CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-5-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

(ii) Question paper is divided into **FIVE** sections – **Section A, B, C, D and E.**

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

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

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

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

(vii) **Section E** – question 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)

Question No. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each.

1. The specific sequence in which amino acids are arranged in a protein is called its [1 mark]

(A) Primary structure

(B) Secondary structure

(C) Tertiary structure

(D) Quaternary structure

Correct Answer: (A) Primary structure

Solution:

Concept:

- The primary structure of a protein is its definite sequence of amino acid residues linked by peptide bonds.
- Secondary, tertiary and quaternary structures describe progressively higher levels of folding or association.

Step 1: Identify what is specified The question refers to the order in which amino acids occur along a polypeptide chain. Reading the chain from its amino end to its carboxyl end gives this sequence; it determines the identity of the protein.

Step 2: Distinguish the other levels Secondary structure describes local arrangements such as the alpha helix and beta sheet. Tertiary structure describes the overall three-dimensional folding of one polypeptide. Quaternary structure describes the association of two or more polypeptide subunits. None names the linear amino acid sequence.

Step 3: Conclusion The sequence is the primary structure. Hence, the correct option is (A).

Quick Tip to Solve: For a question about amino acid order, choose primary; reserve folding and subunit association for higher levels.

2. The correct name of the given reaction is [1 mark]

$$Ar - N_2^+ X^- \xrightarrow{Cu\ CN/KCN} Ar - CN + N_2$$

(A) Sandmeyer's reaction

(B) Gabriel Phthalimide synthesis

(C) Carbyl amine reaction

(D) Hoffmann bromamide degradation reaction

Correct Answer: (A) Sandmeyer's reaction

Solution:

Concept:

- Aryl diazonium salts undergo replacement of their diazonium group with loss of nitrogen gas.
- Sandmeyer reactions use cuprous salts to replace the diazonium group by chloride, bromide or cyanide.

Step 1: Identify the replacement In the displayed reaction the aryl diazonium group is replaced by a cyano group, producing an aromatic nitrile, $ArCN$, and releasing N_2. The copper(I) cyanide reagent identifies the cuprous-salt substitution.

Step 2: Compare the named reactions Gabriel phthalimide synthesis prepares primary amines using a phthalimide salt and an alkyl halide. The carbylamine reaction converts primary amines into isocyanides with chloroform and alcoholic alkali. Hofmann bromamide degradation converts a primary amide into an amine with one fewer carbon atom. These transformations do not match the diazonium-to-nitrile conversion.

Step 3: Conclusion This is Sandmeyer's reaction. Hence, the correct option is (A).

Quick Tip to Solve: Look for an aryl diazonium salt together with a cuprous salt: replacement by cyanide is a Sandmeyer reaction.

3. Out of the following alkenes, the one which will produce tertiary butyl alcohol on acid catalysed hydration is [1 mark]

(A) $CH_3CH_2CH = CH_2$

(B) $CH_3CH = CH_2$

(C) $CH_3–CH = CH–CH_3$

(D) $(CH_3)_2C = CH_2$

Correct Answer: (D) $(CH_3)_2C = CH_2$

Solution:

Concept:

- Acid-catalysed hydration adds water across an alkene double bond in accordance with Markovnikov orientation.

Quick Tip to Solve: Place the hydroxyl group on the more substituted double-bond carbon, then count its three carbon neighbours.

- A tertiary alcohol has its carbon bearing the hydroxyl group bonded to three carbon atoms.

Step 1: Identify the required carbon skeleton Tertiary butyl alcohol is 2-methylpropan-2-ol, $(CH_3)_3COH$. The corresponding alkene is 2-methylpropene, $(CH_3)_2C{=}CH_2$. Proton addition at the terminal carbon gives the stable tertiary carbocation, which is attacked by water and then loses a proton.

Step 2: Check all four alkenes Option (A), but-1-ene, gives butan-2-ol as the major hydration product. Option (B), propene, gives propan-2-ol and has only three carbons. Option (C), but-2-ene, also gives butan-2-ol. Option (D) has the branched four-carbon skeleton needed for tertiary butyl alcohol:

$$(CH_3)_2C{=}CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3COH$$

Step 3: Conclusion 2-Methylpropene produces tertiary butyl alcohol. Hence, the correct option is (D).

Quick Tip to Solve: Place the hydroxyl group on the more substituted double-bond carbon, then count its three carbon neighbours.

4. Auto-oxidation of chloroform in air and light produces a poisonous gas known as [1 mark]

(A) Phosphine

(B) Mustard gas

(C) Phosgene

(D) Tear gas

Correct Answer: (C) Phosgene

Solution:

Concept:

- Chloroform undergoes slow oxidation by atmospheric oxygen when exposed to air and light.
- The oxidation product carbonyl chloride, $COCl_2$, is commonly called phosgene and is poisonous.

Step 1: Write the oxidation reaction The balanced overall reaction is

$$2\,CHCl_3 + O_2 \xrightarrow{light} 2\,COCl_2 + 2\,HCl$$

Thus, oxygen converts chloroform into carbonyl chloride; the equation conserves carbon, hydrogen, chlorine and oxygen atoms.

Step 2: Match the gas to its name Phosgene is the common name of carbonyl chloride, so it matches the oxidation product. Phosphine is PH_3 and would require phosphorus, absent from chloroform. Mustard gas is a sulfur-containing organic compound. Tear gas denotes lachrymatory substances, not the standard named oxidation product of chloroform.

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

Quick Tip to Solve: Remember the pair chloroform plus air and light gives carbonyl chloride, whose common name is phosgene.

5. Transition metals are known to make interstitial compounds. Formation of interstitial compounds makes the transition metal [1 mark]

(A) more hard

(B) more soft

(C) more ductile

(D) more metallic

Correct Answer: (A) more hard

Solution:

Concept:

- Interstitial compounds form when small atoms such as hydrogen, carbon or nitrogen occupy spaces in a transition-metal lattice.
- These compounds are generally very hard and retain metallic conductivity, although their mechanical properties change.

Step 1: Relate lattice occupation to hardness The small atoms fit into interstitial sites between metal atoms. Their presence strengthens and distorts the lattice and impedes the movement of lattice planes relative to one another. The material therefore resists deformation more strongly.

Step 2: Compare the property changes Greater resistance to deformation means increased hardness, matching option (A). Increased softness would mean the opposite change. Greater ductility is not the characteristic result because slipping is hindered. Although metallic conductivity is commonly retained, the phrase more metallic does not describe the characteristic effect of interstitial compound formation.

Step 3: Conclusion Formation of interstitial compounds makes the transition metal harder. Hence, the correct option is (A).

Quick Tip to Solve: Connect small atoms in lattice gaps with restricted slipping of metal layers; restricted slipping means greater hardness.

6. Isotonic solutions have the same [1 mark]

(A) density

(B) refractive index

(C) osmotic pressure

(D) volume

Correct Answer: (C) osmotic pressure

Solution:

Concept:

- Isotonic solutions have equal osmotic pressures at the same temperature.
- For a dilute solution, $\pi = iCRT$, where i is the van't Hoff factor, C molar concentration, R gas constant and T absolute temperature.

Quick Tip to Solve: Associate isotonic with equal osmotic pressure at a common temperature, rather than with equal solution volumes.

Step 1: Apply the definition Two solutions are isotonic when their osmotic pressures are equal at the same temperature:

$$\pi_1 = \pi_2.$$

If separated by a membrane permeable only to the solvent, neither solution draws solvent from the other by a net osmotic flow.

Step 2: Distinguish unrelated properties Osmotic pressure depends on the effective concentration of dissolved particles. Equal osmotic pressure does not require equal density or refractive index, which also depend on the substances present. Nor does it require equal total volume: samples of different volumes can have the same concentration and osmotic pressure. Thus options (A), (B) and (D) are not the defining equality.

Step 3: Conclusion Isotonic solutions have the same osmotic pressure. Hence, the correct option is (C).

Quick Tip to Solve: Associate isotonic with equal osmotic pressure at a common temperature, rather than with equal solution volumes.

7. Which of the following cell was used in Apollo space programme? [1 mark]

(A) Mercury cell

(B) H_2 – O_2 fuel cell

(C) Dry cell

(D) Ni–Cd cell

Correct Answer: (B) H_2 – O_2 fuel cell

Solution:

Concept:

- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy.
- In a hydrogen-oxygen fuel cell, H_2 is the fuel and O_2 is the oxidant; the overall product is water.

Step 1: Identify the Apollo cell The Apollo space programme used the hydrogen-oxygen fuel cell. It provided electrical power while producing water that could be used by the astronauts. The overall cell reaction is

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O.$$

Step 2: Compare the remaining choices A mercury cell and a dry cell are primary cells with reactants stored inside them. A nickel-cadmium cell is a rechargeable secondary cell. These cells do not identify the continuously fed hydrogen-oxygen system used in Apollo, so choices (A), (C) and (D) are rejected.

Step 3: Conclusion The Apollo space programme used the H_2–O_2 fuel cell. Hence, the correct option is (B).

Quick Tip to Solve: Connect Apollo with a fuel cell that supplies both electrical energy and useful water: hydrogen plus oxygen.

8. The rate of a reaction increases sixteen times when the concentration of the reactant increases four times. The order of the reaction is [1 mark]

(A) 2.5

(B) 2.0

(C) 1.5

(D) 0.5

Correct Answer: (B) 2.0

Solution:

Concept:

- For a single-reactant rate law, $r = k[A]^n$, where r is rate, k is the rate constant and n is the order.
- At unchanged temperature, taking a ratio cancels k: $r_2/r_1 = ([A]_2/[A]_1)^n$.

Step 1: Form the rate ratio The concentration becomes four times its initial value while the rate becomes sixteen times its initial value. Therefore,

$$16 = 4^n.$$

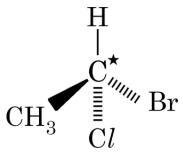
Since $16 = 4^2$, the exponent required in the rate law is fixed.

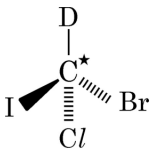
Step 2: Test the listed orders The proposed orders 2.5, 2.0, 1.5 and 0.5 would give rate factors 32, 16, 8 and 2, respectively. Only the order in (B) reproduces the measured sixteenfold increase. Order is an exponent and has no unit.

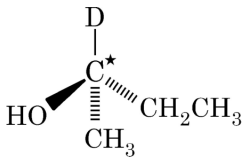
Step 3: Conclusion The reaction is second order, $n = 2.0$. Hence, the correct option is (B).

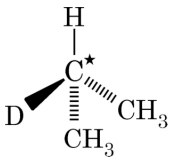
Quick Tip to Solve: Write the rate multiplier and concentration multiplier with the same base: here sixteen is four squared.

9. In which of the following molecules, C atom marked with asterisk is chiral? [1 mark]

(I) 

(II) 

(III) 

(IV) 

(A) I, II, III

(B) I, II, III, IV

(C) II, III, IV

(D) I, III, IV

Correct Answer: (A) I, II, III

Solution:

Concept:

- A tetrahedral carbon is a chiral centre when its four attached groups are all different.
- Deuterium, D, and hydrogen, H, are distinguishable isotopes, but two identical methyl groups remain identical.

