroxyl groups.

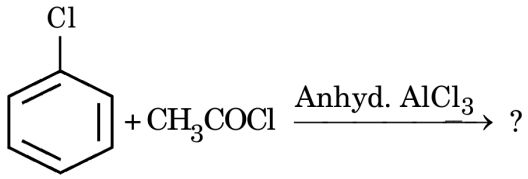
Step 2: (b) Establish five hydroxyl groups On acetylation with acetic anhydride, glucose forms glucose pentaacetate. Each hydroxyl group reacts to form one acetate ester group, $-OCOCH_3$. Introduction of five acetyl groups therefore demonstrates the presence of five $-OH$ groups in a glucose molecule. The formation of a stable pentaacetate also indicates that these hydroxyl groups are attached to different carbon atoms.

Step 3: Conclusion (a) Oxidation with bromine water to gluconic acid establishes an aldehydic group. (b) Formation of glucose pentaacetate on acetylation establishes five hydroxyl groups.

Quick Tip to Solve: Use bromine-water oxidation for the aldehyde evidence and pentaacetate formation to count the five hydroxyl groups.

19. Draw the structures of product(s) in each of the following reactions: [2 marks]

(a) 

(b) 

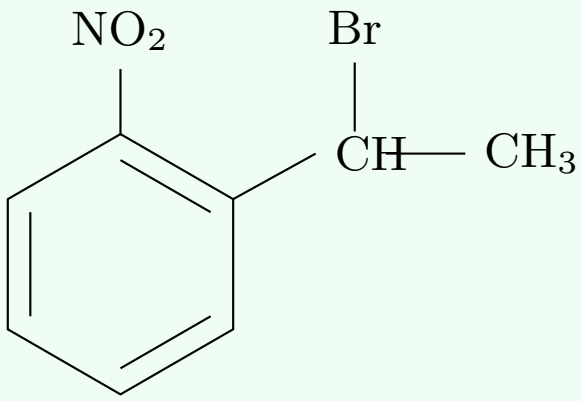
Solution:

Concept:

- With Br_2 and heat, an alkylbenzene undergoes free-radical bromination at the benzylic carbon; the aromatic ring is retained.
- Friedel–Crafts acylation introduces $-COCH_3$ into an aromatic ring using CH_3COCl and anhydrous $AlCl_3$. Chlorine directs substitution to the ortho and para positions.

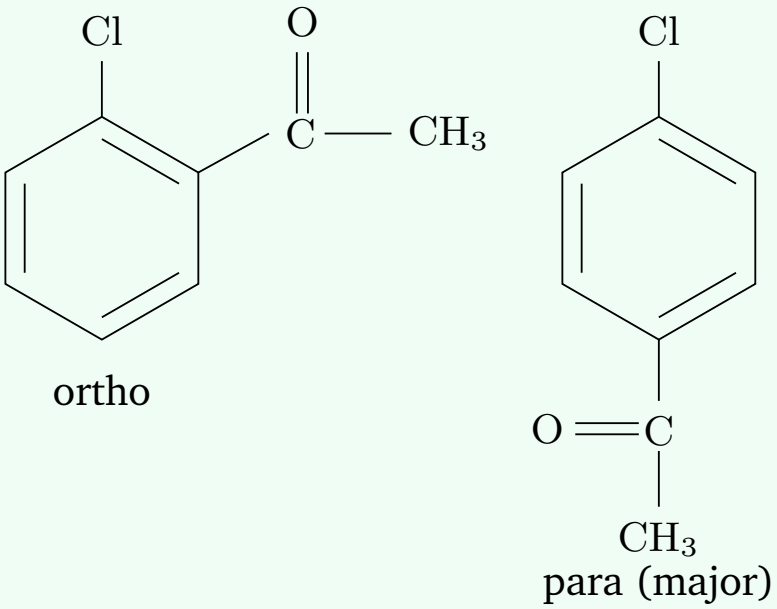
Step 1: Identify the benzylic substitution in (a) The printed side chain is ethyl, $-CH_2CH_3$, rather than methyl. The carbon immediately attached to the benzene ring is benzylic. A hydrogen on this carbon is replaced by bromine because the intermediate benzyl radical is resonance stabilised. The adjacent nitro group stays in its original position. Thus the new side chain is $-CHBrCH_3$; substitution on the terminal methyl carbon is not the expected major reaction.

Quick Tip to Solve: First distinguish heat-driven side-chain bromination from ring substitution; for chlorobenzene acylation, place the acetyl group ortho and para.



Product of reaction (a)

Step 2: Place the acetyl group in (b) Anhydrous $AlCl_3$ activates acetyl chloride to generate the acyl electrophile. Chlorine is deactivating overall but directs electrophilic substitution ortho and para by resonance donation. Accordingly, the products are 2-chloroacetophenone and 4-chloroacetophenone. The para isomer is favoured because it has less steric crowding between chlorine and the acetyl group.



Ortho and para acylation products in reaction (b); para is major

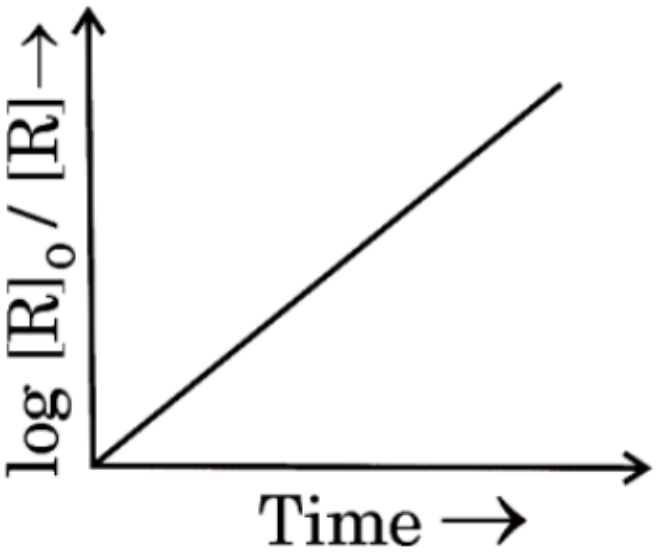
Step 3: Conclusion (a) 1-(1-Bromoethyl)-2-nitrobenzene. (b) 2-Chloroacetophenone and 4-chloroacetophenone (para major); their structures are shown above.

Quick Tip to Solve: First distinguish heat-driven side-chain bromination from ring substitution; for chlorobenzene acylation, place the acetyl group ortho and para.

20. 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, $\ln([R]_0/[R]) = kt$, where $[R]_0$ is the initial concentration, $[R]$ the concentration at time t, and k the rate constant.
- Using common logarithms, the integrated law becomes $\log([R]_0/[R]) = kt/2.303$. A straight line in a plot of this quantity against time identifies first-order kinetics.

Step 1: Read the plotted quantities and determine the order The vertical axis is $\log([R]_0/[R])$, and the horizontal axis is time. The graph is a straight line through the origin. This is the linear form of the integrated first-order rate equation: at $t = 0$, $[R] = [R]_0$, so the logarithm is zero. A zero-order reaction instead gives a straight line of concentration against time, and a second-order reaction gives one of reciprocal concentration against time.

