CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-2-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculators **is not** allowed.

Section A (16 marks)

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

1. When MnO_2 is fused with KOH in air, it gives : [1 mark]

(A) $KMnO_4$

(B) K_2MnO_4

(C) Mn_2O_7

(D) Mn_2O_3

Correct Answer: (B) K_2MnO_4

Solution:

Concept:

- Oxidation in strongly alkaline medium produces manganate(VI), with manganese in oxidation state $+6$.
- The oxygen in air acts as the oxidising agent; potassium hydroxide supplies the alkaline medium and potassium ions.

Step 1: Identify the product of alkaline fusion In MnO_2, manganese is in oxidation state $+4$. Fusion with KOH in air oxidises it to manganate, MnO_4^{2-}, whose potassium salt is green potassium manganate. The balanced reaction is

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O.$$

Step 2: Check the other options Permanganate, $KMnO_4$, contains manganese(VII) and is obtained in a subsequent oxidation of manganate. Mn_2O_7 is manganese(VII) oxide, whereas Mn_2O_3 contains manganese(III); neither represents the alkaline oxidative-fusion product.

Step 3: Conclusion The product is K_2MnO_4; the correct option is (B).

Quick Tip to Solve: Remember the preparation sequence: alkaline fusion first gives green manganate, followed by oxidation to purple permanganate.

2. Ligand $EDTA^{4-}$ is an example of a : [1 mark]

(A) Monodentate ligand

(B) Didentate ligand

(C) Tridentate ligand

(D) Polydentate ligand

Correct Answer: (D) Polydentate ligand

Solution:

Concept:

- Denticity is the number of donor atoms of one ligand that can attach to the same metal ion.

Quick Tip to Solve: Count two nitrogen donors plus four carboxylate oxygen donors; do not confuse the ligand charge with its denticity.

- A ligand with several donor sites is polydentate; EDTA is commonly hexadentate.

Step 1: Count the donor sites The $EDTA^{4-}$ ligand can coordinate through two amine nitrogen atoms and four oxygen atoms, one from each carboxylate group. Thus it has six donor sites available for attachment to a metal ion.

Step 2: Classify the ligand Six donor atoms make EDTA a hexadentate ligand, which belongs to the polydentate category. Monodentate, didentate and tridentate ligands coordinate through one, two and three donor atoms respectively, so options (A), (B) and (C) do not describe EDTA. The charge $4-$ is not its denticity.

Step 3: Conclusion EDTA is a polydentate (hexadentate) ligand; the correct option is (D).

Quick Tip to Solve: Count two nitrogen donors plus four carboxylate oxygen donors; do not confuse the ligand charge with its denticity.

3. Which of the following ligand forms chelate complex ? [1 mark]

(A) $C_2O_4^{2-}$

(B) Cl^-

(C) NO_2^-

(D) NH_3

Correct Answer: (A) $C_2O_4^{2-}$

Solution:

Concept:

- Chelation occurs when a ligand binds to one metal ion through two or more donor atoms and forms a ring.
- Oxalate, $C_2O_4^{2-}$, is a bidentate ligand with two oxygen donor sites.

Step 1: Identify the ring-forming ligand Oxalate coordinates to the same metal ion through an oxygen atom from each carboxylate group. This links the metal to both ends of the ligand and creates a five-membered chelate ring containing the metal, two oxygen atoms and two carbon atoms.

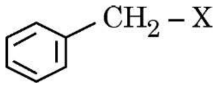
Step 2: Compare the remaining ligands Chloride and ammonia are monodentate ligands, attaching through chlorine and nitrogen respectively. Nitrite, NO_2^-, is ambidentate: it can bind through nitrogen or oxygen, but uses one donor site at a time in the usual CBSE classification. Ambidentate behaviour does not mean chelation.

Step 3: Conclusion Oxalate $C_2O_4^{2-}$ forms a chelate complex; the correct option is (A).

Quick Tip to Solve: Look for two donor sites that can bind simultaneously to one metal; alternative binding through N or O alone is ambidentate behaviour.

4. Which of the following contains sp^2 hybridised carbon bonded to X ? [1 mark]

(A) $CH_2 = CH - CH_2 - X$

(B) 

(C) $CH_2 = CH - X$

(D) $CH_3 - CH_2 - X$

Correct Answer: (C) $CH_2 = CH - X$

Solution:

Concept:

- The hybridisation to inspect is that of the carbon directly bonded to halogen X.
- A carbon in a $C = C$ double bond is sp^2; a saturated carbon with four sigma bonds is sp^3.

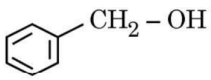
Step 1: Examine the vinyl halide In $CH_2 = CH - X$, the carbon bonded to X is itself part of the double bond. It has three sigma bonds and one pi bond, so its hybridisation is sp^2. This is a vinylic carbon-halogen bond.

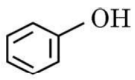
Step 2: Check all other positions In $CH_2 = CH - CH_2 - X$, the halogen is on the saturated allylic CH_2, which is sp^3. In benzyl halide, $C_6H_5CH_2 - X$, it is on the side-chain CH_2, also sp^3, even though the ring carbons are sp^2. The halogen-bearing carbon of $CH_3CH_2 - X$ is likewise sp^3.

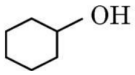
Step 3: Conclusion The compound is $CH_2 = CH - X$; the correct option is (C).

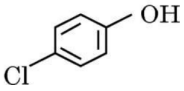
Quick Tip to Solve: Locate the carbon touching X first; a nearby double bond or benzene ring does not determine that carbon's hybridisation.

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

(A) 

(B) 

(C) 

(D) 

(A) Benzyl alcohol $C_6H_5CH_2OH$

(B) Phenol C_6H_5OH

(C) Cyclohexanol $C_6H_{11}OH$

(D) p-Chlorophenol $p - ClC_6H_4OH$

Correct Answer: (D) p-Chlorophenol $p - ClC_6H_4OH$

Solution:

Concept:

- Acid strength increases when the conjugate base is better stabilised.
- Phenoxide ions are resonance stabilised; ordinary alkoxide ions have no comparable delocalisation into an aromatic ring.

Step 1: Compare alcohols with phenols Benzyl alcohol has its hydroxyl group on a saturated CH_2

Quick Tip to Solve: First separate phenols from side-chain alcohols, then compare substituent effects on the stability of their phenoxide ions.

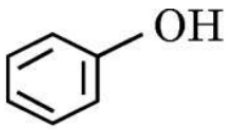
side chain, while cyclohexanol has it on a saturated ring carbon. Their conjugate bases are alkoxide ions. Phenol and p-chlorophenol lose the hydroxyl proton to form phenoxide ions, whose negative charge is delocalised over the aromatic system; these are more acidic than the two alcohols.

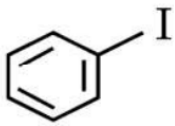
Step 2: Compare the two phenols The chlorine substituent in p-chlorophenol exerts an electron-withdrawing inductive effect that stabilises its conjugate base. Although chlorine also has a resonance donation effect, its net influence increases acidity relative to phenol. Thus p-chlorophenol is more acidic than phenol as well as benzyl alcohol and cyclohexanol.

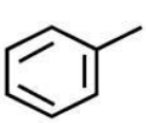
Step 3: Conclusion p-Chlorophenol is the most acidic of the four compounds; the correct option is (D).

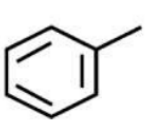
Quick Tip to Solve: First separate phenols from side-chain alcohols, then compare substituent effects on the stability of their phenoxide ions.

6. Anisole reacts with HI to give : [1 mark]

(A)  $+ CH_3 - I$

(B)  $+ CH_3 - OH$

(C)  $+ CH_3 - I$

(D)  $+ CH_3 - OH$

(A) $C_6H_5OH + CH_3I$

(B) $C_6H_5I + CH_3OH$

(C) $C_6H_5CH_2OH + CH_3I$

(D) $C_6H_5CH_2I + CH_3OH$

Correct Answer: (A) $C_6H_5OH + CH_3I$

Solution:

Concept:

- HI cleaves ethers after protonation of the ether oxygen.
- In anisole, iodide attacks the methyl carbon by S_N2, since the aromatic sp^2 carbon cannot undergo the usual backside substitution.

Step 1: Activate the ether and identify the attack site Anisole is $C_6H_5 - O - CH_3$. Protonation of

Quick Tip to Solve: For an aryl methyl ether with HI, preserve the aryl-oxygen bond and replace the oxygen attached to the methyl group with iodine.

oxygen by HI makes the ether linkage susceptible to cleavage. The iodide ion attacks the unhindered methyl carbon and breaks the oxygen-methyl bond, leaving the aromatic carbon-oxygen bond intact.

Step 2: Write and compare the products The reaction is

$$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I.$$

Iodobenzene plus methanol, option (B), would require cleavage at the aromatic carbon and is not formed by this mechanism. Options (C) and (D) contain a benzyl group, $C_6H_5CH_2$, absent from anisole and hence cannot be the products of simple ether cleavage.

Step 3: Conclusion Anisole gives phenol and methyl iodide; the correct option is (A).

Quick Tip to Solve: For an aryl methyl ether with HI, preserve the aryl-oxygen bond and replace the oxygen attached to the methyl group with iodine.

7. Ethanol on heating with conc. H_2SO_4 at 413 K gives : [1 mark]

(A) $C_2H_5OSO_3H$

(B) $C_2H_5-O-CH_3$

(C) $C_2H_5-O-C_2H_5$

(D) $CH_2=CH_2$

Correct Answer: (C) $C_2H_5-O-C_2H_5$

Solution:

Concept:

- Concentrated sulphuric acid catalyses dehydration of ethanol; the product depends on temperature.
- At 413 K, intermolecular dehydration joins two ethanol molecules through an oxygen atom.

