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

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 calculators is **not** allowed.

Section A (16 marks)

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

1. The most stable oxidation state of Iron is: [1 mark]

(A) +2

(B) +3

(C) +4

(D) −2

Correct Answer: (B) +3

Solution:

Concept:

- Iron has atomic number 26 and ground-state configuration $[\mathrm{Ar}]3d^6 4s^2$. The $4s$ electrons are removed before the $3d$ electrons during ion formation.
- A half-filled d^5 subshell has extra stability because of its symmetrical occupancy and exchange energy.

Step 1: Compare the common ions Removing two electrons gives Fe^{2+} : $[\mathrm{Ar}]3d^6$. Removing one more gives Fe^{3+} : $[\mathrm{Ar}]3d^5$, with one electron in each of the five d orbitals.

Step 2: Assess the alternatives The half-filled configuration favours the +3 state in the comparison asked here. The +2 state is also common but does not have this half-filled configuration. The +4 state requires further removal of a d electron, while -2 is not the characteristic stable state of iron in this context.

Step 3: Conclusion The most stable oxidation state in this comparison is $+3$. Hence, the correct option is (B).

Quick Tip to Solve: Write the ion configurations first: the half-filled $3d^5$ configuration identifies Fe^{3+}.

2. The product formed as a result of CH_3MgBr and CO_2 followed by hydrolysis is: [1 mark]

(A) CH_3CHO

(B) CH_3COCH_3

(C) HCOOH

(D) CH_3COOH

Correct Answer: (D) CH_3COOH

Solution:

Concept:

- A Grignard reagent RMgX adds its alkyl group to carbon dioxide to form a magnesium carboxylate.
- Acidic hydrolysis converts the carboxylate to RCOOH; the acid contains one more carbon atom than the alkyl group.

Quick Tip to Solve: Count carbons: methyl Grignard plus carbon dioxide gives a two-carbon carboxylic acid.

Step 1: Form the carboxylate The methyl group of CH_3MgBr attacks the electrophilic carbon of CO_2:

$$CH_3MgBr + CO_2 \longrightarrow CH_3COOMgBr.$$

The carbon of carbon dioxide becomes the carboxyl carbon.

Step 2: Hydrolyse and compare the options On acidic hydrolysis, $CH_3COOMgBr$ gives CH_3COOH. Ethanal and acetone are carbonyl compounds rather than the carboxylic acid produced by this reaction. Formic acid has only one carbon and would not retain the methyl carbon supplied by the reagent.

Step 3: Conclusion The product is ethanoic acid, CH_3COOH. Hence, the correct option is (D).

Quick Tip to Solve: Count carbons: methyl Grignard plus carbon dioxide gives a two-carbon carboxylic acid.

3. Nucleotides are composed of a: [1 mark]

(A) pentose sugar and phosphoric acid

(B) nitrogenous base, pentose sugar and phosphoric acid

(C) nitrogenous base and phosphoric acid

(D) pentose sugar and nitrogenous base

Correct Answer: (B) nitrogenous base, pentose sugar and phosphoric acid

Solution:

Concept:

- A nucleoside contains a nitrogenous base attached to a pentose sugar.
- A nucleotide is a phosphate ester of a nucleoside and therefore has a base, a sugar and a phosphate component.

Step 1: Identify the three components The sugar is ribose in RNA or 2-deoxyribose in DNA. It is bonded to a nitrogenous base, and a phosphate group derived from phosphoric acid is attached to the sugar. These three components together constitute a nucleotide.

Step 2: Distinguish the alternatives Option (A) omits the base, while option (C) omits the sugar. Option (D), sugar plus base, describes a nucleoside and lacks the phosphate group. Only option (B) includes all three components required for a nucleotide.

Step 3: Conclusion A nucleotide contains a nitrogenous base, pentose sugar and phosphoric acid. Hence, the correct option is (B).

Quick Tip to Solve: Use nucleotide = nucleoside + phosphate; nucleoside already includes sugar and base.

4. Which of the following alkyl halides will undergo S_N1 reaction most readily? [1 mark]

(A) $(CH_3)_3 - I$

(B) $(CH_3)_3 - Cl$

(C) $(CH_3)_3 - Br$

(D) $(CH_3)_3 - F$

Correct Answer: (A) $(CH_3)_3 - I$

Solution:

Concept:

- The rate-determining step of an S_N1 reaction is ionisation of the alkyl halide, with departure of the halide ion.
- For a common alkyl framework, leaving-group ability follows $I^- > Br^- > Cl^- > F^-$, and the carbon-halogen bond becomes easier to break towards iodine.

Step 1: Compare the leaving groups The options compare iodide, chloride, bromide and fluoride derivatives. With the alkyl framework held common, the decisive difference is the halogen. Iodide is the most readily departing group because the carbon-iodine bond is the weakest of these carbon-halogen bonds.

Step 2: Check all options The iodide derivative therefore ionises most readily. Bromide also undergoes ionisation but less readily than iodide; chloride is slower still. Fluoride is least favourable because its carbon-fluorine bond is particularly strong and fluoride is a poor leaving group. The relative order is iodide, bromide, chloride, then fluoride.

Step 3: Conclusion The iodide derivative in option (A) undergoes the S_N1 reaction most readily. Hence, the correct option is (A).

Quick Tip to Solve: When the alkyl group is common to all choices, rank the leaving groups: iodide leaves most easily.

5. Phenol dimerises in benzene having van't Hoff factor 0.54. Its degree of association is: [1 mark]

(A) 0.54

(B) 0.46

(C) 0.92

(D) 0.27

Correct Answer: (C) 0.92

Solution:

Concept:

- The van't Hoff factor i is the ratio of actual solute particles after association to the initial particles.
- For dimerisation, if α is the fraction of monomers associated, then $i = 1 - \alpha/2$.

Step 1: Count the particles after dimerisation Start with 1 mol of phenol molecules. If a fraction α associates, unassociated phenol is $1 - \alpha$ mol and the dimers formed are $\alpha/2$ mol. Thus the total particle amount is $1 - \alpha + \alpha/2 = 1 - \alpha/2$.

Quick Tip to Solve: For dimers, double the deficit in van't Hoff factor: $\alpha = 2(1 - i)$.

Step 2: Substitute the given factor Using $i = 0.54$,

$$0.54 = 1 - \frac{\alpha}{2}, \qquad \alpha = 2(1 - 0.54) = 0.92.$$

The value 0.46 is only $\alpha/2$, not the degree of association. The values 0.54 and 0.27 do not satisfy the dimer particle-count equation.

Step 3: Conclusion The degree of association is $\alpha = 0.92$, or 92%. Hence, the correct option is (C).

Quick Tip to Solve: For dimers, double the deficit in van't Hoff factor: $\alpha = 2(1 - i)$.

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6. A reaction $A_2 + B_2 \rightarrow 2AB$ occurs by the following mechanism:

$A_2 \rightarrow A + A$ (slow)

$A + B_2 \rightarrow AB + B$ (fast)

$A + B \rightarrow AB$ (fast)

Its order would be: [1 mark]

(A) 1

(B) 2

(C) Zero

(D) $\frac{1}{2}$

Correct Answer: (A) 1

Solution:

Concept:

- The slow elementary step determines the rate for the stated mechanism.
- The order is the sum of concentration exponents in the rate law; stoichiometric coefficients of an overall reaction alone do not determine it.

Step 1: Write the slow-step rate law The slow step is $A_2 \longrightarrow A + A$. It is an elementary unimolecular step, so its rate law is $r = k[A_2]$. The concentration of B_2 does not appear because it participates only in a subsequent fast step.

Step 2: Determine the order and reject distractors The sole concentration exponent is 1. The overall equation contains two reactants, but it does not make the reaction second order. Zero order would require no concentration dependence, and half order would require a square-root dependence; neither follows from the given slow elementary step.

Step 3: Conclusion The reaction is first order. Hence, the correct option is (A).

Quick Tip to Solve: Use the slow elementary step to write the rate law before looking at the overall equation.

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7. Decarboxylation of sodium benzoate on heating with soda lime gives: [1 mark]

(A) benzene

(B) benzoic acid

(C) benzaldehyde

(D) toluene

Correct Answer: (A) benzene

Solution:

Concept:

- Soda lime is a mixture of sodium hydroxide and calcium oxide used for decarboxylation of sodium carboxylates.
- Heating RCOONa with soda lime gives RH, removing the carboxyl carbon as carbonate.

Step 1: Apply decarboxylation to sodium benzoate For sodium benzoate the group R is phenyl, $\mathrm{C_6H_5}$. Heating removes the carboxylate group and replaces it by hydrogen:

$$\mathrm{C_6H_5COONa + NaOH \xrightarrow[CaO]{\Delta} C_6H_6 + Na_2CO_3}.$$

Step 2: Compare the proposed products The six-carbon benzene ring remains, while the carboxyl carbon enters sodium carbonate. Benzoic acid would result from acidifying benzoate, not soda-lime heating. Benzaldehyde would require conversion to an aldehyde, and toluene would retain an extra carbon as a methyl group; neither describes decarboxylation.

Step 3: Conclusion The product is benzene, $\mathrm{C_6H_6}$. Hence, the correct option is (A).

Quick Tip to Solve: Remove the entire $-\mathrm{COONa}$ group and replace it with H when applying soda-lime decarboxylation.

8. The IUPAC name of $\mathrm{CH_3–CO–CH_2–CHO}$ is: [1 mark]

(A) 1-oxobutanal-3-one

(B) 1-oxobutanal

(C) 3-oxobutanal

(D) 3-oxobutanone

Correct Answer: (C) 3-oxobutanal

Solution:

Concept:

- The aldehyde group has naming priority over the ketone group; it supplies the suffix $-\mathrm{al}$.
- The longest chain containing $-\mathrm{CHO}$ has four carbons and is numbered from the aldehyde carbon.

Step 1: Choose the parent and numbering Write the chain from the aldehyde end as

$$\mathrm{CHO - CH_2 - CO - CH_3}.$$

Quick Tip to Solve: Number from CHO first, then express any additional ketone carbonyl as oxo.

The aldehyde carbon is C-1, the methylene carbon is C-2, the internal carbonyl carbon is C-3 and the methyl carbon is C-4. Thus the parent is butanal.

Step 2: Name the second carbonyl The ketone carbonyl is expressed by the prefix oxo at position 3. A carbonyl at C-1 is already represented by the aldehyde suffix, so adding 1-oxo is redundant. The suffix butanone would incorrectly give naming priority to the ketone. Neither option (A), (B) nor (D) correctly combines the priority rule and the internal carbonyl locant.

Step 3: Conclusion The IUPAC name is $\boxed{\text{3-oxobutanal}}$. Hence, the correct option is (C).

Quick Tip to Solve: Number from CHO first, then express any additional ketone carbonyl as oxo.

