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

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. 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 are classified as water-soluble or fat-soluble according to their solubility.
- Vitamins A, D, E and K are fat-soluble and can be stored in the liver and fatty tissues.

Step 1: Evaluate the assertion Vitamin D is a fat-soluble vitamin. It can be retained in the body's fat stores and liver, so the statement that it cannot be stored is false.

Step 2: Evaluate the reason The reason correctly identifies vitamin D as fat-soluble. Unlike excess water-soluble vitamins, it is not readily eliminated in urine. Thus, the reason is true in the classification used here.

Step 3: Compare the truth values The reason supports storage of vitamin D; it cannot explain the assertion that storage is impossible. Options (A) and (B) require a true assertion, while (C) also incorrectly makes the reason false.

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

Quick Tip to Solve: Recall the fat-soluble group A, D, E and K: their storage immediately rules out the assertion.

2. 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 phthalimide synthesis prepares primary aliphatic amines by alkylation of the phthalimide anion, followed by hydrolysis.
- The alkylation requires nucleophilic substitution of a halide by the nitrogen nucleophile.

Step 1: Evaluate the assertion An aromatic primary amine has its amino group directly attached to an aromatic ring. Gabriel phthalimide synthesis does not prepare such amines from aryl halides under its usual conditions. The assertion is therefore true.

Step 2: Evaluate the reason The phthalimide anion substitutes suitable alkyl halides, but ordinary aryl halides do not undergo this reaction. Their carbon-halogen bond has partial double-bond character and is attached to an sp^2-hybridised carbon. The reason is true.

Step 3: Check the explanatory connection Failure of the required substitution prevents formation of the N-aryl intermediate that would be needed to produce an aromatic primary amine. Thus, the reason directly explains the assertion; option (B) denies this connection, and (C) and (D) assign incorrect truth values.

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

Quick Tip to Solve: In Gabriel synthesis, check whether the halogen is on an alkyl carbon or directly on an aromatic ring.

3. 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 only when reduction of hydrogen ions by that metal is thermodynamically favourable.
- Standard reduction potentials are $E^\circ_{H^+/H_2} = 0\,V$ and $E^\circ_{Cu^{2+}/Cu} = +0.34\,V$.

Step 1: Evaluate the assertion Copper does not release hydrogen gas from dilute mineral acids. Dilute non-oxidising acids cannot oxidise copper through reduction of hydrogen ions. Oxidising acids can attack copper, but their oxidising species are reduced instead of liberating hydrogen. Thus, the assertion is true.

Step 2: Evaluate the reason Here electrode potential means the standard reduction potential of the Cu^{2+}/Cu couple. Its positive value, $+0.34\,V$, makes the reason true.

Step 3: Connect the potential to hydrogen liberation For the proposed reaction $Cu + 2\,H^+ \longrightarrow Cu^{2+} + H_2$, copper would be the anode and hydrogen ions the cathodic reactant:

$$E^\circ_{cell} = 0 - (+0.34) = -0.34\,V.$$

This negative value explains why copper does not displace hydrogen in the stated context. Option (B) incorrectly denies the explanation, while (C) and (D) incorrectly make one statement false.

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

Quick Tip to Solve: Compare a metal's reduction potential with zero: a positive value opposes displacement of hydrogen from dilute acid.

4. 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:

- For a first-order reaction, the integrated rate law is $kt = \ln([A]_0/[A]_t)$, where k is the rate constant and $[A]_0, [A]_t$ are the initial and remaining reactant concentrations.
- The half-life $t_{1/2}$ is the time for the concentration to become half its initial value.

Step 1: Evaluate the assertion At the half-life, $[A]_t = [A]_0/2$. Substituting into the first-order law gives

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

Doubling the initial concentration does not change this time at a fixed temperature, so the assertion is false.

Step 2: Evaluate the reason The initial concentration cancels from the ratio $[A]_0/([A]_0/2) = 2$. Thus, the half-life depends on the rate constant, not on the initial concentration. The reason is true.

Step 3: Relate the two statements The reason contradicts the claimed doubling of half-life. A doubled initial concentration gives twice the initial rate, but also twice the amount to be consumed to reach half concentration. Options (A) and (B) wrongly treat the assertion as true, and (C) reverses both truth values.

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

Quick Tip to Solve: For a first-order reaction at fixed temperature, use $t_{1/2} = 0.693/k$; the starting concentration never enters.

5. 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:

- Vitamins are required in small amounts for normal physiological functions, and their deficiencies cause characteristic disorders.
- Vitamin C is also called ascorbic acid; its deficiency causes scurvy.

Step 1: Identify the vitamin linked to scurvy Scurvy is associated with deficiency of vitamin C, which is needed for normal collagen formation. Deficiency weakens connective tissues and may lead to bleeding gums and poor wound healing. The chemical name to recognise is ascorbic acid.

Step 2: Check the other listed substances Vitamin B1 is thiamine, whose deficiency causes beriberi. Vitamin B2 is riboflavin, whose deficiency is associated with cracking at the corners of the mouth and related symptoms. Glutamic acid is an amino acid, not the vitamin responsible for preventing scurvy. These facts eliminate (A), (B) and (D).

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

Quick Tip to Solve: Link scurvy directly with vitamin C, then recognise ascorbic acid as its chemical name among the options.

6. 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 nitrogenous base, a pentose sugar and a phosphate group.
- Nucleic-acid chains have a sugar-phosphate backbone formed by $3'$-$5'$ phosphodiester linkages between successive nucleotides.

Step 1: Identify the bond that builds the chain A phosphate group links the $3'$-oxygen of the sugar in one nucleotide to the $5'$-oxygen of the sugar in the next. Because the phosphate forms two ester bonds, this connection is called a phosphodiester linkage. Repeated linkages produce a polynucleotide

Quick Tip to Solve: For nucleic acids, separate the backbone bond (phosphodiester) from base-pair bonding (hydrogen bonds).

chain.

Step 2: Distinguish the competing linkages A glycosidic linkage joins a nitrogenous base to its sugar within a nucleotide. Peptide linkages join amino acids in proteins. Hydrogen bonds pair complementary bases between DNA strands; they do not create the covalent nucleotide backbone. Hence, (A), (B) and (C) describe different structural connections.

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

Quick Tip to Solve: For nucleic acids, separate the backbone bond (phosphodiester) from base-pair bonding (hydrogen bonds).

7. 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 is the loss of a protein's native secondary and tertiary structures, usually caused by heat or a change in pH.
- In denaturation the protein loses its native biological activity, while its primary peptide-chain structure remains intact.

Step 1: Examine egg white and milk Heating egg white disrupts the native folding of its proteins, which aggregate and coagulate. Curdling of milk due to acid formation changes the pH and causes its proteins to coagulate. Both are standard examples of protein denaturation in this context.

Step 2: Distinguish clotting and select the combined choice Blood clotting is a regulated biochemical process involving conversion of fibrinogen into fibrin through enzyme action; it is not the usual example of denaturation by heat or pH change. Option (A) alone omits curdling, and (B) alone omits coagulation of egg white. The combined choice includes both listed examples of denaturation.

Step 3: Conclusion Coagulation of egg white and curdling of milk are both examples of protein denaturation. Hence, the correct option is (D).

Quick Tip to Solve: Identify the familiar heat and acid examples: cooked egg white and curdled milk both lose their native protein structure.

8. 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:

- Salicylic acid is 2-hydroxybenzoic acid: its carboxyl group is ortho to the phenolic hydroxyl group.
- In Kolbe's reaction, sodium phenoxide reacts with carbon dioxide under pressure, followed by acidification.

Step 1: Identify the required transformation Phenol must acquire a $-\mathrm{COOH}$ group on the aromatic ring. Convert phenol into sodium phenoxide with sodium hydroxide; treatment with $\mathrm{CO_2}$ at about $400\,\mathrm{K}$ under pressure gives sodium salicylate. Acidification produces salicylic acid.

Step 2: Distinguish the named reactions Reimer–Tiemann reaction normally introduces a $-\mathrm{CHO}$ group, giving salicylaldehyde. Friedel–Crafts reactions introduce alkyl or acyl groups, while coupling with a diazonium salt gives an azo compound. These are not the stated carboxylation of phenol.

Step 3: Conclusion The conversion is accomplished by the Kolbe reaction. Hence, the correct option is (C).

Quick Tip to Solve: Link phenol plus carbon dioxide to salicylic acid; phenol plus chloroform and alkali normally gives salicylaldehyde.

9. 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 group $\mathrm{R{-}CH(OH){-}R'}$, with two carbon groups attached to the carbon bearing hydroxyl.
- Oxidation removes one hydrogen from the hydroxyl group and one from its carbon, forming a carbonyl group without changing the carbon skeleton.

Step 1: Apply oxidation to the alcohol group Chromic anhydride, $\mathrm{CrO_3}$, oxidises a secondary alcohol

Quick Tip to Solve: Count the carbon groups on the hydroxyl-bearing carbon: two groups predict a ketone on ordinary oxidation.

according to

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

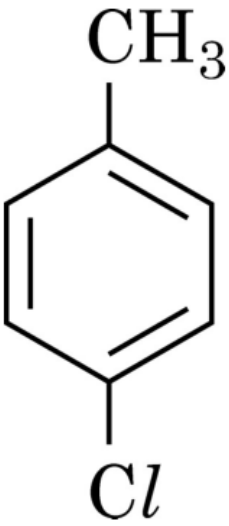
The carbonyl carbon remains bonded to both carbon groups.

Step 2: Compare the product classes A carbonyl group between two carbon groups is a ketone. An aldehyde has a hydrogen on the carbonyl carbon and is the initial oxidation product of a primary alcohol. A carboxylic acid or ester is not formed by this ordinary oxidation of a secondary alcohol; further vigorous oxidation would involve carbon–carbon bond cleavage.

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

Quick Tip to Solve: Count the carbon groups on the hydroxyl-bearing carbon: two groups predict a ketone on ordinary oxidation.

10. 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:

- A disubstituted benzene is numbered to give its substituents the lowest possible set of locants.
- If the same locant set results in either direction, the substituent cited first alphabetically receives the lower locant.