Step 1: Apply the temperature condition At 413 K, ethanol undergoes acid-catalysed intermolecular dehydration. Two molecules lose one molecule of water to form ethoxyethane (diethyl ether):

$$2C_2H_5OH \xrightarrow[413\,K]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O.$$

Step 2: Check the alternatives Ethyl hydrogen sulphate in (A) is associated with reaction of ethanol with the acid at lower temperature. The mixed ether in (B) would require a methyl group source, absent here. Ethene in (D) is the principal dehydration product at the higher temperature 443 K, not the stated 413 K.

Step 3: Conclusion The product is diethyl ether, $C_2H_5 - O - C_2H_5$. Hence, the correct option is (C).

Quick Tip to Solve: Remember ethanol plus concentrated acid: 413 K favours ether; 443 K favours ethene.

8. An azeotropic solution of two liquids has boiling point lower than either of them when it : [1 mark]

(A) is saturated

(B) shows positive deviation from Raoult's law

(C) shows negative deviation from Raoult's law

(D) shows no deviation from Raoult's law

Correct Answer: (B) shows positive deviation from Raoult's law

Solution:

Concept:

- Raoult's law for an ideal binary solution gives $p = x_A p_A^0 + x_B p_B^0$.
- Positive deviation raises vapour pressure; boiling occurs when total vapour pressure equals external pressure.

Step 1: Relate vapour pressure to boiling point When unlike intermolecular attractions are weaker than the attractions in the pure liquids, molecules escape more readily into the vapour. The total vapour pressure exceeds the ideal value: the mixture shows positive deviation from Raoult's law. It therefore reaches the external pressure at a lower temperature.

Step 2: Identify the azeotrope and eliminate other options A sufficiently large positive deviation produces a maximum in vapour pressure and a minimum in boiling temperature, giving a minimum-boiling azeotrope. Negative deviation instead favours a maximum-boiling azeotrope. An ideal solution with no deviation does not give this boiling-point minimum, and saturation does not explain it.

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

Quick Tip to Solve: For a minimum-boiling azeotrope, think higher vapour pressure and positive deviation.

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

(A) 0.80

(B) 0.725

(C) 0.15

(D) 0.0225

Correct Answer: (D) 0.0225

Solution:

Concept:

- For a non-volatile solute, only the solvent contributes to the vapour pressure.
- Raoult's law gives $p = x_1 p^0$; $x_1 + x_2 = 1$, where x_2 is the solute mole fraction.

Step 1: Write the relative lowering Let p^0 be the vapour pressure of pure water and p that of the

Quick Tip to Solve: Use relative lowering directly as solute mole fraction; do not subtract it from one.

solution. Since the solute is non-volatile,

$$\frac{p^0 - p}{p^0} = 1 - \frac{p}{p^0} = 1 - x_1 = x_2.$$

Thus the relative lowering equals the mole fraction of the solute, rather than the mole fraction of water.

Step 2: Substitute and check the options The given relative lowering is 0.0225, so $x_2 = 0.0225$. The water mole fraction is $1 - 0.0225 = 0.9775$. Mole fractions are dimensionless. Values 0.80, 0.725 and 0.15 would each imply a different relative lowering and do not satisfy the given data.

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

Quick Tip to Solve: Use relative lowering directly as solute mole fraction; do not subtract it from one.

10. During electrolysis of aqueous solution of NaCl : [1 mark]

(A) $H_2(g)$ is liberated at cathode

(B) Na is formed at cathode

(C) $O_2(g)$ is liberated at anode

(D) $Cl_2(g)$ is liberated at cathode

Correct Answer: (A) $H_2(g)$ is liberated at cathode

Solution:

Concept:

- Reduction occurs at the cathode, while oxidation occurs at the anode.
- In aqueous sodium chloride, water is reduced preferentially to sodium ions at the cathode.

Step 1: Identify the cathode reaction The solution contains both water and Na^+ ions. Reduction of water is easier than reduction of Na^+ to sodium metal. The cathode reaction is

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

Therefore hydrogen gas is liberated at the cathode, and sodium metal is not deposited.

Step 2: Check the remaining statements In the usual electrolysis of aqueous sodium chloride (brine), chloride ions are oxidised at the anode:

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

Thus chlorine is produced at the anode, not the cathode. Oxygen is not the stated anode product under these conditions. Options (B), (C) and (D) therefore do not describe the standard process.

Step 3: Conclusion $H_2(g)$ is liberated at the cathode. Hence, the correct option is (A).

Quick Tip to Solve: Distinguish aqueous NaCl from molten NaCl: water gives hydrogen at the aqueous cathode.

11. The addition of catalyst during a chemical reaction alters which of the following quantities of the reaction ? [1 mark]

(A) Enthalpy

(B) Activation energy

(C) Entropy

(D) Internal energy

Correct Answer: (B) Activation energy

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with lower activation energy, E_a.
- Enthalpy, entropy and internal energy changes depend on the initial and final states.

Step 1: Explain the kinetic effect Activation energy is the energy barrier between reactants and the activated state. A catalyst introduces an alternative pathway with a lower barrier, increasing the fraction of effective collisions and hence the reaction rate. In the Arrhenius equation $k = Ae^{-E_a/(RT)}$, lowering E_a increases the rate constant at the same temperature.

Step 2: Eliminate the state quantities A catalyst does not change the identities or thermodynamic states of the reactants and products. Consequently it does not alter the reaction enthalpy, entropy or internal energy changes. Those quantities are state-function differences, whereas the activation energy depends on the pathway. Thus (A), (C) and (D) are excluded.

Step 3: Conclusion The catalyst alters activation energy. Hence, the correct option is (B).

Quick Tip to Solve: Ask whether a quantity depends on the reaction path: activation energy does, state changes do not.

12. For the elementary reaction P $\rightarrow$ Q, the rate of disappearance of 'P' increases by a factor of 8 upon doubling the concentration of 'P'. The order of the reaction with respect to 'P' is : [1 mark]

(A) 3

(B) 4

(C) 2

(D) 1

Correct Answer: (A) 3

Solution:

Concept:

- For order n with respect to P, the rate law is $r = k[P]^n$, where k is the rate constant.
- At fixed temperature, multiplying concentration by a multiplies rate by a^n.

Step 1: Compare the two rates Let the original concentration be $[P]$, with rate $r_1 = k[P]^n$. After

Quick Tip to Solve: When concentration doubles, write rate factor as 2 to the order; 8 equals 2 cubed.

doubling it, the rate is $r_2 = k(2[P])^n$. Taking the ratio removes the unchanged rate constant:

$$\frac{r_2}{r_1} = \frac{k(2[P])^n}{k[P]^n} = 2^n.$$

Step 2: Use the observed rate factor The printed observation gives $r_2/r_1 = 8$. Therefore $2^n = 8 = 2^3$, which requires $n = 3$. First, second and fourth orders would give factors 2, 4 and 16, respectively, so those options fail. The experimentally stated concentration dependence supplies the order; it must not be inferred simply from the displayed reaction arrow.

Step 3: Conclusion The order with respect to P is $\boxed{3}$. Hence, the correct option is (A).

Quick Tip to Solve: When concentration doubles, write rate factor as 2 to the order; 8 equals 2 cubed.

13. Assertion (A): Aliphatic primary amines can be prepared by Gabriel phthalimide synthesis.
Reason (R): Alkyl halides undergo nucleophilic substitution with anion formed by phthalimide.

[1 mark]

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

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

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

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

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

Solution:

Concept:

- Gabriel phthalimide synthesis prepares primary aliphatic amines by alkylation of the phthalimide anion, followed by hydrolysis.
- The negatively charged nitrogen acts as a nucleophile; an alkyl halide supplies the alkyl group.

Step 1: Judge the assertion The assertion is true. Phthalimide is treated with alcoholic potassium hydroxide to form its potassium salt. Alkylation and subsequent hydrolysis release a primary amine, RNH_2.

Step 2: Judge the reason The reason is true. The phthalimide anion attacks the alkyl carbon and replaces the halide ion by nucleophilic substitution, producing an N-alkylphthalimide.

Step 3: Check the explanatory link This substitution introduces the required alkyl group on nitrogen. Hydrolysis then removes the phthaloyl protecting group, yielding the aliphatic primary amine. Thus the reason explains how the assertion is achieved; the alternatives denying either statement or their connection are incorrect.

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

Quick Tip to Solve: Recall the sequence: phthalimide anion, alkyl halide, then hydrolysis to a primary amine.

14. Assertion (A): Uracil base is present in DNA.

Reason (R): DNA undergoes self-replication. [1 mark]

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

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

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

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

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

Solution:

Concept:

- DNA normally contains adenine, guanine, cytosine and thymine; RNA contains uracil instead of thymine.
- Complementary base pairing permits each DNA strand to act as a template during replication.

Step 1: Judge the assertion The assertion is false. Uracil is a characteristic pyrimidine base of RNA. In the standard composition of DNA, thymine occupies its place; DNA contains A, G, C and T.

Step 2: Judge the reason The reason is true. DNA undergoes self-replication: the two strands separate and each directs the formation of a complementary strand using base pairing.

Step 3: Check the explanatory link The ability of DNA to replicate does not make uracil a constituent of DNA. Since the assertion itself is false, neither alternative saying that both statements are true can apply. The alternative declaring the reason false also fails.

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

Quick Tip to Solve: Use the base lists first: DNA has thymine, whereas RNA has uracil; then assess replication separately.