9. Dehydration of tertiary alcohols with Cu at 573 K gives: [1 mark]

(A) Alkyne

(B) Alkene

(C) Aldehyde

(D) Ketone

Correct Answer: (B) Alkene

Solution:

Concept:

- A tertiary alcohol has no hydrogen on the carbon bearing the $-\text{OH}$ group.
- Passing alcohol vapour over heated copper at $573\,\text{K}$ distinguishes primary, secondary and tertiary alcohols.

Step 1: Identify the reaction pathway A tertiary alcohol cannot form a carbonyl compound by the usual dehydrogenation because its hydroxyl-bearing carbon has no hydrogen to remove. Under the stated heated-copper conditions, a tertiary alcohol undergoes dehydration, eliminating water.

Step 2: Identify the organic product Loss of $-\text{OH}$ and a hydrogen from an adjacent carbon forms a $\text{C} = \text{C}$ bond, producing an alkene. Aldehydes and ketones arise from primary and secondary alcohol dehydrogenation respectively. A single dehydration introduces one double bond, so an alkyne is not the product of this process.

Step 3: Conclusion The product is an $\boxed{\text{alkene}}$. Hence, the correct option is (B).

Quick Tip to Solve: Check for a hydrogen on the OH-bearing carbon: tertiary alcohols dehydrate.

10. In the Arrhenius equation, when log k is plotted against 1/T, a straight line is obtained whose:

[1 mark]

(A) slope is $\frac{A}{R}$ and intercept is E_a

(B) slope is A and intercept is $\frac{-E_a}{R}$

(C) slope is $\frac{-E_a}{RT}$ and intercept is $\log A$

(D) slope is $\frac{-E_a}{2.303R}$ and intercept is $\log A$

Correct Answer: (D) slope is $\frac{-E_a}{2.303R}$ and intercept is $\log A$

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a is activation energy and R is the gas constant.
- For common logarithms, $\log e = 1/2.303$.

Step 1: Convert the exponential equation Taking common logarithms gives

$$\log k = \log A - \frac{E_a}{2.303R}\frac{1}{T}.$$

The factor 2.303 appears because the graph uses common logarithm, rather than natural logarithm.

Step 2: Compare with the straight-line form With $y = \log k$ and $x = 1/T$, compare with $y = mx + c$. The coefficient of $1/T$ is the constant slope and the remaining term is the intercept. Option (A) uses the frequency factor as the slope and activation energy as intercept; (B) also interchanges unrelated quantities. Option (C) contains T in the alleged slope and misses the logarithm conversion factor.

Step 3: Conclusion The slope is $\boxed{-E_a/(2.303R)}$ and the intercept is $\boxed{\log A}$. Hence, the correct option is (D).

Quick Tip to Solve: For log k use 2.303; for ln k the slope is simply -Ea/R.

11. Phenol on reaction with aqueous bromine at room temperature gives:

[1 mark]

(A) 2-bromophenol

(B) 3-bromophenol

(C) 4-bromophenol

(D) 2,4,6-tribromophenol

Correct Answer: (D) 2,4,6-tribromophenol

Solution:

Concept:

- The $-OH$ group activates the benzene ring by donating electron density through resonance.
- The hydroxyl group directs electrophilic substitution to the ortho and para positions.

Quick Tip to Solve: Aqueous bromine plus phenol means substitution at both ortho sites and the para site.

Step 1: Locate the activated positions In phenol, carbon 1 bears the hydroxyl group. The two ortho positions are C-2 and C-6, while the para position is C-4. These positions are especially electron-rich and readily undergo substitution by bromine.

Step 2: Apply the aqueous reaction conditions With aqueous bromine at room temperature, the strongly activated ring undergoes substitution at all three positions, giving a white precipitate of 2,4,6-tribromophenol. The reaction is

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

Options (A) and (C) describe only monobromination, while (B) incorrectly places bromine at a meta position.

Step 3: Conclusion The product is $\boxed{\text{2,4,6-tribromophenol}}$. Hence, the correct option is (D).

Quick Tip to Solve: Aqueous bromine plus phenol means substitution at both ortho sites and the para site.

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

(A) Secondary structure

(B) Primary structure

(C) Tertiary structure

(D) Quaternary structure

Correct Answer: (B) Primary structure

Solution:

Concept:

- A protein is a polypeptide in which amino-acid residues are joined by peptide bonds.
- The primary structure specifies the identity and order of these residues in each polypeptide chain.

Step 1: Match the description to a structural level The question asks for the specific sequence of amino acids, meaning the order of residues along the chain, conventionally read from the amino terminus to the carboxyl terminus. This sequence is the first level used to describe a protein.

Step 2: Distinguish the other levels Secondary structure describes local arrangements such as an alpha helix or beta sheet. Tertiary structure describes the overall three-dimensional folding of one polypeptide. Quaternary structure describes the association of multiple polypeptide subunits. These levels concern spatial organization rather than the residue sequence itself.

Step 3: Conclusion The sequence is the $\boxed{\text{primary structure}}$. Hence, the correct option is (B).

Quick Tip to Solve: Sequence means primary; local folding, overall folding and subunit assembly are higher levels.

13. Assertion (A): Aniline is a stronger base than ammonia.

Reason (R): The unshared electron pair on nitrogen atom in aniline becomes less available for protonation due to resonance. [1 mark]

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

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

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

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

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

Solution:

Concept:

- A base accepts a proton using an available electron pair.
- Resonance delocalization reduces the availability of the nitrogen lone pair in aniline.

Step 1: Judge the assertion Ammonia has a localized lone pair on nitrogen that can accept a proton. In aniline, this lone pair interacts with the benzene ring and is delocalized. Aniline is consequently a weaker base than ammonia, so the assertion that it is stronger is false.

Step 2: Judge the reason The reason correctly states that resonance makes the unshared electron pair on nitrogen less available for protonation. Donation of this pair into the aromatic ring lowers the tendency of nitrogen to form a coordinate bond with a proton. Therefore, the reason is true.

Step 3: Check the explanation and code The reason accounts for the actual weaker basicity of aniline and contradicts the stronger-basicity claim in the assertion. Codes (A) and (B) require a true assertion, and code (C) requires a false reason. None matches these truth values; the false-assertion, true-reason code does.

Step 4: Conclusion The assertion is false, but the reason is true. Hence, the correct option is $\boxed{\text{(D)}}$.

Quick Tip to Solve: Compare lone-pair availability before judging basicity; resonance in aniline lowers it.

14. Assertion (A): The pK_a of $O_2N–CH_2–COOH$ is lower than that of $CH_3–COOH$.

Reason (R): $–NO_2$ group shows electron withdrawing effect which increases the acidic character of $O_2N–CH_2–COOH$. [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:

- Acid strength increases with K_a, while $pK_a = -\log K_a$ decreases.
- An electron-withdrawing group stabilizes a carboxylate conjugate base through the negative inductive effect.

Step 1: Judge the assertion Nitroacetic acid, $O_2N - CH_2 - COOH$, is stronger than acetic acid, CH_3COOH. Its dissociation constant is therefore greater, making its pK_a lower. The assertion is true.

Step 2: Judge the reason The nitro group withdraws electron density through sigma bonds. In the conjugate base $O_2N - CH_2 - COO^-$, this effect stabilizes the negative charge and favours loss of a proton from the acid. The methyl group in acetic acid instead has an electron-releasing effect. Thus the reason is true.

Step 3: Connect the reason to the assertion Stabilization of the nitroacetic acid conjugate base increases acidity, increases K_a, and therefore decreases pK_a. This directly explains the stated comparison. Option (B) incorrectly denies the explanatory link, while (C) and (D) incorrectly declare one of the two true statements false.

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

Quick Tip to Solve: A withdrawing group stabilizes COO-: stronger acid, larger Ka and smaller pKa.

15. Assertion (A): Transition metals have high enthalpy of atomization.

Reason (R): This is because transition metals have low melting points. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Enthalpy of atomization is the energy required to form gaseous atoms from one mole of a solid metal.
- Strong metallic bonding requires more energy to separate atoms; unpaired d electrons contribute to bonding.

Step 1: Judge the assertion The assertion is true. Transition metals generally have high enthalpies of atomization because their metallic bonds are strong. Participation of both valence s and d electrons, especially unpaired d electrons, increases the strength of interatomic bonding.

Step 2: Judge the reason The reason is false. Transition metals generally have high melting points, not low melting points. Strong metallic bonding explains both the large energy required for atomization and the generally high melting temperatures; exceptions do not support the stated general reason.

Step 3: Check the explanatory link A false reason cannot explain a true assertion. Codes (A) and (B) require both statements to be true and are therefore excluded; code (D) would require a false assertion and a true reason, the opposite of the present truth values.

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

Quick Tip to Solve: For atomization questions, connect stronger metallic bonding with a larger energy needed to separate atoms.

16. Assertion (A): When NaCl is added in water, elevation in boiling point is observed.

Reason (R): Elevation in boiling point is a colligative property. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Boiling occurs when the vapour pressure of a liquid equals the external pressure.
- Elevation in boiling point is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality.

Step 1: Judge the assertion The assertion is true. Dissolving non-volatile NaCl in water lowers the vapour pressure of water at a given temperature. The solution must therefore be heated to a higher temperature to reach the external pressure and boil.

Step 2: Judge the reason The reason is true. Boiling-point elevation depends on the number of solute particles in solution, rather than their chemical identity. NaCl dissociates into Na^+ and Cl^-, increasing the number of dissolved particles.

Step 3: Check the explanatory link The reason identifies boiling-point elevation as a colligative property, but does not explain the physical cause of the rise in boiling point. The explanation requires the lowering of solvent vapour pressure by dissolved non-volatile NaCl, followed by the need for a higher temperature to attain atmospheric pressure. Thus both statements are true, but the given reason does not supply the correct explanation. Code (A) incorrectly treats the classification alone as an explanation, and (C) and (D) incorrectly make one statement false.

Step 4: Conclusion Both statements are true, but the reason does not correctly explain the assertion. Hence, the correct option is (B).

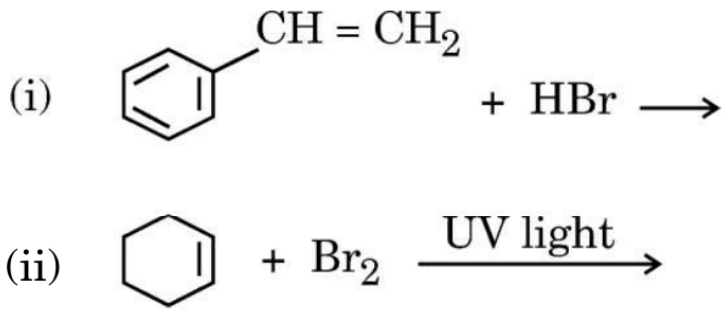
Quick Tip to Solve: For a non-volatile dissolved salt, count its dissolved particles when predicting boiling-point elevation.