Step 1: Check structures I, II and III In I, the starred carbon carries H, CH_3, Br and Cl: all are different. In II, its groups are D, I, Br and Cl, again all different. In III, the groups are D, OH, CH_3 and CH_2CH_3. Methyl and ethyl are different groups, so III also has a chiral starred carbon.

Step 2: Reject structure IV and compare the options In IV, the starred carbon has H, D and two CH_3 groups. Although the two isotopes differ, the repeated methyl groups make this carbon achiral. Thus every option containing IV, namely (B), (C) and (D), fails the four-different-groups test.

Step 3: Conclusion The starred carbon is chiral in I, II and III. Hence, the correct option is (A).

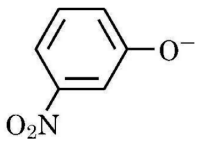
Quick Tip to Solve: List all four groups at the starred carbon; distinguish isotopes, then check for a repeated methyl group.

10. Which of the following species can act as the strongest base? [1 mark]

(A) OH^-

(B) $C_6H_5O^-$

(C) RO^-

(D) 

Correct Answer: (C) RO^-

Solution:

Concept:

- A base accepts a proton. A negative ion with greater electron density available for protonation is generally a stronger base.
- Electron-donating inductive effects increase basicity, while electron-withdrawing effects and resonance stabilization decrease it.

Step 1: Compare alkoxide with hydroxide In RO^-, the alkyl group has a positive inductive effect and pushes electron density towards oxygen. This makes alkoxide a stronger proton acceptor than OH^- in the standard comparison of these anions.

Step 2: Compare the aromatic anions In $C_6H_5O^-$, the negative charge is delocalized by resonance into the aromatic ring, stabilizing phenoxide and reducing its basicity relative to alkoxide. The nitro group in the nitrophenoxide option withdraws electron density, further reducing its proton-accepting tendency. Therefore neither (B) nor (D) exceeds alkoxide, and hydroxide in (A) also falls below it.

Step 3: Conclusion RO^- is the strongest base among the listed species. Hence, the correct option is (C).

Quick Tip to Solve: For these oxygen anions, identify alkyl electron donation first; aromatic resonance and nitro withdrawal reduce basicity.

11. Dilution affects both conductivity as well as molar conductivity. Effect of dilution on both is as follows: [1 mark]

(A) both increase with dilution.

(B) both decrease with dilution.

(C) conductivity increases whereas molar conductivity decreases on dilution.

(D) conductivity decreases whereas molar conductivity increases on dilution.

Correct Answer: (D) conductivity decreases whereas molar conductivity increases on dilution.

Solution:

Concept:

- Conductivity κ measures conduction by the ions present per unit volume of solution.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when c is in mol L^{-1}; it measures conduction associated with one mole of electrolyte.

Quick Tip to Solve: Keep the quantities separate: conductivity refers to ions per unit volume, while molar conductivity refers to one mole.

Step 1: Track conductivity on dilution Adding solvent reduces the number of charge-carrying ions per unit volume, so conductivity κ decreases. This eliminates options (A) and (C), both of which claim that conductivity increases.

Step 2: Track molar conductivity on dilution Molar conductivity increases on dilution because reduced interionic attraction allows ions to move more freely. For weak electrolytes, increased ionization also contributes strongly. Thus conductivity and molar conductivity respond differently: a lower concentration need not imply lower conduction per mole. Option (B) wrongly claims that both decrease.

Step 3: Conclusion Conductivity decreases whereas molar conductivity increases on dilution. Hence, the correct option is (D).

Quick Tip to Solve: Keep the quantities separate: conductivity refers to ions per unit volume, while molar conductivity refers to one mole.

12. Van't Hoff factor for $Na_2SO_4 \cdot 10H_2O$ solution, assuming complete ionization is [1 mark]

(A) 1

(B) 3

(C) 13

(D) 2

Correct Answer: (B) 3

Solution:

Concept:

- The van't Hoff factor i is the ratio of solute particles after dissociation to the number of solute formula units initially dissolved.
- Water of crystallization joins the solvent on dissolution and is not counted as separate solute particles.

Step 1: Write the dissolution products Complete ionization of hydrated sodium sulphate can be represented as

$$\mathrm{Na_2SO_4 \cdot 10\,H_2O} \longrightarrow \mathrm{2\,Na^+ + SO_4{}^{2-} + 10\,H_2O}.$$

Each formula unit provides two sodium ions and one sulphate ion. The ten water molecules become part of the aqueous solvent.

Step 2: Count solute particles and reject distractors There are $2 + 1 = 3$ solute ions for each original formula unit. Thus $i = 3/1$. The value 13 wrongly counts the water of crystallization as solute particles. The value 1 ignores dissociation, whereas 2 omits one of the three ions produced by complete ionization.

Step 3: Conclusion For complete ionization, the van't Hoff factor is $i = 3$. Hence, the correct option is (B).

Quick Tip to Solve: Ignore water of crystallization when counting dissolved solute ions: sodium sulphate gives two sodium ions and one sulphate ion.

13. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): Zr and Hf are of almost similar atomic radii.

Reason (R): This is due to Lanthanoid contraction. [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 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:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series because of poor shielding by $4f$ electrons.
- Atomic size depends on effective nuclear charge as well as the number of occupied shells.

Step 1: Judge the Assertion The Assertion is true. Zr and Hf, the corresponding members of the second and third transition series, have almost equal atomic radii even though hafnium has an additional occupied shell.

Step 2: Judge the Reason The Reason is true. The lanthanoid series precedes hafnium, and its poorly shielding $4f$ electrons allow the increasing nuclear charge to contract the electron cloud.

Step 3: Check the explanatory link This contraction offsets the size increase normally expected on moving down the group from zirconium to hafnium. Thus the Reason directly explains the Assertion; options (B), (C) and (D) incorrectly deny the link or the truth of a statement.

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

Quick Tip to Solve: For the unusually similar sizes of second- and third-series transition elements, check whether intervening lanthanoids offset the extra shell.

14. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): The units of rate constant of a zero order reaction and rate of reaction are the same.

Reason (R): In zero order reaction, the rate of reaction is independent of the concentration of reactants. [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 Assertion (A).

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

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

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

Solution:

Concept:

- For a reaction of order n, the rate law is $r = k[A]^n$, where r is reaction rate, k is the rate constant and $[A]$ is reactant concentration.
- Rate has dimensions of concentration per time, commonly mol $L^{-1}s^{-1}$.

Step 1: Judge the Assertion For zero order, $n = 0$, so

$$r = k[A]^0 = k.$$

Therefore k and the rate have identical units, mol $L^{-1}s^{-1}$. The Assertion is true.

Step 2: Judge the Reason The Reason is true. Changing reactant concentration does not change the rate within the conditions in which the reaction follows zero-order kinetics, since the concentration factor is unity.

Step 3: Check the explanatory link This concentration independence removes the concentration factor from the rate law and gives $r = k$. It therefore explains the common units. Option (B) incorrectly denies this link, while (C) and (D) wrongly classify one statement as false.

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

Quick Tip to Solve: Write the rate law with the actual reaction order before finding units; for zero order the concentration factor becomes exactly unity.

15. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): Inversion of configuration is observed in S_N2 reaction.

Reason (R): The reaction proceeds with the formation of carbocation. [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 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:

- An S_N2 substitution is concerted: bond formation and bond breaking occur in a single step.
- Backside nucleophilic attack reverses the spatial arrangement around the reacting stereogenic carbon, giving inversion of configuration.

Step 1: Judge the Assertion The Assertion is true. The nucleophile approaches from the side opposite the leaving group in an S_N2 reaction. As the leaving group departs, the arrangement of the other groups turns inside out, producing Walden inversion.

Step 2: Judge the Reason The Reason is false. An S_N2 reaction passes through a transition state with partial bonds to the nucleophile and leaving group; it does not form a carbocation intermediate. Carbocation formation instead belongs to the usual S_N1 mechanism.

Step 3: Check the explanatory link The false statement about carbocation formation cannot explain inversion. Backside attack in the concerted mechanism supplies the explanation. Options (A) and (B) incorrectly treat R as true, and (D) incorrectly treats A as false.

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

Quick Tip to Solve: Distinguish the mechanisms by intermediates: concerted backside attack gives inversion in SN2; a carbocation indicates SN1.

16. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): p-methoxyphenol is a stronger acid than p-nitrophenol.

Reason (R): Methoxy group shows +I effect whereas nitro group shows –I effect. [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 Assertion (A).

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

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

Correct Answer: No correct printed option: both Assertion and Reason are false. Methoxy shows -I, not the printed +I, and p-nitrophenol is the stronger acid.

Solution:

Concept:

- Phenol acidity increases when a substituent stabilises the phenoxide conjugate base.
- The nitro group withdraws electrons by $-I$ and $-R$ effects; the methoxy group has a $-I$ effect but donates by $+R$ resonance.

Step 1: Judge the Assertion The Assertion is false. The para nitro group stabilises the negative charge of the phenoxide ion through electron withdrawal and resonance, making p-nitrophenol more acidic than p-methoxyphenol. Para methoxy resonance donation instead makes the conjugate base less favourable.

Step 2: Judge the Reason as printed The Reason is also false. Oxygen in $-\mathrm{OCH_3}$ is electronegative, so methoxy withdraws inductively ($-I$); its electron-donating effect on the aromatic ring is $+R$, not the printed $+I$. The stated $-I$ effect of $-\mathrm{NO_2}$ is correct, but the first clause makes the complete Reason false.

Step 3: Check the available codes There is no explanatory link because both statements are false. Options (A) and (B) require both to be true, (C) requires A to be true, and (D) requires R to be true. None matches the chemically correct judgement of the printed statements.

Step 4: Conclusion Both A and R are false as printed; none of the supplied options is correct.

Quick Tip to Solve: Separate inductive and resonance effects: methoxy has -I but +R, whereas nitro withdraws by both effects.

Section B (10 marks)

17. State:

(a) Kohlrausch law of independent migration of ions.

(b) Faraday's first law of electrolysis. [2 marks]

Solution:

Concept:

- At infinite dilution, ions migrate independently, and each ion makes a definite contribution to an electrolytes limiting molar conductivity.
- Electrolysis connects the mass deposited or liberated at an electrode with the total electric charge passed through the electrolyte.

Step 1: State Kohlrausch law At infinite dilution, each ion contributes independently to the total molar conductivity of an electrolyte, irrespective of the nature of the other ion present. For an electrolyte producing ν_+ cations and ν_- anions per formula unit,

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ.$$

Here Λ_m° is limiting molar conductivity and $\lambda_+^\circ, \lambda_-^\circ$ are the limiting ionic molar conductivities. The coefficients count the respective ions, so contributions must be added with their stoichiometric multiplicities.

Step 2: State Faraday first law The mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte:

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

Here m is the mass, Q is electric charge, Z is the electrochemical equivalent, I is a constant current and t is its duration. Thus doubling the charge doubles the deposited mass for the same substance. With I in amperes and t in seconds, Q is measured in coulombs.

