CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-2-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculator is NOT allowed.

You may use the following values of physical constants wherever necessary :

$c = 3 \times 10^8$ m/s

$h = 6.63 \times 10^{-34}$ J s

$e = 1.6 \times 10^{-19}$ C

$\mu_0 = 4\pi \times 10^{-7}$ T m A^{-1}

$\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 N^{-1} m^{-2}

$\frac{1}{4\pi\varepsilon_0} = 9 \times 10^9$ N m^2 C^{-2}

Mass of electron $(m_e) = 9.1 \times 10^{-31}$ kg.

Mass of neutron $= 1.675 \times 10^{-27}$ kg.

Mass of proton $= 1.673 \times 10^{-27}$ kg.

Avogadro's number $= 6.023 \times 10^{23}$ per gram mole

Boltzmann's constant $= 1.38 \times 10^{-23}$ J K^{-1}

Section A (16 marks)

Question No. ***1 to 16*** *are Multiple Choice type questions carrying* ***1*** *mark each.*

1. Which among the following is a false statement? [1 mark]

(A) Rate of zero order reaction is independent of initial concentration of reactant.

(B) Half-life of a zero order reaction is inversely proportional to the rate constant.

(C) Molecularity of a reaction may be zero.

(D) For a first order reaction, $t_{1/2}$ = 0.693/k.

Correct Answer: (C) Molecularity of a reaction may be zero.

Solution:

Concept:

- Molecularity is the number of reacting species participating in an elementary step and is a positive integer.
- For zero order, rate is k and $t_{1/2} = [A]_0/(2k)$; for first order, $t_{1/2} = 0.693/k$.

Step 1: Check the kinetic statements For a zero-order reaction, rate $= k[A]^0 = k$, so its rate does not depend on the initial concentration: (A) is true. Its half-life is $[A]_0/(2k)$, which is inversely proportional to k at fixed initial concentration: (B) is true. For a first-order reaction, the integrated rate equation gives $t_{1/2} = \ln 2/k = 0.693/k$, so (D) is also true.

Step 2: Identify the false statement An elementary reaction must involve at least one reacting species. Its molecularity may be one, two or, rarely, three, but cannot be zero. Zero order is possible because order is determined experimentally; this does not mean zero molecularity. Thus the claim in (C) is false.

Step 3: Conclusion Molecularity cannot be zero. Hence, the false statement is option (C).

Quick Tip to Solve: Distinguish experimental reaction order from the positive integer count called molecularity.

2. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is [1 mark]

(A) 1F

(B) 3F

(C) 5F

(D) 6F

Correct Answer: (B) 3F

Solution:

Concept:

- The oxidation number decreases during reduction; the decrease per atom equals the number of electrons accepted.
- One faraday, F, is the charge carried by one mole of electrons; charge is $Q = n_e F$.

Quick Tip to Solve: First find Mn oxidation states in both specified species; do not use the five-electron acidic permanganate result.

Step 1: Calculate the oxidation-state change Let the oxidation number of Mn in MnO_4^- be x. Since oxygen is -2, $x - 8 = -1$, giving $x = +7$. In MnO_2, $x - 4 = 0$, giving $x = +4$. Each manganese atom therefore accepts three electrons.

Step 2: Convert electrons into charge One mole of permanganate contains one mole of Mn atoms, so its reduction requires three moles of electrons. Hence

$$Q = 3F.$$

Option (A) represents only one electron per Mn; (C) would reduce Mn from $+7$ to $+2$; (D) represents six electrons and does not match the given product.

Step 3: Conclusion The required charge is $\boxed{3F}$. Hence, the correct option is (B).

Quick Tip to Solve: First find Mn oxidation states in both specified species; do not use the five-electron acidic permanganate result.

3. The element having [Ar]3d^{10}4s^{1} electronic configuration is [1 mark]

(A) Cu

(B) Zn

(C) Cr

(D) Mn

Correct Answer: (A) Cu

Solution:

Concept:

- Atomic number is the total number of electrons in a neutral atom.
- A completely filled $3d^{10}$ subshell helps stabilise the ground-state configuration of copper.

Step 1: Count the electrons The argon core contains 18 electrons. The stated configuration contains another 10 in $3d$ and 1 in $4s$, giving

$$Z = 18 + 10 + 1 = 29.$$

Atomic number 29 is copper, Cu. The configuration is the actual ground-state configuration rather than the simple Aufbau prediction $3d^9 4s^2$.

Step 2: Compare all the alternatives Copper has $[Ar]3d^{10}4s^1$, matching (A). Zinc has $[Ar]3d^{10}4s^2$; chromium has $[Ar]3d^5 4s^1$; manganese has $[Ar]3d^5 4s^2$. Thus none of (B), (C) or (D) matches both the subshell occupation and the total electron count.

Step 3: Conclusion The element is $\boxed{\text{Cu}}$. Hence, the correct option is (A).

Quick Tip to Solve: Add electrons to the argon core first; 18 plus 10 plus 1 immediately identifies atomic number 29.

4. The number of molecules that react with each other in an elementary reaction is a measure of the: [1 mark]

(A) activation energy of the reaction

(B) stoichiometry of the reaction

(C) molecularity of the reaction

(D) order of the reaction

Correct Answer: (C) molecularity of the reaction

Solution:

Concept:

- Molecularity counts the reacting particles participating in a single elementary reaction.
- Order is the sum of the concentration exponents in the experimentally determined rate law.

Step 1: Apply the definition The question explicitly refers to an elementary reaction and asks for the number of molecules reacting with one another. This is the definition of molecularity. For example, a step involving two reacting molecules is bimolecular, whereas a step involving one reacting molecule is unimolecular.

Step 2: Distinguish the other quantities Activation energy, (A), is the energy barrier for a reaction and is not a particle count. Stoichiometry, (B), gives the relative amounts in a balanced equation and need not describe the particles in a particular elementary event. Order, (D), is obtained from the rate law; for an elementary step it may coincide numerically with molecularity, but the definition asked here is specifically molecularity.

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

Quick Tip to Solve: The words elementary reaction and number of reacting particles point directly to molecularity.

5. The diamagnetic species is: [At. No. Co = 27, Fe = 26, Ni = 28] [1 mark]

(A) $[Ni(CN)_4]^{2-}$

(B) $[NiCl_4]^{2-}$

(C) $[Fe(CN)_6]^{3-}$

(D) $[CoF_6]^{3-}$

Correct Answer: (A) $[Ni(CN)_4]^{2-}$

Solution:

Concept:

- A diamagnetic species has all electrons paired; unpaired electrons produce paramagnetism.
- Ligand strength and geometry determine pairing: cyanide is strong-field, while chloride and fluoride are weak-field ligands.

Step 1: Examine the nickel complexes In both nickel complexes, nickel is $+2$, so Ni^{2+} is $3d^8$. In $[Ni(CN)_4]^{2-}$, strong-field cyanide causes pairing and the complex is square planar with dsp^2

Quick Tip to Solve: Count the metal d electrons after finding its oxidation state, then check ligand strength and pairing.

hybridisation. All electrons are paired, making (A) diamagnetic. In $[NiCl_4]^{2-}$, weak-field chloride gives a tetrahedral sp^3 complex with two unpaired electrons, so (B) is paramagnetic.

Step 2: Check iron and cobalt In $[Fe(CN)_6]^{3-}$, iron is $+3$, hence d^5. Even with strong-field cyanide, its low-spin octahedral configuration t_{2g}^5 retains one unpaired electron. In $[CoF_6]^{3-}$, cobalt is $+3$, hence d^6; weak-field fluoride gives high-spin $t_{2g}^4 e_g^2$ with four unpaired electrons. Thus (C) and (D) are also paramagnetic.

Step 3: Conclusion The diamagnetic species is $\boxed{[Ni(CN)_4]^{2-}}$. Hence, the correct option is (A).

Quick Tip to Solve: Count the metal d electrons after finding its oxidation state, then check ligand strength and pairing.

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6. The complex ions $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ are called [1 mark]

(A) Ionization isomers

(B) Linkage isomers

(C) Co-ordination isomers

(D) Geometrical isomers

Correct Answer: (B) Linkage isomers

Solution:

Concept:

- Linkage isomerism arises when an ambidentate ligand binds to the same metal through different donor atoms.
- The nitrite ion can coordinate through nitrogen as nitro or through oxygen as nitrito.

Step 1: Identify the attachment difference The complexes have the same cobalt centre, five ammonia ligands and one nitrite ligand, with the same overall charge. In $[Co(NH_3)_5(NO_2)]^{2+}$, the nitrite binds through nitrogen. In $[Co(NH_3)_5(ONO)]^{2+}$, it binds through oxygen. The change is therefore in the ligand donor atom.

Step 2: Classify and eliminate the alternatives Different donor-atom attachment of an ambidentate ligand produces linkage isomers, (B). Ionization isomers, (A), involve interchange between a coordinated ligand and an external counter-ion. Coordination isomers, (C), involve redistribution of ligands between complex cations and anions. Geometrical isomers, (D), differ in the relative spatial positions of ligands rather than which atom of one ligand binds to the metal.

Step 3: Conclusion The two complex ions are linkage isomers. Hence, the correct option is (B).

Quick Tip to Solve: Read NO2 versus ONO as nitrogen-bound versus oxygen-bound nitrite: the donor atom changes.

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7. What will be formed after oxidation reaction of secondary alcohol with chromic anhydride (CrO_3)?

[1 mark]

(A) Aldehyde

(B) Ketone

(C) Carboxylic acid

(D) Ester

Correct Answer: (B) Ketone

Solution:

Concept:

- A secondary alcohol has the form $R - CH(OH) - R'$, with the hydroxyl-bearing carbon attached to two carbon groups.
- Oxidation removes hydrogen from the hydroxyl group and its carbon, forming a carbonyl group without breaking the carbon skeleton.

Step 1: Identify the oxidation product Chromic anhydride, CrO_3, oxidises the secondary alcohol according to

$$R - CH(OH) - R' + [O] \longrightarrow R - CO - R' + H_2O.$$

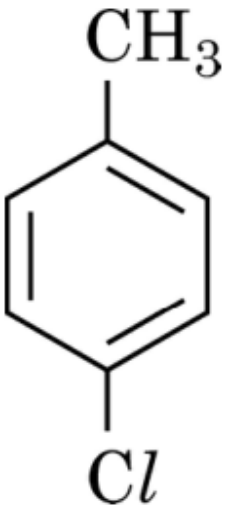
The carbonyl carbon remains bonded to two carbon groups, so the product belongs to the ketone family.

Step 2: Check the other choices An aldehyde has a hydrogen attached to the carbonyl carbon and is the initial oxidation product of a primary alcohol. A carboxylic acid is commonly obtained by further oxidation of a primary alcohol. An ester requires esterification or another ester-forming reaction; it is not the normal product of this oxidation.

Step 3: Conclusion The product is a ketone. Hence, the correct option is (B).

Quick Tip to Solve: Count the carbon groups bonded to the alcohol carbon: two groups give a ketone on oxidation.

8. Which is the correct IUPAC name for [1 mark]



(A) Methylchlorobenzene

(B) Toluene

(C) 1-Chloro-4-Methylbenzene

(D) 1-Methyl-4-Chlorobenzene

Correct Answer: (C) 1-Chloro-4-Methylbenzene

Solution:

Concept:

- For a disubstituted benzene, assign locants to give the lowest set of numbers to the substituents.
- When the two directions give identical locants, alphabetical order decides which substituent receives the lower number.