Step 2: Compare with the equation of a straight line Set $y = \log([R]_0/[R])$ and $x = t$. Comparing $y = (k/2.303)x$ with $y = mx + c$ gives $m = k/2.303$ and $c = 0$. Hence the slope is positive. Its unit is the reciprocal of the time unit used on the horizontal axis, because the logarithm of a concentration ratio is dimensionless.

Step 3: Conclusion (a) The reaction is first order. (b) The slope is $k/2.303$, or $0.4343k$.

Quick Tip to Solve: Check whether the vertical axis uses log or ln: the first-order slope is k/2.303 for log and k for ln.

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

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

Solution:

Concept:

- Name ligands alphabetically before the central metal; neutral ethane-1,2-diamine, abbreviated en, carries no charge.
- Each chlorido ligand has charge -1, and the sulphate counter-ion is ${SO_4}^{2-}$. Indicate the metal oxidation state with a Roman numeral.

Step 1: Determine the charge and oxidation state The compound is $[CoCl_2(en)_2]SO_4$. Since sulphate carries charge -2, the bracketed complex must carry charge $+2$. If cobalt has oxidation state x, then $x + 2(-1) + 2(0) = +2$, giving $x = +4$. The number of chlorido ligands must not be confused with the net complex charge.

Step 2: Assemble the coordination name List chlorido before ethane-1,2-diamine alphabetically. Two chlorido ligands give dichlorido; two ligands whose name already contains numerical prefixes give bis(ethane-1,2-diamine). The complex is cationic, so the metal retains the name cobalt, followed by (IV). Name the sulphate counter-ion after the complex.

Step 3: Conclusion Dichloridobis(ethane-1,2-diamine)cobalt(IV) sulphate.

Quick Tip to Solve: Use sulphate to obtain the complex charge first; then include both negative chlorido charges to find cobalt(IV).

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

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

Solution:

Concept:

- Oxalato is the anionic bidentate ligand ${C_2O_4}^{2-}$; each ligand contributes charge -2.
- An anionic coordination entity uses the metal name ending in -ate; iron becomes ferrate. Name the potassium counter-ion first.

Step 1: Calculate the oxidation state of iron The three potassium ions in $K_3[Fe(C_2O_4)_3]$ supply total charge $+3$. Consequently, the complex ion carries charge -3. With iron oxidation state x, charge balance is $x + 3(-2) = -3$, so $x = +3$. Count three oxalato ligands, each with charge minus two, rather than treating all three together as minus two.

Step 2: Name the cation and complex anion Write potassium first. The three oxalato ligands are denoted tris(oxalato), with parentheses clearly grouping the ligand name. Since the bracketed complex is anionic, use ferrate rather than iron, and append (III) to specify the oxidation state. The potassium count is implied by the chemical composition and does not become a prefix in the salt name.

Step 3: Conclusion Potassium tris(oxalato)ferrate(III).

Quick Tip to Solve: For an oxalato complex, multiply the ligand count by minus two before finding the metal oxidation state.

OR

21(b)(i). Differentiate between :

Double salt and Complex compound [1 mark]

Solution:

Concept:

- A double salt dissociates in water into all its constituent simple ions and loses the identity of the original combined salt.
- A complex compound retains its coordination entity in solution; the ligands remain bound to the central metal within the complex ion.

Step 1: Explain dissociation of a double salt For example, Mohrś salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O$, gives $NH_4{}^+$, Fe^{2+} and $SO_4{}^{2-}$ ions on dissolution. These ions exhibit their usual individual properties. Thus the crystallised double salt does not persist as a distinct coordinated ion in aqueous solution.

Step 2: Contrast a complex compound in solution For example, $K_4[Fe(CN)_6]$ gives potassium ions and the intact $[Fe(CN)_6]^{4-}$ coordination ion. It does not ordinarily dissociate into free Fe^{2+} and free cyanide ions under normal dissolution conditions. The identity and characteristic properties of the coordination entity are retained.

Step 3: Conclusion Double salts produce their constituent simple ions in solution; complex compounds retain a coordinated complex ion.

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

21(b)(ii). Differentiate between :

Didentate ligand and Ambidentate ligand [1 mark]

Solution:

Concept:

- A ligand donates a lone pair to a central metal atom or ion. Denticity counts the donor atoms of one ligand simultaneously attached to that metal.
- The availability of alternative donor atoms does not mean that both bind simultaneously.

Step 1: Didentate ligand A didentate (bidentate) ligand coordinates to the same metal through two donor atoms simultaneously. For example, ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, bonds through both nitrogen atoms and forms a chelate ring.

Step 2: Ambidentate ligand An ambidentate ligand has two different possible donor atoms but coordinates through only one of them at a time. For example, NO_2^- can bind through nitrogen (nitro) or oxygen (nitrito). In either mode it is unidentate; the two possibilities are alternative attachment sites.

Step 3: Conclusion A didentate ligand uses two donor atoms simultaneously; an ambidentate ligand uses one of two alternative donor atoms at a time.

Quick Tip to Solve: For en count two simultaneous metal bonds; for nitrite choose either N or O as the donor.

Section C (21 marks)

22. How can you obtain the following ?

(a) Aniline from ammonium benzoate

(b) Benzene diazonium chloride from nitrobenzene

(c) 2,4,6-tribromoaniline from aniline [3 marks]

Solution:

Concept:

- Heating an ammonium carboxylate gives an amide by loss of water. Hofmann bromamide degradation converts a primary amide into an amine containing one fewer carbon atom.
- Primary aromatic amines undergo diazotisation with nitrous acid at 273–278 K. The $-NH_2$ group strongly activates the benzene ring towards electrophilic substitution.

Step 1: (a) Prepare aniline from ammonium benzoate First heat ammonium benzoate to obtain benzamide. Then treat benzamide with bromine and aqueous sodium hydroxide (Hofmann bromamide reaction):

$$C_6H_5COONH_4 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O.$$

$$C_6H_5CONH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The carbonyl carbon is lost in the degradation, so the product is aniline rather than an amine bearing a carbonyl group.

Step 2: (b) Prepare benzene diazonium chloride from nitrobenzene Reduce nitrobenzene using tin and hydrochloric acid, followed by treatment with alkali to liberate aniline. Diazotise the aniline using sodium nitrite and hydrochloric acid at 273–278 K:

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2 + 2H_2O.$$

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{–}278\ K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

Keep the diazotisation mixture cold because aromatic diazonium salts decompose on warming.

Step 3: (c) Prepare 2,4,6-tribromoaniline from aniline Add bromine water to aniline at room temperature. The activating amino group directs bromination to both ortho positions and the para position, giving a white precipitate:

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

The product has bromine at positions 2, 4 and 6 relative to the amino group. No Lewis-acid catalyst is needed for this strongly activated ring.

Step 4: Conclusion (a) Heating, then $Br_2/NaOH$; (b) reduction, then $NaNO_2/HCl$ at 273–278 K; (c) bromine water gives 2,4,6-tribromoaniline.

Quick Tip to Solve: Use Hofmann degradation for the loss of a carbonyl carbon and keep diazotisation at 273–278 K.

23. 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:

- During electrolysis of aqueous sodium chloride, water is reduced at the cathode and chloride ions are oxidised at the anode.
- Cell potential depends on the activities of species in the overall cell reaction. Conductivity κ measures conduction by ions in unit volume, whereas molar conductivity is defined per mole of electrolyte.