15. Assertion (A): Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
Reason (R): Diazonium salts of aliphatic amines show resonance. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Aromatic diazonium ions receive resonance stabilisation through conjugation with the benzene ring.
- Aliphatic diazonium salts are unstable and readily lose nitrogen; they lack aromatic ring conjugation.

Step 1: Judge the assertion The assertion is true. Aromatic diazonium salts, such as benzenediazonium chloride, can be maintained in cold aqueous solution at about 273–278 K. Aliphatic diazonium salts are much less stable.

Step 2: Judge the reason The reason is false in the stated comparison. An aliphatic alkyl group cannot provide the benzene-ring resonance stabilisation responsible for the greater stability of aromatic diazonium salts. Aliphatic diazonium salts readily decompose with the evolution of nitrogen gas.

Step 3: Check the explanatory link The stabilising resonance relevant here belongs to the aromatic diazonium system, not to the aliphatic system as the reason claims. Therefore both-statement-true options are excluded, and the option calling the assertion false is also excluded.

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

Quick Tip to Solve: Associate the greater diazonium stability with conjugation to an aromatic ring, and remember the cold preparation conditions.

16. Assertion (A): p-nitroaniline is a weaker base than p-toluidine.

Reason (R): The electron withdrawing effect of $-NO_2$ group in p-nitroaniline makes it a weaker base. [1 mark]

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

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

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

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

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

Solution:

Concept:

- An amine is basic because its nitrogen lone pair can accept a proton.
- Electron-withdrawing groups reduce lone-pair availability; electron-donating groups generally enhance it.

Step 1: Judge the assertion The assertion is true. The nitro group in p-nitroaniline withdraws electron density strongly, whereas the methyl group in p-toluidine donates electron density. The nitrogen lone pair is therefore less available for protonation in p-nitroaniline.

Step 2: Judge the reason The reason is true. The para nitro group withdraws electrons by both inductive and resonance effects. Conjugation favours delocalisation of the amino nitrogen lone pair towards the electron-deficient ring, reducing its availability to bind a proton.

Step 3: Check the explanatory link This withdrawal is precisely why p-nitroaniline is the weaker base. The methyl group in p-toluidine produces the opposite tendency by its electron-donating effect. Thus the reason explains the assertion, excluding the option that denies the explanatory link and the options that call either statement 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: Compare how the para substituent affects nitrogen lone-pair availability: nitro withdraws, methyl donates.

Section B (10 marks)

17. A 6% solution of glucose (molar mass = 180 g mol^{-1}) is isotonic with 2.5% solution of an unknown organic substance. Calculate the molecular weight of the unknown organic substance. [2 marks]

Solution:

Concept:

- For a dilute solution, osmotic pressure is $\pi = CRT = \dfrac{wRT}{MV}$, where w is solute mass, M molar mass and V solution volume.
- Isotonic solutions at the same temperature have equal osmotic pressures. For molecular organic solutes, equal pressures imply equal molar concentrations.

Step 1: Express the concentrations Take 100 mL of each solution, using the given percentages as grams of solute per 100 mL solution. The glucose solution contains 6 g, while the unknown solution contains 2.5 g. Let the unknown molar mass be M g mol^{-1}.

Step 2: Apply the isotonic condition At the same temperature and equal solution volume, RT/V cancels from the two osmotic-pressure expressions. Thus the numbers of moles of the molecular solutes are equal:

$$\frac{6}{180} = \frac{2.5}{M}.$$

This uses the usual non-electrolyte treatment of glucose and the unknown organic solute; no additional ionic particle factor is needed.

Step 3: Calculate the molar mass Rearranging the equality gives

$$M = \frac{2.5 \times 180}{6} = 75 \text{ g mol}^{-1}.$$

The lower mass percentage of the unknown still produces the same number of dissolved particles because its molar mass is correspondingly smaller than that of glucose.

Step 4: Conclusion The molecular weight of the unknown organic substance is 75 (molar mass 75 g mol^{-1}).

Quick Tip to Solve: For isotonic molecular solutions, divide each percentage by its molar mass and equate the resulting ratios.

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

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

Solution:

Concept:

- For a first order reaction, $t = (2.303/k)\log(m_0/m_t)$, where k is the rate constant and m_0, m_t are initial and remaining reactant masses.

Quick Tip to Solve: When the mass halves in a first order reaction, use 0.693/k directly and retain the printed power of ten in k.

- The half-life is $t_{1/2} = 0.693/k$, independent of the initial amount for first order kinetics.

Step 1: Identify the fraction remaining The reactant decreases from $5\,\text{g}$ to $2.5\,\text{g}$. Hence $m_t/m_0 = 2.5/5 = 1/2$, so the requested time is one half-life. Mass ratios equal amount ratios for the same reactant; they can therefore be used in the integrated rate equation.

Step 2: Substitute the rate constant Using $k = 1.25 \times 10^{-3}\,\text{s}^{-1}$ and the supplied logarithm,

$$t = \frac{2.303 \times 0.301}{1.25 \times 10^{-3}} = 554.56\,\text{s}.$$

The usual rounded half-life formula gives $t = 0.693/(1.25 \times 10^{-3}) = 554.4\,\text{s}$. The small difference reflects rounding of the logarithm. The units are seconds because the reciprocal of s^{-1} is s.

Step 3: Conclusion The required time is approximately $\boxed{5.54 \times 10^2\,\text{s}}$, or $9.24\,\text{min}$.

Quick Tip to Solve: When the mass halves in a first order reaction, use 0.693/k directly and retain the printed power of ten in k.

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

Solution:

Concept:

- Lanthanoids fill the $4f$ subshell; actinoids fill the $5f$ subshell. In each series, increasing atomic number increases nuclear charge.
- Shielding reduces the nuclear attraction felt by outer electrons. Poor shielding by f electrons causes effective nuclear attraction and contraction to increase across the series.

Step 1: Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic and ionic radii, especially the radii of Ln^{3+} ions, with increasing atomic number from lanthanum to lutetium. Added $4f$ electrons shield the increasing nuclear charge poorly. The stronger effective nuclear attraction pulls the electron cloud closer to the nucleus.

Step 2: Explain the greater actinoid contraction Across the actinoids, electrons are added to the $5f$ subshell while nuclear charge increases. The $5f$ electrons shield one another and outer electrons still less effectively than $4f$ electrons do in lanthanoids. Consequently, the rise in effective nuclear attraction, and hence the element-to-element decrease in size, is greater in the actinoid series. Poor shielding, rather than simply the larger number of electrons, explains the comparison.

Step 3: Conclusion Lanthanoid contraction is the gradual decrease in size across the lanthanoid series; the greater actinoid contraction results from poorer shielding by $5f$ electrons than by $4f$ electrons.

Quick Tip to Solve: Link the shrinking radii to rising nuclear charge and poor f-electron shielding; use 5f versus 4f to explain the comparison.

OR

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

Solution:

Concept:

- Enthalpy of atomization is the enthalpy needed to form one mole of gaseous atoms from an element in its standard state. Stronger metallic bonding requires more energy to break.
- In transition metals, both outer s electrons and d electrons can contribute to metallic bonding; many unpaired d electrons commonly give stronger interatomic bonding.

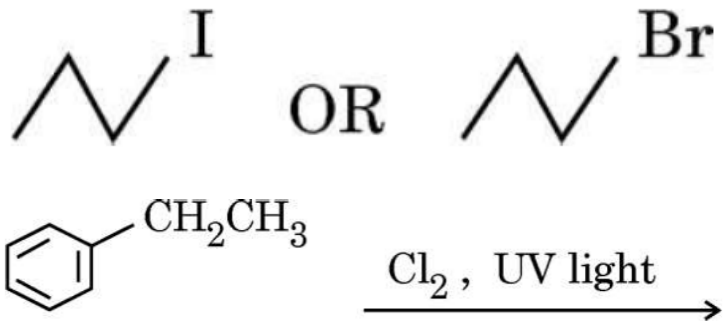
Step 1: Explain high enthalpy of atomization Transition metals generally contain several unpaired electrons in their d orbitals. Participation of these electrons together with outer s electrons in metallic bonding creates strong attractions among metal atoms. Separating the solid completely into isolated gaseous atoms therefore requires considerable energy, producing high enthalpies of atomization. The trend need not be perfectly regular because electronic configuration and bonding strength vary across the series.

Step 2: Identify the minimum in the 3d series Zinc has the configuration $[\mathrm{Ar}]\,3d^{10}4s^{2}$. Its d subshell is completely filled and has no unpaired d electrons. Thus it lacks the strong d-electron contribution to metallic bonding found in the middle of the series, and its metallic bonding is relatively weak. Accordingly, zinc has the lowest enthalpy of atomization among the elements of the 3d series.

Step 3: Conclusion Transition metals have strong metallic bonds due to s- and d-electron participation; $\boxed{\mathrm{Zn}}$ has the lowest enthalpy of atomization in the 3d series.

Quick Tip to Solve: For atomization questions, connect bond strength with unpaired d electrons; Zn has a filled 3d subshell and weak metallic bonding.

20. (a) In the following pair of compounds, which compound undergoes S_N2 reaction faster and why ?
(b) Write the major product in the following :
Ethylbenzene + Cl_2 / UV light $\rightarrow$? [2 marks]



Solution:

Concept:

- In an S_N2 reaction, the nucleophile attacks as the leaving group departs. For the same alkyl group, a weaker carbon-halogen bond and better leaving group increase the rate.
- Chlorination with Cl_2 under UV light proceeds by a free-radical mechanism; benzylic radicals are stabilized by resonance with the aromatic ring.