Step 1: Read the positions on the ring The figure shows a methyl group, $-CH_3$, and a chlorine atom

Quick Tip to Solve: For opposite chloro and methyl groups, write the locant pair 1,4 and give chloro the 1 because c precedes m.

at opposite carbon atoms of a benzene ring. Their relative positions are para, so their locants are 1 and 4 whichever group is chosen first.

Step 2: Resolve the numbering tie Chloro precedes methyl alphabetically; therefore chlorine receives locant 1 and methyl receives locant 4. Methylchlorobenzene omits the required positional information. Toluene denotes methylbenzene without chlorine, while 1-methyl-4-chlorobenzene reverses the preferred alphabetical numbering and citation.

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

Quick Tip to Solve: For opposite chloro and methyl groups, write the locant pair 1,4 and give chloro the 1 because c precedes m.

11. 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 complex has no unpaired electrons; a complex with even one unpaired electron is paramagnetic.
- Determine the metal oxidation state and d-electron count, then consider ligand strength and geometry to find the number of unpaired electrons.

Step 1: Examine the nickel complexes Both nickel complexes contain Ni^{2+}, which has a $3d^8$ configuration. Strong-field CN^- causes pairing in $[Ni(CN)_4]^{2-}$, giving square-planar dsp^2 hybridisation and no unpaired electrons. With weak-field Cl^-, $[NiCl_4]^{2-}$ is tetrahedral with sp^3 hybridisation and two unpaired electrons.

Step 2: Check iron and cobalt In $[Fe(CN)_6]^{3-}$, iron is Fe^{3+}, a d^5 ion. Although cyanide produces a low-spin complex, its t_{2g}^5 arrangement still contains one unpaired electron. In $[CoF_6]^{3-}$, cobalt is Co^{3+}, a d^6 ion; weak-field fluoride gives high-spin $t_{2g}^4 e_g^2$ with four unpaired electrons. Both are paramagnetic.

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

Quick Tip to Solve: Do not equate strong-field ligands with diamagnetism: low-spin iron(III), a d-five ion, still has one unpaired electron.

12. 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:

- An ambidentate ligand has two possible donor atoms but coordinates through only one of them at a time.
- Linkage isomerism occurs when the same ambidentate ligand is attached to the central metal through different donor atoms.

Step 1: Identify the changed attachment Both ions have five ammonia ligands and one nitrite ligand around cobalt. In $[Co(NH_3)_5(NO_2)]^{2+}$, the nitrite group binds through nitrogen. In $[Co(NH_3)_5(ONO)]^{2+}$, it binds through oxygen. Thus the composition is unchanged, but the metal–ligand linkage changes.

Step 2: Exclude the other isomerisms Ionisation isomerism involves exchange between a coordinated ligand and a counter-ion. Coordination isomerism involves exchange of ligands between complex cations and anions. Geometrical isomerism changes the spatial arrangement of ligands without changing their donor atom. None describes the nitrogen-to-oxygen attachment change shown here.

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

Quick Tip to Solve: When the formulas change from NO2 to ONO at the same metal, identify the donor atom first: N versus O signals linkage isomerism.

13. 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:

- The argon core, $[Ar]$, represents 18 electrons. For a neutral atom, its total electron count equals its atomic number.
- Copper has the ground-state configuration $[Ar]3d^{10}4s^1$, with a completely filled $3d$ subshell.

Step 1: Count the electrons The given configuration contains $18 + 10 + 1 = 29$ electrons. The neutral element with atomic number 29 is copper, Cu. Its configuration differs from the simple expected

Quick Tip to Solve: Add the argon core's 18 electrons to the displayed exponents: 18 + 10 + 1 = 29 identifies copper immediately.

filling pattern $[\mathrm{Ar}]3d^9 4s^2$ because the filled $3d$ subshell is especially stable.

Step 2: Check the alternatives Zinc has $[\mathrm{Ar}]3d^{10}4s^2$, so it has one extra electron. Chromium has $[\mathrm{Ar}]3d^5 4s^1$, and manganese has $[\mathrm{Ar}]3d^5 4s^2$. Neither has the given filled $3d^{10}$ subshell and single $4s$ electron together.

Step 3: Conclusion The element is copper, Cu. Hence, the correct option is (A).

Quick Tip to Solve: Add the argon core's 18 electrons to the displayed exponents: 18 + 10 + 1 = 29 identifies copper immediately.

14. 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 is the number of reacting species taking part together in a single elementary reaction step; it is a positive integer.
- Reaction order is the sum of concentration exponents in the experimentally determined rate law and need not equal the molecularity of an overall reaction.

Step 1: Use the elementary-step definition The question explicitly counts molecules reacting with each other in an elementary reaction. One participating molecule gives a unimolecular step, two give a bimolecular step, and three give a termolecular step. This count is the defining feature of molecularity.

Step 2: Distinguish the other quantities Activation energy is the energy barrier to reaction, not a count of molecules. Stoichiometry describes the relative quantities in a balanced chemical equation, which may represent several steps. Order describes the dependence of rate on concentration. For an elementary step order can match molecularity, but the definition given here asks directly for molecularity.

Step 3: Conclusion The number is a measure of the molecularity of the reaction. Hence, the correct option is (C).

Quick Tip to Solve: Underline the words elementary reaction: counting its participating molecules identifies molecularity, whereas rate-law exponents identify order.

15. 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:

- For a zero-order reaction, the rate is $r = k$ and the half-life is $t_{1/2} = [A]_0/(2k)$, where $[A]_0$ is the initial reactant concentration.
- Molecularity counts the reacting species participating in one elementary step; it is a positive integer and cannot be zero.

Step 1: Test the statements about zero order Option (A) is true because the zero-order rate law contains no concentration term. Option (B) is also true: at fixed initial concentration, $t_{1/2} = [A]_0/(2k)$, so the half-life is inversely proportional to k.

Step 2: Distinguish molecularity from order Option (C) is false. An elementary reaction requires at least one reacting species; hence its molecularity is at least one. It is reaction order, an experimentally determined sum of rate-law powers, that may be zero. Option (D) is true because a first-order reaction has $t_{1/2} = \ln 2/k = 0.693/k$.

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

Quick Tip to Solve: Do not confuse zero order with zero molecularity: order comes from the rate law, whereas molecularity counts reacting species.

16. 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:

- Reduction lowers oxidation number by electron gain. The charge for one mole of electrons is one faraday, F.
- Faraday's relation is $Q = n_e F$, where n_e is the amount of electrons transferred in moles.

Step 1: Find the oxidation-state change In MnO_4^-, let the manganese oxidation number be x: $x + 4(-2) = -1$, so $x = +7$. In MnO_2, $x + 2(-2) = 0$, so $x = +4$. Each manganese atom therefore

Quick Tip to Solve: Count the change in manganese oxidation number for the stated product; the familiar five-electron change applies to Mn^{2+}, not MnO_2.

gains three electrons.

Step 2: Convert electron transfer to charge For one mole of MnO_4^-, three moles of electrons are needed. Thus

$$Q = (3\,\text{mol})F = 3F$$

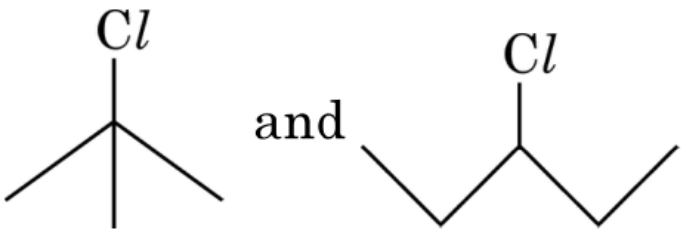
when F is expressed as charge per mole of electrons. Option (A) allows only one electron per ion; options (C) and (D) allow five and six, respectively. None matches reduction from $+7$ to $+4$.

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

Quick Tip to Solve: Count the change in manganese oxidation number for the stated product; the familiar five-electron change applies to Mn^{2+}, not MnO_2.

Section B (10 marks)

17(a). In the following pair of halogen compounds, which compound undergoes S_N1 reaction faster and why? [1 mark]



Solution:

Concept:

- An S_N1 reaction proceeds through carbocation formation in its slow, rate-determining step.
- For simple alkyl carbocations, stability follows tertiary $>$ secondary $>$ primary, owing to the electron-releasing inductive effect and hyperconjugation.

Step 1: Identify the two substrates The left structure is 2-chloro-2-methylpropane, $(CH_3)_3CCl$, a tertiary halide. The right structure is 3-chloropentane, $CH_3CH_2CHClCH_2CH_3$, a secondary halide.

Step 2: Compare carbocation formation Loss of Cl^- from the left compound gives a tertiary carbocation, whereas the right compound gives a secondary carbocation. The three alkyl groups stabilise the tertiary carbocation more effectively, so its formation has a lower activation barrier under comparable S_N1 conditions.

Step 3: Conclusion 2-Chloro-2-methylpropane (the left compound) undergoes S_N1 faster because it forms the more stable tertiary carbocation.

Quick Tip to Solve: For this pair, classify the carbon bonded to chlorine; faster S_N1 ionisation follows the more stable carbocation.

17(b). Arrange the following compounds in increasing order of their reactivity towards S_N2 displacement:

2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane. [1 mark]

Solution:

Concept:

- An S_N2 displacement occurs in one step by backside attack of the nucleophile at the carbon bearing the leaving group.
- With the same leaving group and comparable conditions, steric hindrance gives the reactivity order primary $>$ secondary $>$ tertiary.

Step 1: Classify the carbon bearing bromine 2-Bromo-2-methylbutane is a tertiary bromoalkane, 2-bromopentane is secondary, and 1-bromopentane is primary. All three contain the same leaving group, Br^-, so accessibility of the reacting carbon controls the comparison.

Step 2: Compare access for backside attack The tertiary carbon is shielded by three alkyl groups, making S_N2 attack extremely difficult. The secondary carbon is less crowded, and the primary carbon is most accessible to the approaching nucleophile. Consequently, increasing crowding decreases the displacement rate.

Step 3: Conclusion The increasing order is: 2-bromo-2-methylbutane $<$ 2-bromopentane $<$ 1-bromopentane.

Quick Tip to Solve: For S_N2, count alkyl groups attached directly to the carbon bearing bromine; fewer groups give faster backside attack.

18. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half? [2 marks]

Solution:

Concept:

- Second order with respect to a reactant means that its concentration enters the rate law with power two: $r = k[A]^2$, with other concentration factors held constant.
- At unchanged temperature and other conditions, the rate constant k is unchanged. Therefore $r_2/r_1 = ([A]_2/[A]_1)^2$.

Step 1: Write the initial rate Let the initial concentration of the reactant be a and the initial rate be r_1. Keeping any other reactant concentrations fixed, we can write

$$r_1 = ka^2.$$

The requested change is found by substituting the new concentration into this same rate law, not by changing the rate constant.

Quick Tip to Solve: For an order n, multiply concentration by f and rate by f^n; here square both multipliers, 2 and $1/2$.

Step 2: Double the concentration For part (i), the new concentration is $2a$. Hence

$$r_2 = k(2a)^2 = 4ka^2 = 4r_1.$$

Squaring the concentration multiplier is essential because the order with respect to this reactant is two.

Step 3: Reduce the concentration to half For part (ii), the new concentration is $a/2$. Thus

$$r_3 = k\left(\frac{a}{2}\right)^2 = \frac{ka^2}{4} = \frac{r_1}{4}.$$

Halving the concentration therefore reduces the rate to a quarter of its initial value, provided all other conditions remain the same.

Step 4: Conclusion (i) The rate becomes four times the initial rate. (ii) The rate becomes one-fourth of the initial rate.

Quick Tip to Solve: For an order n, multiply concentration by f and rate by f^n; here square both multipliers, 2 and $1/2$.

19. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured (C). An acidified solution of compound (C) oxidises Na_2SO_3 to (D). Identify (A), (B), (C) and (D). [2 marks]

Solution:

Concept:

- Alkaline oxidation of chromite produces yellow chromate; acidification converts chromate into orange dichromate.
- Acidified dichromate is an oxidising agent: it oxidises sulfite, SO_3^{2-}, to sulfate, SO_4^{2-}, while chromium(VI) is reduced to chromium(III).

Step 1: Identify the yellow fusion product Fusion of chromite with sodium carbonate in air gives sodium chromate, so (A) is Na_2CrO_4. The balanced reaction is

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \longrightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2.$$

Step 2: Identify the two dichromates Acidification converts chromate ions to dichromate ions:

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

Thus (B) is sodium dichromate, $Na_2Cr_2O_7$. Adding potassium chloride gives the less soluble potassium dichromate, which crystallises as orange crystals:

$$Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl.$$

Quick Tip to Solve: Follow the colour change from yellow chromate to orange dichromate, then remember that an oxidant adds oxygen to sulfite to form sulfate.

Hence (C) is $K_2Cr_2O_7$.

Step 3: Identify the oxidation product of sulfite Sulfur changes from oxidation number $+4$ in sulfite to $+6$ in sulfate. The ionic reaction in acidic medium is

$$Cr_2O_7^{2-} + 3\,SO_3^{2-} + 8\,H^+ \longrightarrow 2\,Cr^{3+} + 3\,SO_4^{2-} + 4\,H_2O.$$

The sodium salt corresponding to the sulfate product is sodium sulfate, so (D) is Na_2SO_4.

Step 4: Conclusion (A) Na_2CrO_4, sodium chromate; (B) $Na_2Cr_2O_7$, sodium dichromate; (C) $K_2Cr_2O_7$, potassium dichromate; (D) Na_2SO_4, sodium sulfate.

Quick Tip to Solve: Follow the colour change from yellow chromate to orange dichromate, then remember that an oxidant adds oxygen to sulfite to form sulfate.

20. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex. [At. No. Co = 27, Ni = 28] [2 marks]

Solution:

Concept:

- In valence bond theory, an octahedral complex uses six hybrid orbitals to accept six ligand lone pairs. Inner orbital complexes use two $3d$ orbitals in d^2sp^3 hybridisation; outer orbital complexes use two $4d$ orbitals in sp^3d^2 hybridisation.
- Find the metal-ion configuration by removing $4s$ electrons before $3d$ electrons. Two vacant $3d$ orbitals are necessary for an inner orbital octahedral complex.

Step 1: Examine the cobalt(III) ion Since NH_3 is neutral, cobalt is in oxidation state $+3$ in $[Co(NH_3)_6]^{3+}$. Neutral cobalt has configuration $[Ar]3d^74s^2$, so Co^{3+} is $[Ar]3d^6$. In this complex, the six $3d$ electrons pair in three orbitals, leaving two $3d$ orbitals vacant. These combine with one $4s$ and three $4p$ orbitals to form six d^2sp^3 hybrid orbitals.

Step 2: Examine the nickel(II) ion Nickel is in oxidation state $+2$ in $[Ni(NH_3)_6]^{2+}$. Neutral nickel is $[Ar]3d^84s^2$, so Ni^{2+} is $[Ar]3d^8$. Eight electrons occupy at least four of the five $3d$ orbitals even if pairing occurs; two vacant $3d$ orbitals cannot be obtained. Consequently, the six acceptor orbitals are formed from one $4s$, three $4p$ and two outer $4d$ orbitals, giving sp^3d^2 hybridisation.

Step 3: Conclusion $[Co(NH_3)_6]^{3+}$ is an inner orbital complex with d^2sp^3 hybridisation, whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex with sp^3d^2 hybridisation.

Quick Tip to Solve: First count the metal ion's d electrons: a d^8 ion cannot provide the two empty inner d orbitals needed for octahedral d^2sp^3 hybridisation.

21(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 rate of disappearance of reactant is constant: $-d[A]/dt = k$, where k is the zero order rate constant and $[A]$ is the reactant concentration.
- The integrated rate equation is $[A]_t = [A]_0 - kt$, where $[A]_0$ and $[A]_t$ are the concentrations initially and after time t. Thus the time is the decrease in concentration divided by k.

Step 1: Identify the concentration decrease Both given molar concentrations are in mol L^{-1}, consistent with the units of the rate constant. The amount consumed per litre is

$$[A]_0 - [A]_t = 0.10 - 0.075 = 0.025\,\text{mol L}^{-1}.$$

Use this decrease, rather than the concentration remaining, because kt represents the concentration consumed.

Step 2: Apply the zero order integrated rate equation Rearrange the integrated law and substitute the data:

$$t = \frac{[A]_0 - [A]_t}{k} = \frac{0.025\,\text{mol L}^{-1}}{0.0030\,\text{mol L}^{-1}\text{s}^{-1}} = 8.33\,\text{s}.$$

The concentration units cancel and leave seconds. A logarithm is not used here because the reaction is zero order, so equal amounts of reactant are consumed in equal time intervals.

Step 3: Conclusion The time required for the concentration to fall to $0.075\,\text{M}$ is approximately $8.3\,\text{s}$.

Quick Tip to Solve: For a zero order reaction, calculate the concentration lost first and divide by k; do not use the first order logarithmic formula.

OR

21(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 rate of reaction is $r = k[A]^0 = k$; it does not depend on the reactant concentration under the stated conditions.
- A reaction rate is normalised by the stoichiometric coefficients. For $2\,NH_3 \longrightarrow N_2 + 3\,H_2$, the rates obey $r = -\frac{1}{2}d[NH_3]/dt = d[N_2]/dt = \frac{1}{3}d[H_2]/dt$.

Step 1: Write the balanced decomposition equation The decomposition of ammonia on platinum is represented by

$$2\,NH_3 \xrightarrow{Pt} N_2 + 3\,H_2.$$

Hence formation of one mole of nitrogen accompanies formation of three moles of hydrogen. The

Quick Tip to Solve: Balance ammonia decomposition first: the product coefficients 1 and 3 convert the zero order reaction rate k into the nitrogen and hydrogen formation rates.

product formation rates must therefore have the ratio $1:3$; they cannot both equal the same numerical rate.

Step 2: Relate each production rate to the rate constant Since the order is zero, the reaction rate is $r = k = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$. Multiplying by the coefficient of each product gives

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

Both signs are positive because these species are produced. The coefficient two belongs to ammonia consumption and does not multiply the nitrogen production rate.

Step 3: Conclusion The rates of production of N_2 and H_2 are respectively 2.5×10^{-4} and $7.5 \times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$.

Quick Tip to Solve: Balance ammonia decomposition first: the product coefficients 1 and 3 convert the zero order reaction rate k into the nitrogen and hydrogen formation rates.

Section C (21 marks)

22. A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. [3 marks]

Solution:

Concept:

- The osmotic pressure of a dilute solution is $\pi = iCRT = i(n/V)RT$, where i is the van't Hoff factor, C the molar concentration, n the moles of solute, V the solution volume, R the gas constant and T the absolute temperature.
- Isotonic solutions have equal osmotic pressures at the same temperature. Urea, $\text{CO(NH}_2)_2$, and glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, are non-electrolytes in water, so each has $i = 1$. Equal osmotic pressure therefore requires equal molar concentrations.

Step 1: Calculate the molarity of the urea solution The number of moles in the stated $1\,\text{L}$ of solution is found by dividing the urea mass by its molar mass:

$$n_{\text{urea}} = \frac{15\,\text{g}}{60\,\text{g mol}^{-1}} = 0.25\,\text{mol}.$$

Hence $C_{\text{urea}} = 0.25\,\text{mol L}^{-1}$. The volume given is already the volume of solution, so no density or solvent-volume conversion is required.

Step 2: Use the condition of equal osmotic pressures At the same temperature, equating the osmotic pressures gives

$$C_{\text{urea}}RT = C_{\text{glucose}}RT \quad \Rightarrow \quad C_{\text{glucose}} = 0.25\,\text{mol L}^{-1}.$$

Quick Tip to Solve: For isotonic non-electrolyte solutions with equal volumes, set $m_1/M_1 = m_2/M_2$; here multiply the urea mass by $180/60 = 3$.

Thus one litre of the glucose solution must also contain $0.25\,\text{mol}$ of solute. Equal masses are not required, since osmotic pressure depends on the number of dissolved particles rather than their individual masses.