Section B (10 marks)

17(a). Draw the structures of major monohalo products in each of the following reactions:

(i)

(ii) [2 marks]

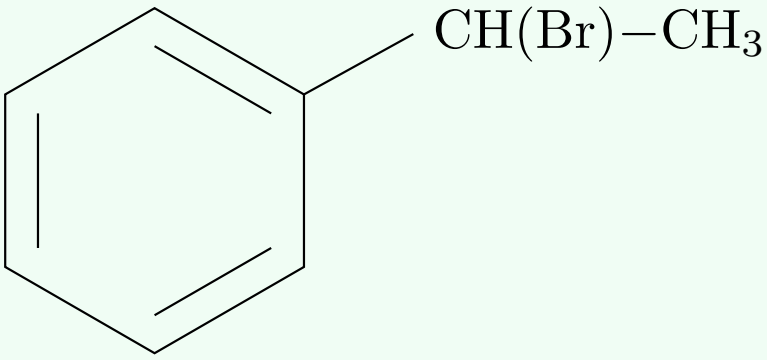


Solution:

Concept:

- In the absence of peroxides, HBr adds to an unsymmetrical alkene by Markovnikov addition.
- Under UV light, bromination can substitute an allylic hydrogen through a resonance-stabilised allylic radical.

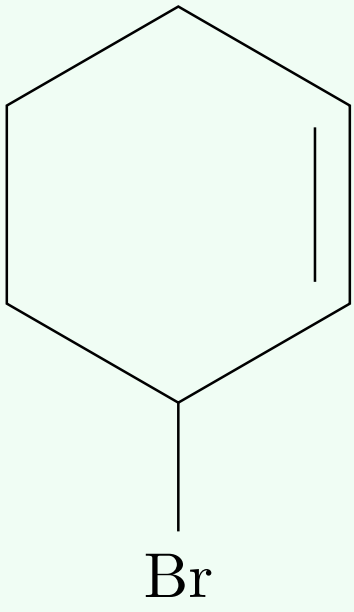
Step 1: Find the product of reaction (i) The substrate is styrene, $C_6H_5CH{=}CH_2$. Addition of a proton to the terminal carbon produces the resonance-stabilised benzylic carbocation $C_6H_5CH^+CH_3$. Bromide then attacks this carbon. The major product is $C_6H_5CH(Br)CH_3$, 1-bromo-1-phenylethane. The reversed orientation would not give this stabilised carbocation; peroxide-induced anti-Markovnikov addition is not indicated.



(i) 1-Bromo-1-phenylethane

Step 2: Find the product of reaction (ii) The substrate is cyclohexene and the specified condition is UV light. Photochemical radical bromination replaces an allylic hydrogen, giving the major monohalo product 3-bromocyclohex-1-ene. The ring double bond is retained. The two allylic positions of cyclohexene are equivalent by symmetry, so substitution at either leads to the same constitutional product. Addition across the double bond would give a dibromo product and is not the requested monohalo reaction.

Quick Tip to Solve: Check the condition: HBr alone gives Markovnikov addition, while UV light signals radical allylic bromination.



(ii) 3-Bromocyclohex-1-ene

Step 3: Conclusion The major products are (i) 1-bromo-1-phenylethane, $C_6H_5CH(Br)CH_3$, and (ii) 3-bromocyclohex-1-ene, with the structures shown above.

Quick Tip to Solve: Check the condition: HBr alone gives Markovnikov addition, while UV light signals radical allylic bromination.

OR

17(b). Give reasons for the following:

(i) Grignard reagent should be prepared under anhydrous conditions.

(ii) Alkyl halides give alcohol with aqueous KOH whereas in the presence of alcoholic KOH, alkenes are formed. [2 marks]

Solution:

Concept:

- Grignard reagents $RMgX$ react rapidly with proton donors such as water.
- Aqueous hydroxide favours nucleophilic substitution; alcoholic KOH favours elimination of a beta hydrogen and the halide.

Step 1: Explain the need for anhydrous conditions The carbon bonded to magnesium in a Grignard reagent has carbanion-like character. It removes a proton from water, destroying the reagent and producing an alkane instead of allowing the intended synthetic reaction:

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X.$$

Quick Tip to Solve: Remember aqueous KOH replaces X by OH, whereas alcoholic KOH removes a beta H together with X.

Hence the apparatus and ether solvent must be dry, and moisture must be excluded during preparation.

Step 2: Explain the effect of aqueous KOH In aqueous medium, OH^- acts predominantly as a nucleophile and replaces the halogen atom. The substitution produces an alcohol:

$$R{-}X + KOH(aq) \longrightarrow R{-}OH + KX.$$

For example, bromoethane gives ethanol.

Step 3: Explain the effect of alcoholic KOH With alcoholic KOH, elimination is favoured, especially on heating. The base removes a hydrogen from a carbon adjacent to the carbon carrying the halogen; loss of halide forms a double bond between these carbons:

$$CH_3CH_2Br + KOH(alc) \xrightarrow{\Delta} CH_2{=}CH_2 + KBr + H_2O.$$

An appropriate beta hydrogen is necessary for this dehydrohalogenation.

Step 4: Conclusion (i) Water converts the Grignard reagent into an alkane, so preparation requires anhydrous conditions. (ii) Aqueous KOH favours substitution to give an alcohol; alcoholic KOH favours beta elimination to give an alkene.

Quick Tip to Solve: Remember aqueous KOH replaces X by OH, whereas alcoholic KOH removes a beta H together with X.

18. What happens when D-glucose is treated with the following reagents?

(a) Br_2 water

(b) HCN [2 marks]

Solution:

Concept:

- The open-chain form of D-glucose is $CHO - (CHOH)_4 - CH_2OH$; its terminal aldehyde group undergoes oxidation and nucleophilic addition.
- Bromine water is a mild oxidising agent, whereas HCN adds across the carbonyl group to form a cyanohydrin.

Step 1: (a) Oxidation with bromine water Bromine water oxidises the aldehyde group of D-glucose to a carboxyl group, giving D-gluconic acid. The terminal primary alcohol group remains unchanged under these mild conditions.

$$CHO - (CHOH)_4 - CH_2OH + Br_2 + H_2O \longrightarrow COOH - (CHOH)_4 - CH_2OH + 2HBr.$$

This reaction establishes the presence of an aldehyde group in glucose.

Step 2: (b) Addition of hydrogen cyanide HCN reacts with the carbonyl group of the open-chain form. Cyanide adds to the carbonyl carbon, followed by protonation of oxygen, producing glucose

Quick Tip to Solve: Track the terminal CHO group: bromine water changes it to COOH, while HCN changes it to CH(OH)CN.

cyanohydrin:

$$\mathrm{CHO-(CHOH)_4-CH_2OH + HCN \longrightarrow HO-CH(CN)-(CHOH)_4-CH_2OH.}$$

The carbonyl oxygen becomes an OH group and the carbonyl carbon gains a CN group; the remaining carbon chain is retained.

Step 3: Conclusion (a) D-glucose forms D-gluconic acid with bromine water. (b) It forms glucose cyanohydrin with HCN.

Quick Tip to Solve: Track the terminal CHO group: bromine water changes it to COOH, while HCN changes it to CH(OH)CN.

19. Write the chemical equations when:

(a) Pentan-3-one is treated with H_2N-NH_2 followed by heating with KOH in high boiling solvent such as ethylene glycol.

(b) Two molecules of $(CH_3)_3C-CHO$ are treated with conc. NaOH. [2 marks]

Solution:

Concept:

- Wolff-Kishner reduction converts a carbonyl group to a methylene group using hydrazine followed by KOH and heat in a high boiling solvent.
- An aldehyde without an alpha-hydrogen undergoes Cannizzaro disproportionation in concentrated alkali: one molecule is reduced to an alcohol and another is oxidised to a carboxylate salt.

Step 1: (a) Reduction of pentan-3-one Pentan-3-one first forms its hydrazone with hydrazine, eliminating water:

$$\mathrm{CH_3CH_2COCH_2CH_3 + H_2NNH_2 \longrightarrow CH_3CH_2C(=NNH_2)CH_2CH_3 + H_2O.}$$

Heating this hydrazone with KOH in ethylene glycol removes nitrogen and replaces the carbonyl-derived group by a methylene group:

$$\mathrm{CH_3CH_2C(=NNH_2)CH_2CH_3 \xrightarrow[\text{ethylene glycol, }\Delta]{\text{KOH}} CH_3CH_2CH_2CH_2CH_3 + N_2.}$$

The five-carbon skeleton is preserved in this Wolff-Kishner reduction.

Step 2: (b) Cannizzaro reaction In $(CH_3)_3CCHO$, the alpha-carbon is bonded to three methyl groups and the aldehyde carbon, so it has no hydrogen. Hence concentrated NaOH causes disproportionation rather than aldol addition:

$$\mathrm{2(CH_3)_3CCHO + NaOH \longrightarrow (CH_3)_3CCH_2OH + (CH_3)_3CCOONa.}$$

One aldehyde molecule supplies the alcohol and the other supplies sodium 2,2-dimethylpropanoate.

Quick Tip to Solve: For concentrated alkali, inspect the carbon next to CHO: absence of alpha-hydrogen signals Cannizzaro reaction.

Step 3: Conclusion (a) Pentan-3-one gives pentane. (b) Two molecules of the aldehyde give 2,2-dimethylpropan-1-ol and sodium 2,2-dimethylpropanoate.

Quick Tip to Solve: For concentrated alkali, inspect the carbon next to CHO: absence of alpha-hydrogen signals Cannizzaro reaction.

20. Calculate the potential of Iron electrode in which the concentration of Fe^{2+} ion is 0.01 M. $E^{\circ}_{Fe^{2+}/Fe} = -0.45$ V at 298 K.
[Given: $\log 10 = 1$**]** [2 marks]

Solution:

Concept:

- For the reduction half-reaction $Fe^{2+} + 2e^- \longrightarrow Fe(s)$, the electron number is $n = 2$.
- At 298 K, the Nernst equation is $E = E^{\circ} - (0.0591/n)\log Q$. The activity of pure solid iron is unity, so $Q = 1/[Fe^{2+}]$.

Step 1: Write the electrode Nernst equation Using the reduction convention for the given standard potential and taking the ion concentration in molarity,

$$E_{Fe^{2+}/Fe} = E^{\circ}_{Fe^{2+}/Fe} - \frac{0.0591}{2}\log\frac{1}{[Fe^{2+}]}$$
$$= E^{\circ}_{Fe^{2+}/Fe} + \frac{0.0591}{2}\log[Fe^{2+}].$$

Solid iron does not appear as a concentration factor in the reaction quotient.

Step 2: Substitute the concentration The concentration is $0.01 = 10^{-2}$ M, so $\log 0.01 = -2$, using the supplied $\log 10 = 1$. Therefore,

$$E = -0.45 + \frac{0.0591}{2}(-2)$$
$$= -0.45 - 0.0591 = -0.5091\,\text{V}.$$

Diluting the reducible ion makes its reduction less favourable, consistent with a potential more negative than the standard value.

Step 3: Conclusion The iron electrode potential at 298 K is $\boxed{-0.5091\,\text{V}}$, approximately -0.51 V.

Quick Tip to Solve: For a metal-ion reduction electrode, use the plus sign before log ion concentration; dilution lowers its potential.