Step 3: Conclusion Kohlrausch law adds independent ionic contributions at infinite dilution; Faraday first law gives $m = ZQ$, or $m = ZIt$ for constant current.

Quick Tip to Solve: Remember the distinguishing condition: infinite dilution for independent ionic migration, and total charge passed for electrode mass.

18. Classify the following sugars into monosaccharides and disaccharides:

Galactose, Glucose, Lactose and Maltose [2 marks]

Solution:

Concept:

- A monosaccharide is a carbohydrate that cannot be hydrolysed to simpler carbohydrate units. Glucose and galactose are single sugar units.

Quick Tip to Solve: Remember lactose as glucose + galactose, and maltose as glucose + glucose; two linked units identify a disaccharide.

- A disaccharide contains two monosaccharide units joined by a glycosidic bond. Hydrolysis breaks this bond and releases the component sugars.

Step 1: Identify the single sugar units Galactose and glucose are monosaccharides. Each is an aldohexose, containing six carbon atoms and an aldehyde group in its open-chain form. Neither can be split by hydrolysis into smaller carbohydrate molecules; consequently, their classification depends on being individual sugar units, rather than on their sweetness or reducing behaviour.

Step 2: Identify the sugars containing two units Lactose is formed from galactose and glucose, whereas maltose is formed from two glucose units. Their glycosidic bonds can be hydrolysed to give these constituent monosaccharides. Both therefore belong to the disaccharide class. The fact that these sugars are reducing sugars does not make them monosaccharides: the classification here is by the number of sugar units.

Step 3: Conclusion Monosaccharides: galactose and glucose. Disaccharides: lactose and maltose.

Quick Tip to Solve: Remember lactose as glucose + galactose, and maltose as glucose + glucose; two linked units identify a disaccharide.

19(a)(i). Carry out the following conversions:

Nitrobenzene to Aniline [1 mark]

Solution:

Concept:

- Reduction of an aromatic nitro group, $-NO_2$, gives the corresponding primary amino group, $-NH_2$.
- Tin and hydrochloric acid provide the reducing medium; subsequent treatment with $NaOH$ liberates the free amine from its salt.

Step 1: Reduce the nitro group Treat nitrobenzene with tin and hydrochloric acid. The nitro group is reduced while the benzene ring remains unchanged. The overall reduction to the free amine can be represented as

$$C_6H_5NO_2 + 6\,[H] \longrightarrow C_6H_5NH_2 + 2\,H_2O.$$

Step 2: Liberate the free amine In the acidic reaction mixture the amine is present as its anilinium salt. Add aqueous sodium hydroxide after reduction to obtain the free amino compound. Thus the reagent sequence is Sn/HCl, followed by $NaOH$.

Step 3: Conclusion Nitrobenzene is converted to aniline by reduction with Sn/HCl, followed by alkaline work-up with $NaOH$.

Quick Tip to Solve: For nitrobenzene to aniline, reduce the nitro group and then basify to release the free amine.

19(a)(ii). Carry out the following conversions:

Aniline to Phenol [1 mark]

Solution:

Concept:

- Aniline undergoes diazotisation with nitrous acid generated from $NaNO_2$ and HCl.
- The diazonium salt is prepared at 273–278 K; warming its aqueous solution replaces the diazonium group by $-OH$.

Step 1: Prepare the diazonium salt Treat aniline with sodium nitrite and hydrochloric acid at 273–278 K:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2Cl + NaCl + 2\,H_2O.$$

The low temperature stabilises benzenediazonium chloride during its preparation.

Step 2: Hydrolyse the diazonium salt Warm the aqueous diazonium salt solution. Water replaces the diazonium group, with evolution of nitrogen:

$$C_6H_5N_2Cl + H_2O \xrightarrow{\text{warm}} C_6H_5OH + N_2 + HCl.$$

This two-stage route introduces the hydroxyl group at the same ring position as the original amino group.

Step 3: Conclusion Aniline is diazotised using $NaNO_2/HCl$ at 273–278 K, and the resulting diazonium salt is warmed with water to form phenol.

Quick Tip to Solve: Keep diazotisation cold, then warm with water: the first stage forms the diazonium salt, and the second forms phenol.

OR

19(b)(i). Write a chemical test to distinguish between Dimethyl amine and Ethanamine. [1 mark]

Solution:

Concept:

- The carbylamine test is given only by primary amines; secondary and tertiary amines do not give this test.
- A primary amine heated with chloroform and alcoholic potassium hydroxide forms a foul-smelling isocyanide.

Step 1: Apply the carbylamine test Heat separate samples of the two amines with chloroform and alcoholic potassium hydroxide. Ethanamine is a primary amine because its nitrogen is bonded to one ethyl group; dimethylamine is secondary because its nitrogen is bonded to two methyl groups.

Step 2: Compare the observations Ethanamine produces a foul-smelling ethyl isocyanide:

$$C_2H_5NH_2 + CHCl_3 + 3\,KOH \longrightarrow C_2H_5NC + 3\,KCl + 3\,H_2O.$$

Quick Tip to Solve: Count the carbon groups attached to nitrogen: only the primary amine ethanamine responds to the carbylamine test.

Dimethylamine does not form an isocyanide under these conditions and hence gives a negative carbylamine test.

Step 3: Conclusion Ethanamine gives the carbylamine test, forming foul-smelling ethyl isocyanide; dimethylamine gives a negative test.

Quick Tip to Solve: Count the carbon groups attached to nitrogen: only the primary amine ethanamine responds to the carbylamine test.

19(b)(ii). Write the product formed when benzene diazonium chloride is treated with KI. [1 mark]

Solution:

Concept:

- In benzenediazonium chloride, the diazonium group can be replaced by iodine on treatment with potassium iodide.
- The reaction releases nitrogen gas. No copper salt catalyst is required for replacement by iodine.

Step 1: Identify the substitution Potassium iodide supplies iodide ions. These replace the diazonium group attached to the benzene ring. The carbon framework of the aromatic ring is retained; iodide replaces the entire diazonium group rather than simply replacing chloride in the salt.

Step 2: Write the balanced reaction The balanced reaction is

$$C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + N_2 + KCl.$$

One molecule of nitrogen is liberated for each molecule of the diazonium salt, and potassium chloride is formed from the remaining ions.

Step 3: Conclusion The organic product is iodobenzene, C_6H_5I, with evolution of nitrogen gas.

Quick Tip to Solve: For a diazonium salt treated with KI, replace the diazonium group by iodine and write nitrogen as the gaseous by-product.

20. Show that in case of a first order reaction, the time taken for completion of 99% reaction is twice the time required for 90% completion of the reaction. (log 10 = 1) [2 marks]

Solution:

Concept:

- For a first order reaction, the integrated rate law is $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0$, $[A]_t$ are the initial and remaining reactant concentrations.
- Percentage completion gives the amount consumed. Thus 90% and 99% completion leave 10% and 1% of the initial reactant, respectively. Both times refer to the same reaction at the same temperature, so k is unchanged.

Step 1: Write the time for 90% completion At 90% completion, $[A]_t = 0.10[A]_0$. Substitute the

Quick Tip to Solve: Convert completion to the fraction remaining first: 90% leaves 0.10 and 99% leaves 0.01; their logarithmic concentration ratios are 1 and 2.

remaining concentration, rather than the amount consumed, in the rate law:

$$t_{90} = \frac{2.303}{k} \log \frac{[A]_0}{0.10[A]_0} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}.$$

Step 2: Write the time for 99% completion and compare At 99% completion, $[A]_t = 0.01[A]_0$. Hence

$$t_{99} = \frac{2.303}{k} \log \frac{[A]_0}{0.01[A]_0} = \frac{2.303}{k} \log 100 = \frac{2(2.303)}{k}.$$

Here $\log 100 = \log(10^2) = 2 \log 10 = 2$. Dividing the two expressions cancels the common rate constant and the factor 2.303:

$$\frac{t_{99}}{t_{90}} = \frac{2(2.303)/k}{2.303/k} = 2.$$

Step 3: Conclusion Therefore, $\boxed{t_{99} = 2t_{90}}$: the time needed for 99% completion is twice that needed for 90% completion in a first order reaction.

Quick Tip to Solve: Convert completion to the fraction remaining first: 90% leaves 0.10 and 99% leaves 0.01; their logarithmic concentration ratios are 1 and 2.

21. Resistance of a conductivity cell filled with 0.2 mol L^{-1} KCl solution is $200\,\Omega$. If the resistance of the same cell when filled with 0.05 mol L^{-1} KCl solution is $620\,\Omega$, calculate the conductivity and molar conductivity of 0.05 mol L^{-1} KCl solution. The conductivity of 0.2 mol L^{-1} KCl solution is 0.0248 S cm^{-1}. [2 marks]

Solution:

Concept:

- Conductivity is $\kappa = G(l/A) = (l/A)/R$, where R is resistance, $G = 1/R$ is conductance, and l/A is the cell constant. The same cell has the same cell constant for both solutions.
- With conductivity in S cm^{-1} and concentration C in mol L^{-1}, molar conductivity is $\Lambda_m = 1000\kappa/C$. The factor 1000 converts litres to cubic centimetres.

Step 1: Determine the cell constant using the known solution For the 0.2 mol L^{-1} KCl solution, $\kappa_1 = 0.0248$ S cm^{-1} and $R_1 = 200\,\Omega$. Therefore

$$\frac{l}{A} = \kappa_1 R_1 = (0.0248)(200) = 4.96\ \text{cm}^{-1}.$$

This geometrical factor applies to the second measurement because the conductivity cell is unchanged.

Step 2: Calculate the conductivity of the dilute solution The 0.05 mol L^{-1} solution has resistance $R_2 = 620\,\Omega$. Thus

$$\kappa_2 = \frac{l/A}{R_2} = \frac{4.96}{620} = 0.00800\ \text{S cm}^{-1}.$$

Its conductivity is lower than that of the concentrated solution, consistent with the larger measured resistance in the same cell.

Quick Tip to Solve: For the same conductivity cell, use $\kappa_1 R_1 = \kappa_2 R_2$, then apply $\Lambda_m = 1000\kappa/C$ with the new solution's concentration.

Step 3: Convert to molar conductivity Use the concentration of the second solution, $C_2 = 0.05\,\text{mol L}^{-1}$:

$$\Lambda_{m,2} = \frac{1000\kappa_2}{C_2} = \frac{1000(0.00800)}{0.05} = 160\,\text{S cm}^2\,\text{mol}^{-1}.$$

Conductivity measures the conductance contribution per unit cell geometry; molar conductivity additionally accounts for the amount of electrolyte present.

Step 4: Conclusion For $0.05\,\text{mol L}^{-1}$ KCl, conductivity is $\boxed{0.00800\,\text{S cm}^{-1}}$ and molar conductivity is $\boxed{160\,\text{S cm}^2\,\text{mol}^{-1}}$.

Quick Tip to Solve: For the same conductivity cell, use $\kappa_1 R_1 = \kappa_2 R_2$, then apply $\Lambda_m = 1000\kappa/C$ with the new solution's concentration.