Step 3: Convert the glucose amount into mass Multiply the required moles by the molar mass of glucose:

$$m_{\text{glucose}} = n_{\text{glucose}} M_{\text{glucose}} = (0.25\,\text{mol})(180\,\text{g mol}^{-1}) = 45\,\text{g}.$$

The molar mass of glucose is three times that of urea, so three times as much mass is needed for the same number of solute molecules in an equal solution volume.

Step 4: Conclusion One litre of the isotonic glucose solution contains $45\,\text{g}$ of glucose.

Quick Tip to Solve: For isotonic non-electrolyte solutions with equal volumes, set $m_1/M_1 = m_2/M_2$; here multiply the urea mass by $180/60 = 3$.

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23. Calculate Λ°_m for acetic acid and its degree of dissociation (α) if its molar conductivity is 48.1 Ω^{-1} cm^2 mol^{-1}.

Given that:

Λ°_m (HCl) = 426 Ω^{-1} cm^2 mol^{-1}

Λ°_m (NaCl) = 126 Ω^{-1} cm^2 mol^{-1}

Λ°_m (CH_3COONa) = 91 Ω^{-1} cm^2 mol^{-1} [3 marks]

Solution:

Concept:

- Kohlrausch's law states that the limiting molar conductivity of an electrolyte is the sum of the independent limiting ionic contributions, with stoichiometric coefficients included.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda^\circ_m$, where Λ_m is its molar conductivity at the given concentration and Λ°_m is its limiting value.

Step 1: Isolate the ionic contributions of acetic acid Acetic acid dissociates into H^+ and CH_3COO^-. Combine the strong-electrolyte data so that the unwanted sodium and chloride contributions cancel:

$$\begin{aligned}
\Lambda^\circ_m(\text{HCl}) &= \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{Cl}^-),\\
\Lambda^\circ_m(\text{CH}_3\text{COONa}) &= \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{Na}^+),\\
\Lambda^\circ_m(\text{NaCl}) &= \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-).
\end{aligned}$$

Thus, add the first two conductivities and subtract the third. This obtains the limiting value without extrapolating the conductivity of the weak acid directly.

Step 2: Substitute the limiting conductivities

$$\begin{aligned}
\Lambda^\circ_m(\text{CH}_3\text{COOH}) &= \Lambda^\circ_m(\text{HCl}) + \Lambda^\circ_m(\text{CH}_3\text{COONa}) - \Lambda^\circ_m(\text{NaCl})\\
&= 426 + 91 - 126\\
&= 391\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}.
\end{aligned}$$

Quick Tip to Solve: For a weak acid, add its sodium salt to a strong acid with the same hydrogen ion, subtract the common sodium salt, then divide the measured conductivity by this limiting value.

All three given values use the same conductivity units, so no unit conversion is required.

Step 3: Calculate the dissociated fraction Use the measured value $48.1\,\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$:

$$\alpha = \frac{48.1}{391} = 0.1230, \qquad 100\alpha = 12.30\%.$$

The units cancel in the ratio. Its value lies between zero and one, as a dissociated fraction must, and indicates that the acid is only partly ionised at the given concentration.

Step 4: Conclusion The limiting molar conductivity of acetic acid is $391\,\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$, and its degree of dissociation is $\alpha \approx 0.123$, or 12.3%.

Quick Tip to Solve: For a weak acid, add its sodium salt to a strong acid with the same hydrogen ion, subtract the common sodium salt, then divide the measured conductivity by this limiting value.

24. (a) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising. Why?
(b) Write two consequences of lanthanoid contraction.
(c) Which element of 3d series has lowest enthalpy of atomisation and why? [3 marks]

Solution:

Concept:

- A reducing agent loses electrons and is oxidised; an oxidising agent accepts electrons and is reduced. The stability of the resulting electronic configuration helps explain the direction of these changes.
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoids, caused by the poor shielding of nuclear charge by $4f$ electrons.
- Enthalpy of atomisation measures the energy needed to form gaseous atoms from the element. Stronger metallic bonding gives a larger value.

Step 1: Explain the opposite behaviour of the two d-four ions **(a)** Both Cr^{2+} and Mn^{3+} have the $3d^4$ configuration, but their accessible stable products differ. Chromium(II) readily loses an electron:

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

The resulting Cr^{3+} has a stable $3d^3$ configuration, with a half-filled lower t_{2g} set in an octahedral environment. Therefore Cr^{2+} acts as a strong reducing agent. In contrast, manganese(III) readily accepts an electron:

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

The resulting Mn^{2+} has the especially stable half-filled $3d^5$ configuration. Thus Mn^{3+} is a strong oxidising agent.

Step 2: State two consequences of lanthanoid contraction **(b)** First, the elements of the second and third transition series have nearly equal radii in corresponding groups; for example, Zr and Hf have very similar sizes and hence closely similar chemical properties. Second, the basic strength of lanthanoid hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. As the Ln^{3+} ion becomes smaller, its

Quick Tip to Solve: For a redox comparison, write the configuration after losing or gaining one electron; the same initial d-electron count need not imply the same redox behaviour.

polarising power increases, the metal–oxygen bond becomes less ionic, and the hydroxide becomes less basic.

Step 3: Identify the weakest metallic bonding in the series **(c)** Zinc has the lowest enthalpy of atomisation in the $3d$ series. Its configuration is $[\mathrm{Ar}]\,3d^{10}4s^2$, with a completely filled $3d$ subshell and no unpaired electrons. Compared with the other members, it has weak metallic bonding, so less energy is needed to separate the solid into gaseous atoms.

Step 4: Conclusion **(a)** Cr^{2+} is oxidised to stable d^3 Cr^{3+}, whereas Mn^{3+} is reduced to stable d^5 Mn^{2+}. **(b)** Lanthanoid contraction produces nearly equal Zr/Hf radii and decreasing hydroxide basicity. **(c)** Zinc has the lowest atomisation enthalpy because its metallic bonding is weak.

Quick Tip to Solve: For a redox comparison, write the configuration after losing or gaining one electron; the same initial d-electron count need not imply the same redox behaviour.

25. Write IUPAC names of the following coordination entities:

(a) $[Fe(en)_2Cl_2]^+$

(b) $[Co(NH_3)_4(H_2O)Br]SO_4$

(c) $[Ni(CN)_4]^{2-}$ [3 marks]

Solution:

Concept:

- In a coordination name, name the ligands in alphabetical order before the central metal. Ignore numerical prefixes such as di-, tetra- and bis- when alphabetising.
- Find the oxidation state of the metal from the total charge of the complex and the charges on the ligands; write it as a Roman numeral in parentheses.
- An anionic coordination entity takes a metal name ending in -ate. Neutral ligands NH_3, H_2O and ethane-1,2-diamine are called ammine, aqua and ethane-1,2-diamine respectively.

Step 1: Name the iron complex **(a)** In $[Fe(en)_2Cl_2]^+$, each ethane-1,2-diamine ligand (en) is neutral and each chlorido ligand has charge -1. If the iron oxidation state is x,

$$x + 2(0) + 2(-1) = +1 \quad \Rightarrow \quad x = +3.$$

Chlorido comes before ethane-1,2-diamine alphabetically. Use bis for the two ligands whose name already contains a numerical component. Since the entity is cationic, retain the name iron. Its name is **dichloridobis(ethane-1,2-diamine)iron(III) ion**.

Step 2: Name the cobalt salt **(b)** In $[Co(NH_3)_4(H_2O)Br]SO_4$, the sulphate ion is SO_4^{2-}, so the coordination entity must have charge $+2$. Ammine and aqua are neutral, while bromido has charge -1:

$$x + 4(0) + 0 - 1 = +2 \quad \Rightarrow \quad x = +3.$$

The alphabetical ligand order is ammine, aqua, bromido. Name the cation first and the sulphate anion second: **tetraammineaquabromidocobalt(III) sulphate**.

Quick Tip to Solve: Determine the complex charge before the oxidation state: the sulphate outside the cobalt brackets makes that complex a cation of charge $+2$, despite the bromido ligand inside.

Step 3: Name the nickel anion **(c)** Each cyanido ligand in $[Ni(CN)_4]^{2-}$ has charge -1. Hence,

$$x + 4(-1) = -2 \quad \Rightarrow \quad x = +2.$$

Four cyanido ligands give tetracyanido. Since the entity is an anion, nickel becomes nickelate. The name is **tetracyanidonickelate(II) ion**.

Step 4: Conclusion **(a)** Dichloridobis(ethane-1,2-diamine)iron(III) ion.

(b) Tetraammineaquabromidocobalt(III) sulphate.

(c) Tetracyanidonickelate(II) ion.

Quick Tip to Solve: Determine the complex charge before the oxidation state: the sulphate outside the cobalt brackets makes that complex a cation of charge $+2$, despite the bromido ligand inside.

26(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 by removing the oxygen atom and adding hydrogen.
- The carbonyl compound first reacts with hydrazine, NH_2NH_2, to form a hydrazone. Heating with KOH in a high-boiling solvent such as ethylene glycol gives the hydrocarbon.

Step 1: Form the hydrazone The carbonyl compound condenses with hydrazine, eliminating water. For a ketone, the reaction is

$$R_2C{=}O + H_2NNH_2 \longrightarrow R_2C{=}NNH_2 + H_2O.$$

The two R groups remain attached to the same carbon throughout the reduction.

Step 2: Heat the hydrazone under basic conditions On heating the hydrazone with KOH in ethylene glycol, nitrogen is evolved and the carbonyl carbon becomes a methylene carbon:

$$R_2C{=}NNH_2 \xrightarrow[\Delta]{\text{KOH, ethylene glycol}} R_2CH_2 + N_2.$$

Thus a ketone gives the corresponding hydrocarbon; an aldehyde RCHO similarly gives RCH_3.

Step 3: Conclusion Wolff–Kishner reduction is the conversion $R_2C{=}O \longrightarrow R_2CH_2$ using hydrazine followed by KOH and heat in ethylene glycol, with evolution of N_2.

Quick Tip to Solve: Associate Wolff–Kishner with hydrazine and hot base: replace only the carbonyl oxygen by two hydrogens, preserving the carbon skeleton.