Step 1: Read the positions in the structure The benzene ring contains a methyl group, $-CH_3$, and a chloro group, $-Cl$, at opposite ring positions. They are therefore in the para arrangement, and the locants are $1, 4$ whichever group is chosen first.

Step 2: Apply the alphabetical tie-break Chloro precedes methyl alphabetically, so chlorine receives locant 1 and methyl receives locant 4. Option (A) omits the necessary position numbers. Option (B), toluene, contains only a methyl group and does not describe the chlorine substituent. Option (D) assigns locant 1 to methyl despite the alphabetical tie-break.

Step 3: Conclusion The correct IUPAC name is 1-chloro-4-methylbenzene. Hence, the correct option is (C).

Quick Tip to Solve: For para chloro and methyl groups, both numberings give 1,4; assign 1 to chloro alphabetically.

9. Which of the following is/are examples of denaturation of protein? [1 mark]

(A) Coagulation of egg white

(B) Curdling of milk

(C) Clotting of blood

(D) Both (A) and (B)

Correct Answer: (D) Both (A) and (B)

Solution:

Concept:

- Denaturation disrupts a protein's secondary and tertiary structure, causing loss of its native biological activity.
- The peptide bonds of the primary structure ordinarily remain intact during denaturation.

Step 1: Recognise the two examples Heating egg white unfolds its proteins and leads to coagulation, so (A) is an example of denaturation. When milk turns sour, the change in acidity destabilises the native protein structure and causes curdling, so (B) is also a standard example.

Step 2: Distinguish blood clotting Blood clotting is a physiological enzyme-mediated process in which soluble fibrinogen is converted into a fibrin network. It is not the standard heat- or pH-induced denaturation example in this question. Choosing either (A) or (B) alone would omit the other valid example; the combined choice includes both.

Step 3: Conclusion Both coagulation of egg white and curdling of milk are examples. Hence, the correct option is (D).

Quick Tip to Solve: Link denaturation with heat or a change in pH: cooked egg white and sour milk are the two examples.

10. The conversion of phenol to salicylic acid can be accomplished by [1 mark]

(A) Reimer-Tiemann reaction

(B) Friedel-Crafts reaction

(C) Kolbe reaction

(D) Coupling reaction

Correct Answer: (C) Kolbe reaction

Solution:

Concept:

- Phenol reacts with sodium hydroxide to form sodium phenoxide, whose ring is activated towards electrophilic substitution.
- In the Kolbe reaction, carbon dioxide introduces a carboxyl group mainly at the ortho position; acidification gives salicylic acid.

Step 1: Identify the required transformation Salicylic acid is 2-hydroxybenzoic acid. Therefore, the conversion must retain the hydroxyl group and introduce $-COOH$ next to it. Sodium phenoxide

Quick Tip to Solve: For phenol, remember carbon dioxide gives ortho-COOH by Kolbe; chloroform gives ortho-CHO by Reimer–Tiemann.

reacts with CO_2 under pressure at about $400\,K$ to form sodium salicylate, which gives salicylic acid on acidification.

Step 2: Compare the named reactions This carboxylation is the Kolbe reaction. The usual Reimer–Tiemann reaction with chloroform gives salicylaldehyde, containing $-CHO$, rather than the required acid. Friedel–Crafts reactions introduce alkyl or acyl groups, while coupling with a diazonium salt forms an azo compound; neither is the required conversion.

Step 3: Conclusion Phenol is converted into salicylic acid by the Kolbe reaction. Hence, the correct option is (C).

Quick Tip to Solve: For phenol, remember carbon dioxide gives ortho-COOH by Kolbe; chloroform gives ortho-CHO by Reimer–Tiemann.

11. Scurvy is caused due to deficiency of [1 mark]

(A) Vitamin B1

(B) Vitamin B2

(C) Ascorbic acid

(D) Glutamic acid

Correct Answer: (C) Ascorbic acid

Solution:

Concept:

- Ascorbic acid is vitamin C, a water-soluble vitamin required for normal connective tissue formation and maintenance.
- A vitamin deficiency is identified by matching the nutrient with its characteristic disease, rather than by its chemical name alone.

Step 1: Identify the nutrient responsible Scurvy results from deficiency of vitamin C, whose chemical name is ascorbic acid. Deficiency affects collagen formation and produces symptoms such as bleeding gums and delayed wound healing. Thus, the chemical name in option (C) matches the required vitamin.

Step 2: Eliminate the other options Vitamin B_1, or thiamine, is associated with beriberi on deficiency. Vitamin B_2, or riboflavin, is associated with conditions such as cheilosis. Glutamic acid is an amino acid and is not vitamin C. Consequently, none of these three choices identifies the deficiency responsible for scurvy.

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

Quick Tip to Solve: Translate ascorbic acid to vitamin C, then recall the direct pair: vitamin C deficiency causes scurvy.

12. Nucleotides are joined together by [1 mark]

(A) Glycosidic linkage

(B) Peptide linkage

(C) Hydrogen bonding

(D) Phosphodiester linkage

Correct Answer: (D) Phosphodiester linkage

Solution:

Concept:

- A nucleotide consists of a pentose sugar, a nitrogenous base and a phosphate group.
- Adjacent nucleotides in a nucleic-acid strand are connected through the sugar–phosphate backbone by $3'-5'$ phosphodiester linkages.

Step 1: Locate the connection between nucleotides The phosphate group forms ester bonds with the $3'$-hydroxyl group of one sugar and the $5'$-hydroxyl group of the next sugar. Since the phosphate participates in two ester bonds, the resulting covalent connection is called a phosphodiester linkage.

Step 2: Distinguish the other bonds A glycosidic linkage connects a nitrogenous base to its sugar within a nucleoside; it does not join successive nucleotides. A peptide linkage connects amino acids in proteins. Hydrogen bonds connect complementary bases across the two DNA strands, whereas the nucleotides along each strand are held together covalently through phosphate.

Step 3: Conclusion Nucleotides are joined by phosphodiester linkages. Hence, the correct option is (D).

Quick Tip to Solve: Distinguish along a strand from across strands: along means phosphodiester, across DNA strands means hydrogen bonds.

13. Assertion (A): Cu cannot liberate H_2 on reaction with dilute mineral acids.

Reason (R): Cu has positive electrode potential. [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:

- A metal displaces hydrogen from a dilute non-oxidising acid when its oxidation, coupled with reduction of H^+, is thermodynamically favourable.

Quick Tip to Solve: For hydrogen displacement, subtract the metal reduction potential from zero; a positive metal potential gives an unfavourable result.

- Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials; $E^\circ_{H^+/H_2} = 0\,\text{V}$.

Step 1: Judge the assertion Copper does not displace hydrogen from dilute mineral acids such as dilute HCl or dilute sulphuric acid. Thus Assertion (A) is true. An oxidising acid may dissolve copper, but its oxidising species is reduced rather than hydrogen ions being reduced to hydrogen gas.

Step 2: Judge the reason The standard reduction potential of Cu^{2+}/Cu is positive, $+0.34\,\text{V}$, relative to the standard hydrogen electrode. Reason (R) is therefore true.

Step 3: Check the explanatory link and options For the proposed reaction $Cu + 2H^+ \rightarrow Cu^{2+} + H_2$, the cell potential is $0 - (+0.34) = -0.34\,\text{V}$. The negative potential makes hydrogen displacement unfavourable under standard conditions, explaining the assertion. Option (B) denies this link, (C) incorrectly makes the reason false, and (D) incorrectly makes the assertion 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: For hydrogen displacement, subtract the metal reduction potential from zero; a positive metal potential gives an unfavourable result.

14. Assertion (A): In a first order reaction, if the concentration of the reactant is doubled, its half-life is also doubled.

Reason (R): The half-life of a reaction does not depend upon the initial concentration of the reactant in a first order reaction. [1 mark]

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

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

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

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

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

Solution:

Concept:

- A first-order reaction obeys $kt = \ln([A]_0/[A]_t)$, where k is the rate constant and $[A]_0$, $[A]_t$ are initial and remaining reactant concentrations.
- At half-life, $[A]_t = [A]_0/2$, so $t_{1/2} = \ln 2/k = 0.693/k$.

Step 1: Judge the assertion Doubling the initial concentration doubles the initial rate of a first-order reaction, but does not double its half-life. At a fixed temperature the rate constant is unchanged, so Assertion (A) is false.

Step 2: Judge the reason Substituting the half-life condition into the integrated rate law gives $kt_{1/2} = \ln([A]_0/([A]_0/2)) = \ln 2$. The initial concentration cancels. Therefore, the half-life is independent of initial concentration and Reason (R) is true.

Quick Tip to Solve: Distinguish rate from half-life: first-order rate changes with concentration, whereas half-life depends only on the rate constant.

Step 3: Check the relation and options The reason directly shows why the claimed doubling of half-life is incorrect: both the original and doubled concentrations give the same ratio of initial to remaining concentration at half completion. Options (A), (B), and (C) all require a true assertion and therefore fail; only (D) gives the correct truth values.

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

Quick Tip to Solve: Distinguish rate from half-life: first-order rate changes with concentration, whereas half-life depends only on the rate constant.

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15. Assertion (A): Vitamin D cannot be stored in our body.

Reason (R): Vitamin D is fat soluble vitamin and is not excreted from the body in urine. [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:

- Vitamins A, D, E and K are fat-soluble and can be stored in the liver and fatty tissues.
- Water-soluble vitamins are generally excreted more readily in urine; this behaviour differs from that of fat-soluble vitamins.

Step 1: Judge the assertion Vitamin D is a fat-soluble vitamin. It can be stored in the liver and adipose tissues, so the statement that it cannot be stored in our body is incorrect. Assertion (A) is false.

Step 2: Judge the reason Reason (R) correctly classifies vitamin D as fat-soluble. In the textbook classification, fat-soluble vitamins are not readily eliminated in urine as water-soluble vitamins are. Thus the given reason is true.

Step 3: Check the relation and options Fat solubility supports storage of vitamin D rather than the assertion that storage is impossible. Since the assertion itself is false, neither (A) nor (B), which make both statements true, can apply. Option (C) reverses the required truth values. Option (D) alone identifies a false assertion and a true reason.

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

Quick Tip to Solve: Remember A, D, E and K together as fat-soluble vitamins; their storage makes claims of obligatory daily replacement suspect.

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16. Assertion (A): Aromatic primary amines cannot be prepared by Gabriel Phthalimide synthesis.
Reason (R): Aryl halides do not undergo nucleophilic substitution reaction with the 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 synthesis forms primary amines by alkylation of the phthalimide anion followed by hydrolysis of the N-alkyl product.
- The nucleophilic substitution step works with suitable alkyl halides, whereas ordinary aryl halides do not undergo this substitution with the phthalimide anion.

Step 1: Judge the assertion To prepare an aromatic primary amine such as aniline by this route, the phthalimide anion would have to replace halide directly on an aromatic ring. Ordinary aryl halides do not react in the required manner, so aromatic primary amines cannot be prepared by Gabriel synthesis. Assertion (A) is true.