Step 1: (a) Increase in pH during electrolysis Water is reduced at the cathode:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-.$$

At the anode, chloride ions give chlorine:

$$2Cl^- \longrightarrow Cl_2 + 2e^-.$$

Hydroxide ions accumulate with sodium ions in solution. Thus $[OH^-]$ increases, $[H^+]$ decreases, and the pH rises.

Step 2: (b) Constant potential of the mercury cell The half-reactions in alkaline medium are

$$Zn(Hg) + 2OH^- \longrightarrow ZnO + H_2O + 2e^-,$$

$$HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-.$$

Adding them gives

$$Zn(Hg) + HgO \longrightarrow ZnO + Hg.$$

Hydroxide ions and water cancel. The overall reaction involves no aqueous ion whose concentration changes during discharge, so the potential stays nearly constant throughout the useful life. In a dry cell, changes in reacting species during discharge cause potential to vary.

Step 3: (c) Decrease in conductivity on dilution Dilution increases the volume occupied by a fixed amount of electrolyte. The number of ions carrying charge per unit volume decreases, so conductivity κ decreases. Although ionic mobility or ionisation may increase on dilution, the reduced ion concentration per unit volume lowers conductivity. Molar conductivity generally increases on dilution because it refers to the conduction associated with one mole of electrolyte.

Step 4: Conclusion (a) Cathodic formation of OH^- raises pH. (b) No changing aqueous-ion concentration occurs in the overall mercury-cell reaction. (c) Dilution reduces charge carriers per unit volume.

Quick Tip to Solve: Cancel OH- from the mercury-cell half-reactions, and distinguish conductivity from molar conductivity.

24. 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:

- For the empirical rate law $r = k[A]^m[B]^n$, m and n are the orders with respect to A and B; they are determined experimentally, not from reaction stoichiometry.
- Compare experiments in which only one initial concentration changes. The overall order is $m + n$, and $k = r/([A]^m[B]^n)$.

Step 1: Find the order with respect to A Compare experiments 1 and 2: $[B]$ remains $0.01\,\text{mol L}^{-1}$, while $[A]$ doubles from 0.01 to $0.02\,\text{mol L}^{-1}$. The rate also doubles:

$$\frac{r_2}{r_1} = \frac{1 \times 10^{-2}}{5 \times 10^{-3}} = 2 = \left(\frac{0.02}{0.01}\right)^m = 2^m.$$

Hence $m = 1$: the reaction is first order with respect to A.

Step 2: Find the order with respect to B Compare experiments 1 and 3: $[A]$ remains $0.01\,\text{mol L}^{-1}$, while $[B]$ doubles. The initial rate remains $5 \times 10^{-3}\,\text{mol L}^{-1}\,\text{min}^{-1}$:

$$\frac{r_3}{r_1} = 1 = \left(\frac{0.02}{0.01}\right)^n = 2^n.$$

Thus $n = 0$: the reaction is zero order with respect to B over the conditions of these experiments. The rate law is therefore $r = k[A]$, and the overall order is $1 + 0 = 1$.

Step 3: Calculate and check the rate constant Using experiment 1,

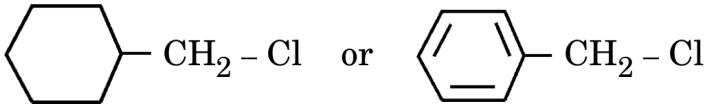
$$k = \frac{r_1}{[A]_1} = \frac{5 \times 10^{-3}\,\text{mol L}^{-1}\,\text{min}^{-1}}{0.01\,\text{mol L}^{-1}} = 0.50\,\text{min}^{-1}.$$

Experiment 2 confirms this value: $k = (1 \times 10^{-2})/0.02 = 0.50\,\text{min}^{-1}$. Experiment 3 gives the same value because changing B does not alter the rate. The concentration units cancel, as expected for a first-order rate constant.

Step 4: Conclusion Order with respect to A: 1; with respect to B: 0; overall order: 1. The rate constant is $\boxed{k = 0.50\,\text{min}^{-1}}$.

Quick Tip to Solve: Compare 1 with 2 for A and 1 with 3 for B; retain inverse minutes because the rates are given per minute.

25. 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:

- S_N1 proceeds through a carbocation; its rate depends on the concentration of the alkyl halide alone.
- S_N2 is a concerted substitution; its rate depends on both the alkyl halide and the nucleophile.
- A carbocation is stabilised when its positive charge can be delocalised by resonance.

Step 1: Compare the kinetics For S_N1, the slow step is ionisation of the carbon–halogen bond, so rate $= k[\mathrm{RCl}]$: the reaction is first order. For S_N2, the nucleophile participates in the single rate-determining step, so rate $= k[\mathrm{RCl}][\mathrm{Nu}^-]$: the reaction is second order.

Step 2: Compare the mechanisms An S_N1 reaction occurs in two steps: departure of the leaving group forms a carbocation, followed by attack of the nucleophile. An S_N2 reaction occurs in one step: backside nucleophilic attack and departure of the leaving group occur together. Thus, S_N1 has a carbocation intermediate, whereas S_N2 does not.

Step 3: Compare the two printed compounds The left compound is cyclohexylmethyl chloride, $\mathrm{C_6H_{11}CH_2Cl}$; the right compound is benzyl chloride, $\mathrm{C_6H_5CH_2Cl}$. Ionisation of benzyl chloride produces $\mathrm{C_6H_5CH_2^+}$. Its positive charge is delocalised into the benzene ring, giving resonance stabilisation. The cyclohexylmethyl carbocation has no corresponding aromatic resonance stabilisation. Stabilisation of the carbocation favours the slow ionisation step of the S_N1 reaction.

Step 4: Conclusion Two differences are first-order versus second-order kinetics, and a two-step carbocation mechanism versus a one-step concerted mechanism. Benzyl chloride undergoes S_N1 faster because it forms a resonance-stabilised benzyl carbocation.

Quick Tip to Solve: For an S_N1 comparison, first draw the carbocation obtained by removing the halide and check for resonance.

26. 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 partially reduces a nitrile, $\mathrm{R-CN}$, to an aldehyde, $\mathrm{R-CHO}$, after hydrolysis.
- Ethanal undergoes aldol addition with dilute NaOH; heating then removes water to give an unsaturated aldehyde.

Quick Tip to Solve: Use the ethanal aldol clue to identify the aldehyde first, then replace CHO by CN to recover the starting nitrile.

- Tollens' reagent detects aldehydes, while the iodoform test requires the appropriate methyl carbonyl or alcohol group.

Step 1: Obtain B from the ethanal clue Two molecules of ethanal first form 3-hydroxybutanal by aldol addition. On heating, this product loses water to form but-2-enal (crotonaldehyde):

$$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$$

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

Hence the structure suggested for B is $CH_3CH = CHCHO$.

Step 2: Identify A and check its formula The carbon atom of the nitrile group becomes the aldehyde carbon on partial reduction. Replace the terminal $-CHO$ of B by $-CN$ to obtain A: $CH_3CH = CHCN$, but-2-enenitrile. It has four carbon atoms, five hydrogen atoms and one nitrogen atom, agreeing with C_4H_5N.

Step 3: Write the required reduction and check the tests Using controlled DIBAL-H reduction followed by hydrolysis,

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

The nitrile group is converted to an aldehyde, with the carbon skeleton and carbon–carbon double bond retained. B gives a positive Tollens' test because it has an aldehyde group. It lacks the CH_3CO- group and is not ethanal, so it does not give the iodoform test.