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

Etard reaction [1 mark]

Solution:

Concept:

- The Etard reaction selectively oxidises the methyl side chain of an aromatic hydrocarbon to an aldehyde.
- Chromyl chloride, CrO_2Cl_2, first forms a complex in a nonaqueous solvent; hydrolysis releases the aldehyde.

Step 1: Form the Etard complex Treat toluene with chromyl chloride in carbon disulphide (CS_2). The benzylic methyl group is oxidised through formation of the Etard complex.

Step 2: Hydrolyse the complex Hydrolysis gives benzaldehyde. The overall organic transformation is

$$C_6H_5CH_3 \xrightarrow[\text{2. hydrolysis}]{\text{1. } CrO_2Cl_2/CS_2} C_6H_5CHO.$$

This controlled oxidation retains the aromatic ring and stops at the aldehyde stage.

Step 3: Conclusion Etard oxidation converts toluene into benzaldehyde using chromyl chloride followed by hydrolysis.

Quick Tip to Solve: Associate Etard with chromyl chloride: the benzylic $-CH_3$ becomes $-CHO$, not $-COOH$.

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

Cannizzaro reaction [1 mark]

Solution:

Concept:

- Aldehydes having no α-hydrogen undergo the Cannizzaro reaction with concentrated alkali.
- It is a disproportionation: one aldehyde molecule is reduced to an alcohol while another is oxidised to a carboxylate salt.

Step 1: Select a suitable aldehyde Benzaldehyde, C_6H_5CHO, has no α-hydrogen and therefore undergoes Cannizzaro reaction on treatment with concentrated aqueous sodium hydroxide.

Step 2: Write the balanced reaction Two molecules of benzaldehyde give one molecule each of benzyl alcohol and sodium benzoate:

$$2C_6H_5CHO + NaOH \xrightarrow{\text{concentrated alkali}} C_6H_5CH_2OH + C_6H_5COONa.$$

The acid product remains as its salt in the strongly basic reaction mixture.

Step 3: Conclusion Cannizzaro reaction is the self-oxidation and self-reduction of an aldehyde lacking α-hydrogen in concentrated alkali, yielding an alcohol and a carboxylate salt.

Quick Tip to Solve: Check for the absence of α-hydrogen first; concentrated alkali then suggests Cannizzaro rather than aldol reaction.

OR

26(B). Write the structures of A, B and C in the following sequence of reactions: [3 marks]

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

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

Solution:

Concept:

- Thionyl chloride converts a carboxylic acid into an acyl chloride; Rosenmund reduction converts an acyl chloride into an aldehyde using $H_2/Pd{-}BaSO_4$.
- An aldehyde condenses with hydrazine to give a hydrazone. DIBAL-H partially reduces a nitrile, yielding an aldehyde on hydrolysis.
- Aldehydes containing α-hydrogen undergo aldol addition with dilute base. Heating the aldol removes water and forms an α,β-unsaturated aldehyde.

Step 1: Sequence (a): form A and reduce it to B Ethanoic acid reacts with thionyl chloride to give ethanoyl chloride, A:

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

Catalytic hydrogenation with palladium supported on barium sulphate stops at ethanal, B:

$$CH_3COCl + H_2 \xrightarrow{Pd-BaSO_4} CH_3CHO + HCl.$$

Step 2: Sequence (a): identify the hydrazine product C Ethanal condenses with hydrazine, replacing the carbonyl oxygen with $=N{-}NH_2$ and eliminating water:

$$CH_3CHO + H_2N{-}NH_2 \longrightarrow CH_3CH{=}N{-}NH_2 + H_2O.$$

C is ethanal hydrazone. Hydrazine alone does not imply Wolff–Kishner reduction: that reduction also needs strong base and heating.

Step 3: Sequence (b): obtain A and perform aldol addition Partial reduction of ethanenitrile by DIBAL-H, followed by hydrolysis, gives ethanal, A:

$$CH_3CN \xrightarrow[2.\ H_2O]{1.\ DIBAL\text{-}H} CH_3CHO.$$

Ethanal has α-hydrogen. Two molecules combine in dilute sodium hydroxide to form 3-hydroxybutanal, B:

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

Step 4: Sequence (b): dehydrate B on heating Heating removes the hydroxyl group at the β-carbon

Quick Tip to Solve: Read every reagent: hydrazine alone gives a hydrazone; dilute NaOH gives an aldol, and the separate heating step dehydrates it.

and a hydrogen at the α-carbon as water:

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

The resulting conjugated aldehyde C is but-2-enal (crotonaldehyde).

Step 5: Conclusion In (a): A $= CH_3COCl$, B $= CH_3CHO$, C $= CH_3CH{=}N{-}NH_2$.
In (b): A $= CH_3CHO$, B $= CH_3CH(OH)CH_2CHO$, C $= CH_3CH{=}CHCHO$.

Quick Tip to Solve: Read every reagent: hydrazine alone gives a hydrazone; dilute NaOH gives an aldol, and the separate heating step dehydrates it.

27(a). Define the following:

(i) Enantiomers

(ii) Racemic mixture [2 marks]

Solution:

Concept:

- Chirality is the property of a molecule whose mirror image cannot be superimposed on it. Enantiomers are related through this mirror-image relationship.
- Optical rotation is the rotation of plane-polarised light. The two enantiomers rotate it equally in opposite directions under identical conditions.

Step 1: Define enantiomers Enantiomers are stereoisomers that are non-superimposable mirror images of each other. Their atomic connectivity is identical, but their three-dimensional arrangements differ. A chiral molecule and its mirror image form such a pair; one is dextrorotatory $(+)$ and the other is laevorotatory $(-)$, with equal magnitudes of specific rotation under the same conditions.

Step 2: Define a racemic mixture A racemic mixture is an equimolar mixture of the two enantiomers of a compound, containing equal amounts of the $(+)$ and $(-)$ forms. Their equal and opposite rotations cancel, so the mixture is optically inactive. This cancellation is external compensation between different molecules; each enantiomer remains chiral. A racemic mixture is often represented by $(\pm)$.

Step 3: Conclusion (i) Enantiomers are non-superimposable mirror-image stereoisomers. (ii) A racemic mixture contains the two enantiomers in a $1:1$ ratio and has zero net optical rotation.

Quick Tip to Solve: Include both essential phrases: non-superimposable mirror images for enantiomers, and an equimolar mixture for a racemate.

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

Solution:

Concept:

- Resonance can give a carbon–halogen bond partial double-bond character, making its cleavage difficult.
- A bond from an sp^2-hybridised carbon is shorter and stronger than the corresponding bond from an sp^3-hybridised carbon.

Step 1: Examine resonance in chlorobenzene A lone pair on chlorine overlaps with the aromatic π-system. Delocalisation gives the $\mathrm{C-Cl}$ bond partial double-bond character, so this bond is stronger and harder to break than the bond in a chloroalkane.

Step 2: Relate bond strength to substitution Chlorine is also bonded directly to an sp^2-hybridised ring carbon, making the $\mathrm{C-Cl}$ bond shorter and stronger. Consequently, displacement of chloride by a nucleophile is difficult under ordinary conditions.

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

Quick Tip to Solve: For an aryl halide, link chlorine's lone-pair delocalisation to partial double-bond character and difficult bond cleavage.

28. (a) Write the product obtained when D-glucose reacts with H_2N-OH.

(b) Amino acids show amphoteric behaviour, why?

(c) Why vitamin C cannot be stored in our body? [3 marks]

Solution:

Concept:

- Hydroxylamine, NH_2OH, condenses with the aldehyde group of open-chain glucose to form an oxime with elimination of water.
- An amino acid contains an acidic carboxyl group, $-\mathrm{COOH}$, and a basic amino group, $-\mathrm{NH_2}$; it can both donate and accept a proton.
- Vitamin C is a water-soluble vitamin. Excess amounts are removed from the body in urine, so it must be supplied regularly in the diet.

Step 1: (a) Form the glucose oxime The small proportion of D-glucose present in its open-chain form contains a terminal aldehyde group. Reaction at this group replaces its carbonyl oxygen by $=\mathrm{N-OH}$; the remaining carbon chain is unchanged:

$$\mathrm{HOCH_2(CHOH)_4CHO + NH_2OH \longrightarrow HOCH_2(CHOH)_4CH{=}NOH + H_2O.}$$

The product is D-glucose oxime. Formation of this derivative is evidence for a carbonyl group in the open-chain form of glucose.

Step 2: (b) Explain the amphoteric character In aqueous solution an amino acid largely exists as

Quick Tip to Solve: For glucose derivatives, change only the aldehyde group: hydroxylamine converts $-\mathrm{CHO}$ to $-\mathrm{CH{=}NOH}$.

the zwitterion $H_3N^+CHRCOO^-$. With an acid its carboxylate group accepts a proton; with a base its ammonium group loses a proton:

$$H_3N^+CHRCOO^- + H^+ \longrightarrow H_3N^+CHRCOOH$$

$$H_3N^+CHRCOO^- + OH^- \longrightarrow H_2NCHRCOO^- + H_2O.$$

Thus it reacts with both acids and bases, which is amphoteric behaviour.

Step 3: (c) Relate storage to water solubility Vitamin C dissolves in the body's aqueous fluids and excess vitamin is readily excreted in urine. Unlike fat-soluble vitamins, it does not accumulate as a substantial body store; a regular dietary supply is therefore necessary.

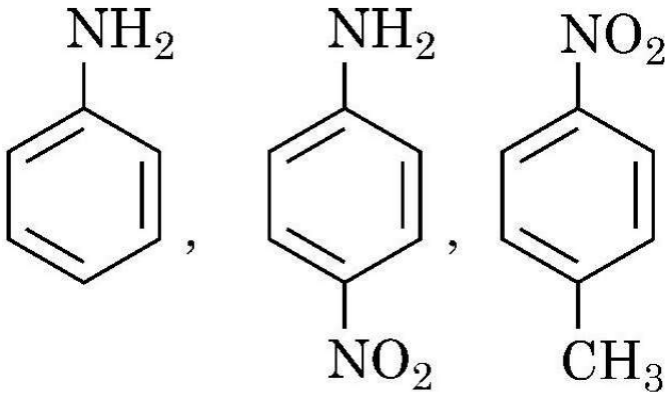
Step 4: Conclusion (a) D-glucose oxime is formed. (b) Amino acids have both acidic and basic groups and react with acids as well as bases. (c) Vitamin C is water-soluble and its excess is excreted in urine.