21. Write two differences between order of reaction and molecularity of reaction. [2 marks]

Solution:

Concept:

- The order of a reaction is the sum of the exponents of reactant concentrations in its experimentally determined rate law.
- Molecularity is the number of reacting species that participate together in a single elementary reaction step.

Step 1: Difference 1: how the quantities are determined Order is determined experimentally from the rate law. For example, if $r = k[A]^x[B]^y$, the overall order is $x + y$; these exponents need not equal the coefficients in the balanced overall equation. Molecularity is determined from the mechanism of an elementary step by counting the reacting atoms, ions or molecules participating in that step. Thus order describes measured rate dependence, whereas molecularity describes a microscopic event.

Step 2: Difference 2: possible values Order can be zero, an integer or a fraction, depending on the experimental rate law. Molecularity is always a positive integer, generally one, two or occasionally three; it cannot be zero or fractional because a reaction event must involve a whole number of reacting species. Molecularity applies to an elementary step, while an overall complex reaction can still have an experimentally defined order.

Step 3: Conclusion Order is obtained experimentally and may be zero, integral or fractional. Molecularity is counted for an elementary step and is always a positive integer.

Quick Tip to Solve: Remember the two comparisons as measured exponents versus counted species, and flexible values versus positive integers.

Section C (21 marks)

22. Compound (A) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compounds (B) and (C). The compound (B) on oxidation with PCC gives compound (D) which upon treatment with dilute NaOH and subsequent heating gives compound (E). Compound (E) on catalytic hydrogenation gives compound (C). The compound (D) is oxidized further to give compound (F) which is found to be a monobasic acid (Molecular weight = 60). Identify the compounds (A), (B), (C), (D), (E) and (F). [3 marks]

Solution:

Concept:

- Lithium aluminium hydride reduces an ester $RCOOR'$ to two alcohols: RCH_2OH and $R'OH$.
- PCC converts a primary alcohol into an aldehyde. An aldehyde containing an alpha hydrogen undergoes aldol addition, followed by dehydration on heating.

Step 1: Identify the acid, aldehyde and first alcohol The monobasic acid (F) has molecular weight 60. Ethanoic acid, CH_3COOH, has molecular weight $2(12) + 4(1) + 2(16) = 60$. Thus (F) is ethanoic acid. Since oxidation of aldehyde (D) gives this acid, (D) is ethanal, CH_3CHO. The primary alcohol

Quick Tip to Solve: Start from the acid of molecular weight 60, work backwards to ethanal and ethanol, then use the aldol product to find the ester alcohol group.

oxidised by PCC to ethanal must be ethanol, so (B) is CH_3CH_2OH. The sequence is

$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow{[O]} CH_3COOH.$$

Step 2: Use the aldol reaction to identify the second alcohol Ethanal reacts with dilute NaOH to form 3-hydroxybutanal; heating removes water to give but-2-enal (crotonaldehyde), which is (E):

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

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

Catalytic hydrogenation reduces both the carbon-carbon double bond and the aldehyde group. Hence (C) is butan-1-ol:

$$CH_3CH{=}CHCHO + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_2OH.$$

Step 3: Reconstruct the original ester The ester must contain the ethanoate portion that produces ethanol and the butyl portion that produces butan-1-ol on reduction. Therefore (A) is butyl ethanoate, $CH_3COOCH_2CH_2CH_2CH_3$. This has six carbons, twelve hydrogens and two oxygens, matching $C_6H_{12}O_2$. Its reduction gives exactly the two required alcohols:

$$CH_3COOCH_2CH_2CH_2CH_3 \xrightarrow{LiAlH_4} CH_3CH_2OH + CH_3CH_2CH_2CH_2OH.$$

Step 4: Conclusion (A) Butyl ethanoate; (B) ethanol; (C) butan-1-ol; (D) ethanal; (E) but-2-enal; (F) ethanoic acid.

Quick Tip to Solve: Start from the acid of molecular weight 60, work backwards to ethanal and ethanol, then use the aldol product to find the ester alcohol group.

23. Answer the following: (any three)

(a) What is peptide linkage?

(b) What type of bonds hold a DNA double helix together?

(c) Which one of the following is a polysaccharide?

Sucrose, Glucose, Starch, Fructose

(d) Give one example each for water-soluble vitamins and fat-soluble vitamins. [3 marks]

Solution:

Concept:

- A peptide linkage joins amino acids by condensation. Complementary bases in DNA form hydrogen bonds between the two strands.
- Polysaccharides contain many monosaccharide units; vitamins are classified according to whether they dissolve in water or fat.

Step 1: (a) Peptide linkage A peptide linkage is the amide bond $-CO-NH-$ formed between the carboxyl group of one amino acid and the amino group of another, with elimination of a water

Quick Tip to Solve: For DNA, distinguish hydrogen bonds between strands from phosphodiester bonds within a strand; remember A, D, E and K as fat-soluble vitamins.

molecule. For example,

$$H_2NCHRCOOH + H_2NCHR'COOH$$

$$\longrightarrow H_2NCHRCONHCHR'COOH + H_2O.$$

The $CO - NH$ connection in the product is the peptide linkage.

Step 2: (b) Bonds holding the DNA double helix together Hydrogen bonds between complementary nitrogenous bases hold the two strands together: adenine pairs with thymine through two hydrogen bonds, while guanine pairs with cytosine through three. The phosphodiester bonds form the sugar-phosphate backbone within each strand; they are not the bonds joining the paired bases across the two strands.

Step 3: (c) Identify the polysaccharide Starch is the polysaccharide. It is a polymer of alpha-D-glucose, consisting of amylose and amylopectin. Glucose and fructose are monosaccharides, whereas sucrose is a disaccharide made from glucose and fructose. Therefore the other three listed substances are not polysaccharides.

Step 4: (d) Examples of vitamins A water-soluble vitamin is vitamin C (ascorbic acid). A fat-soluble vitamin is vitamin A (retinol). Vitamin C dissolves in water, whereas vitamin A dissolves in fat; the latter belongs to the fat-soluble group A, D, E and K. These examples give one vitamin of each requested class.

Step 5: Conclusion The answers are: (a) $-CO - NH-$ peptide bond; (b) hydrogen bonds; (c) starch; (d) vitamin C (water-soluble) and vitamin A (fat-soluble). Any three of these parts may be attempted.

Quick Tip to Solve: For DNA, distinguish hydrogen bonds between strands from phosphodiester bonds within a strand; remember A, D, E and K as fat-soluble vitamins.

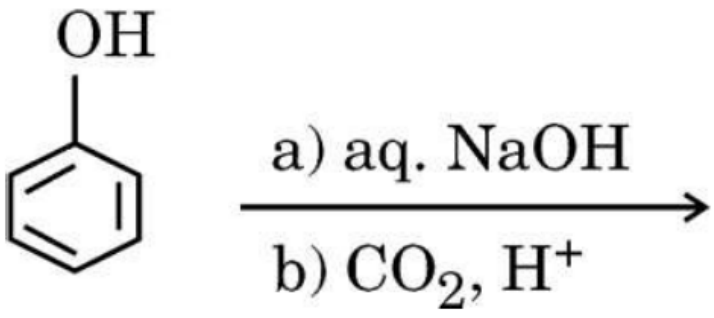
24. (a) Write the mechanism of the following reaction:

$CH_3CH_2OH \xrightarrow{H^+, 443\,K} CH_2{=}CH_2$

(b) Write the main product in each of the following reactions:

(i) $CH_3{-}CH_2{-}CH{=}CH_2 \xrightarrow[b)\ 3H_2O_2/OH^-]{a)\ B_2H_6}$?

(ii) [3 marks]



Solution:

Concept:

- Acid-catalysed dehydration removes water from an alcohol; protonation converts the hydroxyl group into a better leaving group.
- Hydroboration-oxidation adds water across an alkene with anti-Markovnikov orientation. The Kolbe reaction carboxylates sodium phenoxide mainly at the ortho position.

Step 1: (a) Protonation of ethanol The oxygen atom of ethanol accepts a proton from the acid. This forms protonated ethanol, in which water can act as a leaving group:

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2^+.$$

The reaction is carried out at $443\,K$, which favours elimination to ethene.

Step 2: (a) Elimination and regeneration of the catalyst In the standard acid-dehydration scheme, protonated ethanol loses water and then loses a proton from the adjacent carbon to form the double bond:

$$CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2^+ + H_2O,$$

$$CH_3CH_2^+ \longrightarrow CH_2{=}CH_2 + H^+.$$

For a primary alcohol, the unstable primary carbocation need not be a freely existing intermediate: departure of water and removal of the beta hydrogen can occur together. In either description the acid is regenerated and the net reaction is

$$CH_3CH_2OH \xrightarrow[443\,K]{H^+} CH_2{=}CH_2 + H_2O.$$

Step 3: (b)(i) Hydroboration-oxidation product The starting alkene is but-1-ene. In hydroboration, boron attaches preferentially to its less substituted terminal carbon. Oxidation with alkaline hydrogen peroxide replaces the carbon-boron bond with a carbon-oxygen bond without changing this orientation. Hence the main product is butan-1-ol, $CH_3CH_2CH_2CH_2OH$, and not butan-2-ol.

Step 4: (b)(ii) Kolbe reaction product Aqueous NaOH first converts phenol into sodium phenoxide:

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O.$$

Reaction with carbon dioxide gives mainly sodium salicylate. Acidification then gives 2-hydroxybenzoic acid (salicylic acid):

$$C_6H_5ONa \xrightarrow{CO_2} o\text{–}HOC_6H_4COONa$$

$$o\text{–}HOC_6H_4COONa \xrightarrow{H^+} o\text{–}HOC_6H_4COOH.$$

Thus the OH and COOH groups occupy adjacent positions on the benzene ring.

Step 5: Conclusion (a) Protonation followed by water elimination and proton removal gives ethene. (b)(i) Butan-1-ol; (b)(ii) 2-hydroxybenzoic acid (salicylic acid).

Quick Tip to Solve: With diborane followed by alkaline peroxide, put OH on the terminal carbon; with phenoxide and carbon dioxide, put COOH ortho to OH.

25. (a) Write the formula for the following coordination compound:

Potassium tetrahydroxidozincate (II)

(b) Arrange the following complexes in the increasing order of conductivity of their solution:

$[Cr(NH_3)_5Cl]Cl_2$, $[Cr(NH_3)_3Cl_3]$, $[Cr(NH_3)_6]Cl_3$

(c) Identify the type of isomerism exhibited by the following complexes:

(i) $[Co(NH_3)_5NO_2]^{2+}$

(ii) $[Co(en)_3]Cl_3$ [3 marks]

Solution:

Concept:

- Hydroxido is OH^-; determine the complex charge from the metal oxidation state and ligand charges.
- Counterions outside the coordination sphere dissociate. At comparable concentration, more free ions produce greater conductivity.
- An ambidentate ligand produces linkage isomerism; three bidentate en ligands around an octahedral metal can give optical isomerism.