Step 4: Conclusion A is $CH_3CH = CHCN$, but-2-enenitrile. B is $CH_3CH = CHCHO$, but-2-enal.

Quick Tip to Solve: Use the ethanal aldol clue to identify the aldehyde first, then replace CHO by CN to recover the starting nitrile.

27(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:

- Iron has atomic number 26. Fe^{3+} is $3d^5$, whereas Fe^{2+} is $3d^6$.
- F^- is a weak-field ligand; CN^- is a strong-field ligand and promotes pairing in these iron complexes.

Step 1: Analyse the fluoride complex In $[FeF_6]^{3-}$, $x - 6 = -3$, giving iron oxidation state $+3$. Its $3d^5$ electrons remain unpaired with weak-field fluoride. Two vacant $3d$ orbitals are unavailable, so the octahedral complex uses $4s$, three $4p$, and two $4d$ orbitals.

Step 2: Analyse the cyanide complex In $[Fe(CN)_6]^{4-}$, $x - 6 = -4$, giving iron oxidation state $+2$ and $3d^6$. Strong-field cyanide pairs the six electrons in three $3d$ orbitals, leaving two $3d$ orbitals available for octahedral hybridisation with $4s$ and three $4p$ orbitals.

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

Quick Tip to Solve: Find the iron oxidation state before deciding whether ligand-induced pairing leaves two inner d orbitals vacant.

27(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:

- Iron has atomic number 26. Fe^{3+} is $3d^5$, whereas Fe^{2+} is $3d^6$.
- F^- is a weak-field ligand; CN^- is a strong-field ligand and promotes pairing in these iron complexes.

Step 1: Determine the orbitals used with fluoride Fluoride is weak-field, and the $3d^5$ configuration of Fe^{3+} remains high-spin. The complex therefore uses two outer $4d$ orbitals with $4s$ and $4p$, giving sp^3d^2 hybridisation.

Step 2: Determine the orbitals used with cyanide Cyanide is strong-field. The $3d^6$ electrons of Fe^{2+} pair, making two inner $3d$ orbitals available. Their participation with $4s$ and $4p$ gives d^2sp^3 hybridisation. The words inner and outer refer to the shell of the d orbitals used.

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

Quick Tip to Solve: In octahedral iron complexes, identify whether the hybrid orbitals contain 3d (inner) or 4d (outer) orbitals.

27(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:

- Iron has atomic number 26. Fe^{3+} is $3d^5$, whereas Fe^{2+} is $3d^6$.
- F^- is a weak-field ligand; CN^- is a strong-field ligand and promotes pairing in these iron complexes.
- Unpaired electrons produce paramagnetism; a complex with all electrons paired is diamagnetic.

Step 1: Count unpaired electrons in the fluoride complex In $[FeF_6]^{3-}$, iron is Fe^{3+}, with $3d^5$ configuration. Weak-field F^- produces a high-spin octahedral arrangement, $t_{2g}^3e_g^2$. All five d electrons are unpaired, so this complex is paramagnetic.

Step 2: Count unpaired electrons in the cyanide complex In $[Fe(CN)_6]^{4-}$, iron is Fe^{2+}, with $3d^6$ configuration. Strong-field CN^- produces the low-spin arrangement $t_{2g}^6e_g^0$. All six d electrons are paired, so the complex is diamagnetic.

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

Quick Tip to Solve: Compare magnetism by counting unpaired electrons after accounting for both oxidation state and ligand field strength.

OR

27(b). (i) What happens to the colour of complex $[Ti(H_2O)_6]^{3+}$ when heated gradually ?
(ii) Write the electronic configuration for d^5 ion if $\Delta_o < P$.
(iii) Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$.
[Atomic number : Ni = 28] [3 marks]

Solution:

Concept:

- Colour in an octahedral complex can arise from a d-d transition between the lower t_{2g} and upper e_g levels.
- When the octahedral splitting energy Δ_o is smaller than the pairing energy P, electrons occupy the higher orbitals singly before pairing.
- The presence of unpaired electrons causes paramagnetism; a complex with all electrons paired is diamagnetic.

Step 1: Explain the colour change in part (i) In $[Ti(H_2O)_6]^{3+}$, titanium is in the $+3$ oxidation state and has configuration $3d^1$. Its violet colour arises when the single electron absorbs visible light and moves from t_{2g} to e_g. On gradual heating, coordinated water is removed, so the aqua ligand field responsible for this transition is lost. The violet colour consequently fades and the complex becomes colourless.

Step 2: Fill the orbitals for part (ii) Since $\Delta_o < P$, promotion to an e_g orbital costs less energy than pairing in a t_{2g} orbital. The first three electrons occupy the three t_{2g} orbitals separately and the next two occupy the two e_g orbitals separately. Thus the high-spin configuration is

$$t_{2g}^3 e_g^2.$$

All five electrons are unpaired; the low-spin configuration $t_{2g}^5 e_g^0$ does not apply to the stated inequality.

Step 3: Identify bonding and magnetism for part (iii) Carbon monoxide is a neutral ligand, so nickel has oxidation state zero in $[Ni(CO)_4]$. Free nickel has configuration $[Ar]3d^8 4s^2$. In the presence of the strong-field CO ligands, the electrons pair to give a filled $3d^{10}$ set. One $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals which accept the four ligand lone pairs, producing a tetrahedral complex. There are no unpaired electrons, so it is diamagnetic.

Step 4: Conclusion (i) Violet colour fades to colourless on gradual heating. (ii) $t_{2g}^3 e_g^2$. (iii) sp^3 hybridization and diamagnetic behaviour.

Quick Tip to Solve: For d^5, first compare Δ_o with P: the smaller splitting gives five singly occupied orbitals.

28. 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:

- Freezing-point depression obeys $\Delta T_f = K_f m$, where m is the solute molality and K_f is the molal freezing-point depression constant.
- For a dilute aqueous solution with a nonvolatile solute, Raoultś law gives $\Delta p/p^0 = x_2$, where x_2 is the mole fraction of solute particles and p^0 is the pure-solvent vapour pressure.

Step 1: Calculate the solute molality Pure water freezes at $0\,^\circ\mathrm{C}$, while the solution freezes at $-0.3\,^\circ\mathrm{C}$. Hence $\Delta T_f = 0.3\,\mathrm{K}$. The molality is

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

Taking $1\,\mathrm{kg}$ of water therefore gives $n_2 = 0.16129\,\mathrm{mol}$ of solute particles. This basis is convenient because molality is defined per kilogram of solvent.

Step 2: Convert molality to mole fraction The molar mass of water is $18\,\mathrm{g\,mol^{-1}}$, so

$$n_1 = \frac{1000}{18} = 55.5556\,\mathrm{mol}, \qquad x_2 = \frac{n_2}{n_1 + n_2} = \frac{0.16129}{55.5556 + 0.16129} = 0.0028948.$$

The denominator contains the total number of moles, not only the moles of water. In the usual dilute-solution approximation, $x_2 \simeq n_2/n_1 = 0.0029032$, which gives the same answer to the justified precision.

Step 3: Apply Raoult's law at 298 K The required quantity is the absolute lowering of vapour pressure, $\Delta p = p^0 - p$, rather than the solution vapour pressure. Using $p^0 = 24.8\,\mathrm{mm\,Hg}$,

$$\Delta p = p^0 x_2 = 24.8(0.0028948) = 0.07179\,\mathrm{mm\,Hg}.$$

The dilute approximation gives $0.0720\,\mathrm{mm\,Hg}$. Both calculations show that the lowering is small because the solute mole fraction is small.