Quick Tip to Solve: For glucose derivatives, change only the aldehyde group: hydroxylamine converts $-CHO$ to $-CH=NOH$.

Section D (8 marks)

29. 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. [4 marks]

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



Solution:

Concept:

- Basic character depends on the availability of an electron pair for accepting a proton. An amino nitrogen has an available lone pair, whereas nitro nitrogen does not behave as an amine nitrogen.
- The para nitro group withdraws electrons by both inductive and resonance effects, decreasing the availability of the amino nitrogen lone pair.

Step 1: Identify all three printed structures From left to right the structures are aniline, para-nitroaniline and para-nitrotoluene. The third compound contains $-NO_2$ and $-CH_3$, and has no $-NH_2$ group. Its nitro group is only a very weak proton acceptor at oxygen; it cannot be treated as an amino group with an available nitrogen lone pair.

Step 2: Compare the electron-pair availability Aniline can accept a proton at its amino nitrogen. In para-nitroaniline, the strongly electron-withdrawing para $-NO_2$ group draws electron density away through the ring as well as by its inductive effect. This makes the amino lone pair less available than in aniline. Para-nitrotoluene lacks the amino basic centre entirely and is much less basic than either amino compound; its methyl group does not compensate for the absence of that centre.

Quick Tip to Solve: Identify the substituent itself before comparing its effect: the third printed ring has $-NO_2$, not $-NH_2$.

Step 3: Conclusion The increasing order of basic character is

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

Quick Tip to Solve: Identify the substituent itself before comparing its effect: the third printed ring has $-NO_2$, not $-NH_2$.

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

Solution:

Concept:

- For a base, $pK_b = -\log K_b$; a weaker base therefore has a larger pK_b.
- Resonance can reduce the availability of the nitrogen lone pair, whereas an alkyl group increases nitrogen electron density by its positive inductive effect.

Step 1: Examine the lone pair in aniline In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is consequently less available for accepting a proton.

Step 2: Compare methylamine In methylamine, CH_3NH_2, the lone pair is localised on nitrogen and the methyl group supplies electron density by its $+I$ effect. Methylamine accepts a proton more readily and has the larger K_b.

Step 3: Conclusion Aniline is the weaker base, so $pK_b(\text{aniline}) > pK_b(\text{methylamine})$.

Quick Tip to Solve: First compare lone-pair availability, then reverse the basic-strength order when writing the pK_b order.

29(c)(i). 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, basicity depends jointly on the electron-releasing effect of methyl groups and hydration of the conjugate ammonium ion.
- Methyl groups increase electron density, but extensive substitution reduces effective hydration of the protonated base.

Step 1: Compare ammonia with methylamines All three methylamines receive electron density from their methyl groups and are stronger bases than NH_3 in aqueous solution. Ammonia is therefore placed first in increasing basic strength.

Step 2: Include hydration in the comparison The trimethylammonium ion is less effectively hydrated than the less substituted ions. Hence trimethylamine is weaker than methylamine in water, while dimethylamine has the most favourable balance of electron donation and hydration among these

Quick Tip to Solve: For methylamines in water, remember secondary greater than primary greater than tertiary greater than ammonia.

bases.

Step 3: Conclusion

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

Quick Tip to Solve: For methylamines in water, remember secondary greater than primary greater than tertiary greater than ammonia.

OR

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

Solution:

Concept:

- Ammonia undergoes nucleophilic substitution with an alkyl halide to form a primary amine after loss of a proton.
- The amine product remains nucleophilic and can react further with the alkyl halide.

Step 1: Follow the successive alkylations The primary amine initially produced reacts with further alkyl halide to form a secondary amine. Further alkylation gives a tertiary amine and eventually a quaternary ammonium salt. Thus the reaction does not necessarily stop after one alkyl group is introduced.

Step 2: Explain the purity problem The resulting mixture contains different classes of amines and a quaternary ammonium salt, making isolation of one pure amine difficult. Excess ammonia favours the primary amine, but does not make unrestricted ammonolysis a generally selective preparation.

Step 3: Conclusion Ammonolysis gives a mixture of primary, secondary and tertiary amines together with a quaternary ammonium salt, so it is unsuitable for directly obtaining pure amines.

Quick Tip to Solve: When an amine synthesis leaves a nitrogen lone pair, check whether the product can undergo further alkylation.

30. 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. [4 marks]

30(a). Define reverse osmosis. Name one SPM which can be used in the process of reverse osmosis. [2 marks]

Solution:

Concept:

- A semipermeable membrane (SPM) permits solvent molecules to pass through it while retaining the dissolved solute particles.
- Osmotic pressure, π, is the minimum excess pressure applied on the solution side that just stops the net flow of solvent into the solution.

Step 1: Reverse the natural solvent flow In ordinary osmosis, solvent flows from the pure-solvent side, or the more dilute solution, into the more concentrated solution through the SPM. If an external pressure greater than the osmotic pressure is applied on the solution side, solvent is forced to flow in the opposite direction: from the solution through the membrane towards the pure-solvent side. This pressure-driven process is called reverse osmosis. Thus, the required condition is $P_{\text{applied}} > \pi$, not merely equality; at equality the net osmotic flow stops.

Step 2: Name a suitable membrane A cellulose acetate membrane supported over a suitable support can be used as the SPM. It allows water to pass while retaining dissolved salts; the support helps the thin membrane withstand the applied pressure. This is the basis of obtaining fresh water from saline water by reverse osmosis.

Step 3: Conclusion Reverse osmosis is the flow of solvent from a solution towards the pure solvent through an SPM when the pressure applied on the solution exceeds its osmotic pressure. One suitable SPM is a supported cellulose acetate membrane.

Quick Tip to Solve: State both the reversed flow direction and the condition $P_{\text{applied}} > \pi$; name cellulose acetate as the membrane.

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

Solution:

Concept:

- The membrane of a red blood corpuscle is semipermeable, so water moves across it by osmosis.
- A solution with a lower effective solute concentration than the cell contents is hypotonic to the

Quick Tip to Solve: Compare with 0.9% saline: a lower salt concentration causes water entry and swelling of RBCs.

cell; water enters the cell from such a solution.

Step 1: Compare the salt concentrations Approximately 0.9% NaCl solution is isotonic with red blood corpuscles. The given 0.5% NaCl solution is more dilute and therefore hypotonic to the corpuscles.

Step 2: Determine the direction of water movement Water moves from the dilute external solution into the more concentrated cell contents through the cell membrane by endosmosis. As water enters, the cell volume increases; excessive entry can rupture the membrane, causing haemolysis.

Step 3: Conclusion The RBCs swell in 0.5% NaCl solution and may burst because water enters them by osmosis.

Quick Tip to Solve: Compare with 0.9% saline: a lower salt concentration causes water entry and swelling of RBCs.

OR

30(b)(ii). 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 depends on the total concentration of solute particles: $\pi = iCRT$, where i is the van't Hoff factor, C the molar concentration, R the gas constant and T the absolute temperature.
- Dissociation increases the number of solute particles and hence the osmotic pressure at a given formula-unit concentration.

Step 1: Compare the particles produced Potassium chloride is an electrolyte and dissociates in water:

$$\mathrm{KCl} \longrightarrow \mathrm{K^+ + Cl^-}$$

It therefore produces approximately two ions per formula unit, giving $i \approx 2$. Urea, $\mathrm{CO(NH_2)_2}$, is a non-electrolyte and remains molecular, giving $i = 1$.

Step 2: Compare the osmotic pressures Both solutions have the same stated concentration, $C = 1\ \mathrm{mol\ L^{-1}}$. At a common temperature, the larger number of solute particles in the potassium chloride solution gives a greater value of iC. The ideal dissociation model predicts approximately twice the osmotic pressure of urea; exact real-solution values need not have this ratio.

Step 3: Conclusion The $1\ \mathrm{M}$ KCl solution has the higher osmotic pressure because it dissociates into ions, whereas urea does not.

Quick Tip to Solve: For solutions of equal molarity at the same temperature, compare their van't Hoff factors rather than their molar masses.

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

Solution:

Concept:

- A colligative property depends on the number of dissolved solute particles relative to the solvent, rather than the chemical identity of those particles.
- For a dilute solution, osmotic pressure obeys $\pi = (n_{\text{particles}}/V)RT$, where $n_{\text{particles}}$ is the amount of solute particles, V the solution volume, R the gas constant and T the absolute temperature.

Step 1: Identify the controlling quantity At a fixed temperature, the osmotic-pressure expression depends on the number of solute particles per unit volume. The identity or molar mass of the solute does not occur separately in this expression.

Step 2: Apply the definition of a colligative property Dilute solutions containing the same concentration of independently dissolved particles have the same osmotic pressure at the same temperature. If a solute dissociates, the additional ions must be counted; this changes the particle concentration, not the colligative nature of the property.

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

Quick Tip to Solve: Use $\pi = (n_{\text{particles}}/V)RT$ to show immediately that the relevant quantity is particle concentration.

Section E (15 marks)

31(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 molecular formula C_2H_6O permits ethanol and dimethyl ether, but ethanol has the alcohol group required for this oxidation sequence.
- Ethanal, CH_3CHO, gives the iodoform test with iodine and aqueous sodium hydroxide. The characteristic yellow precipitate is iodoform, CHI_3.
- Ethanol undergoes intermolecular dehydration with concentrated H_2SO_4 at $413\,K$ to form ethoxyethane. Excess hydrogen iodide cleaves this ether and converts the alcohol initially formed into an alkyl iodide.

Step 1: Identify the alcohol and its oxidation product Since compound A has molecular formula C_2H_6O, consider ethanol, CH_3CH_2OH, and dimethyl ether, CH_3OCH_3. The subsequent oxidation and

Quick Tip to Solve: Use the yellow iodoform precipitate to identify ethanal, then work backwards to ethanol. Remember that ethanol at $413\,K$ forms an ether, and excess HI converts both ethyl groups of that ether into iodoethane.

ether formation establish that A is ethanol. Its controlled oxidation with CrO_3 gives the two-carbon aldehyde ethanal, so B is CH_3CHO:

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

Here $[O]$ denotes an oxygen equivalent supplied by the oxidising agent. The positive iodoform test of B identifies the aldehyde stage of oxidation; further oxidation to ethanoic acid would not give that test.