Step 2: Judge the reason The carbon bonded to halogen in an aryl halide is sp^2-hybridised, and the carbon-halogen bond has partial double-bond character through resonance. Such a substrate does not undergo the normal nucleophilic displacement needed with the phthalimide anion. Reason (R) is true in the context of Gabriel synthesis.

Step 3: Check the explanatory link and options The failure of the first substitution step prevents formation of the N-aryl intermediate and therefore prevents release of an aromatic primary amine on hydrolysis. The reason directly explains the assertion. Option (B) wrongly denies the explanation; (C) and (D) incorrectly reject a true 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: Check whether the halogen is attached directly to the aromatic ring: an aryl halide cannot supply the substitution step of Gabriel synthesis.

Section B (10 marks)

17. Name the following coordination compounds according to IUPAC norms:

(a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$

(b) $[CrCl_2(en)_2]Cl$ [2 marks]

Solution:

Concept:

- Name ligands before the central metal in alphabetical order, ignoring multiplicative prefixes when deciding that order.
- Neutral ligands NH_3, H_2O, and en are named ammine, aqua, and ethane-1,2-diamine; Cl^- as a ligand is chlorido.
- The metal oxidation state is written in Roman numerals. For a cationic complex, retain the normal metal name and then name the counter-anion.

Step 1: Name compound (a) In $[Co(NH_3)_4(H_2O)Cl]Cl_2$, the two external chloride ions make the complex ion charge $+2$. If cobalt has oxidation state x, then $x + 4(0) + 0 - 1 = +2$, giving $x = +3$. Alphabetical ligand order is ammine, aqua, chlorido, and four ammine ligands require tetraammine. The name is **tetraammineaquachloridocobalt(III) chloride**.

Step 2: Name compound (b) In $[CrCl_2(en)_2]Cl$, one external chloride ion makes the complex charge $+1$. Ethane-1,2-diamine is neutral, so $x + 2(-1) + 2(0) = +1$, giving chromium oxidation state $+3$. Chlorido precedes ethane-1,2-diamine alphabetically. Use dichlorido for the two chloride ligands and bis(ethane-1,2-diamine) for the two chelating ligands. The name is **dichloridobis(ethane-1,2-diamine)chromium(III) chloride**.

Step 3: Conclusion (a) Tetraammineaquachloridocobalt(III) chloride.

(b) Dichloridobis(ethane-1,2-diamine)chromium(III) chloride.

Quick Tip to Solve: Use the chloride ions outside the brackets to find the complex charge before calculating the metal oxidation state; en is neutral.

18. What is meant by the Rate law and Rate constant of a reaction. Identify the order of a reaction if the units of its Rate constant are:

(a) s^{-1}

(b) mol^{-1} L s^{-1} [2 marks]

Solution:

Concept:

- The rate law expresses the experimentally measured rate in terms of reactant concentrations, for example $r = k[A]^m[B]^n$. The powers m, n are experimental orders, not necessarily stoichiometric coefficients.
- The rate constant k is the proportionality constant in the rate law at a specified temperature; it is numerically equal to the rate when each concentration entering the law is unity.

Quick Tip to Solve: Rewrite the units of k as concentration to a power times s^{-1}; that power is 1 minus the order.

Step 1: Define the two quantities For $r = k[A]^m[B]^n$, the dependence of rate on concentration is the rate law and k measures the rate scale at the given temperature. The total reaction order is $N = m + n$. The rate constant is independent of reactant concentration, although its value generally changes with temperature.

Step 2: Use the units to identify order Rate has units mol $L^{-1}s^{-1}$. Therefore $[k] = (\text{mol } L^{-1})^{1-N}s^{-1}$. In (a), s^{-1} has no concentration factor, so $1-N = 0$ and $N = 1$. In (b), $\text{mol}^{-1}L\ s^{-1} = (\text{mol } L^{-1})^{-1}s^{-1}$, so $1 - N = -1$ and $N = 2$.

Step 3: Conclusion The rate law gives rate as a function of concentration and k is its proportionality constant. (a) First order; (b) second order.

Quick Tip to Solve: Rewrite the units of k as concentration to a power times s^{-1}; that power is 1 minus the order.

19. Complete and balance the following chemical equations:

(a) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow$

(b) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow$ [2 marks]

Solution:

Concept:

- Redox balancing requires conservation of both atoms and electric charge. Permanganate is reduced to MnO_2 in neutral or alkaline medium, while thiosulphate is oxidised to sulphate.
- In acidic medium, dichromate is reduced to Cr^{3+}, and Sn^{2+} is oxidised to Sn^{4+}. Electron gains and losses must be equal.

Step 1: Balance reaction (a) The reduction half-reaction is $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$. The oxidation half-reaction is $S_2O_3^{2-} + 10OH^- \rightarrow 2SO_4^{2-} + 5H_2O + 8e^-$. Multiply these by 8 and 3 respectively, add, and cancel 24 electrons and common water and hydroxide terms. This gives

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-.$$

Both sides contain 8 Mn, 6 S, 42 O and 2 H atoms, with total charge -14.

Step 2: Balance reaction (b) Dichromate reduction is $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$. Each tin ion loses two electrons: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$. Multiplying the tin equation by three and adding cancels six electrons, giving

$$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O.$$

The total charge is $+18$ on each side, and all atoms balance.

Step 3: Conclusion (a) Products: $8MnO_2 + 6SO_4^{2-} + 2OH^-$. (b) Products: $2Cr^{3+} + 3Sn^{4+} + 7H_2O$, with the reactant coefficients as printed.

Quick Tip to Solve: After balancing these redox equations, check total charge as well as oxygen: charge is -14 in (a) and +18 in (b).

20(A). The rate constant for a zero order reaction A → P is 0.0030 mol $L^{-1}s^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M? [2 marks]

Solution:

Concept:

- For a zero-order reaction, the disappearance rate is independent of concentration: $-d[A]/dt = k$.
- The integrated zero-order law is $[A]_t = [A]_0 - kt$, where $[A]_0$ and $[A]_t$ are the initial and later concentrations and t is elapsed time.

Step 1: Calculate the concentration decrease The initial concentration is $[A]_0 = 0.10\,\text{mol L}^{-1}$, and the required final concentration is $[A]_t = 0.075\,\text{mol L}^{-1}$. Since $1\,\text{M} = 1\,\text{mol L}^{-1}$, no concentration conversion is required. The amount consumed per unit volume is

$$\Delta[A] = 0.10 - 0.075 = 0.025\,\text{mol L}^{-1}.$$

Step 2: Apply the integrated rate law Rearranging $[A]_t = [A]_0 - kt$ gives

$$t = \frac{[A]_0 - [A]_t}{k} = \frac{0.025\,\text{mol L}^{-1}}{0.0030\,\text{mol L}^{-1}\text{s}^{-1}} = 8.333\ldots\,\text{s}.$$

The concentration units cancel, leaving seconds. A logarithmic expression is unnecessary because this is a zero-order reaction; the concentration falls linearly with time.

Step 3: Conclusion The required time is $\boxed{8.3\,\text{s}}$ (approximately 8.33 s).

Quick Tip to Solve: For zero order, divide the concentration drop by k; do not use the logarithmic first-order formula.

OR

20(B). The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if k = 2.5 × 10^{-4} mol L^{-1} s^{-1}? [2 marks]

Solution:

Concept:

- For a zero-order reaction, the reaction rate is $r = k[A]^0 = k$; it is independent of reactant concentration under the stated conditions.
- For $aA \to bB + cC$, the stoichiometrically normalised rate is $r = -\frac{1}{a}\frac{d[A]}{dt} = \frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt}$.

Step 1: Balance the decomposition and relate rates The balanced decomposition of ammonia is

$$2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2.$$

Hence the common reaction rate is

$$r = -\frac{1}{2}\frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3}\frac{d[\text{H}_2]}{dt}.$$

Quick Tip to Solve: Balance ammonia decomposition first: one N2 and three H2 mean the hydrogen production rate is three times the nitrogen rate.

Nitrogen and hydrogen are formed in a concentration-rate ratio of $1:3$, because every stoichiometric reaction event produces one nitrogen molecule and three hydrogen molecules.

Step 2: Substitute the zero-order rate constant Since the reaction is zero order, $r = k = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$. Therefore

$$\frac{d[\text{N}_2]}{dt} = r = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1},$$
$$\frac{d[\text{H}_2]}{dt} = 3r = 7.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}.$$

These are positive production rates. The stoichiometric factors relate individual species rates to the common reaction rate.

Step 3: Conclusion Rate of production of N_2: $\boxed{2.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}}$. Rate of production of H_2: $\boxed{7.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}}$.

Quick Tip to Solve: Balance ammonia decomposition first: one N2 and three H2 mean the hydrogen production rate is three times the nitrogen rate.

21. Give reasons for the following observations:

(a) p-Chloronitrobenzene reacts with (aq) NaOH at 443 K to give p-nitrophenol whereas chlorobenzene reacts with the same reagent at 623 K and 300 atm.

(b) Main product obtained when chloroethane reacts with KCN is propane nitrile while with AgCN it is ethyl isocyanide. [2 marks]

Solution:

Concept:

- An electron-withdrawing nitro group at the ortho or para position activates an aryl halide towards nucleophilic substitution by stabilising the negatively charged intermediate.
- Cyanide is an ambident nucleophile: it can form a new bond through carbon or nitrogen. The nature of the cyanide reagent determines the predominant product.

Step 1: (a) Explain activation by the para nitro group In chlorobenzene, resonance gives the carbon–chlorine bond partial double-bond character, making its cleavage difficult. Therefore, reaction with aqueous NaOH requires harsh conditions, $623\,\text{K}$ and $300\,\text{atm}$. In p-chloronitrobenzene, the para $-\text{NO}_2$ group withdraws electrons and stabilises, by resonance, the negative charge of the intermediate formed during attack by OH^-. Substitution is consequently easier and occurs at $443\,\text{K}$, giving p-nitrophenol after protonation.

Step 2: (b) Compare KCN and AgCN KCN is predominantly ionic and supplies free CN^-; attack occurs mainly through carbon, giving the nitrile $\text{CH}_3\text{CH}_2\text{C} \equiv \text{N}$. AgCN is predominantly covalent, with carbon bonded to silver, so nitrogen is available for bonding to the ethyl group and ethyl isocyanide,

Quick Tip to Solve: For cyanide substitutions, inspect the atom attached to the alkyl group: R–CN is a nitrile, whereas R–NC is an isocyanide.

$CH_3CH_2N \equiv C$, predominates.

$$CH_3CH_2Cl + KCN \longrightarrow CH_3CH_2CN + KCl,$$
$$CH_3CH_2Cl + AgCN \longrightarrow CH_3CH_2NC + AgCl.$$

Step 3: Conclusion (a) The para nitro group stabilises the substitution intermediate, lowering the required temperature. (b) KCN bonds mainly through carbon to give propanenitrile, whereas AgCN bonds mainly through nitrogen to give ethyl isocyanide.

Quick Tip to Solve: For cyanide substitutions, inspect the atom attached to the alkyl group: R–CN is a nitrile, whereas R–NC is an isocyanide.

Section C (21 marks)

22. Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the number of moles of CO_2 in 540 g of soda water when packed under 3.34×10^5 Pa at the same temperature. [3 marks]

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the partial pressure of the gas, K_H is Henry's law constant and x is its mole fraction in the solution.
- For dissolved carbon dioxide, $x = n_{CO_2}/(n_{CO_2} + n_{H_2O})$. In a dilute solution, the gas amount is very small compared with the water amount.