Section C (21 marks)

22. Write the IUPAC names of the following coordination compounds (any three): [3 marks]

22(a). $[Co(NH_3)_4Cl(NO_2)]Cl$

Solution:

Concept:

- Coordination names list ligands alphabetically before the central metal. Multiplicative prefixes indicate ligand numbers but do not control alphabetical order.
- The metal oxidation state follows from the complex charge and ligand charges and is written in Roman numerals. Name cations before anions; an anionic complex uses a metal name ending in -ate.

Step 1: Determine the oxidation state The chloride outside the coordination sphere is Cl^-, so the complex cation has charge $+1$. Ammine is neutral; chlorido and nitrito each have charge -1. Thus $x - 1 - 1 = +1$, giving cobalt oxidation state $+3$.

Step 2: Assemble the coordination name Four NH_3 ligands give tetraammine. The bound Cl^- is chlorido and the printed NO_2 is the N-bonded nitrito ligand, named nitrito-N (also traditionally nitro). List ligand names alphabetically, ignoring multiplicative prefixes: ammine, chlorido, nitrito. Name the cation before the chloride counter-ion.

Step 3: Conclusion The IUPAC name is $\boxed{\text{tetraamminechloridonitrito-N-cobalt(III) chloride}}$.

Quick Tip to Solve: Balance ligand charges against the complex charge before choosing the Roman numeral in the name.

22(b). $[Ni(NH_3)_6]Cl_2$

Solution:

Concept:

- Coordination names list ligands alphabetically before the central metal. Multiplicative prefixes indicate ligand numbers but do not control alphabetical order.
- The metal oxidation state follows from the complex charge and ligand charges and is written in Roman numerals. Name cations before anions; an anionic complex uses a metal name ending in -ate.

Step 1: Determine the oxidation state Two chloride counter-ions each have charge -1, so the complex cation has charge $+2$. Each NH_3 ligand is neutral; therefore $x + 6(0) = +2$, giving nickel oxidation state $+2$.

Step 2: Assemble the coordination name Six neutral ammonia ligands are named hexaammine. Because the complex is cationic, retain the metal name nickel and append its oxidation state in Roman numerals, (II). Name the coordination cation first and the chloride counter-ion second; the count of counter-ions is not expressed by a prefix in the salt name.

Step 3: Conclusion The IUPAC name is $\boxed{\text{hexaamminenickel(II) chloride}}$.

Quick Tip to Solve: Balance ligand charges against the complex charge before choosing the Roman numeral in the name.

22(c). $K_3[Cr(C_2O_4)_3]$

Solution:

Concept:

- Coordination names list ligands alphabetically before the central metal. Multiplicative prefixes indicate ligand numbers but do not control alphabetical order.
- The metal oxidation state follows from the complex charge and ligand charges and is written in Roman numerals. Name cations before anions; an anionic complex uses a metal name ending in -ate.

Step 1: Determine the oxidation state Three K^+ ions give total charge $+3$, so the complex anion has charge -3. Each oxalato ligand, ${C_2O_4}^{2-}$, has charge -2. Thus $x + 3(-2) = -3$, giving chromium oxidation state $+3$.

Step 2: Assemble the coordination name Name the potassium cation first. The three bidentate oxalato ligands are written tris(oxalato); tris is used with this ligand name. As the coordination entity is an anion, chromium becomes chromate. Append (III) to indicate the oxidation state of chromium, rather than the overall charge of the complex.

Step 3: Conclusion The IUPAC name is $\boxed{\text{potassium tris(oxalato)chromate(III)}}$.

Quick Tip to Solve: Balance ligand charges against the complex charge before choosing the Roman numeral in the name.

22(d). $[Co(en)_2Br_2]^+$

Solution:

Concept:

- Coordination names list ligands alphabetically before the central metal. Multiplicative prefixes indicate ligand numbers but do not control alphabetical order.
- The metal oxidation state follows from the complex charge and ligand charges and is written in Roman numerals. Name cations before anions; an anionic complex uses a metal name ending in -ate.

Step 1: Determine the oxidation state Each ethane-1,2-diamine ligand, abbreviated en, is neutral, and each bromido ligand has charge -1. The printed complex has charge $+1$, so $x + 2(0) + 2(-1) = +1$; hence cobalt has oxidation state $+3$.

Step 2: Assemble the coordination name Two bromide ligands give dibromido. The two en ligands are named bis(ethane-1,2-diamine), using bis and parentheses for this ligand name. Alphabetical ordering places bromido before ethane-1,2-diamine, ignoring di and bis. Because the entity is cationic, retain cobalt and append (III); no counter-ion is supplied in the formula.

Step 3: Conclusion The IUPAC name is dibromidobis(ethane-1,2-diamine)cobalt(III) ion.

Quick Tip to Solve: Balance ligand charges against the complex charge before choosing the Roman numeral in the name.

23. Give the structure of the major product expected from the following reactions:

(a) Reaction of Ethanal with methyl-magnesium bromide followed by hydrolysis.

(b) Hydration of But-1-ene in the presence of dilute sulphuric acid.

(c) Reaction of phenol with bromine water. [3 marks]

Solution:

Concept:

- A Grignard reagent adds its alkyl group to the carbonyl carbon. Hydrolysis of the magnesium alkoxide gives an alcohol.
- Acid-catalysed hydration of an unsymmetrical alkene follows Markovnikov's rule: hydrogen enters the carbon already bearing more hydrogen atoms.
- The $-OH$ group strongly activates phenol toward electrophilic substitution at the two ortho positions and the para position.

Step 1: (a) Add methylmagnesium bromide to ethanal The methyl group from CH_3MgBr attacks the carbonyl carbon of CH_3CHO. This carbon now carries two methyl groups, one hydrogen and an alkoxide oxygen. Hydrolysis protonates the oxygen:

$$CH_3CHO + CH_3MgBr \longrightarrow CH_3CH(OMgBr)CH_3$$

$$CH_3CH(OMgBr)CH_3 \xrightarrow{H_2O} CH_3CH(OH)CH_3.$$

Quick Tip to Solve: Count one extra carbon after Grignard addition; put OH at carbon 2 in but-1-ene hydration; bromine water substitutes all three activated positions of phenol.

Thus a secondary alcohol is formed; the carbon chain grows by one carbon.

Step 2: (b) Hydrate but-1-ene In dilute sulphuric acid, protonation of $CH_2{=}CHCH_2CH_3$ gives the more stable secondary carbocation at carbon 2. Water attacks this carbon and loss of a proton regenerates the acid:

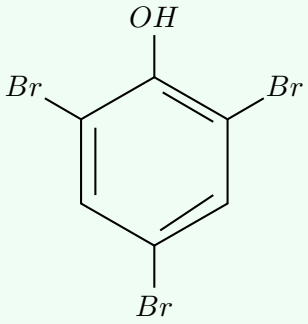
$$CH_2{=}CHCH_2CH_3 + H_2O \xrightarrow{\text{dil. } H_2SO_4} CH_3CH(OH)CH_2CH_3.$$

The hydroxyl group therefore occupies carbon 2, rather than the terminal carbon.

Step 3: (c) Brominate phenol in water Bromine water reacts readily with the activated phenol ring, replacing hydrogen at positions 2, 4 and 6. No Lewis-acid catalyst is needed:

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

Numbering the carbon bearing $-OH$ as carbon 1 fixes the three bromine positions unambiguously. The product separates as a white precipitate.

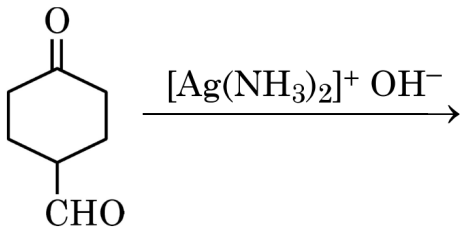


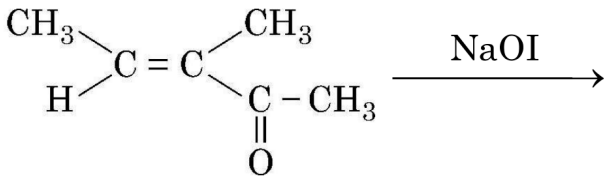
Structure of 2,4,6-tribromophenol

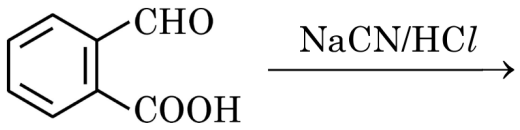
Step 4: Conclusion (a) Propan-2-ol: $CH_3CH(OH)CH_3$. (b) Butan-2-ol: $CH_3CH(OH)CH_2CH_3$. (c) 2,4,6-Tribromophenol: a benzene ring bearing $-OH$ at position 1 and $-Br$ at positions 2, 4 and 6.

Quick Tip to Solve: Count one extra carbon after Grignard addition; put OH at carbon 2 in but-1-ene hydration; bromine water substitutes all three activated positions of phenol.

24. Draw the structures of major product(s) in each of the following reactions: [3 marks]

(a) 

(b) 

(c) 

Solution:

Concept:

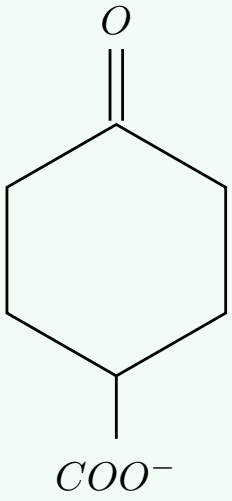
- Tollens' reagent oxidises an aldehyde group $-CHO$ to a carboxylate group $-COO^-$ in alkaline solution. An ordinary ketone is not oxidised.
- Sodium hypoiodite gives the iodoform reaction with a methyl ketone: $RCOCH_3$ becomes $RCOONa$ and CHI_3.
- $NaCN/HCl$ generates hydrogen cyanide. Addition across an aldehyde carbonyl forms the cyanohydrin $RCH(OH)CN$.

Step 1: (a) Oxidise only the aldehyde substituent The printed substrate contains both a ring ketone and a pendant $-CHO$ group at the opposite ring carbon. Tollens' reagent distinguishes these: the aldehyde is oxidised, whereas the ketone carbonyl remains unchanged. The organic product is 4-oxocyclohexane-1-carboxylate, drawn below. The alkaline medium keeps the new group as $-COO^-$; on acidification it would become $-COOH$.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O.$$

Here R denotes the cyclohexanone ring attached to the aldehyde. Silver metal is also deposited.

Quick Tip to Solve: Identify the reactive group before changing the structure: Tollens oxidises CHO, NaOI cleaves COCH3, and HCN adds to CHO while preserving COOH.

