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

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculators is not allowed.

Section A (16 marks)

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

1. Which one of the following first row transition elements is expected to have the highest third ionization enthalpy? [1 mark]

(A) Iron (Z = 26)

(B) Manganese (Z = 25)

(C) Chromium (Z = 24)

(D) Vanadium (Z = 23)

Correct Answer: (B) Manganese (Z = 25)

Solution:

Concept:

- The third ionization enthalpy is the energy required for $M^{2+}(g) \rightarrow M^{3+}(g) + e^{-}$.
- A half-filled $3d^5$ subshell has extra stability; removing an electron from it requires unusually high energy.

Step 1: Compare the divalent ions The configurations after removal of the two outermost electrons are $Fe^{2+} : [Ar]3d^6$, $Mn^{2+} : [Ar]3d^5$, $Cr^{2+} : [Ar]3d^4$ and $V^{2+} : [Ar]3d^3$. The third ionization therefore removes a $3d$ electron from each ion.

Step 2: Identify the most resistant ion For manganese, the third removal breaks the stable half-filled $3d^5$ arrangement. Iron instead forms the stable $3d^5$ ion after this removal. Chromium and vanadium do not start from a half-filled divalent configuration, so neither has this additional resistance.

Step 3: Conclusion Manganese has the highest third ionization enthalpy among these elements. Hence, the correct option is (B).

Quick Tip to Solve: For the third ionization, write the configuration of the divalent ion first; do not compare neutral atoms.

2. Which of the following compounds will give a ketone on oxidation with chromic anhydride (CrO_3)? [1 mark]

(A) $(CH_3)_2CH–CH_2OH$

(B) $CH_3CH_2CH_2OH$

(C) $(CH_3)_3C–OH$

(D) $CH_3–CH_2–CH(OH)–CH_3$

Correct Answer: (D) $CH_3–CH_2–CH(OH)–CH_3$

Solution:

Concept:

- A secondary alcohol has the group R_2CHOH and oxidizes to a ketone, R_2CO.
- The carbon bearing $-OH$ must have one hydrogen for ordinary oxidation to a carbonyl compound

Quick Tip to Solve: Count the carbon groups attached directly to the carbon bearing OH: two carbon groups identify a ketone-forming secondary alcohol.

without carbon-chain cleavage.

Step 1: Classify all four alcohols In (A) and (B), the hydroxyl group is on a terminal CH_2OH group, so both alcohols are primary. Option (C) is tertiary because the hydroxyl-bearing carbon is bonded to three methyl groups. Option (D), butan-2-ol, is secondary.

Step 2: Apply the oxidation rule Butan-2-ol gives butan-2-one:

$$CH_3CH_2CH(OH)CH_3 + [O] \xrightarrow{CrO_3} CH_3CH_2COCH_3 + H_2O.$$

Primary alcohols give aldehydes or, on further oxidation, acids. The tertiary alcohol lacks a hydrogen on its hydroxyl-bearing carbon and does not undergo ordinary oxidation to a ketone.

Step 3: Conclusion Butan-2-ol gives a ketone on oxidation. Hence, the correct option is (D).

Quick Tip to Solve: Count the carbon groups attached directly to the carbon bearing OH: two carbon groups identify a ketone-forming secondary alcohol.

3. Two among the three components of DNA are β-D-2-deoxyribose and a heterocyclic base. The third component is: [1 mark]

(A) Adenine

(B) Phosphoric acid

(C) Sulphuric acid

(D) Uracil

Correct Answer: (B) Phosphoric acid

Solution:

Concept:

- A DNA nucleotide consists of a nitrogenous base, β-D-2-deoxyribose and a phosphate group.
- Base plus sugar forms a nucleoside; addition of phosphate forms a nucleotide.

Step 1: Identify the missing nucleotide component The sugar and heterocyclic base have already been named. The remaining component is phosphoric acid, which supplies phosphate groups to the DNA backbone. These groups link successive sugars through phosphodiester bonds.

Step 2: Eliminate the other choices Adenine is itself a heterocyclic nitrogenous base, so (A) repeats the component already mentioned. Sulphuric acid does not supply the phosphate backbone of DNA. Uracil is a nitrogenous base characteristic of RNA, whereas DNA normally contains thymine; it also cannot supply the missing phosphate component.

Step 3: Conclusion The third component is phosphoric acid. Hence, the correct option is (B).

Quick Tip to Solve: Recall the sequence: base + sugar = nucleoside; nucleoside + phosphate = nucleotide.

4. For an electrolyte undergoing association in a solvent, the van't Hoff factor: [1 mark]

(A) is always greater than one

(B) has negative value

(C) has zero value

(D) is always less than one

Correct Answer: (D) is always less than one

Solution:

Concept:

- The van't Hoff factor i is the ratio of the actual number of solute particles to the number expected without association or dissociation.
- Association combines particles and lowers their number, thereby reducing the colligative effect.

Step 1: Count particles during association If a fraction α of the solute associates into groups of n units, an initial one mole produces $(1-\alpha)+\alpha/n$ moles of particles. Therefore

$$i = 1 - \alpha + \frac{\alpha}{n}.$$

For association, $n > 1$ and $\alpha > 0$, so this value is below one.