Step 2: Write the iodoform reaction of ethanal On warming ethanal with iodine and aqueous sodium hydroxide, its methyl group becomes the yellow precipitate iodoform. The remaining carbon gives sodium methanoate. Thus C is triiodomethane (iodoform), CHI_3, and the balanced equation is

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

Both carbon atoms are accounted for: one appears in iodoform and one in the methanoate ion. This characteristic reaction confirms the identification of B as ethanal.

Step 3: Form the ether at the stated temperature At $413\,K$, concentrated sulphuric acid promotes intermolecular dehydration of two ethanol molecules. One water molecule is removed and an ether linkage is formed, giving D as ethoxyethane (diethyl ether), $C_2H_5OC_2H_5$:

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

The stated temperature is essential: ether formation at $413\,K$ is distinguished from the higher-temperature dehydration of ethanol to ethene.

Step 4: Cleave the ether with excess hydrogen iodide Hydrogen iodide first cleaves the protonated ether to give iodoethane and ethanol. Because HI is present in excess, this ethanol also reacts to form iodoethane:

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

Adding the two reactions gives the overall equation:

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

Thus E is iodoethane (ethyl iodide). The symmetric ether gives the same alkyl iodide from both ethyl groups.

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

Quick Tip to Solve: Use the yellow iodoform precipitate to identify ethanal, then work backwards to ethanol. Remember that ethanol at $413\,K$ forms an ether, and excess HI converts both ethyl groups of that ether into iodoethane.

OR

31(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:

- The $-OH$ group activates the benzene ring of phenol towards electrophilic substitution at its ortho and para positions.
- Hydroboration followed by alkaline peroxide oxidation hydrates an alkene with anti-Markovnikov orientation: the hydroxyl group goes to the less substituted carbon.
- Williamson synthesis forms an ether by nucleophilic substitution of an alkyl halide by an alkoxide ion. The iodoform test detects the $CH_3CH(OH)-$ unit in an alcohol.
- Greater stability of the conjugate base means greater acid strength; resonance stabilises phenoxide, whereas an electron-releasing ethyl group destabilises ethoxide.

Step 1: (a)(i) Nitrate phenol Concentrated nitric acid introduces nitro groups at both ortho positions and the para position of the activated ring:

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

The product is 2,4,6-trinitrophenol, commonly called picric acid. Dilute nitric acid would give mainly mononitration products, so the stated concentration matters.

Step 2: (a)(ii) Hydroborate and oxidise propene Boron adds to the terminal carbon during hydroboration. Oxidation replaces the carbon-boron bond by a carbon-oxygen bond, giving the primary alcohol:

$$CH_3CH{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3CH_2CH_2OH.$$

Thus the product is propan-1-ol; the hydroxyl group is attached to the terminal carbon, rather than to the middle carbon as in acid-catalysed hydration.

Step 3: (a)(iii) Carry out Williamson ether synthesis The tert-butoxide ion attacks the methyl carbon of methyl chloride by the S_N2 mechanism:

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

The ether is 2-methoxy-2-methylpropane. Although the alkoxide is bulky, methyl chloride has an accessible methyl carbon and cannot undergo beta-elimination because it has no beta-carbon.

Step 4: (b) Distinguish the two alcohols with the iodoform test Warm each alcohol separately with iodine and aqueous sodium hydroxide. Butan-2-ol gives a yellow precipitate of iodoform, CHI_3,

Quick Tip to Solve: Check for the $CH_3CH(OH)-$ group before predicting a positive iodoform test; for acidity, compare the stability of the conjugate bases.

because its $CH_3CH(OH)-$ group is first oxidised to a methyl ketone. Butan-1-ol gives no yellow precipitate under this test.

$$CH_3CH(OH)CH_2CH_3 + 4I_2 + 6NaOH \longrightarrow CHI_3 \downarrow + CH_3CH_2COONa + 5NaI + 5H_2O.$$

Butan-1-ol lacks the required methyl-secondary-alcohol arrangement; being a primary alcohol alone does not make an alcohol iodoform-positive.

Step 5: (c) Compare the conjugate bases Ethanol loses a proton to give ethoxide. The ethyl group's positive inductive effect increases electron density on the negatively charged oxygen, making ethoxide less stable than hydroxide, the conjugate base of water. Phenol gives phenoxide, whose negative charge is delocalised by resonance over oxygen and the aromatic ring. Phenoxide is therefore more stabilised, so phenol releases its proton most readily.

Step 6: Conclusion (a) The products are (i) 2,4,6-trinitrophenol, (ii) propan-1-ol and (iii) 2-methoxy-2-methylpropane. (b) Butan-2-ol gives yellow CHI_3 with $I_2/NaOH$; butan-1-ol does not. (c) Increasing acid strength is $\boxed{\text{ethanol} < \text{water} < \text{phenol}}$.

Quick Tip to Solve: Check for the $CH_3CH(OH)-$ group before predicting a positive iodoform test; for acidity, compare the stability of the conjugate bases.

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

Solution:

Concept:

- The aldehyde group, $-CHO$, is the principal functional group; its carbon belongs to the parent chain and is assigned carbon number 1.
- Four carbons give the root but; a carbon-carbon double bond is indicated by en, and the aldehyde suffix is al.

Step 1: Select and number the parent chain The longest chain containing the aldehyde carbon has four carbon atoms. Number from the $-CHO$ end, giving CHO as C-1, the adjacent CH as C-2, the next CH as C-3 and the terminal CH_3 as C-4.

Step 2: Locate the double bond and apply the suffix The double bond lies between C-2 and C-3, so its locant is 2. Combining the four-carbon root, the double-bond locant and the aldehyde suffix gives but-2-enal. No stereochemical prefix is required because the given condensed formula does not specify the geometry about the double bond.

Step 3: Conclusion The IUPAC name of $CH_3 - CH{=}CH - CHO$ is $\boxed{\text{but-2-enal}}$.

Quick Tip to Solve: Count the aldehyde carbon as carbon 1 before locating the double bond; the $-CHO$ carbon is part of the parent chain.

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

Solution:

Concept:

- Tollens' reagent is ammoniacal silver nitrate containing $[Ag(NH_3)_2]^+$; an aldehyde reduces it to metallic silver.
- Propanal, CH_3CH_2CHO, is an aldehyde, whereas propanone, CH_3COCH_3, is a simple ketone and does not reduce Tollens' reagent.

Step 1: Add Tollens' reagent and warm gently Add freshly prepared Tollens' reagent to separate samples in clean test tubes and warm gently in a water bath. Propanal produces a silver mirror on the inner wall as the aldehyde group is oxidised to the carboxylate ion:

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

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 difference in observations identifies the two samples. A carbonyl-group test such as 2,4-DNP would give a precipitate with both and therefore would not distinguish them.

Step 3: Conclusion Use Tollens' test: propanal: silver mirror; propanone: no silver mirror.

Quick Tip to Solve: For an aldehyde-versus-simple-ketone pair, use Tollens' reagent; a general carbonyl test is positive for both compounds.

32(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 a benzylic methyl group into a carboxyl group without changing the benzene ring.
- A Grignard reagent adds an alkyl group to an aldehyde; hydrolysis of the magnesium alkoxide gives an alcohol.
- The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by bromine. Hydrolysis of the alpha-bromo acid gives an alpha-hydroxy acid.

Step 1: (i) Oxidise the side chain of toluene Heat toluene with alkaline potassium permanganate. The methyl side chain is oxidised to potassium benzoate. Acidify the reaction mixture to obtain benzoic acid:

$$C_6H_5CH_3 \xrightarrow{\text{hot alkaline } KMnO_4} C_6H_5COOK \xrightarrow{H_3O^+} C_6H_5COOH.$$

Quick Tip to Solve: Count carbons before choosing the route: ethanol needs one extra carbon, whereas propanal must retain its three-carbon chain.

Step 2: (ii) Convert ethanol into ethanal and add a methyl group Pass ethanol vapour over heated copper at $573\,\mathrm{K}$ to form ethanal by dehydrogenation:

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

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

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

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

Step 3: (iii) Oxidise propanal, brominate and hydrolyse First oxidise propanal to propanoic acid using acidified potassium dichromate:

$$\mathrm{CH_3CH_2CHO} + [\mathrm{O}] \xrightarrow{\mathrm{K_2Cr_2O_7/H^+}} \mathrm{CH_3CH_2COOH}.$$

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

$$\mathrm{CH_3CH_2COOH} \xrightarrow[\text{then } \mathrm{H_2O}]{\mathrm{Br_2/red\ P}} \mathrm{CH_3CHBrCOOH},$$

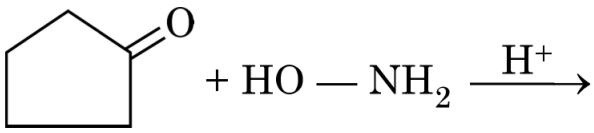
$$\mathrm{CH_3CHBrCOOH} \xrightarrow[\text{then } \mathrm{H_3O^+}]{\mathrm{aq\cdot NaOH}} \mathrm{CH_3CH(OH)COOH}.$$

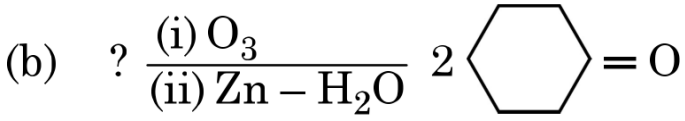
Step 4: Conclusion The final products are (i) $\mathrm{C_6H_5COOH}$, (ii) $\mathrm{CH_3CH(OH)CH_3}$ and (iii) $\mathrm{CH_3CH(OH)COOH}$, respectively.