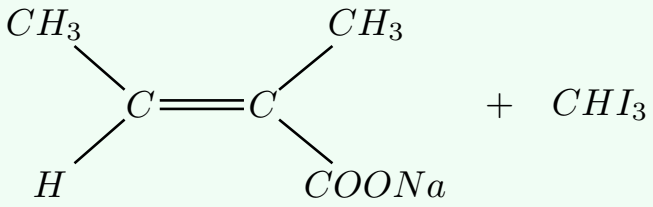


(a) Organic product in the alkaline Tollens medium

Step 2: (b) Cleave the methyl ketone by the iodoform reaction Write the substrate as $RCOCH_3$, where $R = CH_3CH{=}C(CH_3){-}$. The methyl group directly bonded to the carbonyl is successively iodinated, then cleavage produces iodoform and the carboxylate salt. The carbon-carbon double bond is retained:

$$CH_3CH{=}C(CH_3)COCH_3 \xrightarrow{NaOI} CH_3CH{=}C(CH_3)COONa + CHI_3.$$

The organic salt is sodium 2-methylbut-2-enoate. Iodoform, CHI_3, is the characteristic yellow precipitate; both products must be included.



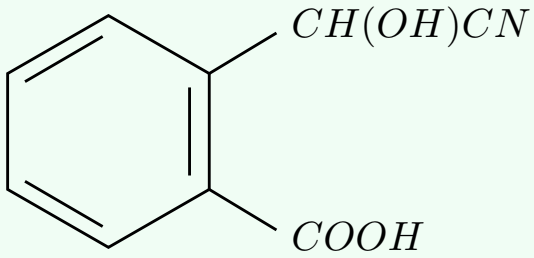
(b) Carboxylate salt and iodoform

Step 3: (c) Form the aldehyde cyanohydrin Cyanide attacks the electrophilic aldehyde carbon, and protonation converts the resulting alkoxide into an alcohol. Thus the original $-CHO$ group becomes $-CH(OH)CN$. The neighbouring $-COOH$ group stays in its original ortho position:

$$o\text{-}HOOC{-}C_6H_4{-}CHO + HCN \longrightarrow o\text{-}HOOC{-}C_6H_4{-}CH(OH)CN.$$

Addition creates a new carbon-carbon bond to the cyanide carbon; the former carbonyl oxygen remains in the hydroxyl group.

Quick Tip to Solve: Identify the reactive group before changing the structure: Tollens oxidises CHO, NaOI cleaves COCH3, and HCN adds to CHO while preserving COOH.



(c) Cyanohydrin with the ortho carboxyl group retained

Step 4: Conclusion The structures are shown below each corresponding step.

(a) 4-Oxocyclohexane-1-carboxylate, with silver deposition.

(b) $CH_3CH{=}C(CH_3)COONa$ and CHI_3.

(c) o-$HOOC{-}C_6H_4{-}CH(OH)CN$.

Quick Tip to Solve: Identify the reactive group before changing the structure: Tollens oxidises CHO, NaOI cleaves COCH3, and HCN adds to CHO while preserving COOH.

25. Calculate the emf of the following cell:

Ni(s) + 2Ag$^+$(0.01 M) $\rightarrow$ Ni^{2+}(0.1 M) + 2Ag(s)

Given that E°$_{cell}$ = 1.05 V, log 10 = 1 [3 marks]

Solution:

Concept:

- The Nernst equation relates the cell potential to its standard potential and the reaction quotient: $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$ at 298 K, where n is the number of electrons transferred.
- Pure solids have unit activity and do not appear in Q. For dilute solutions, ionic activities are represented by their molar concentrations.

Step 1: Identify the electron transfer Nickel is oxidised and silver ions are reduced. The corresponding half-reactions are

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

Thus, two electrons are exchanged per complete cell reaction, so $n = 2$. The coefficient of silver ions also becomes their concentration exponent in the reaction quotient.

Step 2: Calculate the reaction quotient For the reaction as written, the dissolved product is $\mathrm{Ni^{2+}}$ and the dissolved reactant is $\mathrm{Ag^+}$. Therefore,

$$Q = \frac{[\mathrm{Ni^{2+}}]}{[\mathrm{Ag^+}]^2} = \frac{0.1}{(0.01)^2} = 10^3.$$

Nickel and silver metal are omitted because they are pure solids. Using the supplied logarithm, $\log Q = 3\log 10 = 3$.

Quick Tip to Solve: Square the silver-ion concentration in Q, and use $n = 2$: both follow from the balanced cell reaction.

Step 3: Substitute into the Nernst equation Using the usual room-temperature form of the Nernst equation, substitute the standard cell potential, electron count and quotient:

$$E_{\text{cell}} = 1.05 - \frac{0.0591}{2} \times 3$$
$$= 1.05 - 0.08865 = 0.96135\,\text{V}.$$

The positive logarithm lowers the potential below the standard value, as expected for this relatively large product-to-reactant quotient.

Step 4: Conclusion The emf of the cell is $\boxed{E_{\text{cell}} \approx 0.961\,\text{V}}$, or approximately $0.96\,\text{V}$.

Quick Tip to Solve: Square the silver-ion concentration in Q, and use $n = 2$: both follow from the balanced cell reaction.

26. Account for the following:

(a) Haloalkanes react with AgCN to form isocyanide as main product.

(b) Allyl chloride shows high reactivity towards S_N1 reaction.

(c) Haloarenes are extremely less reactive towards nucleophilic substitution reactions. [3 marks]

Solution:

Concept:

- Cyanide is an ambident nucleophile: its carbon and nitrogen ends can form a bond. The nature of the cyanide reagent determines which end principally attacks.
- An S_N1 reaction proceeds through a carbocation; resonance stabilisation of that intermediate increases the ease of ionisation.
- Nucleophilic substitution depends on carbon-halogen bond strength, the stability of possible intermediates, and access to the carbon bearing the halogen.

Step 1: Explain isocyanide formation with silver cyanide (a) $AgCN$ is predominantly covalent. Its carbon end is bonded to silver, leaving the nitrogen end available for attack on the haloalkane. Consequently, the alkyl group bonds to nitrogen and an isocyanide is the main product:

$$R{-}X + AgCN \longrightarrow R{-}NC + AgX.$$

This differs from ionic KCN, whose free cyanide ion chiefly attacks through carbon to give $R{-}CN$, a nitrile.

Step 2: Explain the reactivity of allyl chloride (b) In allyl chloride, departure of chloride forms an allylic carbocation. Its positive charge is delocalised over two carbon atoms through resonance:

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

This stabilises the carbocation formed in the slow, ionisation step of the S_N1 reaction. The reduced energy required for this step explains the high reactivity of allyl chloride.

Quick Tip to Solve: Link each reason to its decisive feature: covalent $AgCN$, a resonance-stabilised allyl cation, and a strong aryl carbon-halogen bond.

Step 3: Explain the low reactivity of haloarenes (c) A halogen lone pair is conjugated with the aromatic ring. Resonance gives the carbon-halogen bond partial double-bond character, making it shorter and stronger than the corresponding bond in a haloalkane. Also, the bonded aromatic carbon is sp^2-hybridised; its greater s-character strengthens the bond relative to an sp^3 carbon-halogen bond. Ordinary S_N1 substitution is unfavourable because loss of halide would produce a highly unstable aryl carbocation. Ordinary S_N2 substitution is difficult because the aromatic ring obstructs the necessary backside attack at the carbon bearing halogen. Hence haloarenes resist nucleophilic substitution under ordinary conditions.

Step 4: Conclusion $AgCN$ chiefly reacts through nitrogen, giving isocyanide; allyl chloride reacts readily by S_N1 because of allylic carbocation resonance; haloarenes react poorly because of their strong carbon-halogen bonds and unfavourable ordinary S_N1 and S_N2 pathways.

Quick Tip to Solve: Link each reason to its decisive feature: covalent $AgCN$, a resonance-stabilised allyl cation, and a strong aryl carbon-halogen bond.

27. The rate constant of a reaction quadruples when the temperature changes from 300 K to 320 K. Calculate the activation energy for this reaction.

[log 2 = 0.30, log 4 = 0.60, 2.303 R = 19.15 J K^{-1} mol^{-1}] [3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For the same reaction at two temperatures, taking common logarithms and eliminating A gives $\log(k_2/k_1) = \dfrac{E_a}{2.303R}(1/T_1 - 1/T_2)$.

Step 1: Identify the temperature and rate-constant ratio Take $T_1 = 300\,\text{K}$ and $T_2 = 320\,\text{K}$. The rate constant at the higher temperature is four times its initial value, so $k_2/k_1 = 4$. Hence $\log(k_2/k_1) = \log 4 = 0.60$, using the value supplied in the question. The temperatures already use the absolute Kelvin scale required by the Arrhenius equation.

Step 2: Rearrange the two-temperature equation Since $1/T_1 - 1/T_2 = (T_2 - T_1)/(T_1T_2)$, solving for the activation energy gives

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

Use the higher-temperature rate constant in the numerator of the logarithm and the higher temperature in T_2. Both the logarithm and $T_2 - T_1$ are then positive, yielding a positive activation energy.

Step 3: Substitute and calculate the activation energy Substituting $2.303R = 19.15\,\text{J K}^{-1}\text{mol}^{-1}$ gives

$$\begin{aligned} E_a &= 19.15 \times 0.60 \times \frac{300 \times 320}{320 - 300} \\ &= 19.15 \times 0.60 \times 4800 \\ &= 55152\,\text{J mol}^{-1}. \end{aligned}$$

Quick Tip to Solve: Use $k_2/k_1 = 4$ directly, and simplify $T_1T_2/(T_2 - T_1) = 4800\,\text{K}$ before multiplying.

The temperature factor has units of kelvin, cancelling the inverse-kelvin unit of R. Dividing the resulting energy by 1000 converts joules per mole to kilojoules per mole.

Step 4: Conclusion The activation energy is $\boxed{E_a = 55.152\,\text{kJ mol}^{-1} \approx 55.2\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Use $k_2/k_1 = 4$ directly, and simplify $T_1T_2/(T_2 - T_1) = 4800\,\text{K}$ before multiplying.

28. A compound 'X' with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify 'X' and give the IUPAC name of the product. Write the reaction involved. [3 marks]

Solution:

Concept:

- In the Hinsberg test, benzenesulphonyl chloride, $C_6H_5SO_2Cl$, distinguishes primary, secondary and tertiary amines by sulphonamide formation and solubility in alkali.
- A primary amine forms a sulphonamide with an acidic nitrogen-bound hydrogen; a secondary amine forms a sulphonamide without an $N-H$ bond. The latter does not form a soluble salt with alkali.

Step 1: Identify the class of amine The formation of a solid sulphonamide which is insoluble in alkali identifies a secondary amine. A primary amine would give a product containing an acidic $N-H$ bond, which dissolves in alkali by salt formation. A tertiary amine lacks the nitrogen-bound hydrogen required to form this sulphonamide, so it does not account for the stated reaction.

Step 2: Use the molecular formula A secondary amine has the structure $R - NH - R'$. The printed molecular formula is C_3H_9N, so its three carbon atoms must be divided between two alkyl groups as one carbon and two carbons. Thus the groups are methyl and ethyl, giving $CH_3-NH-CH_2CH_3$. This contains three carbons, nine hydrogens and one nitrogen, and its IUPAC name is N-methylethanamine.