Step 1: Calculate the mole fraction of carbon dioxide Both the pressure and Henry's law constant are given in pascals at the same temperature, 298 K, so no pressure conversion is needed. Applying Henry's law,

$$x_{CO_2} = \frac{p}{K_H} = \frac{3.34 \times 10^5}{1.67 \times 10^8} = 2.00 \times 10^{-3}.$$

The mole fraction is dimensionless because the pressure units cancel. Its small value confirms that the soda water is a dilute solution of the gas.

Step 2: Convert the water amount to moles Using the usual dilute-solution approximation for soda water, take the given 540 g as the mass of water; the contribution of dissolved gas to this mass is small. With $M_{H_2O} = 18\ \text{g mol}^{-1}$,

$$n_{H_2O} = \frac{540}{18} = 30.0\ \text{mol}.$$

Step 3: Determine the dissolved gas amount Write the mole-fraction relation before making the dilute approximation:

$$0.002 = \frac{n_{CO_2}}{30 + n_{CO_2}},$$
$$0.002(30 + n_{CO_2}) = n_{CO_2},$$
$$n_{CO_2} = \frac{0.060}{0.998} = 0.06012\ \text{mol}.$$

Equivalently, neglecting the gas amount in the denominator gives $n_{CO_2} \simeq 0.002 \times 30 = 0.060$ mol;

Quick Tip to Solve: First calculate p/K_H to obtain the gas mole fraction; then multiply by the solvent moles when the solution is dilute.

both approaches give the same quoted result at the usual precision for this calculation.

Step 4: Conclusion The amount of dissolved carbon dioxide is approximately $\boxed{6.0 \times 10^{-2}\,\text{mol}}$.

Quick Tip to Solve: First calculate p/K_H to obtain the gas mole fraction; then multiply by the solvent moles when the solution is dilute.

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23. Give reasons:

(a) Fuel cells are preferred for production of electrical energy than thermal plants.

(b) Iron does not rust even if zinc coating is broken in a galvanized pipe.

(c) In the experimental determination of electrolytic conductance, Direct Current (DC) is not used.

[3 marks]

Solution:

Concept:

- A fuel cell converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy through electrode reactions.
- A metal more easily oxidised than iron can protect it sacrificially. Zinc has a more negative standard reduction potential than iron.
- Conductance measurements require the electrolyte composition and electrode conditions to remain effectively unchanged during measurement.

Step 1: (a) Compare fuel cells with thermal plants Fuel cells convert chemical energy directly into electrical energy, avoiding the intermediate conversion into heat and then mechanical work used in a thermal power plant. Thus, their conversion efficiency is higher and less energy is lost in these intermediate stages. They are also less polluting; for example, a hydrogen–oxygen fuel cell produces water as its reaction product, whereas combustion-based thermal plants release pollutants. These advantages make fuel cells preferable for electrical energy production.

Step 2: (b) Explain protection at a break in the zinc coating Zinc is more readily oxidised than iron. Even when a small break exposes iron to moist air, electrically connected zinc acts as the sacrificial anode and oxidises preferentially:

$$\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^{-}.$$

The electrons supplied by zinc keep the exposed iron cathodic and prevent its oxidation to iron ions, which would initiate rusting. Therefore, the protection continues while sufficient zinc remains in electrical contact with the iron, even though the physical coating has been broken.

Step 3: (c) Explain why direct current is avoided A direct current causes sustained electrolysis: ions are discharged at the electrodes, electrode products accumulate and concentration changes develop near the electrode surfaces. This produces electrode polarisation and changes the effective resistance, so the measured value does not represent the original electrolyte conductance accurately. Alternating current is used instead; rapid reversal of current greatly reduces net electrolysis and polarisation, allowing reliable measurement.

Step 4: Conclusion (a) Fuel cells are efficient and less polluting. (b) Zinc protects exposed iron

Quick Tip to Solve: In a scratched galvanised coating, identify the more reactive metal as the anode; zinc corrodes first and supplies electrons to the iron.

by sacrificial oxidation. (c) DC causes electrolysis and polarisation, so AC is used for conductance measurements.

Quick Tip to Solve: In a scratched galvanised coating, identify the more reactive metal as the anode; zinc corrodes first and supplies electrons to the iron.

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

(b) What is lanthanoid contraction?

(c) Zn, Cd and Hg are soft metals. Why? [3 marks]

Solution:

Concept:

- The standard reduction potential refers to the reaction $\mathrm{Mn}^{2+} + 2\mathrm{e}^{-} \longrightarrow \mathrm{Mn}$; a highly negative value means that reduction is comparatively unfavourable.
- Lanthanoid contraction is a size trend across the lanthanoid series, while the strength of metallic bonding influences the hardness of a metal.

Step 1: Explain the negative manganese potential Manganese has the configuration $[\mathrm{Ar}]3d^5 4s^2$, whereas Mn^{2+} is $[\mathrm{Ar}]3d^5$. This half-filled $3d$ subshell has extra stability. Oxidation of manganese to this stable ion is favoured, and the reverse reduction of Mn^{2+} to metal is correspondingly difficult. Consequently, $E^{\circ}_{\mathrm{Mn}^{2+}/\mathrm{Mn}} = -1.18\,\mathrm{V}$ is unusually negative relative to its neighbouring d-block elements.

Step 2: Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic radii and, especially, the radii of Ln^{3+} ions with increasing atomic number from lanthanum to lutetium. The added $4f$ electrons shield the increasing nuclear charge poorly. The increasing effective nuclear attraction therefore draws the electron cloud closer to the nucleus.

Step 3: Explain the softness of group 12 metals Zn, Cd and Hg possess completely filled d^{10} subshells. Their filled d subshells do not contribute effectively to the strong metallic bonding associated with partially filled d orbitals. Their metallic bonding is consequently relatively weak, giving low enthalpies of atomisation and explaining their softness.

Step 4: Conclusion The negative Mn potential reflects the stable half-filled Mn^{2+} ion; lanthanoid contraction is the progressive decrease in size; weak metallic bonding accounts for the softness of Zn, Cd and Hg.

Quick Tip to Solve: For manganese, write the ion configuration first: the stable half-filled d subshell belongs to Mn(II), so its reduction potential is negative.

25(a). Using valence bond theory, explain the hybridization and magnetic behaviour of the following:

(i) $[Co(NH_3)_6]Cl_3$

(ii) $K_2[NiCl_4]$

[At. no.: Co = 27, Ni = 28] [2 marks]

Solution:

Concept:

- In valence bond theory, ligand electron pairs occupy vacant hybrid orbitals of the central metal ion. Magnetic behaviour depends on the number of unpaired metal electrons.
- Find the metal oxidation state before writing its d-electron configuration; inner-orbital octahedral complexes use d^2sp^3, whereas tetrahedral complexes use sp^3.

Step 1: Analyse the cobalt(III) complex In $[Co(NH_3)_6]Cl_3$, the three chloride counterions show that cobalt is Co^{3+}. Its configuration is $[Ar]3d^6$. For this Co(III) complex, ammonia causes the 3d electrons to pair, leaving two vacant 3d orbitals. These combine with one 4s and three 4p orbitals to give d^2sp^3 hybridisation. Six ammonia lone pairs form six coordinate bonds in an octahedral, inner-orbital complex. All the metal electrons are paired, so it is diamagnetic.

Step 2: Analyse the nickel(II) complex In $K_2[NiCl_4]$, the complex anion has charge -2, so nickel is Ni^{2+}, with configuration $[Ar]3d^8$. Chloride is a weak-field ligand and does not pair the two unpaired 3d electrons. One 4s and three 4p orbitals hybridise to form four sp^3 orbitals for the chloride lone pairs. The complex is tetrahedral and paramagnetic, with two unpaired electrons.

Step 3: Conclusion $[Co(NH_3)_6]^{3+}$: d^2sp^3, octahedral, diamagnetic. $[NiCl_4]^{2-}$: sp^3, tetrahedral, paramagnetic (two unpaired electrons).

Quick Tip to Solve: Count counterion charges first: cobalt is +3 and nickel is +2; confusing these changes both the d count and the magnetic prediction.

25(b). Write the electronic configuration of d^5 ion when $\Delta_o > P$. [1 mark]

Solution:

Concept:

- For an octahedral complex, the lower-energy orbitals are t_{2g} and the higher-energy orbitals are e_g.
- When the octahedral splitting Δ_o exceeds pairing energy P, electrons pair in t_{2g} before occupying e_g.

Step 1: Apply the strong-field condition The inequality $\Delta_o > P$ means that pairing an electron in a lower orbital costs less energy than promoting it to the upper set. The ion therefore adopts the low-spin arrangement.

Step 2: Distribute the five d electrons The first three electrons occupy the three t_{2g} orbitals singly. The fourth and fifth electrons pair in two of these orbitals, leaving one unpaired electron. No electron occupies e_g, so the subshell population is $t_{2g}^5e_g^0$.

Step 3: Conclusion The required low-spin configuration is $\boxed{t_{2g}^5e_g^0}$, with one unpaired electron.

Quick Tip to Solve: For low-spin d5, fill the lower octahedral set to five electrons before putting any electron in the upper set.

26(a). Define the following:

(i) Enantiomers

(ii) Racemic mixture [2 marks]

Solution:

Concept:

- Enantiomerism is a form of stereoisomerism: identical connectivity can give different spatial arrangements that are non-superimposable mirror images.
- Optical rotation is the rotation of plane-polarised light. Equal amounts of two enantiomers cancel their equal and opposite rotations.

Step 1: Define enantiomers Enantiomers are stereoisomers that are non-superimposable mirror images of each other. They have the same bonding sequence but differ in the three-dimensional arrangement of groups. For example, the two configurations of a chiral molecule such as 2-butanol form an enantiomeric pair. Under identical conditions, the two members rotate plane-polarised light by equal magnitudes in opposite directions.

Step 2: Define a racemic mixture A racemic mixture is an equimolar mixture of the two enantiomers of a chiral compound, that is, a 1:1 mixture of its dextrorotatory and laevorotatory forms. The clockwise rotation produced by one enantiomer is exactly cancelled by the anticlockwise rotation produced by the other. Thus the mixture is optically inactive by external compensation, even though each enantiomer separately is optically active.

Step 3: Conclusion Enantiomers are non-superimposable mirror-image stereoisomers. A racemic mixture contains equal amounts of the two enantiomers and has zero net optical rotation.

Quick Tip to Solve: In the racemic definition, include both the 1:1 composition and cancellation of optical rotation; optical inactivity alone is insufficient.

26(b). Why is chlorobenzene resistant to nucleophilic substitution reaction? [1 mark]

Solution:

Concept:

- Resonance delocalises a lone pair on chlorine into the benzene ring, giving the carbon-chlorine bond partial double-bond character.
- The chlorine-bearing carbon is sp^2-hybridised; its bond to chlorine is shorter and stronger than the corresponding bond in an alkyl chloride.

Step 1: Examine the bond In chlorobenzene, conjugation between a chlorine lone pair and the ring strengthens the $C-Cl$ bond. Breaking this bond is therefore more difficult than breaking the ordinary single bond in a haloalkane.