Step 1: Compare the two alkyl halides The pair consists of 1-iodopropane and 1-bromopropane, with the same primary propyl group. Thus steric hindrance at the reacting carbon is comparable. 1-Iodopropane undergoes S_N2 faster because the $C-I$ bond is weaker than the $C-Br$ bond and I^- is a better leaving group than Br^-. The comparison is due to the halogen, rather than a difference in alkyl substitution.

Step 2: Write the major photochemical chlorination product UV light causes homolytic cleavage of chlorine. Hydrogen abstraction from the benzylic CH_2 group of ethylbenzene gives the resonance-stabilized radical $C_6H_5-\dot{C}H-CH_3$, which reacts with chlorine to give

$$C_6H_5CH_2CH_3 + Cl_2 \xrightarrow{\text{UV light}} C_6H_5CHClCH_3 + HCl.$$

Benzylic substitution is favored over terminal side-chain substitution because the corresponding radical is more stable. These conditions favor side-chain chlorination; ring chlorination requires an electrophilic catalyst.

Step 3: Conclusion (a) $\boxed{\text{1-iodopropane}}$ reacts faster. (b) The major product is $\boxed{C_6H_5CHClCH_3}$, 1-chloro-1-phenylethane.

Quick Tip to Solve: For equal alkyl groups, compare leaving groups in SN2; with chlorine and UV light, substitute a benzylic hydrogen in ethylbenzene.

21. Define the following terms :

(a) Denaturation of protein

(b) Invert sugar [2 marks]

Solution:

Concept:

- A protein has a specific three-dimensional conformation maintained by interactions such as hydrogen bonds. This shape is essential for its biological activity.
- Sucrose hydrolysis gives one molecule each of glucose and fructose; the resulting mixture has optical rotation opposite to that of sucrose.

Step 1: Define denaturation of protein Denaturation is the loss of the native conformation and biological activity of a protein under the influence of heat, a change in pH, or certain chemicals. Secondary and tertiary structures are disrupted, while the primary structure, namely the amino-acid sequence joined by peptide bonds, remains intact. Coagulation of egg white on heating is a familiar example.

Step 2: Define invert sugar Invert sugar is the equimolar mixture of glucose and fructose obtained by hydrolysis of sucrose. The reaction is

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6\ (\text{glucose}) + C_6H_{12}O_6\ (\text{fructose}).$$

Sucrose is dextrorotatory, but its hydrolysis mixture is laevorotatory because the negative rotation of fructose outweighs the positive rotation of glucose. This change in the direction of optical rotation is called inversion.

Step 3: Conclusion (a) Denaturation: loss of native protein conformation and biological activity without breaking the primary peptide-chain structure. (b) Invert sugar: the equimolar glucose-fructose mixture formed by sucrose hydrolysis.

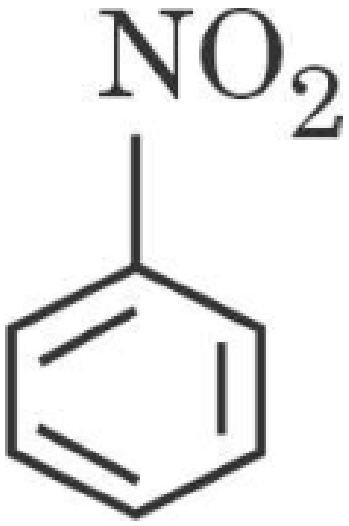
Quick Tip to Solve: For denaturation mention shape and activity; for invert sugar mention both constituent sugars and inversion of optical rotation.

Section C (21 marks)

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

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

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



$$A \xrightarrow[273-278\,K]{NaNO_2 + HCl} B$$

Solution:

Concept:

- KCN substitutes bromide through the carbon atom of cyanide, forming a nitrile with one additional carbon. Partial hydrolysis converts the nitrile to an amide.
- Hofmann bromamide degradation converts an amide into a primary amine with one fewer carbon atom. Diazotisation of aniline at $273 - 278\,K$ gives benzenediazonium chloride.

Step 1: Identify A and B in sequence (a) Ethyl bromide undergoes nucleophilic substitution with KCN:

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

Thus A is propanenitrile, $CH_3CH_2C \equiv N$. Partial hydrolysis stops at the amide rather than proceeding to the carboxylate, so B is propanamide, $CH_3CH_2C(=O)NH_2$. The carbon of the nitrile becomes the carbonyl carbon of this amide.

Step 2: Identify C in sequence (a) B reacts with bromine and sodium hydroxide by Hofmann

Quick Tip to Solve: Track carbon count in (a): KCN adds one carbon, partial hydrolysis retains it, and Hofmann degradation removes the carbonyl carbon.

bromamide degradation:

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

Therefore C is ethanamine, $CH_3CH_2NH_2$. The carbonyl carbon is lost, so this product contains two carbon atoms.

Step 3: Identify A, B and C in sequence (b) Fe and HCl reduce the nitro group of nitrobenzene to an amino group; A is aniline, $C_6H_5NH_2$. Sodium nitrite and hydrochloric acid generate nitrous acid, which diazotises aniline at the printed low temperature. B is benzenediazonium chloride, $C_6H_5N \equiv N^+\,Cl^-$. Ethanol reduces the diazonium group to hydrogen, giving C as benzene, C_6H_6:

$$C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

Nitrogen gas is released and ethanol is oxidised to ethanal.

Step 4: Conclusion (a) A: $CH_3CH_2C \equiv N$, B: $CH_3CH_2CONH_2$, C: $CH_3CH_2NH_2$. (b) A: $C_6H_5NH_2$, B: $C_6H_5N_2^+Cl^-$, C: C_6H_6.

Quick Tip to Solve: Track carbon count in (a): KCN adds one carbon, partial hydrolysis retains it, and Hofmann degradation removes the carbonyl carbon.

23. Write the reaction involved in the following :

(a) Wolff-Kishner reduction

(b) Decarboxylation reaction

(c) Cannizzaro reaction [3 marks]

Solution:

Concept:

- Wolff-Kishner reduction replaces a carbonyl group by a methylene group using hydrazine and strong base on heating.
- Decarboxylation of a sodium carboxylate with soda lime removes its carboxyl carbon. Cannizzaro disproportionation occurs for aldehydes without an alpha hydrogen in concentrated alkali.

Step 1: Write Wolff-Kishner reduction An aldehyde or ketone is first treated with hydrazine to form a hydrazone. Heating with KOH in a high-boiling solvent such as ethylene glycol converts it into the corresponding hydrocarbon, with nitrogen evolution:

$$R_2C = O + H_2NNH_2 \xrightarrow[\Delta]{\text{KOH, ethylene glycol}} R_2CH_2 + N_2 + H_2O.$$

For example, acetone gives propane:

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

The carbon skeleton is retained and the carbonyl oxygen is removed.

Quick Tip to Solve: Write reagents above each arrow: hydrazine/KOH, soda lime/heat, and concentrated alkali distinguish these three named reactions.

Step 2: Write decarboxylation reaction Heating the sodium salt of a carboxylic acid with soda lime, a mixture of NaOH and CaO, produces an alkane with one fewer carbon atom:

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

For example, sodium ethanoate gives methane:

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

The carboxyl carbon is removed from the organic molecule and appears in sodium carbonate.

Step 3: Write Cannizzaro reaction An aldehyde lacking an alpha hydrogen undergoes self-oxidation and self-reduction in concentrated alkali. One aldehyde molecule is oxidised to a carboxylate salt and another is reduced to a primary alcohol. Benzaldehyde gives sodium benzoate and benzyl alcohol:

$$2\mathrm{C_6H_5CHO} + \mathrm{NaOH} \xrightarrow{\text{conc.}} \mathrm{C_6H_5COONa} + \mathrm{C_6H_5CH_2OH}.$$

Benzaldehyde has no alpha hydrogen, so it satisfies the condition for this disproportionation reaction.

Step 4: Conclusion Wolff-Kishner: carbonyl compound to hydrocarbon using hydrazine/KOH and heat. Decarboxylation: sodium carboxylate to an alkane using soda lime and heat. Cannizzaro: an aldehyde without alpha hydrogen to an alcohol and carboxylate in concentrated alkali, as shown above.

Quick Tip to Solve: Write reagents above each arrow: hydrazine/KOH, soda lime/heat, and concentrated alkali distinguish these three named reactions.

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

(a) Phenol from chlorobenzene

(b) Salicylaldehyde from phenol

(c) 2-Methoxyacetophenone from anisole

(d) Picric acid from phenol [3 marks]

Solution:

Concept:

- Chlorobenzene undergoes alkaline hydrolysis at high temperature and pressure; acidification of sodium phenoxide gives phenol.
- The Reimer–Tiemann reaction introduces CHO ortho to OH. Friedel–Crafts acylation introduces COCH3 into anisole at ortho and para positions.
- Concentrated nitric acid nitrates phenol at positions 2, 4 and 6, forming picric acid.

Step 1: (a) Phenol from chlorobenzene Heat chlorobenzene with aqueous sodium hydroxide at 623 K

Quick Tip to Solve: Match the added group with its reagent: CHO needs chloroform/alkali, COCH3 needs acetyl chloride/AlCl3, and three NO2 groups need concentrated nitric acid.

and approximately 300 atm, then acidify:

$$C_6H_5Cl + 2NaOH \xrightarrow[300\,atm]{623\,K} C_6H_5ONa + NaCl + H_2O,$$
$$C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl.$$

Acidification converts the phenoxide ion into the neutral phenol molecule.

Step 2: (b) Salicylaldehyde from phenol Treat phenol with chloroform and aqueous sodium hydroxide on heating, followed by acidification. The Reimer–Tiemann reaction gives the ortho formyl product:

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

This equation represents the overall conversion after acid work-up; salicylaldehyde is 2-hydroxybenzaldehyde.