Step 1: Balance the charges for (a) Zinc has oxidation state $+2$. Four hydroxido ligands contribute -4, so the complex has charge $+2-4=-2$. Its formula is therefore $[Zn(OH)_4]^{2-}$. Two potassium cations neutralise this charge, giving $K_2[Zn(OH)_4]$.

Step 2: Count the free ions for (b) The neutral complex $[Cr(NH_3)_3Cl_3]$ does not dissociate into ions. In $[Cr(NH_3)_5Cl]Cl_2$, one complex cation and two chloride counterions form, giving three ions per formula unit. In $[Cr(NH_3)_6]Cl_3$, one complex cation and three chloride counterions form, giving four ions. Coordinated chlorido ligands remain inside the coordination sphere and must not be counted as freely dissociated chloride. Hence, at comparable concentration, the increasing conductivity order is

$$[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]Cl_2 < [Cr(NH_3)_6]Cl_3.$$

Step 3: Identify the ligand behaviour for (c) (i) The nitrite ligand in $[Co(NH_3)_5NO_2]^{2+}$ is ambidentate. It can bind through nitrogen (nitro) or oxygen (nitrito), producing linkage isomerism. The composition stays the same, while the donor atom changes.

(ii) In $[Co(en)_3]Cl_3$, en is ethane-1,2-diamine, a bidentate ligand. Its three chelate rings give an octahedral arrangement with two non-superimposable mirror images, conventionally denoted Δ and Λ. These are optical isomers; the external chloride ions do not cause this stereoisomerism.

Step 4: Conclusion (a) $K_2[Zn(OH)_4]$. (b) The conductivity order is neutral complex, dichloride salt, then trichloride salt. (c) (i) Linkage isomerism; (ii) optical isomerism.

Quick Tip to Solve: Count only the complex ion and the counterions outside the brackets when comparing conductivity; nitrite can bind through N or O.

26. (a) Which of the following is an allylic halide?

(i) CH_3–CH=CH–Br

(ii) CH_2=CH–CH(Br)–CH_3

(b) Out of chlorobenzene and 2,4,6-trinitrochlorobenzene, which is more reactive towards nucleophilic substitution and why?

(c) Which isomer of C_4H_9Cl has the lowest boiling point? [3 marks]

Solution:

Concept:

- An allylic halide has halogen on an sp^3 carbon adjacent to a carbon-carbon double bond; a vinylic halide has halogen directly on a double-bond carbon.
- Ortho and para electron-withdrawing nitro groups stabilise the anionic intermediate in nucleophilic aromatic substitution.
- Among isomeric haloalkanes, greater branching generally reduces surface contact and London dispersion attractions, lowering the boiling point.

Step 1: Locate the bromine-bearing carbon in (a) In (i), $CH_3 - CH = CH - Br$, Br is directly bonded to an sp^2 carbon of the double bond. Thus (i) is a vinylic halide. In (ii), $CH_2 = CH - CH(Br) - CH_3$, Br is on the saturated sp^3 carbon immediately next to the double bond. Therefore compound (ii) is the allylic halide; proximity alone is insufficient unless the halogen-bearing carbon is adjacent to, rather than part of, the double bond.

Step 2: Explain the substitution reactivity in (b) 2,4,6-Trinitrochlorobenzene is more reactive towards nucleophilic substitution than chlorobenzene. Its nitro groups at positions 2 and 6 (ortho) and 4 (para) withdraw electron density by inductive and resonance effects. They make the carbon bearing chlorine more susceptible to nucleophilic attack and stabilise the negative charge of the addition intermediate by resonance. Loss of chloride then restores aromaticity. Chlorobenzene lacks this stabilisation, and resonance gives its C–Cl bond partial double-bond character, making substitution difficult.

Step 3: Compare branching of the isomers in (c) The C_4H_9Cl isomers include 1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane and 2-chloro-2-methylpropane. The last, $(CH_3)_3CCl$, is tert-butyl chloride and has the most compact arrangement. This reduces effective intermolecular surface contact and weakens dispersion attractions relative to the other isomers. Consequently less thermal energy is needed to separate its molecules, and it has the lowest boiling point.

Step 4: Conclusion (a) (ii), $CH_2 = CH - CH(Br) - CH_3$. (b) 2,4,6-Trinitrochlorobenzene, because its nitro groups stabilise the nucleophilic-substitution intermediate. (c) 2-Chloro-2-methylpropane (tert-butyl chloride).

Quick Tip to Solve: First locate the carbon carrying halogen: adjacent to the double bond means allylic; directly on the double bond means vinylic.

27. The following initial rate data were obtained for the reaction:

$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$

(a) What is the order with respect to NO and Br_2 in the reaction?

(b) Calculate the rate constant (k).

(c) Determine the rate of reaction when concentration of NO and Br_2 are 0.4 M and 0.2 M, respectively.

[3 marks]

$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$

Expt. No.	$[NO]/mol\ L^{-1}$	$[Br_2]/mol\ L^{-1}$	Initial Rate $(mol\ L^{-1}\ s^{-1})$
1	0·05	0·05	$1{\cdot}0 \times 10^{-3}$
2	0·05	0·15	$3{\cdot}0 \times 10^{-3}$
3	0·15	0·05	$9{\cdot}0 \times 10^{-3}$

Solution:

Concept:

- Use $r = k[NO]^m[Br_2]^n$, where m, n are experimentally determined orders and k is the rate constant.
- Compare experiments holding one reactant concentration constant; the rate ratio gives the power of the other concentration ratio.
- For total order three, the units of k are $L^2\,mol^{-2}\,s^{-1}$.

Step 1: Find the individual orders in (a) Experiments 1 and 2 have the same $[NO] = 0.05\,mol\,L^{-1}$. Bromine increases from 0.05 to 0.15 while rate increases from 1.0×10^{-3} to $3.0 \times 10^{-3}\,mol\,L^{-1}\,s^{-1}$. Thus $3 = 3^n$, giving $n = 1$. Experiments 1 and 3 keep bromine at 0.05 and triple NO from 0.05 to 0.15. Rate increases ninefold, giving $9 = 3^m$, so $m = 2$. The rate law is therefore $r = k[NO]^2[Br_2]$, with overall order three. These powers follow the data, not merely the balanced equation.

Step 2: Calculate the rate constant in (b) Using experiment 1,

$$k = \frac{r}{[NO]^2[Br_2]} = \frac{1.0 \times 10^{-3}}{(0.05)^2(0.05)} = 8.0\,L^2\,mol^{-2}\,s^{-1}.$$

The denominator is $1.25 \times 10^{-4}\,mol^3\,L^{-3}$. Dividing rate units by concentration cubed gives the stated units. As a consistency check, experiment 2 gives $3.0 \times 10^{-3}/[(0.05)^2(0.15)] = 8.0$, and experiment 3 gives the same constant.

Step 3: Substitute the specified concentrations in (c) For $[NO] = 0.4\,mol\,L^{-1}$ and $[Br_2] = 0.2\,mol\,L^{-1}$, use the experimentally established rate law:

$$r = 8.0(0.4)^2(0.2) = 8.0(0.16)(0.2) = 0.256\,mol\,L^{-1}\,s^{-1}.$$

As a ratio check against experiment 1, NO is eight times higher and bromine is four times higher. Thus rate is multiplied by $8^2 \times 4 = 256$, agreeing with $256 \times 10^{-3} = 0.256$.

Step 4: Conclusion The orders are 2 in NO and 1 in Br_2; $k = 8.0\,L^2\,mol^{-2}\,s^{-1}$, and the requested rate is $0.256\,mol\,L^{-1}\,s^{-1}$.

Quick Tip to Solve: Use experiments 1 and 2 for bromine order, then 1 and 3 for NO order; square only the NO concentration in the final substitution.

28. When a certain conductivity cell was filled with 0.05 M KCl solution, it has a resistance of 100 ohm at 25°C. When the same cell was filled with 0.02 M $AgNO_3$ solution, the resistance was 90 ohm. Calculate the conductivity and molar conductivity of $AgNO_3$ solution.

(Given: Conductivity of 0.05 M KCl solution = 1.35×10^{-2} ohm^{-1} cm^{-1}) [3 marks]

Solution:

Concept:

- Conductivity is related to resistance by $\kappa = G(l/A) = (l/A)/R$, where $G = 1/R$ is conductance and l/A is the cell constant.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when κ is in $\Omega^{-1}\,\text{cm}^{-1}$ and concentration c is in $\text{mol}\,\text{L}^{-1}$.

Step 1: Determine the cell constant using KCl The KCl solution calibrates the geometry of the conductivity cell. Using its known conductivity and measured resistance,

$$\frac{l}{A} = \kappa_{\text{KCl}} R_{\text{KCl}} = (1.35 \times 10^{-2})(100) = 1.35\,\text{cm}^{-1}.$$

This cell constant depends on the separation and area of the electrodes, so it remains the same when the solution is replaced.

Step 2: Calculate conductivity of silver nitrate For the same cell filled with $0.02\,\text{M}$ silver nitrate, $R = 90\,\Omega$. Hence

$$\kappa_{\text{AgNO}_3} = \frac{l/A}{R} = \frac{1.35}{90} = 1.50 \times 10^{-2}\,\Omega^{-1}\,\text{cm}^{-1}.$$

Its lower resistance corresponds to higher conductivity than that of the KCl calibration solution.

Step 3: Convert conductivity to molar conductivity Use the concentration of the silver nitrate solution, not the concentration of the calibration solution. The factor 1000 converts litres to cubic centimetres:

$$\Lambda_m = \frac{1000\kappa}{c} = \frac{1000 \times 1.50 \times 10^{-2}}{0.02} = 750\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}.$$

The units follow by dividing conductivity by concentration expressed in $\text{mol}\,\text{cm}^{-3}$.

Step 4: Conclusion For $AgNO_3$, $\boxed{\kappa = 1.50 \times 10^{-2}\,\Omega^{-1}\,\text{cm}^{-1}}$ and $\boxed{\Lambda_m = 750\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}}$.

Quick Tip to Solve: First find the cell constant from KCl; use the AgNO3 concentration only in the final molar-conductivity calculation.

Section D (8 marks)

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

29. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds whereas 'The Crystal Field Theory' for coordination compounds is based on the effect of different crystal fields (provided by ligands taken as point charges), on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields. The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron. Coordination compounds find extensive applications in metallurgical processes, analytical and medicinal chemistry.

Answer the following questions: [4 marks]

29(a). What is crystal field splitting energy? [1 mark]

Solution:

Concept:

- In a free metal ion, the five d-orbitals have equal energy (they are degenerate).
- Ligand interactions split these orbitals into groups of different energies; the gap is the crystal field splitting energy.

Step 1: Identify the ligand-induced splitting When ligands approach the central metal ion, their interaction with its d-orbitals depends on orbital orientation. Thus the originally degenerate orbitals no longer all have the same energy.