Step 2: Consider substitution pathways An S_N1 pathway would require a highly unstable phenyl cation. The benzene ring also obstructs the usual backside approach needed for S_N2 substitution at the aryl carbon. Thus ordinary nucleophilic substitution conditions are ineffective.

Quick Tip to Solve: For an aryl halide, discuss resonance and the aryl carbon before invoking ordinary alkyl-halide substitution rules.

Step 3: Conclusion Chlorobenzene resists nucleophilic substitution mainly because resonance gives its short, strong $C - Cl$ bond partial double-bond character.

Quick Tip to Solve: For an aryl halide, discuss resonance and the aryl carbon before invoking ordinary alkyl-halide substitution rules.

27(A)(a). Explain the following reactions and write chemical equation involved:

Wolff-Kishner reduction [1 mark]

Solution:

Concept:

- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group.
- Hydrazine followed by heating with potassium hydroxide in ethylene glycol provides strongly basic reducing conditions.

Step 1: Form the hydrazone The carbonyl compound first condenses with hydrazine, $H_2N - NH_2$, to form a hydrazone with loss of water.

Step 2: Reduce the carbonyl group On heating with KOH in ethylene glycol, the hydrazone loses nitrogen and gives the corresponding hydrocarbon. For acetone:

$$\mathrm{CH_3COCH_3 + H_2NNH_2} \xrightarrow[\Delta]{\text{KOH, ethylene glycol}} \mathrm{CH_3CH_2CH_3 + N_2 + H_2O}.$$

Step 3: Conclusion Wolff-Kishner reduction replaces $> C = O$ by $> CH_2$; acetone gives propane.

Quick Tip to Solve: Remember hydrazine plus base and heat for Wolff-Kishner reduction; the carbon skeleton remains unchanged.

27(A)(b). Explain the following reactions and write chemical equation involved:

Etard reaction [1 mark]

Solution:

Concept:

- The Etard reaction oxidises the methyl side chain of toluene to an aldehyde.
- Chromyl chloride, CrO_2Cl_2, in a non-aqueous solvent forms an intermediate complex, which is hydrolysed.

Step 1: Carry out controlled oxidation Treat toluene with chromyl chloride in carbon disulphide. The methyl group forms an Etard complex rather than undergoing complete oxidation to a carboxylic acid.

Step 2: Hydrolyse the complex Hydrolysis of the complex yields benzaldehyde. The overall conversion is represented as:

$$\mathrm{C_6H_5CH_3} \xrightarrow[\mathrm{CS_2}]{\mathrm{CrO_2Cl_2}} \text{Etard complex} \xrightarrow{\mathrm{H_2O}} \mathrm{C_6H_5CHO}.$$

Quick Tip to Solve: Associate chromyl chloride with stopping side-chain oxidation at the aldehyde stage in the Etard reaction.

The aromatic ring remains unchanged during this side-chain oxidation.

Step 3: Conclusion In the Etard reaction, toluene gives benzaldehyde using CrO_2Cl_2, followed by hydrolysis.

Quick Tip to Solve: Associate chromyl chloride with stopping side-chain oxidation at the aldehyde stage in the Etard reaction.

27(A)(c). Explain the following reactions and write chemical equation involved:

Cannizzaro reaction [1 mark]

Solution:

Concept:

- Aldehydes without an alpha-hydrogen undergo the Cannizzaro reaction in concentrated alkali.
- It is disproportionation: one aldehyde molecule is oxidised to a carboxylate and another is reduced to an alcohol.

Step 1: Check the aldehyde Benzaldehyde has no alpha-hydrogen and therefore undergoes Cannizzaro disproportionation instead of ordinary aldol condensation.

Step 2: Write the balanced equation With concentrated sodium hydroxide:

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

One molecule gives sodium benzoate by oxidation; the other gives benzyl alcohol by reduction. The carboxyl product remains a salt in the alkaline reaction mixture.

Step 3: Conclusion Cannizzaro reaction gives an alcohol and a carboxylate salt from an aldehyde lacking alpha-hydrogen; benzaldehyde gives benzyl alcohol and sodium benzoate.

Quick Tip to Solve: Check for absence of alpha-hydrogen and use concentrated alkali before identifying a Cannizzaro reaction.

OR

27(B). Write the structures of A, B and C in the following sequence of reactions:

(a) $CH_3COOH \rightarrow (SOCl_2)$ A $\rightarrow (H_2, Pd\text{-}BaSO_4)$ B $\rightarrow (H_2N\text{-}NH_2)$ C

(b) $CH_3CN \rightarrow$ (1. DIBAL-H, 2. H_2O) A $\rightarrow$ (Dil. NaOH) B $\rightarrow (\Delta)$ C [3 marks]

$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow{H_2,\ Pd\text{-}BaSO_4} B \xrightarrow{H_2N\text{–}NH_2} C$$

$$CH_3CN \xrightarrow[2.\ H_2O]{1.(DIBAL\text{–}H)} A \xrightarrow{\text{Dil. NaOH}} B \xrightarrow{\Delta} C$$

Solution:

Concept:

- Thionyl chloride gives an acyl chloride; Rosenmund reduction gives an aldehyde, which forms a hydrazone with hydrazine.
- DIBAL-H and hydrolysis convert a nitrile to an aldehyde. Dilute alkali gives an aldol; heating dehydrates it to an unsaturated aldehyde.

Step 1: Identify A in sequence (a) Thionyl chloride replaces the hydroxyl group of ethanoic acid by chlorine:

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl.$$

Thus $A = CH_3 - C(=O) - Cl$, ethanoyl chloride.

Step 2: Identify B and C in sequence (a) Rosenmund reduction gives $B = CH_3 - CHO$, ethanal. It reacts with hydrazine to give its hydrazone:

$$CH_3CHO + H_2NNH_2 \longrightarrow CH_3CH = NNH_2 + H_2O.$$

Hence $C = CH_3 - CH = N - NH_2$. Hydrazine alone gives a hydrazone, not a hydrocarbon.

Step 3: Identify A and B in sequence (b) DIBAL-H followed by water converts CH_3CN into ethanal, so $A = CH_3 - CHO$. Two ethanal molecules undergo aldol addition in dilute sodium hydroxide:

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

Thus $B = CH_3 - CH(OH) - CH_2 - CHO$, 3-hydroxybutanal.

Step 4: Identify C in sequence (b) Heating dehydrates the aldol:

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

Therefore $C = CH_3 - CH = CH - CHO$, but-2-enal (crotonaldehyde).

Step 5: Conclusion (a) $A = CH_3COCl$, $B = CH_3CHO$, $C = CH_3CH = NNH_2$.
(b) $A = CH_3CHO$, $B = CH_3CH(OH)CH_2CHO$, $C = CH_3CH = CHCHO$.

Quick Tip to Solve: Distinguish hydrazone formation from Wolff-Kishner reduction: hydrazine alone does not remove the carbonyl oxygen as a methylene group.

28. Define the following terms:

(a) Native protein

(b) Nucleotide

(c) Essential amino acid [3 marks]

Solution:

Concept:

- A protein has a specific three-dimensional structure maintained by interactions between its amino-acid residues.
- A nucleotide contains a nitrogenous base, a pentose sugar and a phosphate group; a nucleoside contains only the base and sugar.
- Essential amino acids must be supplied in food because the human body cannot synthesise them in sufficient amounts.

Step 1: Define native protein (a) A native protein is a protein in its natural, biologically active state, with its characteristic secondary and tertiary structures intact. Its specific folded conformation enables it to perform its biological function. For example, a native enzyme has an appropriately shaped active site. Denaturation disrupts this natural folded structure and generally causes loss of biological activity without necessarily breaking the peptide bonds of the primary structure.

Step 2: Define nucleotide (b) A nucleotide is the basic structural unit of a nucleic acid, consisting of a nitrogenous base linked to a pentose sugar and one or more phosphate groups. In the nucleic-acid building units, the phosphate is attached to the sugar. Thus, a nucleotide is a phosphorylated nucleoside: nucleoside = base + sugar, whereas nucleotide = base + sugar + phosphate. DNA contains deoxyribose and RNA contains ribose.

Step 3: Define essential amino acid (c) An essential amino acid is an amino acid that the human body cannot synthesise in an adequate amount and must therefore obtain through the diet. For example, valine and leucine are essential amino acids. The term essential refers to dietary requirement, not to whether other amino acids are important for making proteins.

Step 4: Conclusion (a) Native protein: naturally folded, biologically active protein. (b) Nucleotide: nitrogenous base + pentose sugar + phosphate. (c) Essential amino acid: an amino acid that must be obtained from the diet.

Quick Tip to Solve: Remember: adding phosphate to a nucleoside makes a nucleotide; essential means diet-supplied.

Section D (8 marks)

29(a). Read the passage and answer: The spontaneous flow of the solvent through a semipermeable membrane from a pure solvent to a solution or from a dilute solution to a concentrated solution is called osmosis. The phenomenon of osmosis can be demonstrated by taking two eggs of the same size. In an egg, the membrane below the shell and around the egg material is semipermeable. The outer hard shell can be removed by putting the egg in dilute hydrochloric acid. After removing the hard shell, one egg is placed in distilled water and the other in a saturated salt solution. After some time, the egg placed in distilled water swells-up while the egg placed in salt solution shrinks. The external pressure applied to stop the osmosis is termed as osmotic pressure (a colligative property). Reverse osmosis takes place when the applied external pressure becomes larger than the osmotic pressure.

(a) Define reverse osmosis. Name one SPM which can be used in the process of reverse osmosis.

[2 marks]

Solution:

Concept:

- In osmosis, solvent crosses a semipermeable membrane from the dilute side to the concentrated side.
- Osmotic pressure, π, is the minimum opposing pressure required to stop solvent flow; reverse osmosis requires applied pressure greater than π.

Step 1: Reverse the direction of solvent flow Reverse osmosis is the process in which solvent is forced through a semipermeable membrane from a solution towards the pure-solvent side, or from a more concentrated solution towards a more dilute solution, by applying an external pressure greater than its osmotic pressure on the solution side. The membrane permits solvent molecules to cross while retaining dissolved solute. Merely applying pressure equal to the osmotic pressure stops osmosis; it does not reverse the flow.

Step 2: Name a suitable membrane A cellulose acetate membrane is a suitable semipermeable membrane for reverse osmosis. Such a membrane is used to allow water to pass while holding back dissolved salts. When sufficient pressure is applied to saline water, water passes through the membrane and is collected on the other side, providing the basis of desalination.

Step 3: Conclusion Reverse osmosis is pressure-driven solvent flow from the concentrated solution towards the pure-solvent or dilute side through an SPM when $P_{\text{applied}} > \pi$. One suitable SPM is a cellulose acetate membrane.

Quick Tip to Solve: For reverse osmosis, state both the reversed direction and pressure greater than osmotic pressure.

29(b). What do you expect to happen when red blood corpuscles (RBC's) are placed in 0.5% NaCl solution? [1 mark]

Solution:

Concept:

- The red-cell membrane is semipermeable, so a difference in solute concentration drives water across it.
- A 0.9% NaCl solution is approximately isotonic with red blood cells; a 0.5% solution is hypotonic.

Step 1: Compare the external solution with the cell The 0.5% NaCl solution has a lower solute concentration and lower osmotic pressure than the fluid inside the red blood corpuscles. It is therefore hypotonic relative to them.