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

Quick Tip to Solve: Use a $1\,\mathrm{kg}$ water basis: first find solute moles from $\Delta T_f/K_f$, then apply Raoultś law.

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 $-OH$ group donates electron density to the benzene ring through resonance and activates the ortho and para positions toward electrophilic substitution.
- Under strongly substituting conditions, phenol forms products substituted at all three activated positions: 2, 4 and 6.

Step 1: Treat phenol with bromine water Phenol reacts readily with bromine water at room temperature, without a Lewis acid catalyst. Bromine replaces the hydrogen atoms at the two ortho positions and the para position. Bromine water is decolourised and a white precipitate of 2,4,6-tribromophenol appears. The balanced equation is

$$C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3HBr.$$

The three bromine atoms in the product occupy positions 2, 4 and 6 relative to the hydroxyl group.

Step 2: Treat phenol with concentrated nitric acid Concentrated nitric acid nitrates phenol at all three activated positions to form 2,4,6-trinitrophenol, commonly called picric acid, a yellow compound. The balanced equation is

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

Concentrated acid gives the trisubstituted product; the ortho- and para-nitrophenol mixture associated with dilute nitric acid is not the product under the stated conditions.

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: Keep the reagent strength in view: bromine water and concentrated nitric acid both occupy phenolś 2, 4 and 6 positions.

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

Solution:

Concept:

- A nucleophile donates an electron pair to an electron-deficient species; the oxygen atom of an alcohol ROH has lone pairs available for donation.
- The methyl carbocation CH_3^+ is an electrophile with an empty orbital on carbon.

Step 1: Form the carbon-oxygen bond The alcohol oxygen donates one lone pair to the positively charged methyl carbon. The electron-flow arrow starts at the oxygen lone pair and ends at the carbon of CH_3^+, forming a new $O - C$ bond:

$$R - O(:) - H + CH_3^+ \longrightarrow [R - O(H) - CH_3]^+.$$

Oxygen now has three bonds and carries the positive charge; this intermediate is an oxonium ion.

Step 2: Remove the proton A base removes the proton attached to oxygen, and the electrons of the $O - H$ bond return to oxygen. This gives the neutral ether $R - O - CH_3$:

$$[R - O(H) - CH_3]^+ \longrightarrow R - O - CH_3 + H^+.$$

This equation abbreviates proton transfer to a base in the medium. The initial bond formation explicitly demonstrates the nucleophilic role of the alcohol.

Step 3: Conclusion Alcohol attacks CH_3^+ through an oxygen lone pair, forming an oxonium ion which loses a proton to give $R - O - CH_3$.

Quick Tip to Solve: Draw electron flow from the alcohol oxygen lone pair to the carbocation carbon, then remove the oxygen-bound proton.

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 participates in resonance with the aromatic ring.
- Resonance gives the aryl carbon–oxygen bond partial double-bond character.

Step 1: Examine the carbon–oxygen bond Delocalisation of an oxygen lone pair into the benzene ring strengthens and shortens the $C - O$ bond compared with the corresponding bond in an alcohol. The carbon attached to oxygen is also sp^2-hybridised.

Step 2: Relate bond strength to cleavage The stronger bond with partial double-bond character is difficult to break. Thus the usual substitution reactions of alcohols involving replacement of the hydroxyl group do not occur readily with phenol.

Step 3: Conclusion Phenols do not undergo the usual $C - OH$ cleavage reactions because resonance gives the $C - O$ bond partial double-bond character and makes it stronger.

Quick Tip to Solve: For phenol, discuss resonance in the C–O bond, not simply the acidity of the O–H bond.

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 $ZnCl_2$.
- Turbidity indicates formation of a water-insoluble alkyl chloride; tertiary alcohols react fastest.

Step 1: Identify the alcohol classes Butan-1-ol is a primary alcohol, whereas 2-methylpropan-2-ol is a tertiary alcohol. Treat separate samples with Lucas reagent at room temperature and observe the appearance of turbidity.

Step 2: Compare the observations 2-Methylpropan-2-ol produces immediate turbidity because it readily forms the tertiary alkyl chloride. Butan-1-ol gives no turbidity at room temperature because a primary alcohol reacts very slowly under these conditions. Heating is not needed for this comparison.

Step 3: Conclusion Immediate turbidity identifies 2-methylpropan-2-ol; no turbidity at room temperature identifies butan-1-ol.

Quick Tip to Solve: Keep both samples at room temperature: immediate cloudiness is the diagnostic tertiary-alcohol result.

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 linkage is the amide group $-CO-NH-$ joining amino-acid residues.
- Denaturation disrupts the native folding of a protein and causes loss of biological activity.

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

$$H_2N-CHR-COOH + H_2N-CHR'-COOH$$

$$\longrightarrow H_2N-CHR-CO-NH-CHR'-COOH + H_2O.$$

The newly formed amide group connects the two amino-acid residues.

Step 2: Define denatured protein A denatured protein is a protein whose native secondary and

Quick Tip to Solve: Distinguish denaturation, which alters folding, from hydrolysis, which breaks peptide linkages.

tertiary structures have been disrupted, for example by heating or a change in pH, so that it loses its biological activity. The primary structure, that is, the amino-acid sequence joined by peptide linkages, remains intact during ordinary denaturation. Coagulation of egg white on heating is a familiar example.

Step 3: Conclusion (i) Peptide linkage: the $-CO-NH-$ linkage between amino-acid residues. (ii) Denatured protein: a protein that has lost its native folding and biological activity while retaining its primary structure.

Quick Tip to Solve: Distinguish denaturation, which alters folding, from hydrolysis, which breaks peptide linkages.

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

Solution:

Concept:

- Amphoteric substances react with both acids and bases.
- Amino acids contain an acidic carboxyl group and a basic amino group and commonly exist as zwitterions.

Step 1: Identify the acid and base sites The carboxyl group $-COOH$ can donate a proton, while the amino group $-NH_2$ can accept one. Internal proton transfer produces the zwitterion $H_3N^+ - CHR - COO^-$, which has both positive and negative charged groups.

Step 2: Explain reaction with both reagents In an acidic medium the $-COO^-$ group accepts a proton; in a basic medium the $-NH_3^+$ group donates a proton to the base. Consequently the amino acid can act either as a base or as an acid.

Step 3: Conclusion Amino acids show amphoteric behaviour because they possess both acidic and basic groups and can react with both bases and acids.

Quick Tip to Solve: In a zwitterion, COO-minus accepts H-plus and NH3-plus donates H-plus; this gives both behaviours.

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

Solution:

Concept:

- Protein shape and intermolecular interactions affect water solubility.
- Fibrous proteins generally perform structural roles; globular proteins commonly perform functional roles.

Step 1: Describe fibrous proteins Fibrous proteins have polypeptide chains arranged in long, thread-like fibres or sheets. They are generally insoluble in water and provide structural support. Keratin in hair and wool is an example.

Quick Tip to Solve: Use the paired comparison: fibrous means thread-like and insoluble; globular means compact and soluble.

Step 2: Describe globular proteins Globular proteins have polypeptide chains folded into compact, roughly spherical shapes. They are generally soluble in water; examples include insulin and albumin. Thus molecular shape and water solubility provide the requested distinction.