Step 3: (c) 2-Methoxyacetophenone from anisole React anisole with acetyl chloride in the presence of anhydrous aluminium chloride:

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

Friedel–Crafts acylation gives both ortho and para products because the methoxy group is ortho/para directing. Separate the required ortho isomer from the mixture; the para isomer is generally the major product.

Step 4: (d) Picric acid from phenol Treat phenol with concentrated nitric acid:

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

The hydroxyl group activates the ring. Substitution at both ortho positions and the para position forms 2,4,6-trinitrophenol, also called picric acid.

Step 5: Conclusion The preparations use alkaline hydrolysis and acidification, Reimer–Tiemann formylation, Friedel–Crafts acetylation, and strong nitration, respectively. Any three of the equations satisfy the question.

Quick Tip to Solve: Match the added group with its reagent: CHO needs chloroform/alkali, COCH3 needs acetyl chloride/AlCl3, and three NO2 groups need concentrated nitric acid.

25. Give reasons for the following :

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

(b) Racemic mixture is optically inactive.

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

Solution:

Concept:

- Inductive and resonance effects play different roles: electron withdrawal influences overall reactivity, whereas relative stability of substitution intermediates determines orientation.
- Enantiomers rotate plane-polarised light by equal amounts in opposite directions under identical conditions.
- Allylic resonance stabilises the developing positive charge during carbon–chlorine bond cleavage and facilitates nucleophilic substitution.

Step 1: (a) Explain chlorine's ortho/para directing effect Chlorine is electronegative and withdraws electrons through the sigma bonds by its negative inductive effect, $-I$. This lowers the ring's overall electron density and makes chlorobenzene less reactive than benzene towards electrophilic substitution. However, chlorine also donates a lone pair into the aromatic ring by resonance, its $+R$ effect. This increases electron density particularly at the ortho and para positions. The sigma complexes formed by ortho or para attack have an additional resonance contributor in which chlorine donates a lone pair; the corresponding meta complex lacks this stabilisation. Hence chlorine deactivates the ring overall but directs an entering electrophile to ortho and para positions.

Step 2: (b) Explain optical inactivity of a racemic mixture A racemic mixture contains equal amounts of the two enantiomers. If one enantiomer rotates plane-polarised light clockwise through $+\alpha$, the other produces an equal anticlockwise rotation, $-\alpha$, at the same concentration and path length. Their rotations cancel:

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

Thus the mixture shows no net optical rotation even though each enantiomer is individually optically active. This cancellation is called external compensation.

Step 3: (c) Compare hydrolysis of allyl and n-propyl chlorides In allyl chloride, $CH_2{=}CHCH_2Cl$, the carbon bearing chlorine is adjacent to a double bond. During substitution, developing positive charge is delocalised over the allylic system. The allyl carbocation, where an ionisation pathway operates, has the resonance contributors

$$CH_2{=}CHCH_2^+ \longleftrightarrow {}^+CH_2CH{=}CH_2.$$

Allylic resonance also stabilises the transition state for direct nucleophilic displacement. In $CH_3CH_2CH_2Cl$, no adjacent double bond provides such stabilisation. Consequently carbon–chlorine bond cleavage/substitution has a lower activation barrier for allyl chloride, so it is hydrolysed more readily.

Step 4: Conclusion Chlorine directs ortho/para through resonance despite inductive deactivation; equal enantiomer rotations cancel in a racemate; and allylic resonance accelerates hydrolysis relative

Quick Tip to Solve: Separate overall activation from orientation for chlorine, and look for an adjacent double bond when comparing substitution rates.

to n-propyl chloride.

Quick Tip to Solve: Separate overall activation from orientation for chlorine, and look for an adjacent double bond when comparing substitution rates.

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

Solution:

Concept:

- Raoult's law for a non-volatile solute is $p = x_1 p^\circ$, where p° is the pure solvent's vapour pressure and x_1 is the solvent mole fraction.
- Complete dissociation of a 1:1 electrolyte, $\mathrm{AB} \rightarrow \mathrm{A}^+ + \mathrm{B}^-$, gives two solute particles per formula unit, so the van't Hoff factor is $i = 2$.

Step 1: Count the solute particles after dissociation The solute is a strong electrolyte and the question specifies complete dissociation. Each mole of AB therefore produces one mole of each ion:

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

Thus 1 mol of AB gives 2 mol of dissolved particles. Use this effective particle amount rather than the initial formula-unit amount when calculating the mole fraction; the solvent amount remains 50 mol.

Step 2: Calculate the solvent mole fraction Total moles of independently dissolved species are $50 + 2 = 52$ mol. Hence

$$x_1 = \frac{n_1}{n_1 + in_2} = \frac{50}{50 + 2(1)} = \frac{50}{52} = \frac{25}{26}.$$

Both numerator and denominator are mole amounts, so this fraction is dimensionless. Including the ions in the denominator accounts for their increased vapour-pressure lowering.

Step 3: Apply Raoult's law at the given temperature The given pure-solvent pressure at $283\,\mathrm{K}$ is $p^\circ = 100$ mm Hg. Therefore

$$p = x_1 p^\circ = \frac{25}{26} \times 100 = 96.1538 \text{ mm Hg}.$$

The pressure lowering is $100 - 96.1538 = 3.8462$ mm Hg, consistent with the solute-particle mole fraction $2/52$. The often-used dilute approximation $\Delta p/p^\circ \simeq in_2/n_1$ would give $p \simeq 96$ mm Hg; retaining the full mole-fraction denominator gives the value calculated above.

Step 4: Conclusion The vapour pressure of the solution at $283\,\mathrm{K}$ is $\boxed{96.15 \text{ mm Hg}}$, approximately 96 mm Hg in the dilute-solution approximation.

Quick Tip to Solve: First multiply solute moles by the number of ions formed; then put solvent moles over solvent plus effective solute moles.

27. Calculate emf of the following cell:

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

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

Solution:

Concept:

- The cell emf is the cathode reduction potential minus the anode reduction potential: $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}}$.
- At 298 K, the Nernst equation is $E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - (0.0591/n)\log Q$, where n is the electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify the electrode reactions Tin has the more positive standard reduction potential, so tin ions are reduced at the cathode while zinc is oxidised at the anode:

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

The overall reaction is $\mathrm{Zn(s) + Sn^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Sn(s)}$, so $n = 2$.

Step 2: Calculate the standard emf and reaction quotient Using reduction potentials for both electrodes,

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

For this reaction the dissolved product is zinc ion and the dissolved reactant is tin ion. Hence, using the given molar concentrations,

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

Step 3: Apply the Nernst equation At the usual temperature of 298 K for this calculation,

$$E_{\mathrm{cell}} = 0.62 - \frac{0.0591}{2} \times 2 = 0.5609\,\mathrm{V}.$$

Since $Q > 1$, the concentration correction lowers the emf below the standard value; this also checks the sign of the correction.

Step 4: Conclusion The emf of the given cell is $\boxed{0.561\,\mathrm{V}}$ (approximately $0.56\,\mathrm{V}$).

Quick Tip to Solve: Write the balanced cell reaction first: zinc ions go in the numerator of Q, and two electrons make n = 2.

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

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

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy and R the gas constant.
- For two temperatures, $\log(k_2/k_1) = \dfrac{E_a}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$. Temperatures must be in kelvin; at unchanged reactant concentrations, the rate ratio equals the rate-constant ratio.

Step 1: Convert temperatures and identify the ratio The reaction rate triples, so at the same reactant concentrations $k_2/k_1 = 3$. Convert Celsius temperatures to absolute temperatures:

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

Use the given common logarithm $\log 3 = 0.48$. Celsius values cannot be substituted into the reciprocal-temperature terms.

Step 2: Rearrange the two-temperature equation Since $T_2 > T_1$, the reciprocal-temperature difference is positive:

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{T_2 - T_1}{T_1 T_2} = \frac{10}{290 \times 300}\,\text{K}^{-1}.$$

Rearranging gives

$$E_a = \frac{(2.303R)\log(k_2/k_1)\,T_1 T_2}{T_2 - T_1}.$$

This arrangement retains the positive sign required for the activation-energy barrier.

Step 3: Substitute the given data Using $2.303R = 19.15\,\text{J K}^{-1}\,\text{mol}^{-1}$,

$$\begin{aligned} E_a &= \frac{19.15 \times 0.48 \times 290 \times 300}{10} \\ &= 79970.4\,\text{J mol}^{-1} \\ &= 79.9704\,\text{kJ mol}^{-1}. \end{aligned}$$

The kelvin factor from $T_1T_2/(T_2 - T_1)$ cancels the inverse kelvin in the supplied gas-constant factor.

Step 4: Conclusion The activation energy is $\boxed{E_a \approx 80.0\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Convert both temperatures to kelvin before multiplying them; the 10-degree difference alone stays numerically unchanged.

Section D (8 marks)

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

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

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

Solution:

Concept:

- Reducing sugars reduce Tollens' reagent or Fehling's solution and are themselves oxidised.
- A free anomeric centre permits formation of an open-chain carbonyl form; glucose and fructose are examples of reducing monosaccharides.

Step 1: State the chemical criterion A sugar is called reducing when it can act as the reducing agent towards Tollens' reagent or Fehling's solution. The reagent is reduced while the sugar is oxidised.

Step 2: Connect the criterion to examples Glucose reduces these reagents through its accessible aldehyde form. Fructose also gives a positive test because in alkaline solution it can rearrange into aldose forms. Thus reducing behaviour is not restricted to sugars named as aldehydes in their usual open-chain structures.