Step 2: Determine the direction of water flow Water enters the corpuscles through their semipermeable membranes by osmosis, from the more dilute external solution into the relatively concentrated cell contents. The cells consequently swell and may burst, releasing haemoglobin; this bursting is called haemolysis. Shrinkage would occur in a hypertonic solution, so it is not the expected effect here.

Step 3: Conclusion The RBCs absorb water by osmosis, swell and may burst (haemolysis) in the hypotonic 0.5% NaCl solution.

Quick Tip to Solve: Compare NaCl concentration with 0.9 percent: below it makes RBCs swell; above it makes them shrink.

OR

29(b). Which one of the following will have higher osmotic pressure in 1M KCl or 1M urea solution. Justify your answer. [1 mark]

Solution:

Concept:

- At the same temperature, osmotic pressure obeys $\pi = iCRT$, where i is the van't Hoff factor, C is molar concentration, R is the gas constant and T is absolute temperature.
- Dissociation of an electrolyte increases the number of dissolved particles; urea is a non-electrolyte.

Step 1: Count the solute particles KCl dissociates in water as $\mathrm{KCl} \rightarrow \mathrm{K}^{+} + \mathrm{Cl}^{-}$. Ideally, one formula unit gives two ions, so its van't Hoff factor is approximately 2. Urea remains as undissociated molecules and has $i = 1$.

Step 2: Compare osmotic pressures Both solutions have the same molar concentration, $C = 1\,\mathrm{mol\,L^{-1}}$. At the same temperature, π is proportional to i. Thus, ideally, $\pi_{\mathrm{KCl}}/\pi_{\mathrm{urea}} \approx 2$. Real ionic interactions can make the ratio differ from exactly two, but KCl still produces more solute particles and the greater osmotic pressure.

Step 3: Conclusion $1\,\mathrm{M}$ KCl has higher osmotic pressure than $1\,\mathrm{M}$ urea at the same temperature because KCl dissociates into two ions whereas urea does not dissociate.

Quick Tip to Solve: For equal molarity and temperature, compare particle production, using the factor i in $\pi = iCRT$.

29(c). Why osmotic pressure is a colligative property? [1 mark]

Solution:

Concept:

- A colligative property depends on the number of solute particles rather than their chemical identity.
- For a dilute solution, $\pi = (n/V)RT$, with n the amount of dissolved solute particles, V the solution volume and T the absolute temperature.

Step 1: Use the osmotic-pressure relation The relation $\pi = (n/V)RT$ shows that at a fixed temperature the osmotic pressure is determined by the concentration of dissolved particles. It does not depend on which chemical substance supplies those particles.

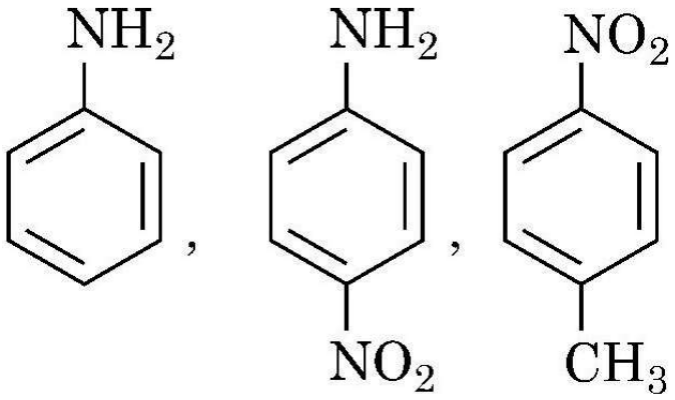
Step 2: Account for dissociation when needed For a dissociating or associating solute, write $\pi = iCRT$. The factor i accounts for the changed particle count. Thus two dilute solutions with equal concentrations of solute particles have the same osmotic pressure at the same temperature, even if their solutes have different chemical identities.

Step 3: Conclusion Osmotic pressure is a colligative property because, at a given temperature, it depends on the number of solute particles per unit volume and not on their chemical nature.

Quick Tip to Solve: Use $\pi = nRT/V$ to show that particle concentration, rather than solute identity, controls osmotic pressure.

30(a). Read the passage and answer: Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Greater the value of K_b or smaller the value of pK_b, stronger is the base. Amines are more basic than alcohols, ethers, esters, etc. The basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in aqueous solutions. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron releasing groups such as -CH_3, -OCH_3, -NH_2, etc., increase the basicity while electron-withdrawing substituents such as -NO_2, -CN, halogens etc., decrease the basicity of amines. The effect of these substitute is more at p- than at m- position.

(a) Arrange the following in the increasing order of their basic character. Give reason: [2 marks]



Solution:

Concept:

- A Lewis base donates an available electron pair; the basicity of an aromatic amine depends on the availability of the nitrogen lone pair for protonation.
- The nitro group, $-NO_2$, withdraws electrons by inductive and resonance effects, reducing the basicity of an amino group at the para position.

Step 1: Identify the three printed compounds The structures are aniline, para-nitroaniline and para-nitrotoluene, respectively. The last structure bears a nitro group and a methyl group; it has no amino group. Therefore it must not be treated as para-toluidine, which would contain $-NH_2$. Para-nitrotoluene is an extremely weak base compared with either of the two aromatic amines: nitro nitrogen has no available lone pair to donate, and protonation of nitro oxygen is much less favourable than protonation of amine nitrogen.

Step 2: Compare the two aromatic amines In aniline, the nitrogen lone pair is partly delocalised into the benzene ring. Para-nitroaniline has an additional strongly electron-withdrawing $-NO_2$ group, which withdraws electron density through both $-I$ and $-R$ effects. This makes the amino lone pair less available to accept a proton than in unsubstituted aniline. The electron-releasing methyl group of para-nitrotoluene does not supply an amino nitrogen and therefore does not make it more basic than these amines.

Step 3: Conclusion The increasing order of basic character is

$$p\text{-nitrotoluene} < p\text{-nitroaniline} < \text{aniline}.$$

Quick Tip to Solve: First identify whether the substituent is NO2 or NH2; the third printed structure has no amino group.

30(b). Why pK_b of aniline is more than that of methylamine? [1 mark]

Solution:

Concept:

- $pK_b = -\log_{10} K_b$: a smaller base dissociation constant K_b means a larger pK_b.
- An available nitrogen lone pair accepts a proton; resonance delocalisation lowers its availability.

Step 1: Examine aniline In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less readily available for bonding to a proton, so aniline is a relatively weak base.

Step 2: Examine methylamine In methylamine, CH_3NH_2, the lone pair is not delocalised into an aromatic ring. The methyl group releases electron density by its positive inductive effect, increasing nitrogen electron density and favouring proton acceptance. Thus methylamine has a larger K_b.

Step 3: Conclusion Aniline is less basic than methylamine; hence $K_b(\text{aniline}) < K_b(\text{methylamine})$ and $pK_b(\text{aniline}) > pK_b(\text{methylamine})$.

Quick Tip to Solve: Convert basicity to pKb only at the end: weaker base means smaller Kb and larger pKb.

30(c). Arrange the following in the increasing order of their basic character in an aqueous solution: $(CH_3)_3N$, $(CH_3)_2NH$, NH_3, CH_3NH_2 [1 mark]

Solution:

Concept:

- In water, amine basicity depends on electron donation by alkyl groups and on hydration of the protonated amine.
- The $+I$ effect increases nitrogen electron density, while hydration stabilises the conjugate acid.

Step 1: Include the methyl-group effect Methyl groups donate electron density towards nitrogen, making methylamines better proton acceptors than ammonia. However, counting methyl groups alone is insufficient for an aqueous solution.

Step 2: Include hydration and steric effects The protonated tertiary amine is less effectively hydrated because three methyl groups hinder access of water to its charged nitrogen and it has fewer N–H bonds. For the methylamine series, the combined effects give dimethylamine the greatest basicity, followed by methylamine, trimethylamine and ammonia.

Step 3: Conclusion The increasing order in aqueous solution is

$$NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH.$$

Quick Tip to Solve: For methylamines in water, remember secondary > primary > tertiary > ammonia; reverse it for increasing order.

OR

30(c). Why ammonolysis of alkyl halides is not a good method to prepare pure amines? [1 mark]

Solution:

Concept:

- Ammonolysis is nucleophilic substitution of an alkyl halide by ammonia, followed by removal of a proton.
- The primary amine produced still has a nitrogen lone pair and can undergo further alkylation.

Step 1: Track the first substitution Ammonia reacts with RX to give a primary amine RNH_2. This product is itself a nucleophile and can attack another molecule of the alkyl halide.

Step 2: Track successive substitutions Further alkylation gives a secondary amine R_2NH, a tertiary amine R_3N, and finally a quaternary ammonium salt $R_4N^+X^-$. Consequently the reaction generally yields a mixture that is difficult to separate. Excess ammonia favours the primary amine but does not make the method generally selective for a single pure amine.

Step 3: Conclusion Ammonolysis is unsuitable for preparing pure amines because successive alkylation produces a mixture of primary, secondary and tertiary amines and quaternary ammonium salts.

Quick Tip to Solve: Follow nitrogen after the first substitution: its lone pair survives, so further alkylation is possible.

Section E (15 marks)

31(A)(a). Calculate the standard Gibbs energy ($\Delta_r G^\circ$) of the following reaction at 25 °C:

Au(s) + Ca^{2+}(1M) → Au^{3+}(1M) + Ca(s)

$E^\circ_{Au^{3+}/Au}$ = +1.5 V, $E^\circ_{Ca^{2+}/Ca}$ = -2.87 V

Predict whether the reaction will be spontaneous or not at 25 °C.

[1 F = 96500 C mol^{-1}] [3 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- For a balanced reaction, $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and $F = 96500\,\text{C}\,\text{mol}^{-1}$.
- A negative Gibbs energy indicates a spontaneous forward reaction under the stated conditions; a positive value indicates a non-spontaneous forward reaction.

Step 1: Balance the electron transfer Gold is oxidised and calcium ions are reduced in the stated direction:

$$\text{Au(s)} \longrightarrow \text{Au}^{3+} + 3e^-,$$
$$\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca(s)}.$$

The printed skeletal equation must be balanced before using the electron count. Multiplying the first half-reaction by 2 and the second by 3 gives

$$2\text{Au(s)} + 3\text{Ca}^{2+}\text{(aq)} \longrightarrow 2\text{Au}^{3+}\text{(aq)} + 3\text{Ca(s)},$$

so $n = 6$.

Step 2: Calculate the potential and Gibbs energy For the forward reaction, calcium is the cathode and gold is the anode. Reduction potentials are not multiplied when balancing half-reactions. Thus

$$E^\circ_{\text{cell}} = -2.87 - (+1.50) = -4.37\,\text{V}.$$

Hence

$$\begin{aligned}\Delta_r G^\circ &= -6(96500)(-4.37)\\ &= +2530230\,\text{J}\,\text{mol}^{-1}\\ &= +2530.23\,\text{kJ}\,\text{mol}^{-1}.\end{aligned}$$

This value is per mole of the balanced reaction written above. At the stated unit concentrations, $Q = 1$, so the Gibbs energy equals the standard value.