Step 3: Write the reaction and name the product Replacement of the amine's nitrogen-bound hydrogen by the benzenesulphonyl group produces the tertiary sulphonamide:

$$CH_3NHCH_2CH_3 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2N(CH_3)CH_2CH_3 + HCl.$$

Alkali used in the test neutralises the liberated hydrogen chloride. The product has methyl and ethyl substituents on its nitrogen and is named N-ethyl-N-methylbenzenesulphonamide. Its nitrogen has no remaining hydrogen, so the product cannot lose an acidic proton to give a soluble salt in alkali.

Step 4: Conclusion X is N-methylethanamine, $CH_3NHCH_2CH_3$. The product is N-ethyl-N-methylbenzenesulphonamide, $C_6H_5SO_2N(CH_3)CH_2CH_3$, which is insoluble in alkali.

Quick Tip to Solve: An alkali-insoluble Hinsberg sulphonamide points to a secondary amine; divide the three carbons of C_3H_9N into methyl and ethyl groups.

Section D (8 marks)

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

29(a). Case: The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. Similarly the charge on the complex is the sum of the charges of the constituent parts i.e. the sum of the charges on the central metal ion and its surrounding ligands. Based on this, the complex is called neutral if the sum of the charges of the constituents is equal to zero. However, for an anion or cationic complex, the sum of the charges of the constituents is equal to the charge on the coordination sphere.

(a) Define ambidentate ligand with an example. [1 mark]

Solution:

Concept:

- A ligand donates an electron pair from a donor atom to the central metal ion to form a coordinate bond.
- An ambidentate ligand has two different possible donor atoms, but coordinates through only one of them at a time.

Step 1: Define the ligand An ambidentate ligand is a monodentate ligand that can attach to the metal ion through either of two different donor atoms. The alternative attachment sites must not be confused with simultaneous attachment through two atoms, which characterises a bidentate ligand.

Step 2: Give an example The nitrite ion, NO_2^-, is ambidentate. It can coordinate through nitrogen as a nitro ligand or through oxygen as a nitrito ligand. In either form only one donor atom of a particular nitrite ion binds to the metal.

Step 3: Conclusion An ambidentate ligand can coordinate through either of two different donor atoms, one at a time; NO_2^- is an example, binding through nitrogen or oxygen.

Quick Tip to Solve: For nitrite, name the two alternative donor atoms, N and O, and specify that only one binds at a time.

29(b). What type of isomerism is shown by $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$? [1 mark]

Solution:

Concept:

- Ionisation isomers arise when a ligand inside the coordination sphere exchanges places with a counter-ion outside it.
- Such isomers have the same overall composition but release different ions when dissolved in water.

Step 1: Compare the coordination spheres In $[Co(NH_3)_5Cl]SO_4$, chloride is coordinated to cobalt and sulphate is the counter-ion. In $[Co(NH_3)_5SO_4]Cl$, sulphate is coordinated and chloride is the counter-ion. Thus chloride and sulphate exchange their positions inside and outside the square brackets.

Quick Tip to Solve: Compare what is inside and outside the brackets: exchange of a coordinated ligand with a counter-ion indicates ionisation isomerism.

Step 2: Compare the ions released Their dissociation can be represented as

$$[Co(NH_3)_5Cl]SO_4 \longrightarrow [Co(NH_3)_5Cl]^{2+} + {SO_4}^{2-}$$

and

$$[Co(NH_3)_5SO_4]Cl \longrightarrow [Co(NH_3)_5SO_4]^{+} + Cl^{-}.$$

The first releases sulphate ions and the second releases chloride ions. This difference in the ions formed in solution is the defining feature of ionisation isomerism.

Step 3: Conclusion The two complexes exhibit ionisation isomerism because coordinated chloride and counter-ion sulphate interchange their positions.

Quick Tip to Solve: Compare what is inside and outside the brackets: exchange of a coordinated ligand with a counter-ion indicates ionisation isomerism.

29(c). Define Chelate effect. How does it affect the stability of complex? [2 marks]

Solution:

Concept:

- A chelating ligand is a di- or polydentate ligand that binds the same metal ion through two or more donor atoms and forms one or more rings containing the metal.
- The chelate effect is the enhanced stability of a complex containing chelating ligands compared with a comparable complex containing monodentate ligands.

Step 1: Define the chelate effect When two or more donor atoms of one ligand attach to the same central metal ion, a ring is formed. The enhanced stability resulting from such ring formation is called the chelate effect. For example, ethane-1,2-diamine, abbreviated en, has two nitrogen donor atoms. Both can bind to the same metal, forming a five-membered chelate ring, whereas ammonia binds through only one nitrogen atom.

Step 2: Explain the effect on stability Complexes with chelating ligands are generally more stable than comparable complexes with monodentate ligands having similar donor atoms. A chelating ligand remains attached through its other donor atom if one metal-donor bond temporarily breaks, making complete dissociation less favourable. Chelate formation also commonly gives a favourable entropy change when several monodentate ligands are replaced by fewer chelating ligands and the displaced ligands are released into solution. Thus the equilibrium tends to favour the chelated complex, giving a higher formation constant under comparable conditions.

Step 3: Conclusion The chelate effect is the enhanced stability associated with ring formation by multidentate ligands. It increases the stability of the complex relative to a comparable complex with monodentate ligands.

Quick Tip to Solve: Link chelate effect to two points: a multidentate ligand forms rings, and these chelated complexes generally have greater stability.

OR

29(c). Find the coordination number and oxidation state of chromium in $Na_3[Cr(C_2O_4)_3]$. [2 marks]

Solution:

Concept:

- Coordination number is the number of donor atoms directly bonded to the central metal ion; it is not simply the number of ligand molecules.
- Oxalato, $C_2O_4{}^{2-}$, is a bidentate ligand with charge -2. Oxidation state follows from the algebraic sum of ionic charges.

Step 1: Count the donor atoms In $Na_3[Cr(C_2O_4)_3]$, the coordination sphere contains three oxalato ligands. Each oxalato ligand attaches to chromium through two oxygen donor atoms, forming a chelate ring. Thus the donor-atom count is obtained from three ligands multiplied by two donor atoms per ligand:

$$\text{Number of donor atoms} = 3 \times 2.$$

The three sodium ions are outside the coordination sphere and do not contribute to this count.

Step 2: Balance the charge of the complex Each sodium ion has charge $+1$, so electrical neutrality requires the complex ion $[Cr(C_2O_4)_3]^{3-}$ to have charge -3. Let chromium have oxidation state x. The three oxalato ligands together contribute charge -6, giving

$$x + 3(-2) = -3.$$

Solving the charge balance gives $x = -3 + 6$. Count ligand charge separately from ligand denticity: the two quantities answer different parts of the question.

Step 3: Conclusion The coordination number of chromium is $\boxed{6}$, and its oxidation state is $\boxed{+3}$.

Quick Tip to Solve: For oxalato complexes, count two donor atoms per ligand, but use a charge of -2 per ligand in the oxidation-state equation.

30(a). Case: Certain organic compounds are required in small amounts in our diet but their deficiency causes specific disease. These compounds are called vitamins. Most of the vitamins cannot be synthesized in our body but plants can synthesize almost all of them. So they are considered as essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us. All the vitamins are generally available in our diet. The term 'vitamin' was coined from the words vital + amine, since the earlier identified compounds had amino group. Vitamins are classified into two groups depending upon their solubility in water or fat namely – fat soluble vitamins and water soluble vitamins.

(a) What is the other name of vitamin B_6? [1 mark]

Solution:

Concept:

- Vitamin names and their numbered B-series designations identify the same dietary compounds.

Quick Tip to Solve: Read the B-vitamin subscript first: B6 is pyridoxine, whereas B1 is thiamine.

- The standard name of vitamin B_6 is pyridoxine; vitamin B_1 is thiamine.

Step 1: Identify the printed vitamin The question asks for the alternate name of vitamin B_6. Read the subscript carefully before recalling the name because different members of the B group have different chemical names.

Step 2: Recall the standard name Associate B_6 with pyridoxine. Do not substitute thiamine: thiamine names B_1, a different vitamin. The requested response is the alternate name, so no deficiency disease or dietary source is needed.

Step 3: Conclusion Vitamin B_6 is also called $\boxed{\text{pyridoxine}}$.

Quick Tip to Solve: Read the B-vitamin subscript first: B6 is pyridoxine, whereas B1 is thiamine.

30(b). Name the vitamin whose deficiency causes increased blood clotting time. [1 mark]

Solution:

Concept:

- Vitamins are essential dietary factors whose deficiencies can disrupt specific physiological functions.
- Vitamin K supports the formation of blood-clotting factors, including prothrombin, needed for normal coagulation.

Step 1: Connect the symptom with coagulation Increased blood-clotting time means that blood takes longer than normal to form a clot. Therefore, identify the vitamin involved in producing the clotting factors rather than a vitamin associated with vision or bone formation.

Step 2: Identify the deficient vitamin Vitamin K is needed for normal synthesis of functional clotting factors. Its deficiency impairs the coagulation process and can cause excessive bleeding because a clot forms less readily. This directly matches the symptom named in the question.

Step 3: Conclusion The deficient vitamin is $\boxed{\text{vitamin K}}$.

Quick Tip to Solve: Link vitamin K with coagulation: delayed clotting or excessive bleeding points to its deficiency.

30(c). Xerophthalmia is caused by the deficiency of which vitamin? Give two sources of this vitamin. [2 marks]

Solution:

Concept:

- Vitamin A is a fat-soluble vitamin required for normal vision and maintenance of the epithelial tissues of the eyes.
- Xerophthalmia is associated with vitamin A deficiency. Dietary vitamin A can come from animal foods or from carotene-rich plant foods.

Step 1: Identify the vitamin from the eye disorder Xerophthalmia involves abnormal dryness of the

Quick Tip to Solve: For xerophthalmia, recall vitamin A and name one carotene-rich plant source and one animal source, such as carrots and fish liver oil.

eyes; severe deficiency can damage the cornea. Vitamin A helps maintain healthy ocular surface tissues and is also important for vision. A shortage of this vitamin therefore accounts for the disorder mentioned. Distinguish this eye condition from scurvy, which is associated with deficiency of vitamin C.

Step 2: Give two suitable dietary sources Two suitable sources are carrots and fish liver oil. Carrots contain beta-carotene, a provitamin that the body can convert into vitamin A, while fish liver oil supplies vitamin A directly. Both therefore contribute to the dietary supply of this vitamin, even though the chemical form supplied differs. State both names explicitly to answer the second demand.

Step 3: Conclusion Xerophthalmia is caused by deficiency of vitamin A. Two sources are carrots and fish liver oil.

Quick Tip to Solve: For xerophthalmia, recall vitamin A and name one carotene-rich plant source and one animal source, such as carrots and fish liver oil.

OR

30(c). Why can't vitamin C be stored in our body? Name the disease caused by the deficiency of this vitamin. [2 marks]

Solution:

Concept:

- Vitamin C, also called ascorbic acid, belongs to the water-soluble group of vitamins.
- Water-soluble vitamins are not stored appreciably in the body: excess amounts are eliminated through urine, so a regular dietary supply is required.