Step 3: Conclusion Reducing sugars are sugars that reduce Tollens' reagent and Fehling's solution, undergoing oxidation themselves.

Quick Tip to Solve: Define reducing sugars by the reagent they reduce, and remember that fructose also gives the alkaline reducing-sugar tests.

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

Solution:

Concept:

- A monosaccharide is a carbohydrate that cannot be hydrolysed into simpler carbohydrate units.
- A disaccharide yields two monosaccharide units on hydrolysis; its classification depends on the number of constituent sugar units.

Quick Tip to Solve: Count sugar units rather than carbon atoms: fructose and galactose are single units; sucrose and lactose each contain two.

Step 1: Identify the single-unit sugars Fructose is a ketohexose and galactose is an aldohexose. Each is a single monosaccharide unit and neither can be hydrolysed into simpler carbohydrates.

Step 2: Identify the two-unit sugars Sucrose consists of glucose and fructose units linked through a glycosidic bond. Lactose consists of glucose and galactose units. On hydrolysis each gives two monosaccharide units, so both are disaccharides.

Step 3: Conclusion $\boxed{\text{Monosaccharides: Fructose, Galactose}}$. $\boxed{\text{Disaccharides: Sucrose, Lactose}}$.

Quick Tip to Solve: Count sugar units rather than carbon atoms: fructose and galactose are single units; sucrose and lactose each contain two.

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

[2 marks]

Solution:

Concept:

- A polysaccharide contains many monosaccharide units joined by glycosidic bonds. On hydrolysis, glycogen yields glucose.
- Storage polysaccharides provide a reserve of carbohydrate: starch serves this function in plants, whereas glycogen serves it in animals.

Step 1: Identify the storage carbohydrate Glycogen is the polysaccharide stored in animal tissues, especially in the liver and muscles. It is a polymer of α-D-glucose and has a branched structure similar to the amylopectin component of starch, though glycogen is more highly branched.

Step 2: Explain the name Starch is the principal carbohydrate reserve in plants. Glycogen performs the corresponding role in animals: when energy is needed, its stored glucose units can be released and used in metabolism. Thus the word animal identifies the organisms in which the reserve occurs, and starch expresses the similarity in composition and storage function; it does not mean that animal tissues store plant starch.

Step 3: Conclusion The polysaccharide is $\boxed{\text{glycogen}}$. It is called animal starch because it is the carbohydrate storage material in animals and is structurally and functionally similar to starch in plants.

Quick Tip to Solve: Pair the storage polymers with their organisms: plants store starch; animals store glycogen.

OR

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

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

Solution:

Concept:

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

Step 1: Name the C-1 isomers The two forms are α-D-glucose and β-D-glucose, called anomers. Cyclisation converts the aldehyde carbon into the hemiacetal carbon C-1. The forms retain the same configurations at the other stereocentres and differ only in the orientation of the hydroxyl group attached to C-1.

Step 2: Identify the functional group from oxidation Glucose is oxidised by bromine water to gluconic acid. The terminal $-\mathrm{CHO}$ group of the open-chain form becomes $-\mathrm{COOH}$, while the carbon chain is retained. This mild oxidation establishes the presence of an aldehyde group, rather than identifying one of the alcoholic hydroxyl groups. The cyclic and open-chain forms remain in equilibrium, so the reaction is possible even though glucose mainly exists in cyclic forms.

Step 3: Conclusion (i) The isomers are α-D-glucose and β-D-glucose (anomers). (ii) Bromine-water oxidation detects the aldehyde group, $\boxed{-\mathrm{CHO}}$.

Quick Tip to Solve: For glucose, connect C-1 configurational changes with anomers and bromine water with aldehyde oxidation.

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

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

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

Solution:

Concept:

- A transition element has a partially filled d subshell in its atom or in at least one of its common ions.
- A completely filled d^{10} subshell does not satisfy the transition-element criterion.

Step 1: Check copper and its ion Copper has configuration $[Ar]3d^{10}4s^{1}$, but Cu^{2+} has configuration $[Ar]3d^{9}$. Its common divalent ion therefore has an incomplete d subshell, which is sufficient for classification as a transition element.

Step 2: Check zinc and its ion Zinc has configuration $[Ar]3d^{10}4s^{2}$, and its common ion Zn^{2+} is $[Ar]3d^{10}$. Both have filled d subshells. Merely belonging to the d block is therefore insufficient to make zinc a transition element.

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

Quick Tip to Solve: Check common ionic configurations as well as the neutral atom before classifying a d-block element.

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

Solution:

Concept:

- The outer ns and penultimate $(n-1)d$ orbitals in transition elements have comparable energies.
- An oxidation state depends on the number of electrons that can participate in bonding or be removed.

Step 1: Compare the available orbitals The energy difference between the ns and $(n-1)d$ orbitals is small. Consequently, both the outer s electrons and different numbers of d electrons can participate in bond formation, depending on the reacting species and the stability of the products.

Step 2: Connect electron participation with oxidation states Participation of different numbers of these electrons produces a variety of oxidation states. For example, manganese shows states from $+2$ to $+7$: its $3d^5 4s^2$ configuration provides s and d electrons for bonding. The availability of d electrons, in addition to s electrons, is the essential reason for this variability.

Step 3: Conclusion Transition elements show variable oxidation states because their ns and $(n-1)d$ orbitals have comparable energies, allowing different numbers of s and d electrons to participate in bonding.

Quick Tip to Solve: Use the small ns-to-d energy gap to explain why more than the outermost electrons take part in bonding.

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

[2 marks]

Solution:

Concept:

- The standard potential $E^\circ_{M^{2+}/M}$ reflects the overall energetics of converting a metal into its aqueous divalent ion.
- Transition-metal oxidation states commonly differ by one unit, whereas those of non-transition elements commonly differ by two units.

Step 1: Explain the irregular electrode potentials Formation of $M^{2+}(aq)$ from $M(s)$ involves atomisation of the metal, the first and second ionisation steps, and hydration of the ion. The corresponding enthalpies do not change smoothly or compensate uniformly from V to Zn. Their combined effect produces the irregular trend in standard electrode potentials. Differences in electronic stability, including half-filled and filled d subshells, contribute to the non-uniform ionisation and hydration energetics.

Step 2: Compare the steps between oxidation states Transition elements can use different numbers of s and d electrons, so successive oxidation states often differ by one unit; manganese, for example, exhibits $+2, +3, +4, +5, +6, +7$. Non-transition elements generally have oxidation states differing by

Quick Tip to Solve: For electrode potentials consider all three energy contributions; for oxidation-state variability compare one-unit and two-unit changes.

two units, as illustrated by tin in $+2$ and $+4$, or phosphorus in $+3$ and $+5$. This is the characteristic comparison; it is not a claim that every element exhibits every possible state.

Step 3: Conclusion (i) The irregular trend arises from the irregular combined variation in atomisation, ionisation and hydration enthalpies. (ii) Transition-metal oxidation states commonly differ by one unit, while non-transition-element states commonly differ by two units.

Quick Tip to Solve: For electrode potentials consider all three energy contributions; for oxidation-state variability compare one-unit and two-unit changes.

OR

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

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

Solution:

Concept:

- A reducing agent loses electrons and is oxidised; an oxidising agent gains electrons and is reduced. Stability of the product configuration helps explain the direction.
- In neutral or weakly alkaline medium, permanganate forms MnO_2, while iodide forms iodate, IO_3^-.

Step 1: (i) Compare the configurations reached by electron transfer Both given ions are $3d^4$. Chromium(II) readily loses one electron:

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

The resulting Cr^{3+} has the stable $3d^3$ configuration (in its usual octahedral environment, t_{2g}^3). Hence Cr^{2+} is strongly reducing. Manganese(III) instead readily accepts one electron:

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

The half-filled $3d^5$ configuration of Mn^{2+} is particularly stable; therefore Mn^{3+} is strongly oxidising.

Step 2: (ii) Balance the ionic reaction The half-reactions in non-acidic medium are

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

Multiply the first by two, add and cancel electrons, water and hydroxide common to both sides. Two manganese atoms gain six electrons in total, matching the six electrons lost by iodine. The final equation conserves each element and total charge: the charge is -3 on each side.

Step 3: Conclusion (i) Cr^{2+} forms stable $3d^3$ Cr^{3+}; Mn^{3+} forms half-filled $3d^5$ Mn^{2+}. (ii)

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

Quick Tip to Solve: Use the printed water reactant to recognise the non-acidic permanganate reaction; check atoms and charge after cancelling the half-reactions.

Section E (15 marks)

31. Answer any five of the following :

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

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

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

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

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

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

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

Solution:

Concept:

- Crystal field splitting competes with pairing energy P; a smaller splitting favours maximum unpaired electrons.
- Ligand charges determine the metal oxidation state. Neutral ethane-1,2-diamine (en) occupies two adjacent coordination sites through its two nitrogen donors.
- Heteroleptic complexes contain different ligand types; optical isomers are non-superimposable mirror images.

Step 1: (a) Relate the splitting energies For the same metal ion, oxidation state and ligands, tetrahedral splitting is smaller than octahedral splitting:

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

The tetrahedral arrangement has fewer ligands and their approach does not point directly at the d-orbital axes.

Step 2: (b) Name the platinum salt Two nitrate ions require a complex cation of charge $+2$. With two chlorido ligands of charge -1 each and two neutral en ligands, $x - 2 = +2$, so platinum is in oxidation state $+4$. Ligands are named in alphabetical order, disregarding multiplicative prefixes; the compound is dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate.