Step 3: Conclusion For $2\text{Au} + 3\text{Ca}^{2+} \rightarrow 2\text{Au}^{3+} + 3\text{Ca}$, $\Delta_r G^\circ = +2530.23\,\text{kJ}\,\text{mol}^{-1}$. The forward reaction is not spontaneous at 25°C under the stated conditions.

Quick Tip to Solve: Balance Au losing 3 electrons against Ca gaining 2: use n = 6, but never multiply electrode potentials.

31(A)(b). Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silverware in an aluminium pan containing an inert electrolytic solution such as NaCl? The standard electrode potential for half reaction:

$Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-}$ **is** -0.71 **V and for**

$Al^{3+} + 3e^- \longrightarrow 2Al(s)$ **is** -1.66 **V.** [2 marks]

Solution:

Concept:

- A spontaneous galvanic reaction has positive cell potential: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- The more negative reduction potential identifies the metal that is more readily oxidised. Aluminium supplies electrons, while silver sulphide accepts them to regenerate metallic silver.

Step 1: Identify the oxidation and reduction Silver sulphide is reduced according to

$$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}.$$

Aluminium acts as the anode and is oxidised: $Al(s) \rightarrow Al^{3+} + 3e^-$. The printed aluminium reduction half-reaction has an extra coefficient 2 before Al; the balanced aluminium couple uses one Al atom. Its supplied reduction potential remains $-1.66\,V$.

Step 2: Calculate the cell potential and interpret it Using the given standard reduction potentials,

$$E^\circ_{\text{cell}} = (-0.71) - (-1.66) = +0.95\,V.$$

Thus $\Delta_r G^\circ = -nFE^\circ_{\text{cell}} < 0$, so aluminium can reduce the tarnish. Balancing electron transfer gives

$$3Ag_2S + 2Al \rightarrow 6Ag + 2Al^{3+} + 3S^{2-}.$$

Contact between the silverware and aluminium permits electron flow; the inert electrolyte provides ionic conduction without itself being the reducing agent.

Step 3: Conclusion Yes. Aluminium can remove the silver sulphide tarnish by reducing it to silver, since the standard cell potential is $+0.95\,V$.

Quick Tip to Solve: Subtract the aluminium reduction potential from the silver sulphide reduction potential; do not multiply electrode potentials when balancing electrons.

OR

31(B)(a). Define the following:

(i) Cell potential

(ii) Fuel cell [2 marks]

Solution:

Concept:

- An electrochemical cell has two electrodes with different electrode potentials; their difference drives electron transfer through the external circuit.
- A fuel cell converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy through electrode reactions.

Step 1: Define cell potential Cell potential is the difference between the electrode potentials of the cathode and anode of an electrochemical cell. With both electrode potentials written as reduction potentials,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}.$$

It is measured in volts. The potential difference measured when no current is drawn from the cell is its electromotive force (emf); this is the maximum potential difference available from the cell under those conditions.

Step 2: Define fuel cell A fuel cell is a galvanic cell in which the chemical energy of the combustion reaction between a fuel and an oxidant is converted directly into electrical energy. The reactants are supplied continuously to the electrodes, allowing the cell to operate while the supply continues. For example, a hydrogen-oxygen fuel cell uses hydrogen as the fuel and oxygen as the oxidant and produces water through the overall reaction $2H_2 + O_2 \rightarrow 2H_2O$.

Step 3: Conclusion (i) Cell potential is the cathode-anode electrode potential difference. (ii) A fuel cell is a galvanic cell that directly converts the energy of continuously supplied fuel and oxidant into electricity.

Quick Tip to Solve: Include both electrode potentials in the first definition and continuous reactant supply with direct electrical conversion in the second.

31(B)(b). Calculate emf of the following cell at 25 °C:

Zn(s) | Zn^{2+}(0.1 M) || Cd^{2+}(0.01 M) | Cd(s)

Given: $E^\circ_{Cd^{2+}/Cd}$ = -0.40 V, $E^\circ_{Zn^{2+}/Zn}$ = -0.76 V

[log 10 = 1] [3 marks]

Solution:

Concept:

- The cathode has the higher reduction potential. Standard cell emf is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Quick Tip to Solve: Write the overall reaction first: zinc ions are products, so their concentration belongs in the numerator of the Nernst quotient.

Step 1: Establish the cell reaction and electron transfer Since $-0.40\,\text{V} > -0.76\,\text{V}$, cadmium ions undergo reduction at the cathode, while zinc undergoes oxidation at the anode:

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

The overall reaction is $\text{Zn(s)} + \text{Cd}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cd(s)}$. Hence $n = 2$; neither metallic zinc nor metallic cadmium appears in the concentration quotient.

Step 2: Calculate the standard cell emf Both given potentials are reduction potentials, so

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

This value applies to standard conditions. The actual ion concentrations differ from the standard state and therefore require the Nernst correction.

Step 3: Substitute the concentrations in the Nernst equation From the balanced forward cell reaction,

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

Taking the dilute-solution activities as represented by the stated molar concentrations and using $\log 10 = 1$,

$$E_{\text{cell}} = 0.36 - \frac{0.0591}{2}\log 10$$
$$= 0.36 - 0.02955 = 0.33045\,\text{V}.$$

The correction lowers the emf because the product-ion concentration is larger than the reactant-ion concentration. The resulting positive emf agrees with the direction of the written cell.

Step 4: Conclusion The emf of the given Zn-Cd cell at 25°C is $E_{\text{cell}} = 0.33045\,\text{V} \approx 0.330\,\text{V}$.

Quick Tip to Solve: Write the overall reaction first: zinc ions are products, so their concentration belongs in the numerator of the Nernst quotient.

32(A). An organic compound 'A', molecular formula C_2H_6O oxidises with CrO_3 to form a compound 'B'. Compound 'B' on warming with iodine and aqueous solution of NaOH gives a yellow precipitate of compound 'C'. When compound 'A' is heated with conc. H_2SO_4 at 413 K gives a compound 'D', which on reaction with excess HI gives compound 'E'. Identify compounds 'A', 'B', 'C', 'D' and 'E' and write chemical equations involved. [5 marks]

Solution:

Concept:

- A primary alcohol undergoes controlled oxidation to an aldehyde. The two constitutional isomers of $\text{C}_2\text{H}_6\text{O}$ are ethanol and dimethyl ether; formation of an aldehyde identifies the alcohol.
- Ethanal gives the iodoform test: iodine in aqueous sodium hydroxide converts its CH_3CO unit into yellow iodoform, CHI_3.

Quick Tip to Solve: Use the yellow iodoform precipitate to identify ethanal first; then read 413 K as ether formation and excess HI as conversion of both ethyl groups to iodoethane.

- At $413\,\mathrm{K}$, concentrated sulphuric acid promotes intermolecular dehydration of ethanol to ethoxyethane. Excess hydrogen iodide cleaves the ether and converts the resulting ethanol into iodoethane.

Step 1: Identify A and its oxidation product B Compound A must be ethanol, CH_3CH_2OH. Dimethyl ether has the same molecular formula but does not undergo the stated oxidation to an aldehyde giving the iodoform test. Controlled oxidation of the primary alcohol gives ethanal, compound B:

$$CH_3CH_2OH + [O] \xrightarrow{CrO_3} CH_3CHO + H_2O.$$

Here $[O]$ denotes the oxygen equivalent supplied by the oxidising reagent. Ethanal contains the required methyl carbonyl group. Further oxidation can give ethanoic acid, but the specified positive iodoform reaction identifies the aldehyde stage in this sequence.

Step 2: Identify the yellow precipitate C On warming ethanal with iodine and aqueous sodium hydroxide, the three hydrogens of its methyl group are replaced by iodine, followed by cleavage in the alkaline medium. The insoluble yellow product is iodoform (triiodomethane), compound C. Sodium methanoate is the other organic product. The balanced overall equation is

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

Thus the yellow precipitate is CHI_3, not an iodide salt: sodium iodide remains dissolved in the reaction mixture.

Step 3: Identify the dehydration product D Two ethanol molecules undergo intermolecular dehydration at the stated temperature, forming ethoxyethane (diethyl ether), compound D:

$$2CH_3CH_2OH \xrightarrow[413\,\mathrm{K}]{\text{conc. } H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O.$$

The temperature is decisive: at $413\,\mathrm{K}$ the ether is the expected product, whereas the higher-temperature dehydration of ethanol produces ethene.

Step 4: Identify E using excess HI Hydrogen iodide first cleaves the protonated ether into iodoethane and ethanol. Excess HI then converts this ethanol into a second molecule of iodoethane:

$$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5I + C_2H_5OH,$$
$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O.$$

Therefore the balanced overall equation is

$$C_2H_5OC_2H_5 + 2HI \longrightarrow 2C_2H_5I + H_2O.$$

Compound E is iodoethane (ethyl iodide). Because the ether is symmetrical, both ethyl groups give the same organic iodide.

Step 5: Conclusion $A = CH_3CH_2OH$ (ethanol), $B = CH_3CHO$ (ethanal), $C = CHI_3$ (iodoform), $D = C_2H_5OC_2H_5$ (ethoxyethane), and $E = C_2H_5I$ (iodoethane).

Quick Tip to Solve: Use the yellow iodoform precipitate to identify ethanal first; then read 413 K as ether formation and excess HI as conversion of both ethyl groups to iodoethane.

OR

32(B). (a) Write chemical equations of the following reactions:

(i) Phenol is treated with conc. HNO_3

(ii) Propene is treated with B_2H_6 followed by oxidation by H_2O_2/OH^-.

(iii) Sodium t-butoxide is treated with CH_3Cl.

(b) Give a simple chemical test to distinguish between butan-1-ol and butan-2-ol.

(c) Arrange the following in increasing order of acid strength:

phenol, ethanol, water [5 marks]

Solution:

Concept:

- Phenol activates its ring towards electrophilic substitution at the ortho and para positions; concentrated nitric acid gives the trinitro derivative.
- Hydroboration followed by alkaline peroxide oxidation adds water across an alkene in the anti-Markovnikov orientation. Williamson synthesis forms an ether by reaction of an alkoxide with a suitable alkyl halide.
- Alcohols containing the $CH_3CH(OH)-$ group give the iodoform test. Acid strength increases when the conjugate base is better stabilised.

Step 1: (a)(i) Nitration of phenol The hydroxyl group directs substitution to positions 2, 4 and 6. With concentrated nitric acid, phenol forms 2,4,6-trinitrophenol, commonly called picric acid:

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

The product retains the phenolic hydroxyl group; three ring hydrogens are replaced by nitro groups.

Step 2: (a)(ii) Hydroboration and oxidation of propene Boron attaches preferentially to the less substituted terminal carbon. Oxidation replaces the carbon-boron bond by a carbon-oxygen bond, yielding propan-1-ol:

$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2/OH^-]{1.\ B_2H_6} CH_3CH_2CH_2OH.$$

Thus the hydroxyl group is on the terminal carbon, rather than the middle carbon as in acid-catalysed hydration.

Step 3: (a)(iii) Williamson ether synthesis The tert-butoxide ion attacks the methyl carbon of chloromethane and displaces chloride by an S_N2 reaction:

$$(CH_3)_3CONa + CH_3Cl \longrightarrow (CH_3)_3COCH_3 + NaCl.$$

The ether is 2-methoxy-2-methylpropane (methyl tert-butyl ether). The alkyl halide is methyl chloride, so there is no competing elimination involving a beta hydrogen on that halide.