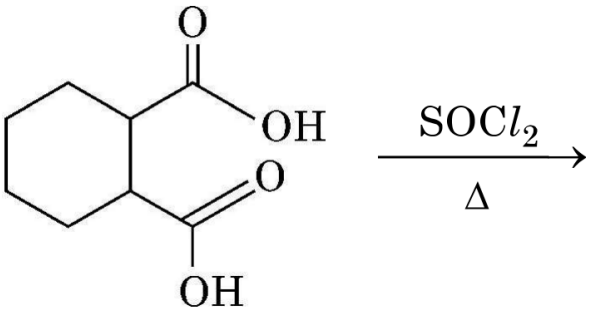
Quick Tip to Solve: Count carbons before choosing the route: ethanol needs one extra carbon, whereas propanal must retain its three-carbon chain.

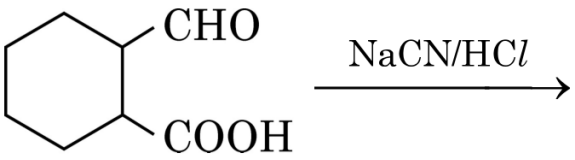
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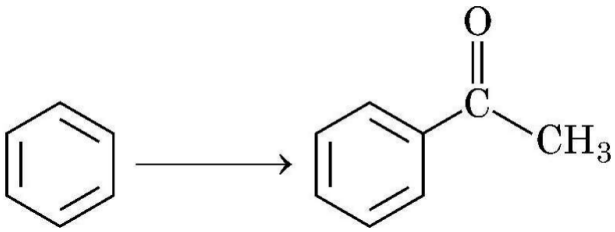
32(B). Complete each synthesis by giving missing starting material, reagent or products: [5 marks]

(a) 

(b) 

(c) 

(d) 

(e) 

Solution:

Concept:

- Hydroxylamine forms an oxime with a carbonyl compound; hydrogen cyanide adds across a carbonyl group to form a cyanohydrin.
- Reductive ozonolysis cleaves an alkene at its double bond, converting each alkene carbon into a carbonyl carbon.
- Thionyl chloride replaces the hydroxyl group of a carboxylic acid by chlorine. Friedel–Crafts acylation introduces an acyl group into benzene using an anhydrous Lewis acid catalyst.

Quick Tip to Solve: Reverse ozonolysis by joining the two carbonyl carbons with a double bond. In the other reactions track only the functional group selected by the reagent.

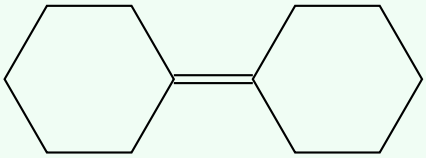
Step 1: (a) Form the oxime of cyclopentanone Hydroxylamine reacts with the ketone carbonyl group by addition followed by loss of water. The carbonyl $C{=}O$ group is replaced by $C{=}N{-}OH$, while the five-membered ring remains unchanged:

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

Step 2: (b) Reconstruct the alkene from the two ketones Reverse ozonolysis by removing the two carbonyl oxygens and joining the carbonyl carbons with a double bond. The starting alkene is cyclohexylidenecyclohexane, shown below:

$$\text{cyclohexylidenecyclohexane} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} 2\,\text{cyclohexanone}.$$

Neither alkene carbon has a hydrogen, so both fragments are ketones rather than aldehydes.



Cyclohexylidenecyclohexane: the required starting alkene in (b)

Step 3: (c) Convert both carboxyl groups into acid chlorides Heating with thionyl chloride replaces the hydroxyl of each $-COOH$ group by chlorine. The product is cyclohexane-1,2-dicarbonyl dichloride:

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

Both $-COCl$ groups occupy adjacent ring positions; both carbonyl oxygens remain.

Step 4: (d) Add hydrogen cyanide to the aldehyde group The reagents generate HCN. Cyanide attacks the aldehyde carbon, then oxygen is protonated. Thus $-CHO$ becomes $-CH(OH)CN$; the adjacent carboxyl group is unchanged:

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

The hydroxyl and cyano groups attach to the former aldehyde carbon outside the ring.

Step 5: (e) Acetylate benzene Use acetyl chloride, CH_3COCl, with anhydrous aluminium chloride. This Friedel–Crafts acylation replaces a ring hydrogen by $-COCH_3$:

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

Aqueous work-up releases acetophenone from its catalyst complex.

Step 6: Conclusion The entries are (a) cyclopentanone oxime, (b) the alkene drawn above, (c) the adjacent diacid chloride, (d) the aldehyde cyanohydrin, and (e) CH_3COCl/anhydrous $AlCl_3$.

Quick Tip to Solve: Reverse ozonolysis by joining the two carbonyl carbons with a double bond. In the other reactions track only the functional group selected by the reagent.

33(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:

- Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, with both electrode values written as reduction potentials.
- Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of moles of electrons transferred per mole of balanced reaction and $F = 96500\,\text{C mol}^{-1}$.

Step 1: Balance the electron transfer Gold is oxidised and calcium ions are reduced in the direction asked. Their half-reactions are

$$\begin{aligned} \text{Au(s)} &\longrightarrow \text{Au}^{3+}(\text{aq}) + 3\,\text{e}^- \\ \text{Ca}^{2+}(\text{aq}) + 2\,\text{e}^- &\longrightarrow \text{Ca(s)}. \end{aligned}$$

The printed reaction is a skeletal equation. Multiply the oxidation by 2 and the reduction by 3 to cancel six electrons:

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

Thus $n = 6$ for the balanced reaction in the smallest whole-number coefficients. Stoichiometric multiplication does not multiply electrode potentials.

Step 2: Calculate the potential and Gibbs energy Use calcium reduction at the cathode and gold oxidation at the anode for the specified direction:

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

Therefore,

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

Here one mole of reaction means consumption of two moles of gold and three moles of calcium ions. The positive Gibbs energy means the forward direction is thermodynamically unfavourable under the stated standard conditions.

Step 3: Conclusion $\boxed{\Delta_r G^\circ = +2.53 \times 10^3\,\text{kJ mol}^{-1}}$ for the balanced reaction. The reaction is not spontaneous at 25 °C under standard conditions; the reverse direction is spontaneous.

Quick Tip to Solve: Balance the 3-electron gold change and 2-electron calcium change before using $-nFE^\circ$: their least common multiple gives $n = 6$.

33(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 metal with the more negative standard reduction potential can act as the reducing agent by undergoing oxidation.
- A positive E°_{cell} gives $\Delta_r G^\circ = -nFE^\circ_{\text{cell}} < 0$, favouring the forward redox reaction.

Step 1: Identify oxidation and reduction The silver sulphide layer is reduced to metallic silver, while aluminium is oxidised. The printed aluminium half-reaction has an extra coefficient 2 before Al; its atom-balanced form is $Al^{3+} + 3e^- \longrightarrow Al$. Using the stated electrode potential for this couple, the balanced overall change is

$$3Ag_2S(s) + 2Al(s) \longrightarrow 6Ag(s) + 3S^{2-}(aq) + 2Al^{3+}(aq).$$

Six electrons are transferred from aluminium to the tarnish.

Step 2: Evaluate the driving potential Using the supplied reduction potentials,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{Ag_2S/Ag} - E^\circ_{Al^{3+}/Al} \\ &= -0.71 - (-1.66) = +0.95\,\text{V}. \end{aligned}$$

The positive potential favours reduction of the tarnish. Contact with the aluminium pan provides an electron path; the inert electrolyte carries ions and completes the conducting circuit.

Step 3: Conclusion Yes. Aluminium reduces the Ag_2S tarnish to silver because $E^\circ_{\text{cell}} = +0.95$ V. Aluminium is consumed as the reducing agent.

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

OR

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

(i) Cell potential

(ii) Fuel cell [2 marks]

Solution:

Concept:

- An electrochemical cell develops a potential difference between its two electrodes owing to their different tendencies to undergo reduction.

Quick Tip to Solve: For cell potential mention the two electrodes; for a fuel cell include both direct energy conversion and continuous reactant supply.

- A fuel cell converts the chemical energy of continuously supplied reactants directly into electrical energy.

Step 1: Define cell potential Cell potential is the potential difference between the cathode and anode of an electrochemical cell. In terms of electrode 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 called its electromotive force (emf). Thus emf refers to the open-circuit value, without a voltage drop caused by current through the cell.

Step 2: Define a fuel cell A fuel cell is a galvanic cell in which a fuel and an oxidising agent are continuously supplied to the electrodes, converting their chemical energy directly into electrical energy. It can operate while reactants are supplied and products are removed. For example, a hydrogen–oxygen fuel cell uses H_2 as fuel and O_2 as oxidant; its overall reaction is

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O\,(l).$$

Step 3: Conclusion (i) Cell potential is the cathode-to-anode potential difference. (ii) A fuel cell is a galvanic cell that generates electricity directly from a continuously supplied fuel and oxidant.

Quick Tip to Solve: For cell potential mention the two electrodes; for a fuel cell include both direct energy conversion and continuous reactant supply.

33(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:

- For the cell as written, the left electrode is the anode and the right electrode is the cathode; $E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$.
- At 25 °C, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$. Here n is the electron-transfer number and Q is the reaction quotient; pure solids have unit activity.

Step 1: Write the cell reaction Zinc is oxidised on the left and cadmium ions are reduced on the right:

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

On adding these half-reactions,

$$\text{Zn}\,(s) + \text{Cd}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cd}\,(s).$$

Quick Tip to Solve: Write the overall reaction first: zinc ions are products, so the quotient is $[Zn^{2+}]/[Cd^{2+}] = 10$, not its reciprocal.

Thus $n = 2$. The standard emf is

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

Step 2: Apply the concentration correction Only the dissolved ions enter the reaction quotient, because zinc and cadmium are pure solids. Using concentrations in place of activities as usual for this calculation,

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

Since $\log 10 = 1$, the Nernst equation gives

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

The product-ion concentration is greater than the reactant-ion concentration, so $Q > 1$ and the concentration correction lowers the emf below its standard value. This also checks the sign of the logarithmic term.

Step 3: Conclusion The cell emf at $25\,^\circ\text{C}$ is $\boxed{E_{\text{cell}} \approx 0.330\,\text{V}}$.

Quick Tip to Solve: Write the overall reaction first: zinc ions are products, so the quotient is $[\text{Zn}^{2+}]/[\text{Cd}^{2+}] = 10$, not its reciprocal.