Step 3: (c) Apply VBT to nickel carbonyl Carbon monoxide is neutral, so nickel has oxidation state zero. In the VBT account, its electrons pair to give a filled $3d^{10}$ shell, leaving the $4s$ and three $4p$ orbitals available for sp^3 hybridisation. Four CO ligands donate electron pairs into these hybrids. Thus $[Ni(CO)_4]$ is tetrahedral and, since there are no unpaired electrons, diamagnetic.

Step 4: (d) Identify the isomerism Both the cation and anion are complex ions, so ligands can interchange between their metal coordination spheres. The compound shows coordination isomerism; an illustrative partner is $[Cr(NH_3)_6][Co(CN)_6]$.

Step 5: (e) Fill the octahedral d orbitals When $\Delta_o < P$, promotion to the higher e_g level costs less

Quick Tip to Solve: Count donor atoms, not ligand molecules: two en ligands plus two chlorido ligands give six coordination sites and an octahedral platinum complex.

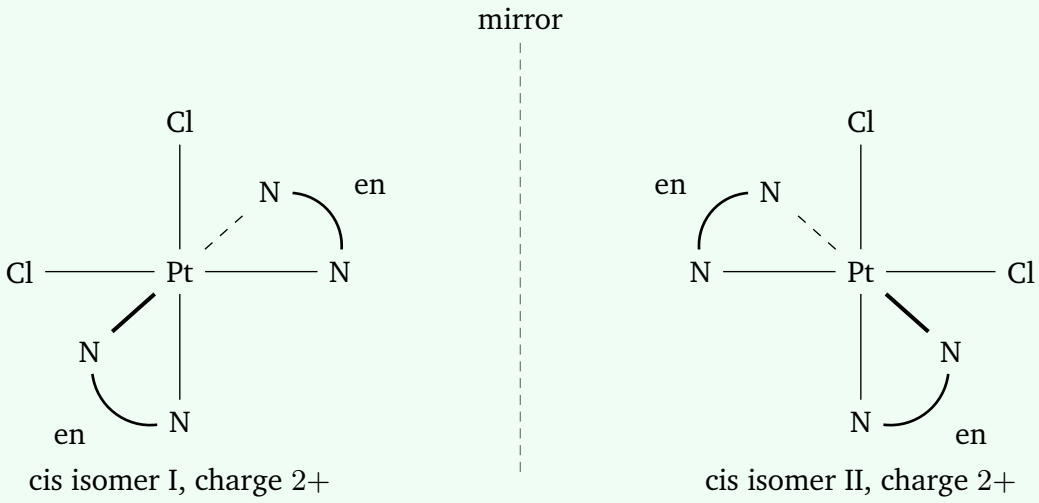
energy than pairing in t_{2g}. Three electrons singly fill t_{2g}; the fourth occupies e_g:

$$d^4: \quad t_{2g}^3 e_g^1.$$

All four electrons are unpaired, so this is a high-spin complex.

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

Step 7: (g) Construct the optical isomers The optically active form is cis-$[PtCl_2(en)_2]^{2+}$. The two chlorido ligands occupy adjacent octahedral positions. Each curved connection in the drawing joins the two nitrogen donors of one en ligand; solid and dashed bonds distinguish front and rear equatorial directions. Reflection reverses the arrangement of the two chelate rings, producing the two non-superimposable optical isomers. Each drawn complex carries charge $2+$. The trans arrangement does not give this pair of optical isomers.



Optical mirror images of cis-$[PtCl_2(en)_2]^{2+}$; each N–N curved link represents one en chelate.

Step 8: Conclusion (a) $\Delta_t = 4\Delta_o/9$. (b) Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate. (c) Tetrahedral, sp^3, diamagnetic. (d) Coordination isomerism. (e) $t_{2g}^3 e_g^1$, high spin. (f) $[Co(NH_3)_4Cl_2]^+$, with two ligand types. (g) The cis optical mirror-image pair is drawn above. Any five parts may be selected as requested.

Quick Tip to Solve: Count donor atoms, not ligand molecules: two en ligands plus two chlorido ligands give six coordination sites and an octahedral platinum complex.

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

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

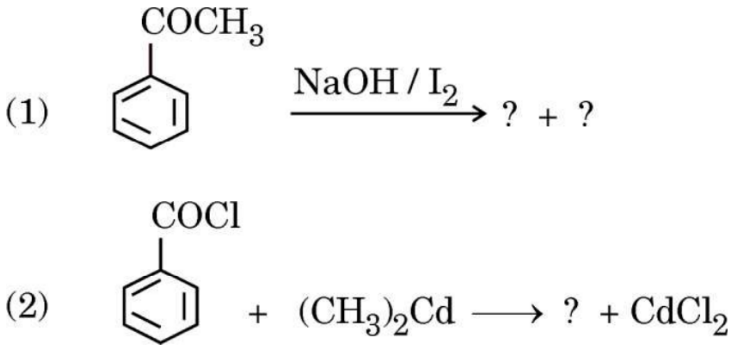
(2) The alpha (α) hydrogen atoms of aldehydes are acidic in nature.

(ii) Write the products in the following reactions :

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

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

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



Solution:

Concept:

- An aldehyde has a hydrogen directly attached to its carbonyl carbon; its oxidation to a carboxylic acid preserves the carbon skeleton. Ketone oxidation normally requires cleavage of a carbon-carbon bond.
- An alpha hydrogen is attached to the carbon next to the carbonyl group. Its removal gives an enolate ion whose negative charge is delocalised between carbon and oxygen.
- The iodoform reaction converts a methyl ketone $RCOCH_3$ into $RCOONa$ and yellow CHI_3 with iodine and sodium hydroxide. Dialkylcadmium converts an acyl chloride into a ketone.

Step 1: (i)(1) Compare oxidation of aldehydes and ketones Aldehydes possess a hydrogen atom on the carbonyl carbon. Oxidation replaces this hydrogen by a hydroxyl group without breaking any carbon-carbon bond:

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

Therefore even mild oxidising agents such as Tollens' reagent oxidise aldehydes readily. In a ketone, both groups attached to the carbonyl carbon are carbon groups, so this hydrogen is absent. Oxidation of a ketone requires breaking a carbon-carbon bond and generally needs vigorous conditions and a strong oxidising agent. This bond cleavage makes oxidation of ketones more difficult.

Step 2: (i)(2) Explain acidity of alpha hydrogens The electron-withdrawing carbonyl group facilitates removal of an alpha hydrogen as a proton. For example, removal of an alpha proton from ethanal gives the following resonance-stabilised enolate ion:

$$CH_3CHO \rightleftharpoons H^+ + CH_2CHO^-.$$

Quick Tip to Solve: Identify the methyl ketone group before using alkaline iodine; always write the carboxylate salt as the product in the alkaline medium.

Its resonance contributors can be written as

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

The negative charge is thus delocalised over the alpha carbon and the electronegative oxygen. Stabilisation of this conjugate base explains the acidic character of the alpha hydrogens, compared with hydrogen atoms of ordinary alkanes. The alpha hydrogen is distinct from the hydrogen directly bonded to the carbonyl carbon.

Step 3: (ii)(1) Apply the iodoform reaction to acetophenone Acetophenone, $C_6H_5COCH_3$, contains the methyl ketone group. In alkaline iodine the three methyl hydrogens are replaced by iodine; cleavage then produces sodium benzoate and iodoform. The balanced overall reaction is

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

Since the reaction medium is alkaline, the benzoic acid fragment is present as its sodium salt. Iodoform separates as a yellow precipitate.

Step 4: (ii)(2) React benzoyl chloride with dimethylcadmium Dimethylcadmium transfers methyl groups to the acyl chloride and gives a ketone. The organic product is acetophenone, $C_6H_5COCH_3$. Including the stoichiometric coefficients gives

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

Unlike the reaction of an acyl chloride with excess Grignard reagent, this reaction stops at the ketone stage.

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

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

Ethanal gives no such effervescence because it does not behave as a carboxylic acid. Passing the evolved gas through limewater makes it milky, confirming carbon dioxide if required.

Step 6: Conclusion Aldehydes oxidise readily because oxidation does not require carbon-carbon bond cleavage; their alpha hydrogens are acidic because the conjugate enolate ion is resonance-stabilised. The products are (ii)(1) sodium benzoate and iodoform, and (ii)(2) acetophenone. Sodium hydrogen carbonate gives effervescence with ethanoic acid but not with ethanal.

Quick Tip to Solve: Identify the methyl ketone group before using alkaline iodine; always write the carboxylate salt as the product in the alkaline medium.

OR

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

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

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

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

(v) Write the main product in the following reaction: [5 marks]

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4} ?$$

Solution:

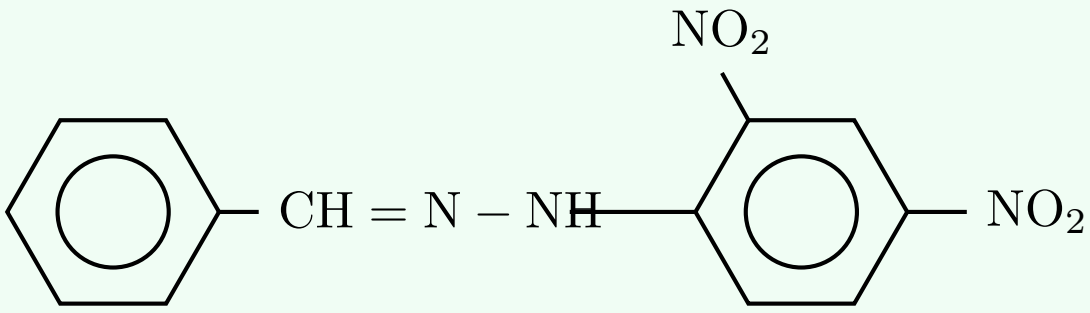
Concept:

- Carbonyl compounds condense with 2,4-dinitrophenylhydrazine to form hydrazones: the carbonyl $C=O$ becomes $C=N-NHAr$, with elimination of water. Here Ar is the phenyl group bearing nitro groups at positions 2 and 4 relative to the hydrazino attachment.
- Addition of CN^- to the electrophilic carbonyl carbon depends on both its positive character and accessibility. Electron-releasing alkyl groups and bulky substituents decrease the rate of nucleophilic addition.
- Grignard reagents add to carbon dioxide to give magnesium carboxylates, which yield carboxylic acids on acidification. The iodoform test identifies the CH_3CO- group, while $NaBH_4$ normally reduces aldehydes and ketones without reducing an ester group.