Step 1: Explain why vitamin C is not stored Because vitamin C is water soluble, its excess can pass into the urine and is excreted instead of accumulating in fatty tissues. It therefore cannot be stored in appreciable amounts for long-term use, unlike the fat-soluble vitamins. A regular supply through food is needed to replace the amounts used and lost. Water solubility is the relevant property asked for here.

Step 2: Identify the deficiency disease Deficiency of vitamin C causes scurvy. Vitamin C supports normal collagen formation, so a deficiency weakens connective tissues. Typical consequences include bleeding gums and poor wound healing. These symptoms connect the dietary shortage with the disease and distinguish it from vitamin A deficiency, which affects the eyes.

Step 3: Conclusion Vitamin C is not stored appreciably because it is water soluble and excess is excreted in urine. Its deficiency causes scurvy.

Quick Tip to Solve: Use the pair water soluble and urinary loss to explain storage; remember vitamin C deficiency as scurvy with bleeding gums.

Section E (15 marks)

31. Attempt any five of the following:

(a) Ce(III) is easily oxidised to Ce(IV). Comment.

(b) $E^\circ(Mn^{2+}/Mn)$ is –1.18 V. Why is this value highly negative in comparison to neighbouring d block elements?

(c) Which element of 3d series has lowest enthalpy of atomisation and why?

(d) What happens when sodium chromate is acidified?

(e) Zn, Cd and Hg are soft metals. Why?

(f) Why is permanganate titration not carried out in the presence of HCl?

(g) The lower oxides of transition metals are basic whereas the highest are amphoteric/acidic. Give reason. [5 marks]

Solution:

Concept:

- Electronic configuration influences the stability of oxidation states; half-filled and completely filled subshells are especially stable.
- The enthalpy of atomisation reflects the strength of metallic bonding. More electrons available for metal-metal bonding generally strengthen this bonding.
- Chromate-dichromate conversion is an acid-base equilibrium, while acidic permanganate is a powerful oxidising agent. Increasing metal oxidation state increases the covalent character and acidity of its oxides.

Step 1: Explain the oxidation of cerium in part (a) Ce^{3+} has configuration $[Xe]4f^1$. On losing this remaining $4f$ electron it forms Ce^{4+}, which has the stable noble-gas configuration $[Xe]4f^0$. This stability favours the formation of the +4 oxidation state and explains why Ce(III) can be oxidised to Ce(IV).

Step 2: Relate the manganese potential to its configuration in part (b) The reduction represented by the potential is $Mn^{2+} + 2\,e^- \longrightarrow Mn$. The ion Mn^{2+} has the especially stable half-filled configuration $[Ar]3d^5$. Reduction would destroy this stable ionic configuration, so reduction to the metal is relatively unfavourable. Conversely, formation of Mn^{2+} from manganese is favoured. Hence $E^\circ(Mn^{2+}/Mn) = -1.18\,V$ is highly negative compared with neighbouring elements.

Step 3: Identify the element in part (c) Zinc has the lowest enthalpy of atomisation in the 3d series. Its configuration is $[Ar]3d^{10}4s^2$; the completely filled $3d$ subshell has no unpaired electrons to contribute effectively to strong metallic bonding. Its relatively weak metal-metal bonding requires the least energy to separate the solid into gaseous atoms.

Step 4: Write the acidification equilibrium in part (d) Yellow chromate ions are converted into orange dichromate ions when sodium chromate is acidified:

$$2\,CrO_4{}^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7{}^{2-} + H_2O.$$

Adding acid increases the concentration of H^+, shifting this equilibrium to the right. Thus the yellow solution becomes orange.

Quick Tip to Solve: Write the electronic configuration first for (a), (b), (c) and (e). For (d) and (f), a balanced ionic equation directly supports the explanation; distinguish equilibrium conversion from oxidation.

Step 5: Explain the softness in part (e) Zn, Cd and Hg have completely filled d^{10} subshells. Their d electrons contribute little to strong metallic bonding compared with the unpaired d electrons of many other d-block metals. Consequently their metallic bonding is relatively weak, and these metals are soft; mercury is liquid at room temperature.

Step 6: Identify the competing oxidation in part (f) Acidic permanganate oxidises chloride ions from HCl to chlorine. For example,

$$2\,MnO_4^- + 16\,H^+ + 10\,Cl^- \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,Cl_2.$$

This side reaction consumes permanganate in addition to that required by the substance being titrated, causing an erroneous titre. Therefore dilute sulphuric acid, rather than hydrochloric acid, is used to acidify a permanganate titration.

Step 7: Connect oxidation state and oxide character in part (g) In low oxidation states the metal has a relatively low charge and metal-oxygen bonding is predominantly ionic. Such oxides contain oxide ions that accept protons and are basic, as in MnO. As the oxidation state rises, the metal's polarising power rises and the metal-oxygen bonds become more covalent. The oxides become amphoteric or acidic: Cr_2O_3 is amphoteric and CrO_3 is acidic. Thus basic character decreases and acidic character increases with increasing oxidation state.

Step 8: Conclusion Any five responses may be selected from the seven explanations above: stable $4f^0$ Ce(IV); stable $3d^5$ manganese(II); weak bonding in zinc; yellow chromate changing to orange dichromate; weak bonding in the d^{10} metals; oxidation of chloride by permanganate; and increasing covalency and acidity of oxides at higher oxidation states.

Quick Tip to Solve: Write the electronic configuration first for (a), (b), (c) and (e). For (d) and (f), a balanced ionic equation directly supports the explanation; distinguish equilibrium conversion from oxidation.

32(a)(i). Ishan's automobile radiator is filled with 1.0 kg of water. How many grams of ethylene glycol (Molar mass = 62 g mol^{-1}) must Ishan add to get the freezing point of the solution lowered to –2.8 °C. K_f for water is 1.86 K kg mol^{-1}. [3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = T_f^\circ - T_f = iK_f m$, where T_f° and T_f are the freezing points of the pure solvent and solution, K_f is the cryoscopic constant and m is molality.
- Ethylene glycol, $HOCH_2CH_2OH$, is a nonelectrolyte and does not dissociate in water, so its van't Hoff factor is $i = 1$. Molality is moles of solute per kilogram of solvent, not per kilogram of solution.

Step 1: Calculate the required depression Pure water freezes at $0\,^\circ$C, while the required solution freezing point is $-2.8\,^\circ$C. Therefore,

$$\Delta T_f = 0 - (-2.8) = 2.8\,K.$$

Quick Tip to Solve: Use $w = \Delta T_f MW/K_f$ with the water mass W in kilograms. Take the depression as positive and do not add the glycol mass to the solvent mass used in molality.

The depression is positive even though the solution freezing point is negative. A temperature difference has the same numerical value in kelvin and degrees Celsius.

Step 2: Determine the molality and amount of glycol With $i = 1$ and $K_f = 1.86\,\text{K kg mol}^{-1}$,

$$m = \frac{\Delta T_f}{K_f} = \frac{2.8}{1.86} = 1.5054\,\text{mol kg}^{-1}.$$

The mass of water, which is the solvent, is $1.0\,\text{kg}$. Hence the number of moles of ethylene glycol needed is

$$n = m \times \text{mass of solvent in kg} = 1.5054 \times 1.0 = 1.5054\,\text{mol}.$$

Step 3: Convert the amount into grams Multiplying by the given molar mass $M = 62\,\text{g mol}^{-1}$, we obtain

$$w = nM = \frac{2.8 \times 1.0 \times 62}{1.86} = 93.33\,\text{g}.$$

As a check, $93.33/62$ moles in $1.0\,\text{kg}$ of water gives a depression of approximately $1.86 \times 1.5054 = 2.8\,\text{K}$, as required.

Step 4: Conclusion Ishan must add approximately $93.3\,\text{g}$ of ethylene glycol to the radiator water (about $93\,\text{g}$ to two significant figures) to lower the freezing point to $-2.8\,^\circ\text{C}$.

Quick Tip to Solve: Use $w = \Delta T_f MW/K_f$ with the water mass W in kilograms. Take the depression as positive and do not add the glycol mass to the solvent mass used in molality.

32(a)(ii). What type of deviation from Raoult's law is shown by ethanol and acetone mixture? Give reason. [2 marks]

Solution:

Concept:

- Raoult's law for an ideal liquid mixture is $p_i = x_i p_i^0$, where p_i is the partial vapour pressure, x_i the liquid mole fraction and p_i^0 the vapour pressure of the pure component.
- Positive deviation occurs when unlike-molecule attractions are weaker than the attractions they replace, so molecules escape into the vapour more readily.

Step 1: Examine the interactions before mixing In pure ethanol, molecules are associated through intermolecular hydrogen bonds involving their $-\text{OH}$ groups. These attractions hold the molecules in the liquid and reduce their tendency to escape into the vapour.

Step 2: Compare the interactions after adding acetone On mixing, acetone molecules enter between ethanol molecules and disrupt some of the ethanol-ethanol hydrogen bonds. The ethanol-acetone attractions are weaker overall than the interactions in the unmixed liquids. Consequently, the molecules have a greater escaping tendency and the vapour pressure of the mixture is higher than that predicted by Raoult's law. The weakening of cohesion is also consistent with an endothermic enthalpy of mixing, $\Delta H_{\text{mix}} > 0$.

Step 3: Conclusion The ethanol-acetone mixture shows positive deviation from Raoult's law be-

Quick Tip to Solve: For ethanol mixed with acetone, connect disruption of ethanol hydrogen bonds to easier escape of molecules and hence positive deviation.

cause acetone disrupts the hydrogen bonding between ethanol molecules, weakening the effective intermolecular attractions and increasing the vapour pressure.

Quick Tip to Solve: For ethanol mixed with acetone, connect disruption of ethanol hydrogen bonds to easier escape of molecules and hence positive deviation.

OR

32(b). (i) Boiling point of water at 750 mm Hg pressure is 99.68 °C. How much sucrose (Molar mass = 342 $\mathrm{g\,mol^{-1}}$) is to be added to 500 g of water such that it boils at 100 °C? (K_b for water = 0.52 $\mathrm{K\,kg\,mol^{-1}}$)

(ii) State Henry's law and write its any one application. [5 marks]

Solution:

Concept:

- Adding a non-volatile solute lowers the solvent vapour pressure. Therefore a higher temperature is needed for it to equal the external pressure, giving elevation of boiling point, $\Delta T_b = K_b m$.
- Molality is $m = n_s/W$, where n_s is the number of moles of solute and W is the solvent mass in kilograms. For solute mass w_s and molar mass M_s, $n_s = w_s/M_s$.
- Henry's law relates the partial pressure p of a gas above a liquid to its mole fraction x dissolved in the liquid: $p = K_H x$ at a fixed temperature, with K_H the Henry's law constant.

Step 1: (i) Determine the required boiling-point elevation At $750\,\mathrm{mm\,Hg}$, the elevation above the pure-water boiling point is

$$\Delta T_b = 100.00 - 99.68 = 0.32\,\mathrm{K}.$$

Sucrose does not dissociate in water, so $i = 1$. Temperature differences in kelvin and degrees Celsius are equal.