Step 2: Define the energy separation Crystal field splitting energy is the energy difference between the two sets of d-orbitals produced by the ligand field. In an octahedral complex it is written $\Delta_o = E(e_g) - E(t_{2g})$, where t_{2g} is the lower-energy set and e_g the higher-energy set.

Step 3: Conclusion Crystal field splitting energy is the energy gap between the two sets of metal d-orbitals formed in a crystal field.

Quick Tip to Solve: Define the separation between the orbital sets, rather than merely saying that the orbitals split.

29(b). Give reason for the violet colour of the complex $[Ti(H_2O)_6]^{3+}$ on the basis of crystal field theory. [1 mark]

Solution:

Concept:

- In $[Ti(H_2O)_6]^{3+}$, neutral water ligands leave titanium in oxidation state $+3$, with configuration $3d^1$.
- An octahedral field splits the metal d-orbitals into lower t_{2g} and higher e_g levels.

Step 1: Locate the single d electron The six water ligands produce an octahedral field. The single d-electron of Ti^{3+} occupies the lower-energy t_{2g} level, leaving the higher-energy e_g level empty.

Quick Tip to Solve: For a colour question, connect the d-electron configuration, visible absorption and complementary observed colour.

Step 2: Explain absorption and the observed colour The electron absorbs visible light with energy $h\nu = \Delta_o$ and is promoted from t_{2g} to e_g. This is a d-d transition. Absorption removes the appropriate yellow-green component from incident white light; the remaining transmitted light gives the complementary violet appearance.

Step 3: Conclusion The complex is violet because its $3d^1$ titanium ion undergoes a visible-light $t_{2g} \rightarrow e_g$ transition and the transmitted light has the complementary violet colour.

Quick Tip to Solve: For a colour question, connect the d-electron configuration, visible absorption and complementary observed colour.

29(c). $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why. [Atomic No.: Cr = 24, Ni = 28] [2 marks]

Solution:

Concept:

- An ion or complex with unpaired electrons is paramagnetic; a complex with all electrons paired is diamagnetic.
- Find the metal oxidation state first. Neutral NH_3 gives Cr^{3+}, while four CN^- ligands in a complex of charge -2 give Ni^{2+}.

Step 1: Explain the chromium complex Chromium has ground-state configuration $[Ar]3d^5 4s^1$; removal of three electrons gives Cr^{3+} : $[Ar]3d^3$. In the octahedral complex $[Cr(NH_3)_6]^{3+}$, the three electrons occupy the three lower t_{2g} orbitals singly: $t_{2g}^3 e_g^0$. There are three unpaired electrons, so it is paramagnetic.

Step 2: Explain the nickel complex Nickel has configuration $[Ar]3d^8 4s^2$, so Ni^{2+} is $[Ar]3d^8$. Cyanide is a strong-field ligand. In $[Ni(CN)_4]^{2-}$, the $3d$ electrons pair so that one $3d$ orbital becomes available for dsp^2 hybridisation. The complex is square planar and all eight d-electrons are paired. Therefore it is diamagnetic; applying the free-ion arrangement without considering the strong ligand field would give the wrong conclusion.

Step 3: Conclusion $[Cr(NH_3)_6]^{3+}$ has three unpaired electrons and is paramagnetic, whereas square-planar $[Ni(CN)_4]^{2-}$ has no unpaired electrons and is diamagnetic.

Quick Tip to Solve: Count unpaired electrons in the complex after finding oxidation state and ligand-field arrangement, not in the neutral atom.

OR

29(c). Explain why $[Fe(CN)_6]^{3-}$ is an inner orbital complex, whereas $[Fe(H_2O)_6]^{3+}$ is an outer orbital complex. [Atomic No.: Fe = 26] [2 marks]

Solution:

Concept:

- For iron, $Z = 26$: $Fe = [Ar]3d^6 4s^2$. Removal of two $4s$ electrons and one $3d$ electron gives $Fe^{3+} = [Ar]3d^5$.
- In valence bond theory, octahedral inner orbital complexes use d^2sp^3 hybridisation involving two $3d$ orbitals; outer orbital complexes use sp^3d^2 involving two $4d$ orbitals.

Step 1: Apply the strong-field ligand effect In $[Fe(CN)_6]^{3-}$, cyanide is a strong-field ligand. It causes pairing of the five $3d$ electrons into three $3d$ orbitals, leaving two $3d$ orbitals vacant. These two inner orbitals combine with one $4s$ and three $4p$ orbitals to form six d^2sp^3 hybrids that accept ligand lone pairs. The complex is low spin, with one unpaired electron.

Step 2: Apply the weak-field ligand effect In $[Fe(H_2O)_6]^{3+}$, water is a weak-field ligand and does not cause pairing of the $3d^5$ electrons. All five $3d$ orbitals remain singly occupied, so no pair of vacant inner $3d$ orbitals is available. The metal instead uses one $4s$, three $4p$ and two outer $4d$ orbitals to form sp^3d^2 hybrids. The complex is high spin, with five unpaired electrons.

Step 3: Conclusion Therefore $[Fe(CN)_6]^{3-}$ is an inner orbital d^2sp^3 complex, whereas $[Fe(H_2O)_6]^{3+}$ is an outer orbital sp^3d^2 complex.

Quick Tip to Solve: First find the metal-ion d count; then ask whether the ligand leaves two inner d orbitals vacant.

30. Batteries and fuel cells are very useful forms of galvanic cell. Any battery or cell that we use as a source of electrical energy is basically a galvanic cell. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries – primary batteries and secondary batteries.

In the primary batteries, the reaction occurs only once and after use over a period of time the battery becomes dead and cannot be reused again, whereas the secondary batteries are rechargeable.

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. To solve this problem, galvanic cells are designed in such a way that energy of combustion of fuels is directly converted into electrical energy, and these are known as fuel cells. One such fuel cell was used in the Apollo space programme.

Answer the following questions: [4 marks]

30(a). How do primary batteries differ from secondary batteries? [1 mark]

Solution:

Concept:

- A battery supplies electrical energy through a spontaneous oxidation-reduction reaction.

Quick Tip to Solve: Use the reversibility of the discharge reaction as the main distinction, then state rechargeability.

- Rechargeability depends on whether an external current can reverse the discharge reaction and regenerate the active materials.

Step 1: Identify primary batteries In a primary battery, the discharge reaction is effectively irreversible under normal use. Once its reactants are consumed, the battery becomes exhausted and cannot be recharged for repeated use. A dry cell is a standard example.

Step 2: Identify secondary batteries A secondary battery has a reversible discharge reaction. Passing an external current in the opposite direction regenerates its active materials, allowing it to be charged and discharged repeatedly. A lead storage battery is a standard example.

Step 3: Conclusion Primary batteries are non-rechargeable, whereas secondary batteries are rechargeable because their discharge reactions can be reversed.

Quick Tip to Solve: Use the reversibility of the discharge reaction as the main distinction, then state rechargeability.

30(b). The cell potential of Mercury cell is 1.35 V, and remains constant during its life. Give reason.

[1 mark]

Solution:

Concept:

- Cell potential depends on the activities of the species in the net cell reaction through the Nernst equation.
- Pure solids and pure liquid mercury have essentially constant activity during operation at a fixed temperature.

Step 1: Write the net mercury-cell reaction The net discharge reaction is

$$\mathrm{Zn(Hg)} + \mathrm{HgO}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Hg}(l).$$

Hydroxide ions consumed at one electrode are regenerated at the other and cancel from the net reaction.

Step 2: Explain the constant reaction quotient The net reaction involves no dissolved ions whose concentration changes as discharge proceeds. Consequently, the effective activities of the reactants and products remain essentially constant during the useful life of the cell. Its reaction quotient, and therefore its potential at fixed temperature, do not vary appreciably.

Step 3: Conclusion The mercury cell maintains approximately $1.35\,\mathrm{V}$ because its overall reaction has no ions in solution whose changing concentration would alter the cell potential.

Quick Tip to Solve: Write the overall reaction and cancel hydroxide ions before explaining why the potential stays constant.

30(c). Write the reactions involved in the recharging of the lead storage battery. [2 marks]

Solution:

Concept:

- Charging a secondary battery requires an external source to drive the reverse of its spontaneous discharge reaction.
- In a discharged lead storage battery, both plates contain $PbSO_4$; charging restores Pb, PbO_2 and sulfuric acid.

Step 1: Reduce lead sulfate at the negative plate During charging, the negative plate receives electrons and acts as the cathode of the electrolytic process. Lead sulfate is reduced to metallic lead:

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

The regenerated lead is the negative electrode material needed for subsequent discharge.

Step 2: Oxidise lead sulfate at the positive plate The positive plate loses electrons and acts as the anode during charging. Its lead sulfate is converted into lead dioxide:

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

Electrons cancel when the two half-reactions are added. Sulfate ions and hydrogen ions regenerate sulfuric acid in the electrolyte.

Step 3: Conclusion The overall recharging reaction is

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

Thus the original electrode materials and electrolyte are restored.

Quick Tip to Solve: Reverse the discharge reactions and check that electrons cancel and both lead atoms are conserved.

OR

30(c). Write two advantages of fuel cells over other galvanic cells. [2 marks]

Solution:

Concept:

- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy through electrode reactions.
- In a hydrogen-oxygen fuel cell, the overall reaction is $2H_2 + O_2 \rightarrow 2H_2O$. Its product is water.

Step 1: Advantage 1: continuous operation A fuel cell keeps supplying electrical energy as long as fuel and oxidant are fed to it and products are removed. Ordinary galvanic batteries have a finite amount of reactants stored inside them and cease supplying current when these reactants are exhausted. Thus,

Quick Tip to Solve: Link continuous reactant feed to long operation, and use the hydrogen-oxygen reaction to justify the clean product.

a fuel cell gives a sustained supply without repeatedly replacing a discharged cell or interrupting use to recharge it.

Step 2: Advantage 2: clean electricity generation A hydrogen-oxygen fuel cell produces water as its reaction product. It avoids polluting combustion gases and the spent chemical materials associated with many conventional galvanic cells. This advantage refers to the hydrogen-oxygen fuel cell: its overall reaction has no carbon-containing product and does not produce smoke during operation.

Step 3: Conclusion Two advantages are continuous electricity generation while fuel and oxidant are supplied, and pollution-free operation of the hydrogen-oxygen fuel cell, whose product is water.

Quick Tip to Solve: Link continuous reactant feed to long operation, and use the hydrogen-oxygen reaction to justify the clean product.

Section E (15 marks)

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

(1) The melting and boiling points of Zn, Cd and Hg are low.

(2) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

(3) E° value of Cu^{2+}/Cu is + 0.34 V.

(ii) Complete and balance the following chemical equations:

(1) $KMnO_4 \xrightarrow{heat}$?

(2) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow$? [5 marks]

Solution:

Concept:

- Metallic bonding depends on participation of valence electrons; filled d subshells contribute little to the strong bonding characteristic of many transition metals.
- Oxidation or reduction is favoured when it leads to a particularly stable configuration, such as d^3 for Cr^{3+} or half-filled d^5 for Mn^{2+}.
- The standard electrode potential depends on the overall energy balance involving atomisation, ionisation and hydration; balanced redox equations conserve both atoms and charge.