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 the paired comparison: fibrous means thread-like and insoluble; globular means compact and soluble.

OR

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

Solution:

Concept:

- Secondary structure describes the local folding pattern of the polypeptide backbone.
- Hydrogen bonds involving backbone $\mathrm{C}=\mathrm{O}$ and $\mathrm{N}-\mathrm{H}$ groups stabilise these arrangements.

Step 1: Identify the helical arrangement One secondary structure is the α-helix. The polypeptide backbone coils into a helix stabilised by hydrogen bonds within the chain, while amino-acid side groups project outward.

Step 2: Identify the sheet arrangement The other common secondary structure is the β-pleated sheet. Extended portions of polypeptide chains lie alongside one another and are held together by hydrogen bonds. These are local backbone arrangements, distinct from the overall tertiary folding of a protein.

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

Quick Tip to Solve: Remember the two shape names: alpha is a helix and beta is a pleated sheet.

Section E (15 marks)

31(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:

- Chromate, $\mathrm{CrO_4^{2-}}$, is yellow; dichromate, $\mathrm{Cr_2O_7^{2-}}$, is orange. Their equilibrium depends on the acidity of the solution.
- A transition element has an incompletely filled d subshell in its atom or at least one of its oxidation states. Half-filled d^5 and d^3 configurations can give special stability.

Quick Tip to Solve: Write the electron configuration on both sides of each reduction couple before comparing its potential.

Step 1: Explain the orange-to-yellow change Adding an alkali supplies OH^-, which removes H^+ and favours chromate formation. The balanced reaction is

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

Chromium remains in the +6 oxidation state, so the colour change is an acid-base equilibrium change, rather than reduction of chromium.

Step 2: Explain why Zn, Cd and Hg are non-transition elements Their atoms have outer configurations $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$, respectively. On forming their usual divalent ions, the two outer s electrons are removed and the d^{10} subshell remains completely filled. Thus neither the atoms nor their usual ions contain an incomplete d subshell, so they do not satisfy the definition of transition elements.

Step 3: Compare the manganese and chromium couples Mn^{3+} is $3d^4$, whereas Mn^{2+} has the especially stable half-filled $3d^5$ configuration. Reduction of Mn^{3+} therefore produces a more stable ion and is strongly favoured, giving the highly positive reduction potential $+1.57\,V$. In contrast, Cr^{3+} has a stable $3d^3$ configuration and its reduction to Cr^{2+}, $3d^4$, loses that stability. This reduction is much less favourable, so its standard reduction potential is much lower.

Step 4: Conclusion Alkali converts orange dichromate to yellow chromate; Zn, Cd and Hg retain filled d subshells; and the relative stability of Mn^{2+} and Cr^{3+} explains the difference in the reduction potentials.

Quick Tip to Solve: Write the electron configuration on both sides of each reduction couple before comparing its potential.

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

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

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

Solution:

Concept:

- Disproportionation means that the same species is simultaneously oxidised and reduced. Manganese has oxidation state +6 in manganate, MnO_4^{2-}.
- Potassium permanganate decomposes on heating to potassium manganate, manganese dioxide and oxygen. Balance atoms and charge when writing ionic equations.

Step 1: Disproportionation in acidic medium Green manganate ions yield purple permanganate ions and brown manganese dioxide:

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

Two manganese atoms are oxidised from +6 to +7, losing two electrons in total; the third is reduced from +6 to +4, gaining those two electrons. Both atom counts and the total charge of -2 are conserved.

Quick Tip to Solve: For manganate disproportionation, remember the manganese oxidation-state pattern: +6 becomes +7 and +4.

Step 2: Heating potassium permanganate On heating, solid potassium permanganate decomposes according to

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

Oxygen gas is evolved, and the residue contains green potassium manganate and brown manganese dioxide. The equation conserves two potassium atoms, two manganese atoms and eight oxygen atoms.

Step 3: Conclusion Acidic manganate gives permanganate and MnO_2; heated $KMnO_4$ gives K_2MnO_4, MnO_2 and oxygen, as shown in the balanced equations.

Quick Tip to Solve: For manganate disproportionation, remember the manganese oxidation-state pattern: $+6$ becomes $+7$ and $+4$.

OR

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

Solution:

Concept:

- Misch metal is an alloy rich in lanthanoid metals. Its usefulness depends on the properties of the alloy rather than those of a single pure element.
- The standard composition is about 95 percent lanthanoid metals and about 5 percent iron, with traces of other elements.

Step 1: State the composition Misch metal contains approximately 95 percent lanthanoid metals, chiefly cerium and lanthanum, and about 5 percent iron. It also contains traces of sulphur, carbon, calcium and aluminium. Thus it is a mixture of metals formed as an alloy, not the name of a pure lanthanoid.

Step 2: Give one use Misch metal is used in magnesium-based alloys for making bullets and shells. This is a standard application of the lanthanoid-rich alloy; stating this single use is sufficient for the requested application.

Step 3: Conclusion Misch metal is an alloy of about 95 percent lanthanoid metals and 5 percent iron, with traces of other elements; it is used in magnesium-based alloys for bullets and shells.

Quick Tip to Solve: Remember the approximate 95:5 lanthanoid-to-iron composition and state one concrete alloy application.

31(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, so the requested oxidation state is +6. In an ordinary oxoanion, each oxygen atom has oxidation state -2.
- The sum of the oxidation states of all atoms equals the net charge of the ion.

Step 1: Select a chromium oxoanion Choose the chromate ion, CrO_4^{2-}, which contains one chromium atom and four oxygen atoms. Its net ionic charge is -2, which must be included when calculating the oxidation state.

Step 2: Verify the chromium oxidation state Let chromium have oxidation state x. Then

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

This equals the group number of chromium. The charge on the whole ion is -2; it is distinct from the +6 oxidation state of the chromium atom.

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

Quick Tip to Solve: Include the ionic charge in the oxidation-state equation: for chromate, x - 8 = -2.

31(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 during the catalytic cycle.
- Vanadium can readily change its oxidation state, allowing its oxide to participate in electron transfer during oxidation reactions.

Step 1: Identify the relevant property of vanadium Vanadium in V_2O_5 is in the +5 oxidation state. It can be reduced to the +4 state and then reoxidised to +5. This ability to undergo reversible changes in oxidation state is the principal reason for its catalytic action.

Step 2: Explain a catalytic cycle For example, in oxidation of sulphur dioxide, the oxide transfers oxygen and is subsequently regenerated:

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

These steps provide an alternative pathway for the overall oxidation. Since V_2O_5 is regenerated, it is not consumed in the net reaction.

Step 3: Conclusion V_2O_5 acts as a catalyst because vanadium readily changes between oxidation

Quick Tip to Solve: Connect variable oxidation states to a reversible catalytic cycle, rather than merely naming the property.

states, especially +5 and +4, and the oxide is regenerated in the catalytic cycle.

Quick Tip to Solve: Connect variable oxidation states to a reversible catalytic cycle, rather than merely naming the property.

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

Solution:

Concept:

- Enthalpy of atomisation is the energy required to form one mole of gaseous atoms from the element in its standard state.
- Stronger metallic bonding requires more energy to separate the atoms.

Step 1: Identify the electrons involved Transition elements have several valence electrons, including electrons in the $(n-1)d$ and ns orbitals. Their unpaired electrons participate in strong interatomic metallic bonding.