Step 2: Calculate the moles and mass of sucrose Convert the solvent mass to kilograms: $500\,\mathrm{g} = 0.500\,\mathrm{kg}$. Using $K_b = 0.52\,\mathrm{K\,kg\,mol^{-1}}$, first find the required molality:

$$m = \frac{\Delta T_b}{K_b} = \frac{0.32}{0.52} = 0.61538\,\mathrm{mol\,kg^{-1}}.$$

The moles of sucrose are

$$n_s = mW = 0.61538 \times 0.500 = 0.30769\,\mathrm{mol}.$$

Its required mass is

$$w_s = n_s M_s = 0.30769 \times 342 = 105.23\,\mathrm{g}.$$

The mass in the molality denominator is that of water, not the total solution mass.

Step 3: (ii) State Henry's law and explain an application At constant temperature, the mole fraction of a dissolved gas is directly proportional to its partial pressure above the liquid: $p = K_H x$. Carbonated beverages are bottled under high pressure of CO_2. The higher partial pressure increases the mole

Quick Tip to Solve: Use 99.68 degrees Celsius as the pure-water reference at 750 mm Hg, and convert only the 500 g of solvent to kilograms before applying molality.

fraction of dissolved CO_2, enabling a larger quantity of gas to dissolve in the beverage. Opening the bottle lowers the pressure and excess gas escapes as bubbles.

Step 4: Conclusion (i) Approximately $105.2\,g$ of sucrose must be added to $500\,g$ of water. (ii) Henry's law is $p = K_H x$ at constant temperature; bottling carbonated beverages under high CO_2 pressure is one application.

Quick Tip to Solve: Use 99.68 degrees Celsius as the pure-water reference at 750 mm Hg, and convert only the 500 g of solvent to kilograms before applying molality.

33(a). An organic compound (A) with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Fehling solution and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid.

(i) Identify the compound (A) and write its IUPAC name.

(ii) Write the reaction of compound (A) with

(1) 2,4-Dinitrophenyl hydrazine and

(2) Fehling solution

(iii) Write the equation of compound (A) when it undergoes Cannizzaro reaction. [5 marks]

Solution:

Concept:

- 2,4-Dinitrophenylhydrazine gives a hydrazone with an aldehyde or ketone; this identifies the carbonyl group.
- Cannizzaro disproportionation occurs with aldehydes lacking an alpha-hydrogen: one molecule is oxidised to a carboxylate and another is reduced to an alcohol.
- Vigorous oxidation converts an aldehyde group and an alkyl side chain attached to benzene into carboxyl groups. Aromatic aldehydes ordinarily do not reduce Fehling solution.

Step 1: (i) Identify the structure from the consistent tests 2,4-DNP establishes a carbonyl group; Cannizzaro reaction establishes an aldehyde without an alpha-hydrogen. Oxidation to benzene-1,2-dicarboxylic acid requires adjacent aldehyde and alkyl groups. The formula therefore identifies $o - C_2H_5C_6H_4CHO$, IUPAC name 2-ethylbenzaldehyde: $C_6H_4 + C_2H_5 + CHO = C_9H_{10}O$. Vigorous oxidation converts both side chains into adjacent COOH groups. The ethyl hydrogens are not alpha to the aldehyde carbonyl because the benzene ring separates these groups.

Step 2: (ii)(1) Write the 2,4-DNP reaction Let $Ar = o - C_2H_5C_6H_4$ and $D = C_6H_3(NO_2)_2$, the nitro groups being at positions 2 and 4. Acid-catalysed condensation eliminates water:

$$ArCHO + H_2N{-}NH{-}D \xrightarrow{H^+} ArCH{=}N{-}NH{-}D + H_2O.$$

The yellow/orange product is the 2,4-dinitrophenylhydrazone.

Step 3: (ii)(2) Examine the printed Fehling test The printed Fehling-positive statement conflicts with the other evidence. 2-Ethylbenzaldehyde is an aromatic aldehyde and does not reduce Fehling solution under the usual test conditions: no brick-red Cu_2O precipitate forms. Thus no positive

Quick Tip to Solve: Use the two adjacent carboxyl groups in the oxidation product to locate CHO and ethyl; then check the aromatic-aldehyde exception before assigning a Fehling result.

Fehling equation can correctly be assigned to this compound. No ordinary aldehyde satisfies all the printed tests simultaneously; the formula, Cannizzaro reaction and oxidation product consistently identify 2-ethylbenzaldehyde.

Step 4: (iii) Write the Cannizzaro reaction In concentrated sodium hydroxide, one aldehyde molecule is oxidised and another reduced:

$$2\mathrm{ArCHO} + \mathrm{NaOH} \xrightarrow{\text{conc.}} \mathrm{ArCOONa} + \mathrm{ArCH_2OH}.$$

With $\mathrm{Ar} = \mathrm{o} - \mathrm{C_2H_5C_6H_4}$, the products are sodium 2-ethylbenzoate and (2-ethylphenyl)methanol. The equation balances atoms and charge, and the ethyl group is retained.

Step 5: Conclusion (A) is 2-ethylbenzaldehyde on the consistent structural evidence. It forms the DNP hydrazone and gives sodium 2-ethylbenzoate and (2-ethylphenyl)methanol in Cannizzaro reaction. The printed positive Fehling claim is inconsistent; the correct result is negative.

Quick Tip to Solve: Use the two adjacent carboxyl groups in the oxidation product to locate CHO and ethyl; then check the aromatic-aldehyde exception before assigning a Fehling result.

OR

33(b)(i). Account for the following:

(1) The alpha (α)-hydrogens of aldehydes and ketones are acidic in nature.

(2) Oxidation of aldehydes is easier than ketones. [2 marks]

Solution:

Concept:

- An alpha-hydrogen is attached to the carbon immediately next to the carbonyl carbon. Acidity depends on the stability of the anion remaining after proton removal.
- Aldehydes contain a hydrogen attached directly to the carbonyl carbon; ketones contain two carbon substituents at that carbon.

Step 1: (1) Explain the acidity of alpha-hydrogens The electron-withdrawing carbonyl group polarises the neighbouring bonds. Removal of an alpha-hydrogen as $\mathrm{H^+}$ gives an enolate ion whose negative charge is delocalised between the alpha-carbon and oxygen:

$$\mathrm{R{-}CO{-}CH_2^-} \longleftrightarrow \mathrm{R{-}C(O^-){=}CH_2}.$$

Here R can be hydrogen for an aldehyde or an alkyl group for a ketone. Resonance stabilisation of this conjugate base, especially the contributor with charge on electronegative oxygen, makes the alpha-hydrogens acidic compared with ordinary alkane hydrogens.

Step 2: (2) Explain the easier oxidation of aldehydes An aldehyde has a hydrogen bonded to its carbonyl carbon. It is readily oxidised to a carboxylic acid without breaking a carbon-carbon bond:

$$\mathrm{RCHO} + [\mathrm{O}] \longrightarrow \mathrm{RCOOH}.$$

Quick Tip to Solve: For acidity look at the carbon next to C=O; for oxidation look for the hydrogen directly on the carbonyl carbon.

A ketone has no hydrogen on its carbonyl carbon. Oxidising it generally requires cleavage of a carbon-carbon bond, which is more difficult and needs strong oxidising agents and vigorous conditions. Aldehydes therefore undergo oxidation more readily than ketones; the crucial difference is the hydrogen directly attached to the carbonyl carbon, not the presence or absence of alpha-hydrogens.

Step 3: Conclusion Alpha-hydrogens are acidic because their removal produces a resonance-stabilised enolate ion. Aldehydes oxidise more easily because they form carboxylic acids without carbon-carbon bond cleavage, whereas ketone oxidation requires such cleavage.

Quick Tip to Solve: For acidity look at the carbon next to C=O; for oxidation look for the hydrogen directly on the carbonyl carbon.

33(b)(ii). Arrange the following in:

(1) Decreasing reactivity towards nucleophilic addition reaction: propanal, acetone, benzaldehyde.

(2) Increasing order of boiling point: Propane, Ethanol, Dimethyl ether, Propanal. [2 marks]

Solution:

Concept:

- Nucleophilic addition begins with attack on the electrophilic carbonyl carbon. Electron donation and steric crowding reduce its reactivity.
- Boiling point increases with the strength of intermolecular attraction. Hydrogen bonding is stronger than ordinary dipole interactions among these compounds.

Step 1: Compare carbonyl reactivity Propanal is an aliphatic aldehyde: its carbonyl carbon is bonded to one alkyl group and one hydrogen. It is relatively accessible and has no resonance donation from an aromatic ring. In benzaldehyde, conjugation with the benzene ring decreases the electrophilic character of the carbonyl carbon, so it reacts less readily than propanal. Acetone has two electron-donating methyl groups; their positive inductive effect reduces the carbonyl carbon's electrophilicity, while the two groups also hinder nucleophilic approach. For these compounds, the aldehydes react more readily than the ketone.

Step 2: Compare intermolecular forces Propane is nonpolar and has only weak dispersion forces. Dimethyl ether is polar, giving stronger attractions than propane, but has no hydrogen bonded to oxygen and cannot hydrogen-bond with itself. Propanal has a strongly polar carbonyl group and stronger intermolecular attractions than dimethyl ether. Ethanol contains an $O-H$ group and forms intermolecular hydrogen bonds, requiring the most energy for separation into vapour among these four substances.

Step 3: Conclusion (1) Decreasing reactivity: Propanal $>$ Benzaldehyde $>$ Acetone.

(2) Increasing boiling point: Propane $<$ Dimethyl ether $<$ Propanal $<$ Ethanol.

Quick Tip to Solve: For this set, place the aliphatic aldehyde first in reactivity and the hydrogen-bonding alcohol last in increasing boiling point.

33(b)(iii). Give simple chemical test to distinguish between Benzoic acid and Benzaldehyde. [1 mark]

Solution:

Concept:

- Carboxylic acids react with aqueous sodium hydrogen carbonate to liberate carbon dioxide; ordinary aldehydes do not show this acid-base reaction.
- Gas evolution provides a direct observation to distinguish the acidic $-\mathrm{COOH}$ group from the aldehyde $-\mathrm{CHO}$ group.

Step 1: Add sodium hydrogen carbonate Place small samples of benzoic acid and benzaldehyde in separate test tubes and add aqueous $\mathrm{NaHCO_3}$ to each. Observe whether gas bubbles are released. Benzoic acid is sufficiently acidic to react with hydrogen carbonate, whereas benzaldehyde does not contain a carboxylic acid group.

Step 2: Identify the positive reaction Benzoic acid gives brisk effervescence of carbon dioxide according to

$$\mathrm{C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2 \uparrow}.$$

Benzaldehyde gives no such effervescence under the same conditions. The evolved carbon dioxide can be confirmed by passing it through limewater, which turns milky.

Step 3: Conclusion The sodium hydrogen carbonate test distinguishes them: benzoic acid releases $\mathrm{CO_2}$ with brisk effervescence, while benzaldehyde does not.

Quick Tip to Solve: Choose bicarbonate when distinguishing a carboxylic acid from an aldehyde: look for carbon dioxide bubbles, not a colour change.