Step 1: (i)(1) Low melting and boiling points Zn, Cd and Hg have the general valence configuration $(n-1)d^{10}ns^2$. Their filled d subshells contain no unpaired electrons, so the d electrons contribute little to metallic bonding compared with metals having partially filled d subshells. The resulting weaker metallic bonds and relatively low enthalpies of atomisation account for their low melting and boiling points.

Step 2: (i)(2) Opposite redox behaviour of the two d-four ions Both Cr^{2+} and Mn^{3+} have $3d^4$ configurations. Chromium(II) readily loses an electron to form chromium(III), with the stable $3d^3$ configuration:

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

By donating an electron it reduces another species and therefore acts as a strong reducing agent.

Quick Tip to Solve: For the redox comparison, write the configuration after electron loss or gain; for dichromate, balance oxygen with water and hydrogen with hydrogen ions.

Manganese(III), in contrast, readily gains an electron to form manganese(II), with the stable half-filled $3d^5$ configuration:

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

By accepting an electron it oxidises another species and therefore acts as a strong oxidising agent.

Step 3: (i)(3) Positive standard potential of copper Converting copper metal into aqueous $\mathrm{Cu^{2+}}$ requires atomisation followed by removal of two electrons. Copper has a high enthalpy of atomisation and high total ionisation enthalpy, including the energy needed to remove the second electron from the stable $3d^{10}$ configuration of $\mathrm{Cu^+}$. The hydration enthalpy of $\mathrm{Cu^{2+}}$ does not compensate sufficiently for these energy requirements. Hence oxidation of Cu to $\mathrm{Cu^{2+}}$ is unfavourable relative to hydrogen under standard conditions, and the reverse reduction has a positive standard potential:

$$\mathrm{Cu^{2+} + 2e^- \rightarrow Cu}, \qquad E^\circ = +0.34\,\mathrm{V}.$$

Step 4: (ii)(1) Thermal decomposition of potassium permanganate On heating, potassium permanganate forms potassium manganate, manganese dioxide and oxygen:

$$\mathrm{2KMnO_4} \xrightarrow{\text{heat}} \mathrm{K_2MnO_4 + MnO_2 + O_2}.$$

The equation conserves two K atoms, two Mn atoms and eight O atoms on each side. Manganese is reduced from $+7$ to $+6$ and $+4$, while part of the oxygen is oxidised from -2 to zero.

Step 5: (ii)(2) Oxidation of iodide by dichromate In acidic solution, dichromate is reduced to chromium(III), while iodide is oxidised to iodine. The half-reactions are

$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O},$$
$$\mathrm{6I^- \rightarrow 3I_2 + 6e^-}.$$

Adding and cancelling the six electrons gives

$$\mathrm{Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O}.$$

The net charge is $+6$ on both sides, and all Cr, I, O and H atoms are balanced.

Step 6: Conclusion The explanations follow from weak metallic bonding, formation of stable d^3 and d^5 ions, and the unfavourable energy balance for copper oxidation. The equation products are $\mathrm{K_2MnO_4 + MnO_2 + O_2}$ on heating, and $\mathrm{2Cr^{3+} + 3I_2 + 7H_2O}$ for acidic dichromate with iodide, with coefficients as balanced above.

Quick Tip to Solve: For the redox comparison, write the configuration after electron loss or gain; for dichromate, balance oxygen with water and hydrogen with hydrogen ions.

OR

31(b). (i) Out of Cu_2Cl_2 and $CuCl_2$, which is more stable in aqueous solution and why?
(ii) Write the general electronic configuration of f-block elements.
(iii) Predict which of the following will be coloured in aqueous solution and why?
Sc^{3+}, Fe^{3+}, Zn^{2+}
[Atomic number: Sc = 21, Fe = 26, Zn = 30]
(iv) How can you obtain potassium dichromate from sodium chromate?
(v) Why do transition metals and their compounds show catalytic activities? [5 marks]

Solution:

Concept:

- The stability of a metal ion in water depends on the energy required to form it and the energy released on hydration. A more negative hydration enthalpy can favour a higher oxidation state.
- In f-block elements the differentiating electron enters an inner f subshell. The general configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- In the usual CBSE explanation, partially filled d orbitals allow transitions between energy levels split by ligands, producing colour. Variable oxidation states and surface adsorption help transition metals act as catalysts.

Step 1: (i) Compare the aqueous stability of copper chlorides $CuCl_2$, containing copper(II), is more stable in aqueous solution than Cu_2Cl_2, containing copper(I). The hydration enthalpy of Cu^{2+} is much more negative than that of Cu^+; this compensates for the energy required to remove the second electron. Copper(I) therefore tends to disproportionate in water:

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s).$$

Thus, the comparison must include hydration, even though the isolated Cu^+ ion has a filled $3d^{10}$ configuration.

Step 2: (ii) State the f-block configuration The general electronic configuration is

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2.$$

Here n denotes the outermost principal shell. The $(n-2)f$ subshell is filled progressively, while the $(n-1)d$ subshell can contain zero or one electron. For the lanthanoids and actinoids, the inner subshells being filled are $4f$ and $5f$, respectively.

Step 3: (iii) Determine the configurations and colour of the ions Remove the outer $4s$ electrons before the $3d$ electrons when forming these ions:

$$Sc^{3+} : [Ar]\, 3d^0,$$
$$Fe^{3+} : [Ar]\, 3d^5,$$
$$Zn^{2+} : [Ar]\, 3d^{10}.$$

Fe^{3+} is coloured because its partially filled d subshell permits electronic transitions involving the split

Quick Tip to Solve: For ion colour, remove the 4s electrons first and count the remaining 3d electrons; for aqueous copper stability, compare hydration as well as electronic configuration.

d levels in aqueous complexes. Sc^{3+} has no d electrons and Zn^{2+} has a completely filled d subshell, so neither supports the usual d-d transitions; both are colourless in aqueous solution.

Step 4: (iv) Prepare potassium dichromate from sodium chromate First acidify aqueous sodium chromate with sulphuric acid to convert chromate into sodium dichromate:

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

Then treat the sodium dichromate solution with potassium chloride:

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

Potassium dichromate is less soluble than sodium dichromate, so it crystallises from the concentrated solution on cooling and can be separated.

Step 5: (v) Explain catalytic activity Transition metals can adopt variable oxidation states, allowing them to form intermediate compounds with reactants and subsequently regenerate the catalyst. This provides an alternative reaction pathway with a lower activation energy. Their metal surfaces also adsorb reactants, bringing them together and weakening bonds that must break. These features explain the catalytic activity of transition metals and many of their compounds; for example, iron catalyses ammonia synthesis and V_2O_5 catalyses the oxidation of SO_2 to SO_3.

Step 6: Conclusion (i) $CuCl_2$ is more stable in water owing to the greater hydration of Cu^{2+}. (ii) The general configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. (iii) Only Fe^{3+} is coloured among the given ions. (iv) Acidify sodium chromate, then add KCl and crystallise $K_2Cr_2O_7$. (v) Variable oxidation states, intermediate formation and adsorption account for catalytic activity.

Quick Tip to Solve: For ion colour, remove the 4s electrons first and count the remaining 3d electrons; for aqueous copper stability, compare hydration as well as electronic configuration.

32(a). (i) At the same temperature, CO_2 gas is more soluble in water than O_2 gas. Which one of them will have higher value of K_H and why?

(ii) How does the size of blood cells change when placed in an aqueous solution containing more than 0.9% (mass/volume) sodium chloride?

(iii) 1 molal aqueous solution of an electrolyte A_2B_3 is 60% ionized. Calculate the boiling point of the solution.

(Given: K_b for H_2O = 0.52 K kg mol^{-1}) [5 marks]

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the partial pressure of the gas and x its mole fraction in solution. At a given temperature and pressure, a larger K_H means a smaller solubility.
- Osmosis is the movement of water through a semipermeable membrane from the solution of lower solute concentration to that of higher solute concentration. A hypertonic solution draws water out of blood cells.

Quick Tip to Solve: For partial ionization, first count the total ions per formula unit, then use $i = 1 + (n-1)\alpha$; add the calculated boiling-point elevation to $100\,^\circ$C.

- Elevation of boiling point is $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b is the solvent's ebullioscopic constant and m is the molality. For dissociation into n ions, $i = 1 + (n-1)\alpha$, with α the fraction ionized.

Step 1: (i) Compare Henry's law constants At the same gas pressure, Henry's law gives $x = p/K_H$. Thus solubility is inversely related to K_H. The question states that carbon dioxide is more soluble in water than oxygen at the same temperature. Therefore oxygen has the higher Henry's law constant: $K_H(\mathrm{O_2}) > K_H(\mathrm{CO_2})$. A higher constant represents a smaller dissolved mole fraction for a given partial pressure, rather than a greater solubility.

Step 2: (ii) Apply osmosis to blood cells An aqueous sodium chloride solution of approximately 0.9% (mass/volume) is isotonic with blood cells. A solution containing more than this concentration is hypertonic relative to the cell contents. The cell membrane acts as a semipermeable membrane, so water moves from inside the cells into the more concentrated external solution by exosmosis. The cells consequently lose water and shrink; this shrinking of red blood cells is called crenation.

Step 3: (iii) Count particles after ionization One formula unit of $\mathrm{A_2B_3}$ produces two A ions and three B ions on complete ionization, hence five ions in all. The degree of ionization is $\alpha = 60/100 = 0.60$. Starting with one mole of electrolyte, 0.40 mole remains unionized, while the ionized 0.60 mole produces $5(0.60) = 3.00$ moles of ions. The total particle amount is therefore 3.40 moles per initial mole of solute:

$$i = (1-\alpha) + 5\alpha = 1 + 4\alpha = 1 + 4(0.60) = 3.40.$$

This calculation accounts for partial ionization; using $i = 5$ would incorrectly assume complete ionization.

Step 4: (iii) Calculate the elevation and final boiling point With $m = 1\,\mathrm{mol\,kg^{-1}}$ and $K_b = 0.52\,\mathrm{K\,kg\,mol^{-1}}$,

$$\Delta T_b = iK_b m = 3.40 \times 0.52 \times 1 = 1.768\,\mathrm{K}.$$

Add the elevation to the normal boiling point of pure water, $100\,^\circ\mathrm{C}$. A temperature difference has the same numerical value in kelvin and degrees Celsius, so

$$T_b = 100 + 1.768 = 101.768\,^\circ\mathrm{C}.$$

Step 5: Conclusion (i) Oxygen has the higher K_H, because it is less soluble. (ii) The blood cells shrink due to exosmosis in the hypertonic sodium chloride solution. (iii) The solution boils at $101.768\,^\circ\mathrm{C}$, approximately $101.77\,^\circ\mathrm{C}$, at normal atmospheric pressure.

Quick Tip to Solve: For partial ionization, first count the total ions per formula unit, then use $i = 1 + (n-1)\alpha$; add the calculated boiling-point elevation to $100\,^\circ\mathrm{C}$.