Step 2: Relate bonding to atomisation Separating the atoms of the metal into individual gaseous atoms requires breaking these strong interactions. A large amount of energy is therefore absorbed during atomisation.

Step 3: Conclusion Transition elements have high enthalpies of atomisation because their numerous unpaired d electrons, along with s electrons, produce strong metallic bonding.

Quick Tip to Solve: Link the number of bonding valence electrons to metallic bond strength, then to atomisation energy.

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

Solution:

Concept:

- Chromate and dichromate ions interconvert with a change in the acidity of the solution.
- Acidification shifts the chromate–dichromate equilibrium towards dichromate.

Step 1: Acidify sodium chromate Treat an aqueous solution of sodium chromate with dilute sulphuric acid. The yellow chromate solution becomes orange as dichromate ions are formed.

Step 2: Write the balanced reaction

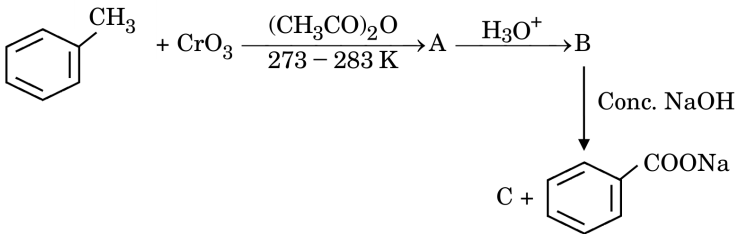
$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

The ionic change is $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$. Thus two chromate units combine in acidic medium.

Step 3: Conclusion Sodium dichromate is prepared by acidifying sodium chromate solution with dilute sulphuric acid.

Quick Tip to Solve: Remember the colour direction: acid changes yellow chromate into orange dichromate.

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



Solution:

Concept:

- Chromium trioxide in acetic anhydride oxidises the methyl side chain of toluene to the protected aldehyde, benzylidene diacetate.
- Acidic hydrolysis removes the acetate groups to give benzaldehyde.
- An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction in concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: Identify the protected oxidation product A The starting aromatic compound is toluene, $C_6H_5CH_3$. With CrO_3 in acetic anhydride at 273–283 K, its side chain gives benzylidene diacetate. Hence $A = C_6H_5CH(OCOCH_3)_2$. This is the diacetate derivative of benzaldehyde; it is not benzoic acid.

Step 2: Hydrolyse A to identify B Acidic hydrolysis regenerates the aldehyde group from the protected derivative:

$$C_6H_5CH(OCOCH_3)_2 + H_2O \xrightarrow{H_3O^+} C_6H_5CHO + 2CH_3COOH.$$

Therefore B is benzaldehyde.

Step 3: Identify the Cannizzaro product C Benzaldehyde has no alpha hydrogen because the carbon adjacent to its aldehyde group belongs to the aromatic ring. Concentrated sodium hydroxide therefore causes disproportionation:

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

One aldehyde molecule is reduced to benzyl alcohol while the other is oxidised to sodium benzoate, the product already shown in the paper.

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: When benzaldehyde and concentrated NaOH appear together, pair sodium benzoate with benzyl alcohol.

32(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:

- Electron donation by the hydroxyl oxygen in a carboxyl group reduces the electrophilicity of its carbonyl carbon.
- Acid strength increases when the conjugate base formed by loss of H^+ is more stable.

Step 1: Explain the behaviour of the carboxyl carbonyl group (I) The lone pair on the hydroxyl oxygen participates in resonance with the carbonyl group. This delocalisation decreases the positive character of the carbonyl carbon. Therefore carboxylic acids do not readily undergo the characteristic nucleophilic addition reactions of aldehydes and ketones; their carbonyl group cannot be treated as an isolated aldehyde or ketone group.

Step 2: Compare the conjugate bases (II) Ethanoic acid loses a proton to form the ethanoate ion, CH_3COO^-. Its negative charge is delocalised over two oxygen atoms through two equivalent resonance structures, giving substantial stabilisation. Ethanol forms ethoxide, $CH_3CH_2O^-$, in which the charge remains localised on one oxygen. The ethyl group also has an electron-releasing inductive effect, which destabilises the negative charge.

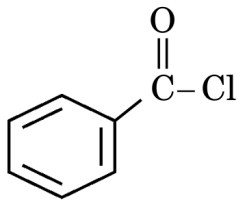
Step 3: Conclusion (I) Resonance lowers the electrophilicity of the carboxyl carbonyl carbon. (II) Ethanoic acid is stronger than ethanol because its conjugate base, ethanoate, is resonance stabilised, whereas ethoxide is not.

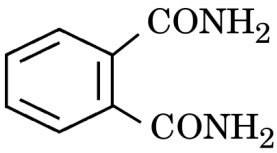
Quick Tip to Solve: For acidity comparisons, remove the acidic proton and compare the stability of the two resulting anions.

OR

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

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

(II)  $+ (CH_3)_2Cd \rightarrow$

(III)  strong heating $\longrightarrow$

Solution:

Concept:

- Dehydration removes water from two carboxylic acid molecules to form an acid anhydride. Phosphorus pentoxide, written as P_4O_{10}, is a dehydrating agent.
- An acid chloride reacts with a dialkylcadmium reagent to form a ketone. Strong heating of adjacent amide groups favours formation of a cyclic imide.

Step 1: (I) Dehydrate ethanoic acid The two ethanoic acid molecules combine with elimination of water. Their acyl groups become joined through an oxygen atom, giving ethanoic anhydride (acetic anhydride):

$$2CH_3COOH \xrightarrow[\text{heat}]{P_4O_{10}} CH_3COOCOCH_3 + H_2O.$$

The water shown in the net equation is taken up by the dehydrating reagent. The organic product contains two acetyl groups.

Step 2: (II) React benzoyl chloride with dimethylcadmium A methyl group replaces chlorine in benzoyl chloride, while the carbonyl group remains intact. The organic product is acetophenone, $C_6H_5COCH_3$. A balanced equation using both methyl groups is

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

Dialkylcadmium gives the ketone without the further addition characteristic of a Grignard reagent.

Step 3: (III) Heat the ortho diamide strongly The two neighbouring amide groups undergo intramolecular condensation. One nitrogen remains between the two carbonyl groups in a five-membered imide ring; the other leaves as ammonia:

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

Here $C_6H_4(CO)_2NH$ denotes cyclic phthalimide, whose $-CO-NH-CO-$ chain joins adjacent

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

positions of the benzene ring.

Step 4: Conclusion The products are (I) ethanoic anhydride, (II) acetophenone (with $CdCl_2$), and (III) phthalimide with ammonia.

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

32(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 an aldehyde or ketone carbonyl group to a methylene group using hydrazine and strong base on heating.
- Soda-lime decarboxylation removes the carboxyl carbon of a sodium carboxylate; the alkane has one carbon fewer than the original acid.

Step 1: (I) Wolff-Kishner reduction The carbonyl compound first forms a hydrazone with hydrazine, NH_2NH_2. Heating it with KOH in ethylene glycol replaces $C = O$ by CH_2, releasing nitrogen. The overall reaction for a ketone is

$$R - CO - R_2 + NH_2NH_2 \xrightarrow[\text{ethylene glycol, heat}]{KOH} R - CH_2 - R_2 + N_2 + H_2O.$$

For an aldehyde, set $R_2 = H$, so the product is RCH_3.