Step 1: (i) Form the benzaldehyde hydrazone Benzaldehyde reacts with the terminal $-NH_2$ group of 2,4-dinitrophenylhydrazine. The product is

$$C_6H_5CH=N-NHC_6H_3(NO_2)_2,$$

where the two NO_2 groups are ortho and para to $-NH-$ on the second ring. The aldehydic hydrogen remains attached to the carbon of the $CH=N$ group. The labelled structure is shown below.



Benzaldehyde 2,4-dinitrophenylhydrazone; nitro groups lie at positions 2 and 4 on the right ring.

Step 2: (ii) Compare nucleophilic addition of HCN The tert-butyl group in $(CH_3)_3C-COCH_3$

Quick Tip to Solve: For this substrate, mark the ketone and ester carbonyls separately: $NaBH_4$ converts only the ketone to CH(OH), so keep the entire ester group intact.

produces greater steric obstruction and a stronger electron-releasing effect than a methyl group in acetone. This reduces access of cyanide to the carbonyl carbon and reduces its electrophilicity. Ethanal has only one alkyl group and one small hydrogen attached to its carbonyl carbon, so it is more reactive than either ketone. Thus the increasing order is

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

Step 3: (iii) Carboxylate phenyl magnesium bromide Treat phenyl magnesium bromide with carbon dioxide in dry ether, then hydrolyse the magnesium salt using dilute acid:

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

Carbon dioxide supplies the additional carbon of the carboxyl group. Acidification is done after carboxylation because moisture or acid would otherwise destroy the Grignard reagent.

Step 4: (iv) Distinguish the two aldehydes using iodoform Warm each sample with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3; benzaldehyde gives no yellow iodoform precipitate. Ethanal contains the required CH_3CO- arrangement, whereas benzaldehyde does not:

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 \downarrow + HCOONa + 3NaI + 3H_2O.$$

Tollens' reagent would not distinguish this pair because both compounds are aldehydes and give a positive test.

Step 5: (v) Reduce the ketone group selectively Sodium borohydride reduces the ketone carbonyl of ethyl acetoacetate to a secondary alcohol. The ester group $-COOC_2H_5$ remains unchanged under these conditions. Acidic work-up protonates the alkoxide, giving

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

The main product is ethyl 3-hydroxybutanoate. Reduction creates a stereogenic centre; in the absence of a chiral reagent the product is a racemic mixture.

Step 6: Conclusion (i) The hydrazone is $C_6H_5CH = N - NHC_6H_3(NO_2)_2$, with nitro groups at 2 and 4. (ii) The order is $(CH_3)_3CCOCH_3 < CH_3COCH_3 < CH_3CHO$. (iii) Use CO_2 in dry ether followed by acidification. (iv) Ethanal gives yellow iodoform; benzaldehyde does not. (v) The product is $CH_3CH(OH)CH_2COOC_2H_5$.

Quick Tip to Solve: For this substrate, mark the ketone and ester carbonyls separately: $NaBH_4$ converts only the ketone to CH(OH), so keep the entire ester group intact.

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

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

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$. The conductivity is $\kappa = G(l/A)$, where l/A is the cell constant. A cell constant in cm^{-1} gives conductivity in S cm^{-1}.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$, where c is the molar concentration in mol L^{-1}. The factor 1000 converts litres to cubic centimetres.
- Faraday's first law relates the mass transformed at an electrode to the total charge passed. One faraday, F, is the charge of one mole of electrons, approximately $96485\,\text{C mol}^{-1}$.

Step 1: (i) Calculate conductance and conductivity The measured resistance is $R = 100\,\Omega$, so the conductance of the solution is

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

Multiply this conductance by the given cell constant:

$$\kappa = G\frac{l}{A} = (0.0100)(0.0354) = 3.54 \times 10^{-4}\,\text{S cm}^{-1}.$$

Resistance is a property of the particular cell and solution together; multiplying its reciprocal by the cell constant removes the geometrical dependence.

Step 2: (i) Convert conductivity to molar conductivity The concentration is $c = 0.05\,\text{mol L}^{-1}$. One litre contains $1000\,\text{cm}^3$, so the volume containing one mole is $1000/c$ cubic centimetres. Thus

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

The units follow from S cm^{-1} × cm^3 mol^{-1}. No limiting molar conductivity or degree of dissociation is needed because the measured resistance directly supplies the conductivity.

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

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

Here m is the mass deposited or liberated, Q is charge, I is current, t is time and Z is the electrochemical equivalent of the substance. Thus, for the same electrode process, doubling the charge doubles the amount transformed.

Step 4: (ii) Count the electrons required for permanganate reduction In MnO_4^-, the four oxygen atoms contribute an oxidation-state sum of -8. Therefore manganese has oxidation state $+7$, since $x - 8 = -1$. In Mn^{2+}, manganese has oxidation state $+2$, so each manganese atom gains five electrons.

Quick Tip to Solve: Use $\Lambda_m = 1000(\text{cell constant})/(Rc)$ directly, then count the fall in manganese oxidation state from $+7$ to $+2$ to obtain the electron requirement.

The balanced reduction half-reaction in acidic medium is

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

Both sides have net charge $+2$, and manganese, oxygen and hydrogen are balanced. Hence reduction of one mole of permanganate requires five moles of electrons. As one mole of electrons carries one faraday, the required charge is $5F$, approximately 4.82×10^5 C.

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

Quick Tip to Solve: Use $\Lambda_m = 1000(\text{cell constant})/(Rc)$ directly, then count the fall in manganese oxidation state from $+7$ to $+2$ to obtain the electron requirement.

OR

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

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

Solution:

Concept:

- Molar conductivity is $\Lambda_m = \kappa \times 1000/c$, where κ is conductivity in S cm^{-1} and c is concentration in mol L^{-1}. The factor 1000 converts litres to cubic centimetres.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^0$, where Λ_m^0 is its limiting molar conductivity. At infinite dilution the weak electrolyte is effectively completely dissociated.
- During discharge of a lead storage battery, oxidation occurs at the lead anode and reduction at the lead dioxide cathode. Sulphuric acid supplies $\mathrm{H^+}$ and $\mathrm{SO_4^{2-}}$; both electrodes form lead sulphate.

Step 1: (i) Calculate molar conductivity The stated conductivity is $\kappa = 5.25 \times 10^{-5}$ S cm^{-1}, and the concentration is $c = 0.0025$ mol L^{-1}. Thus

$$\begin{aligned}\Lambda_m &= \frac{\kappa \times 1000}{c} \\ &= \frac{5.25 \times 10^{-5} \times 1000}{0.0025} \\ &= 21.0\,\text{S cm}^2\ \text{mol}^{-1}.\end{aligned}$$

Conductivity measures conduction per unit geometry of the solution; molar conductivity accounts for the amount of electrolyte present. The latter must be used in the dissociation ratio.

Step 2: (i) Compare with complete dissociation Using the given $\Lambda_m^0 = 390$ S cm^2 mol^{-1},

$$\alpha = \frac{21.0}{390} = 0.05385, \qquad 100\alpha = 5.385\%.$$

The identical conductivity units cancel, so α is dimensionless. This small fraction is consistent with

Quick Tip to Solve: First multiply conductivity by 1000 and divide by concentration; divide the resulting molar conductivity by 390. For the battery, balance two electrons in each half-reaction before adding them.

acetic acid being a weak electrolyte: only a small portion of the dissolved acid forms ions at this concentration.

Step 3: (ii) Write the discharge half-reactions At the negative lead anode, lead is oxidised from oxidation state zero to $+2$, releasing two electrons:

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

At the positive lead dioxide cathode, lead is reduced from $+4$ to $+2$:

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

The acidic medium provides the hydrogen ions needed to convert the oxygen of lead dioxide into water. Electrons leave the anode and reach the cathode through the external circuit.

Step 4: (ii) Add the half-reactions Add the reactions and cancel the two electrons produced and consumed. The combined ionic reaction consumes four hydrogen ions and two sulphate ions, equivalent to two molecules of sulphuric acid. Hence the overall discharge reaction is

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

The atoms and charge balance in both half-reactions. Sulphuric acid is consumed during discharge, so its concentration decreases. On charging, these reactions are reversed, restoring lead and lead dioxide at the respective electrodes.

Step 5: Conclusion (i) The degree of dissociation is $\boxed{\alpha \approx 0.0538}$, or approximately $\boxed{5.38\%}$. (ii) During discharge, the anode converts Pb to $\mathrm{PbSO_4}$, the cathode converts $\mathrm{PbO_2}$ to $\mathrm{PbSO_4}$, and the overall reaction is $\mathrm{Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O}$.

Quick Tip to Solve: First multiply conductivity by 1000 and divide by concentration; divide the resulting molar conductivity by 390. For the battery, balance two electrons in each half-reaction before adding them.