OR

32(b). (i) The vapour pressures of A and B at 25°C are 75 mm Hg and 25 mm Hg, respectively. If A and B are mixed such that the mole fraction of A in the mixture is 0.4, then calculate the mole fraction of B in vapour phase.

(ii) Define colligative property. Which colligative property is preferred for the molar mass determination of macromolecules?

(iii) Why are equimolar solutions of sodium chloride and glucose not isotonic? [5 marks]

Solution:

Concept:

- For an ideal liquid solution, Raoult's law gives $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$, where x is the liquid-phase mole fraction and p^0 is the pure-component vapour pressure at the same temperature.
- Dalton's law gives the vapour-phase mole fraction $y_B = p_B/(p_A + p_B)$. A vapour mole fraction need not equal the corresponding liquid mole fraction.
- Colligative properties depend on the number of solute particles relative to solvent particles, rather than on the chemical identity of the solute. Osmotic pressure obeys $\pi = iCRT$, where i is the van't Hoff factor, C the molarity, R the gas constant and T the absolute temperature.

Step 1: (i) Calculate the partial vapour pressures The liquid mole fractions sum to unity, so $x_B = 1 - 0.4 = 0.6$. Applying Raoult's law to both components at $25°$C,

$$p_A = 0.4 \times 75 = 30\,\text{mm Hg},$$
$$p_B = 0.6 \times 25 = 15\,\text{mm Hg},$$
$$P = p_A + p_B = 45\,\text{mm Hg}.$$

Both liquids contribute to the total pressure; using the pure vapour pressures directly would ignore their liquid-phase compositions.

Step 2: (i) Obtain the vapour-phase composition The required fraction is the fraction of the total vapour pressure contributed by B:

$$y_B = \frac{p_B}{P} = \frac{15}{45} = \frac{1}{3} \approx 0.333.$$

As a check, $y_A = 30/45 = 2/3$, and $y_A + y_B = 1$. A has the larger pure vapour pressure and hence is enriched in the vapour: its vapour fraction exceeds its liquid fraction, while B's vapour fraction is below 0.6.

Step 3: (ii) Define the property and select the preferred method A colligative property is a property of a dilute solution that depends only on the number of dissolved solute particles relative to the number of solvent particles, and not on the nature of the solute. Examples include relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure.

Osmotic pressure is preferred for determining the molar masses of macromolecules. For a non-

Quick Tip to Solve: First calculate each partial pressure from its liquid mole fraction, then divide by total pressure for vapour composition; for tonicity, compare particle concentrations using iC.

electrolyte of mass w dissolved to give solution volume V,

$$\pi = \frac{wRT}{MV}, \qquad M = \frac{wRT}{\pi V}.$$

Even very dilute macromolecular solutions give a measurable osmotic pressure, whereas their boiling-point elevations and freezing-point depressions are very small. Osmotic pressure can also be measured at room temperature, avoiding heating that may damage sensitive macromolecules.

Step 4: (iii) Compare the particle concentrations Isotonic solutions have equal osmotic pressures at the same temperature. Glucose does not dissociate in water, so its van't Hoff factor is $i = 1$. Sodium chloride dissociates into Na^+ and Cl^-, giving more dissolved particles per mole; for complete dissociation, $i = 2$.

Therefore, at equal molarity C and temperature, $\pi_{\text{glucose}} = CRT$, whereas $\pi_{\text{NaCl}} \approx 2CRT$ in the ideal dilute limit. The sodium chloride solution has the higher osmotic pressure, so the equimolar solutions are not isotonic. Deviations from ideal dissociation may change the numerical factor, but do not make equal formula-unit concentrations equal particle concentrations.

Step 5: Conclusion (i) The mole fraction of B in the vapour phase is $\boxed{y_B = 1/3 \approx 0.333}$. (ii) A colligative property depends on the relative number of solute particles; $\boxed{\text{osmotic pressure}}$ is preferred for macromolecular molar masses. (iii) Equimolar NaCl and glucose solutions are not isotonic because NaCl dissociation produces more particles and hence a higher osmotic pressure.

Quick Tip to Solve: First calculate each partial pressure from its liquid mole fraction, then divide by total pressure for vapour composition; for tonicity, compare particle concentrations using iC.

33. Answer any five questions of the following:

(a) N,N-diethyl-benzenesulphonamide is insoluble in alkali. Give reason.

(b) Aniline does not undergo Friedel-Crafts reaction. Why?

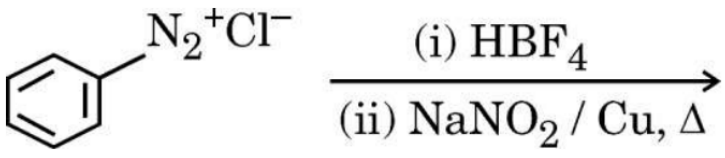
(c) Write a simple chemical test to distinguish between methylamine and aniline.

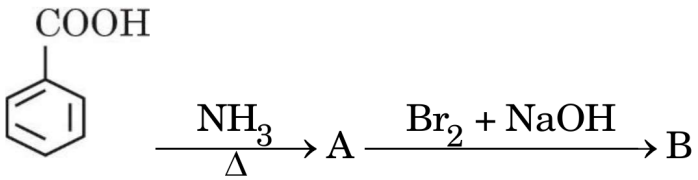
(d) Write the chemical reaction involved in Gabriel phthalimide synthesis.

(e) How will you convert aniline to p-bromoaniline?

(f) Complete the following reaction:

(g) Write the structures of A and B in the following reaction: [5 marks]





Solution:

Concept:

- Sulphonamides dissolve in alkali when an acidic hydrogen attached to nitrogen can be removed to form an ionic salt.
- The amino group reacts with Lewis acids; protection by acetylation controls electrophilic substitution in aniline.
- Gabriel synthesis gives primary alkylamines, while Hofmann bromamide degradation converts a primary amide into an amine with one fewer carbon atom.

Step 1: (a) Explain insolubility in alkali The structure is $C_6H_5SO_2N(C_2H_5)_2$. Both hydrogen atoms originally attached to nitrogen have been replaced by ethyl groups, so there is no $N-H$ hydrogen. It cannot lose an acidic proton to form a water-soluble salt with alkali. Therefore, N,N-diethylbenzenesulphonamide remains insoluble in alkali.

Step 2: (b) Explain the failure of Friedel-Crafts reaction The lone pair on the nitrogen of aniline coordinates with the Lewis acid catalyst $AlCl_3$, forming a salt-like complex. This makes the amino substituent strongly electron withdrawing and deactivates the benzene ring towards electrophilic substitution. Thus aniline does not undergo the usual Friedel-Crafts alkylation or acylation with this catalyst.

Step 3: (c) Distinguish methylamine and aniline Treat separate samples with nitrous acid, generated from $NaNO_2$ and dilute HCl, at 273–278 K. Methylamine releases nitrogen gas with brisk effervescence:

$$CH_3NH_2 + HNO_2 \longrightarrow CH_3OH + N_2 \uparrow + H_2O.$$

Aniline forms a stable benzenediazonium salt at this low temperature, without immediate nitrogen evolution:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

The diazonium solution may be coupled with alkaline beta-naphthol to give an orange-red azo dye, confirming aniline. The carbylamine test would not distinguish these two compounds because both are primary amines.

Step 4: (d) Write Gabriel phthalimide synthesis Phthalimide reacts with alcoholic potassium hydroxide to form potassium phthalimide. Alkylation with an alkyl halide $R-X$, followed by hydrolysis, gives a primary amine:

$$C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK + H_2O,$$
$$C_6H_4(CO)_2NK + R-X \longrightarrow C_6H_4(CO)_2NR + KX,$$
$$C_6H_4(CO)_2NR + 2NaOH \longrightarrow C_6H_4(COONa)_2 + RNH_2.$$

Here R is an alkyl group. The alkylation step does not work with ordinary aryl halides, so this method is not used to prepare aniline.

Step 5: (e) Convert aniline to para-bromoaniline First protect the amino group by acetylation with acetic anhydride. Brominate acetanilide with bromine in acetic acid, isolate the major para product,

Quick Tip to Solve: Read the entire reagent sequence: NaNO2/Cu after diazonium tetrafluoroborate gives nitrobenzene, whereas heating the salt alone gives fluorobenzene.

and hydrolyse the acetyl group:

$$\begin{aligned} C_6H_5NH_2 &\xrightarrow{(CH_3CO)_2O} C_6H_5NHCOCH_3 \\ &\xrightarrow{Br_2/CH_3COOH} \text{p-}BrC_6H_4NHCOCH_3 \\ &\xrightarrow{H_2O/H^+,\ \text{heat}} \text{p-}BrC_6H_4NH_2. \end{aligned}$$

After acid hydrolysis, neutralise to obtain the free amine. Protection reduces the strong activating effect of $-NH_2$, preventing the direct formation of 2,4,6-tribromoaniline with bromine water.

Step 6: (f) Complete the diazonium reaction Fluoroboric acid first converts benzenediazonium chloride to benzenediazonium tetrafluoroborate. Treatment with sodium nitrite in the presence of copper and heat replaces the diazonium group by a nitro group:

$$C_6H_5N_2^+Cl^- \xrightarrow{HBF_4} C_6H_5N_2^+BF_4^- \xrightarrow{NaNO_2/Cu,\ \Delta} C_6H_5NO_2.$$

Thus the product under the complete printed reagent sequence is nitrobenzene. Heating the tetrafluoroborate alone would give fluorobenzene; the printed second reagent, sodium nitrite with copper, instead introduces $-NO_2$.

Step 7: (g) Identify A and B Benzoic acid first forms ammonium benzoate with ammonia. Heating eliminates water to form benzamide, so $A = C_6H_5C(=O)NH_2$. Bromine and sodium hydroxide then cause Hofmann bromamide degradation, giving aniline, $B = C_6H_5NH_2$:

$$\begin{aligned} C_6H_5COOH + NH_3 &\xrightarrow{\Delta} C_6H_5CONH_2 + H_2O, \\ C_6H_5CONH_2 + Br_2 + 4NaOH &\longrightarrow C_6H_5NH_2 \\ &\quad +2NaBr + Na_2CO_3 + 2H_2O. \end{aligned}$$

The carbonyl carbon is removed during degradation; the phenyl group remains attached to nitrogen in the product.

Step 8: Conclusion (a) No acidic $N-H$ hydrogen; (b) complex formation with $AlCl_3$ deactivates aniline; (c) cold nitrous acid gives nitrogen with methylamine and a diazonium salt with aniline; (d) Gabriel synthesis gives RNH_2; (e) acetylation, bromination and hydrolysis give para-bromoaniline; (f) nitrobenzene; (g) A is benzamide and B is aniline. Any five of these parts may be selected.

Quick Tip to Solve: Read the entire reagent sequence: NaNO2/Cu after diazonium tetrafluoroborate gives nitrobenzene, whereas heating the salt alone gives fluorobenzene.