Step 2: (II) Decarboxylation reaction Heat a sodium carboxylate with soda lime, an intimate mixture of NaOH and CaO:

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

For example, sodium ethanoate gives methane:

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

The carboxyl carbon becomes carbonate, explaining the loss of one carbon from the organic product.

Step 3: Conclusion Wolff-Kishner reduction gives RCH_2R_2 from $RCOR_2$; soda-lime decarboxylation gives RH from RCOONa.

Quick Tip to Solve: Keep the carbonyl carbon in Wolff-Kishner reduction, but remove the carboxyl carbon when predicting soda-lime products.

33(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:

- The standard cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$, using reduction potentials for both electrodes.
- At 25°C, $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q$, where n is electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify oxidation and reduction Zinc is oxidised and lead(II) ions are reduced:

$$\begin{aligned} \text{Zn(s)} &\longrightarrow \text{Zn}^{2+} + 2e^{-}, \\ \text{Pb}^{2+} + 2e^{-} &\longrightarrow \text{Pb(s)}. \end{aligned}$$

Thus zinc is the anode, lead is the cathode and $n = 2$. Both tabulated values are reduction potentials, so the negative anode value must be subtracted.

Step 2: Calculate the standard cell potential Use the lead reduction potential for the cathode and the zinc reduction potential for the anode:

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

The positive standard value is consistent with zinc reducing lead(II) ions in the stated reaction.

Step 3: Apply the concentration correction For the reaction as written, zinc ions are products and lead ions are reactants. Therefore

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

Omit solid zinc and solid lead from this quotient. Substituting the supplied $\log 5 = 0.6990$,

$$\begin{aligned} E_{\text{cell}} &= 0.63 - \frac{0.0591}{2}\log 5 \\ &= 0.63 - 0.02955(0.6990) \\ &= 0.63 - 0.02065545\,\text{V}. \end{aligned}$$

Since $Q > 1$, the concentration correction lowers the potential relative to its standard value, providing a check on the sign.

Step 4: Conclusion The galvanic cell potential is $\boxed{E_{\text{cell}} \approx 0.609\,\text{V}}$ at 25°C.

Quick Tip to Solve: Write Q as product-ion concentration divided by reactant-ion concentration; for this cell Q = 5 and n = 2.

33(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: the mass m deposited or liberated at an electrode is directly proportional to the charge q passed through the electrolyte.
- One faraday $F \approx 96485\,\mathrm{C\,mol^{-1}}$ is the charge carried by one mole of electrons; use the electron requirement in the balanced half-reaction.

Step 1: State the law mathematically For a given electrolyte and electrode reaction,

$$m \propto q, \qquad m = Zq = ZIt,$$

where Z is the electrochemical equivalent, I is the current and t is the time for which it flows. Thus doubling the charge passed doubles the mass deposited or liberated, provided the same electrode reaction occurs.

Step 2: Determine the electrons required per permanganate ion In $\mathrm{MnO_4^-}$, oxygen contributes -8 altogether, so manganese has oxidation state $+7$. In $\mathrm{Mn^{2+}}$, it has oxidation state $+2$. Reduction therefore requires a gain of five electrons per manganese atom. The balanced acidic half-reaction is

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

Consequently, one mole of permanganate requires five moles of electrons, each carrying one faraday of charge.

Step 3: Conclusion The electricity required to reduce one mole of $\mathrm{MnO_4^-}$ to $\mathrm{Mn^{2+}}$ is $\boxed{5F}$, approximately $4.82 \times 10^5\,\mathrm{C}$.

Quick Tip to Solve: Count the fall in manganese oxidation state: $+7$ to $+2$ means five electrons and hence five faradays per mole.

OR

33(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: $G = 1/R$, measured in siemens (S).
- Conductivity κ and cell constant l/A are related by $\kappa = G(l/A)$, where l is the electrode separation and A is the effective electrode area. Thus $l/A = \kappa R$.

Quick Tip to Solve: Multiply the given conductivity directly by resistance to find the cell constant; keep the printed power of ten unchanged.

Step 1: Calculate the conductance The cell resistance is $R = 1000\,\Omega$, so its conductance is

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

This is the conductance of this particular cell, which depends on its geometry as well as the solution.

Step 2: Use conductivity to obtain the cell constant At 298 K the given conductivity is $\kappa = 0.125 \times 10^{-3}\,\text{S cm}^{-1}$. Hence

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

The units follow from $\text{S}\,\Omega = 1$, leaving inverse centimetres. The given concentration identifies the standard solution; it does not need to enter a separate molar-conductivity calculation.

Step 3: Conclusion The cell constant is $\boxed{0.125\,\text{cm}^{-1}}$.

Quick Tip to Solve: Multiply the given conductivity directly by resistance to find the cell constant; keep the printed power of ten unchanged.

33(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 $\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s)$, the number of electrons transferred is $n = 2$.
- At 25°C, the Nernst equation is $E = E^\circ - (0.0591/n)\log Q$. The activity of a pure solid is unity, so here $Q = 1/[\text{Mg}^{2+}]$, using the concentration relative to its standard value.

Step 1: Form the reaction quotient The requested potential is labelled $E_{\text{Mg}^{2+}/\text{Mg}}$, so use the reduction reaction and the printed standard potential $E^\circ = +2.36\,\text{V}$. With $[\text{Mg}^{2+}] = 1 \times 10^{-4}\,\text{M}$,

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

The half-cell notation does not change the reduction-potential convention specified by the subscript.

Step 2: Substitute into the Nernst equation Applying the concentration correction gives

$$\begin{aligned} E_{\text{Mg}^{2+}/\text{Mg}} &= 2.36 - \frac{0.0591}{2}\log(10^4) \\ &= 2.36 - (0.02955)(4) \\ &= 2.36 - 0.1182 = 2.2418\,\text{V}. \end{aligned}$$

Lower ion concentration decreases this reduction potential below its given standard value, consistent with the negative correction obtained above.

Quick Tip to Solve: For a metal-ion reduction use n = 2 here and subtract 0.1182 V from the printed standard potential; preserve its given sign.

Step 3: Conclusion Using the standard potential supplied in the question, $\boxed{E_{Mg^{2+}/Mg} = +2.242\,V}$ (approximately $+2.24\,V$).

Quick Tip to Solve: For a metal-ion reduction use n = 2 here and subtract 0.1182 V from the printed standard potential; preserve its given sign.

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

[1 mark]

Solution:

Concept:

- Metallic conduction is due to the motion of mobile electrons through a lattice of positive metal ions.
- Conductance G and resistance R are reciprocals: $G = 1/R$. Increased scattering of electrons raises resistance and lowers conductance.

Step 1: Consider the effect of heating on the lattice When temperature rises, the metal ions vibrate more vigorously about their lattice positions. The moving electrons undergo more frequent collisions with these vibrating ions, so their motion through the conductor is hindered.

Step 2: Relate the resistance change to conductance Increased collisions increase the resistance of an ordinary metallic conductor. Since $G = 1/R$, its electrical conductance decreases as temperature increases. Cooling has the reverse effect because the lattice vibrations become smaller.

Step 3: Conclusion The electrical conductance of a metallic conductor decreases with increasing temperature.

Quick Tip to Solve: In metals, heating increases lattice vibrations and electron scattering: resistance rises, so conductance falls.