Step 4: (b) Distinguish the two alcohols by the iodoform test Warm each sample with iodine and aqueous sodium hydroxide. Butan-2-ol gives a yellow precipitate of iodoform, CHI_3, because it contains the $CH_3CH(OH)-$ group and is oxidised to butan-2-one. Butan-1-ol gives no yellow

Quick Tip to Solve: For the iodoform test, look specifically for a methyl group bonded to the carbon bearing OH; a secondary alcohol alone is not sufficient.

precipitate because it lacks this group. For the positive test:

$$CH_3CH(OH)CH_2CH_3 + 4I_2 + 6NaOH$$

$$\longrightarrow CHI_3 \downarrow + CH_3CH_2COONa + 5NaI + 5H_2O.$$

Step 5: (c) Compare conjugate-base stability Ethanol's electron-releasing ethyl group increases electron density on the oxygen of ethoxide, making it less stable than hydroxide. Ethanol is therefore weaker as an acid than water. Phenoxide is stabilised by delocalisation of its negative charge over oxygen and the aromatic ring, so phenol is more acidic than either. These effects establish the requested increasing order.

Step 6: Conclusion (a) The products are picric acid, propan-1-ol and methyl tert-butyl ether, respectively. (b) Butan-2-ol gives a yellow iodoform precipitate; butan-1-ol does not. (c) Increasing acid strength: $\boxed{\text{ethanol} < \text{water} < \text{phenol}}$.

Quick Tip to Solve: For the iodoform test, look specifically for a methyl group bonded to the carbon bearing OH; a secondary alcohol alone is not sufficient.

33(A)(a). Give IUPAC name of CH_3-CH=CH-CHO. [1 mark]

Solution:

Concept:

- An aldehyde is named using the suffix $-\text{al}$; the carbon of the $-\text{CHO}$ group must be included in the parent chain.
- Number the chain from the aldehyde carbon as carbon 1. Specify the position of a carbon-carbon double bond by its lower carbon number.

Step 1: Select and number the parent chain The structure $CH_3 - CH{=}CH - CHO$ has four carbon atoms in the longest chain containing the aldehyde group. Counting from the $-\text{CHO}$ end gives CHO as carbon 1, the two alkene carbons as carbons 2 and 3, and the methyl carbon as carbon 4. The four-carbon parent therefore has the root but.

Step 2: Locate the double bond and apply the suffix The double bond lies between carbons 2 and 3, so its locant is 2 and the unsaturation is expressed by $-2\text{-en}-$. The aldehyde suffix is $-\text{al}$. Numbering from the methyl end would assign the aldehyde carbon a higher number and is incorrect. No geometrical descriptor can be assigned from this condensed formula alone.

Step 3: Conclusion The IUPAC name is $\boxed{\text{but-2-enal}}$.

Quick Tip to Solve: Start numbering at the CHO carbon before locating the double bond; the aldehyde carbon is part of the four-carbon chain.

33(A)(b). Give a simple chemical test to distinguish between propanal and propanone. [1 mark]

Solution:

Concept:

- Tollens' reagent is ammoniacal silver nitrate containing $[Ag(NH_3)_2]^+$. Aldehydes reduce this complex to metallic silver.
- Propanal contains the aldehyde group $-CHO$, whereas propanone is a ketone; a simple ketone does not give Tollens' test.

Step 1: Perform Tollens' test Add freshly prepared Tollens' reagent to separate samples of propanal and propanone in clean test tubes and warm gently in a water bath. Propanal produces a silver mirror on the inner wall, or a deposit of metallic silver. Its aldehyde group is oxidised to the propanoate ion in the alkaline medium:

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$
$$\longrightarrow CH_3CH_2COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Step 2: Compare the observation for propanone Propanone gives no silver mirror under the same conditions because its ketone group is not oxidised by this mild reagent. The different silver-deposition observations distinguish the samples. A general carbonyl test such as 2,4-DNP would give a precipitate with both compounds and would therefore not distinguish them.

Step 3: Conclusion Use Tollens' reagent: propanal gives a silver mirror, whereas propanone gives no silver mirror.

Quick Tip to Solve: Choose an aldehyde oxidation test to distinguish an aldehyde from a ketone; a test detecting any carbonyl group is insufficient.

33(A)(c). How will you convert the following:

(i) Toluene to benzoic acid

(ii) Ethanol to propan-2-ol

(iii) Propanal to 2-hydroxy propanoic acid [3 marks]

Solution:

Concept:

- Strong oxidation converts an alkyl side chain having a benzylic hydrogen into a carboxyl group; oxidation of a primary alcohol can be stopped at the aldehyde.
- A Grignard reagent adds its alkyl group to an aldehyde; subsequent acidic hydrolysis gives an alcohol with a new carbon-carbon bond.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by bromine. Hydrolysis of that alpha bromo acid gives an alpha hydroxy acid.

Step 1: (i) Oxidise the toluene side chain Heat toluene with alkaline potassium permanganate and

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then acidify the benzoate formed:

$$C_6H_5CH_3 \xrightarrow[\Delta]{KMnO_4/OH^-} C_6H_5COO^- \xrightarrow{H^+} C_6H_5COOH.$$

Oxidation changes the methyl side chain to the carboxyl group while leaving the benzene ring intact. Acidification is necessary to obtain the free acid from its salt.

Step 2: (ii) Form ethanal, then add a methyl group Pass ethanol vapour over heated copper at $573\,K$ to form ethanal by dehydrogenation:

$$CH_3CH_2OH \xrightarrow[573\,K]{Cu} CH_3CHO + H_2.$$

Treat ethanal with methylmagnesium bromide in dry ether, then hydrolyse the addition product with dilute acid:

$$CH_3CHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH(OMgBr)CH_3,$$

$$CH_3CH(OMgBr)CH_3 \xrightarrow{H_3O^+} CH_3CH(OH)CH_3.$$

The added methyl group supplies the third carbon, and the carbonyl carbon becomes the secondary alcohol carbon. Water must be excluded during Grignard addition because it destroys the reagent.

Step 3: (iii) Introduce hydroxyl at the alpha carbon First oxidise propanal to propanoic acid with acidified potassium dichromate:

$$CH_3CH_2CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3CH_2COOH.$$

Carry out alpha bromination with bromine and red phosphorus, followed by aqueous work-up. Then replace bromine by hydroxyl using aqueous alkali and acidify:

$$CH_3CH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Br_2/\text{red P}} CH_3CHBrCOOH,$$

$$CH_3CHBrCOOH \xrightarrow[\text{(ii) } H^+]{\text{(i) aq. KOH}} CH_3CH(OH)COOH.$$

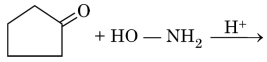
All three original carbon atoms are retained; the hydroxyl group is placed on carbon 2, adjacent to the carboxyl carbon.

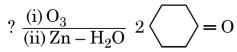
Step 4: Conclusion The products are benzoic acid, C_6H_5COOH; propan-2-ol, $CH_3CH(OH)CH_3$; and 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$, respectively.

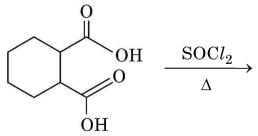
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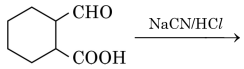
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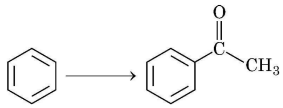
33(B). Complete each synthesis by giving missing starting material, reagent or products: [5 marks]

(a) 

(b) 

(c) 

(d) 

(e) 

Solution:

Concept:

- Hydroxylamine condenses with a carbonyl compound to form an oxime, replacing $C=O$ by $C=N-OH$.
- Reductive ozonolysis cleaves an alkene double bond and converts each of its two carbons into a carbonyl carbon.
- Thionyl chloride converts carboxylic acid groups to acid chloride groups; cyanide adds to an aldehyde to form a cyanohydrin.
- Friedel-Crafts acylation uses an acyl chloride and anhydrous aluminium chloride to introduce an acyl group on benzene.

Step 1: (a) Condensation with hydroxylamine Cyclopentanone reacts with NH_2OH in an acid-catalysed condensation to give cyclopentanone oxime and water. The five-membered carbon ring remains unchanged and the former carbonyl carbon now bears $=N-OH$:

$$\text{cyclopentanone} + NH_2OH \xrightarrow{H^+} \text{cyclopentanone oxime} + H_2O.$$

The oxime has formula C_5H_9NO. The nitrogen of hydroxylamine becomes bonded to the original carbonyl carbon.

Step 2: (b) Reconstruct the alkene from two cyclohexanones The starting material is cyclohexylidenecyclohexane: two cyclohexane rings joined by a double bond between one carbon of each ring. Its condensed structural representation is

$$(CH_2)_5C=C(CH_2)_5,$$

where each $(CH_2)_5$ chain closes back onto its adjacent alkene carbon to form a six-membered

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ring. Ozonolysis followed by Zn/H_2O cleaves this joining double bond and yields two molecules of cyclohexanone. Each alkene carbon has two carbon substituents, so both fragments are ketones.

Step 3: (c) Replace both carboxyl hydroxyl groups by chlorine The product is cyclohexane-1,2-dicarbonyl dichloride. At the two adjacent ring carbons, each printed $-COOH$ group becomes $-COCl$; the ring remains unchanged. With sufficient thionyl chloride:

$$C_6H_{10}(COOH)_2 + 2SOCl_2 \xrightarrow{\Delta} C_6H_{10}(COCl)_2 + 2SO_2 + 2HCl.$$

Thus the two carbonyl oxygen atoms are retained, whereas the two hydroxyl groups are replaced by chlorine atoms.

Step 4: (d) Add hydrogen cyanide to the aldehyde group $NaCN/HCl$ generates hydrogen cyanide. The aldehyde substituent $-CHO$ becomes $-CH(OH)CN$, while the neighbouring $-COOH$ group remains unchanged:

$$C_6H_{10}(CHO)(COOH) + HCN \longrightarrow C_6H_{10}[CH(OH)CN](COOH).$$

The two substituents remain attached to adjacent carbons of the cyclohexane ring. Cyanide attacks the aldehyde carbonyl carbon and protonation converts the oxygen into hydroxyl. The carboxyl group does not undergo ordinary cyanohydrin addition.

Step 5: (e) Acylate benzene Use acetyl chloride, CH_3COCl, with anhydrous $AlCl_3$, followed by aqueous work-up:

$$C_6H_6 + CH_3COCl \xrightarrow{\text{anhydrous } AlCl_3} C_6H_5COCH_3 + HCl.$$

Aluminium chloride generates the electrophilic acetyl species. Substitution of a benzene hydrogen by $-COCH_3$ gives acetophenone, the printed ketone product. Acetic anhydride with anhydrous aluminium chloride is also a suitable acylating system.

Step 6: Conclusion (a) Cyclopentanone oxime; (b) cyclohexylidenecyclohexane; (c) cyclohexane-1,2-dicarbonyl dichloride; (d) the cyanohydrin with adjacent $-CH(OH)CN$ and $-COOH$ substituents; (e) CH_3COCl and anhydrous $AlCl_3$, followed by work-up.

Quick Tip to Solve: In reverse ozonolysis, erase the two carbonyl oxygens and join their carbonyl carbons with a double bond; preserve each surrounding ring exactly.