Step 2: Check the alternatives Particle numbers remain positive, ruling out negative and zero values in (B) and (C). A factor greater than one, as in (A), describes an increase in particle count, as occurs in dissociation. The value one corresponds to no association and is excluded by the stated ongoing association.

Step 3: Conclusion For a solute undergoing association, $0 < i < 1$. Hence, the correct option is (D).

Quick Tip to Solve: Association joins particles: fewer particles mean a smaller colligative effect and a van't Hoff factor below one.

5. For the reaction X + 2Y $\rightarrow$ P, the differential form equation of the rate law is: [1 mark]

(A) $\frac{2\,d[P]}{dt} = -\frac{d[Y]}{dt}$

(B) $-\frac{d[P]}{dt} = -\frac{d[X]}{dt}$

(C) $+\frac{d[X]}{dt} = -\frac{d[P]}{dt}$

(D) $-\frac{2\,d[Y]}{dt} = +\frac{d[P]}{dt}$

Correct Answer: Both (A) and (C) satisfy the printed stoichiometric rate relations; a unique single option cannot be selected.

Solution:

Concept:

- The reaction rate equals the concentration-change rate divided by the stoichiometric coefficient, with a minus sign for reactants.

Quick Tip to Solve: First divide each concentration derivative by its own stoichiometric coefficient; then rearrange to test every option.

- For $X + 2Y \rightarrow P$, $r = -d[X]/dt = -\frac{1}{2}d[Y]/dt = d[P]/dt$.

Step 1: Derive the concentration-change relations Each mole of product formed consumes one mole of X and two moles of Y. Thus

$$\frac{d[X]}{dt} = -\frac{d[P]}{dt}, \qquad \frac{d[Y]}{dt} = -2\frac{d[P]}{dt}.$$

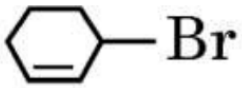
The signs distinguish depletion of reactants from formation of product; these are stoichiometric rate relations, not a concentration-dependent kinetic rate law.

Step 2: Test every printed option Option (A), $2d[P]/dt = -d[Y]/dt$, follows from the second relation. Option (C), $d[X]/dt = -d[P]/dt$, is exactly the first relation. Option (B) incorrectly gives the same sign to the rates of disappearance of product and reactant. In (D), multiplying $d[Y]/dt$ by -2 gives $4d[P]/dt$, not $d[P]/dt$.

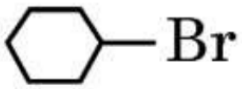
Step 3: Conclusion Both (A) and (C) are correct as printed. The listed options therefore do not give a unique correct choice.

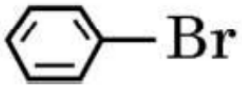
Quick Tip to Solve: First divide each concentration derivative by its own stoichiometric coefficient; then rearrange to test every option.

6. The compound which undergoes S_N1 reaction most rapidly is: [1 mark]

(A) 

(B) 

(C) 

(D) 

(A) 3-Bromocyclohex-1-ene (allylic bromide)

(B) (Bromomethyl)cyclohexane

(C) Bromocyclohexane

(D) Bromobenzene

Correct Answer: (A) 3-Bromocyclohex-1-ene (allylic bromide)

Solution:

Concept:

- The slow step of an S_N1 reaction is ionization of the carbon–halogen bond to form a carbocation.
- Greater stability of the carbocation generally favours faster S_N1 substitution for comparable leaving groups.

Step 1: Identify the carbocations from the structures In (A), bromine is attached to a saturated ring carbon adjacent to the double bond: this is an allylic bromide. Loss of bromide produces a carbocation whose positive charge is delocalized over the allylic system by resonance. Option (B) would initially give a primary cyclohexylmethyl carbocation, and (C) an ordinary secondary cyclohexyl carbocation.

Step 2: Compare the resonance effect The allylic carbocation in (A) is stabilized by resonance, whereas the initially formed cations from (B) and (C) lack that stabilization. In (D), bromine is directly attached to an aromatic carbon; forming a phenyl cation is highly unfavourable, and the aryl carbon–bromine bond also has partial double-bond character. Bromobenzene therefore resists ordinary S_N1 substitution.

Step 3: Conclusion The allylic bromide, 3-bromocyclohex-1-ene, reacts most rapidly. Hence, the correct option is (A).

Quick Tip to Solve: Locate the carbon bonded to Br: an allylic carbon is beside a double bond, whereas an aryl carbon is part of the aromatic ring.

7. Acetic acid reacts with PCl_5 to give: [1 mark]

(A) Cl–CH_2–COCl

(B) Cl–CH_2–COOH

(C) CH_3–COCl

(D) CCl_3–COOH

Correct Answer: (C) CH_3–COCl

Solution:

Concept:

- Phosphorus pentachloride converts a carboxylic acid RCOOH into the corresponding acyl chloride RCOCl.
- The hydroxyl group of the carboxyl group is replaced by chlorine while the carbon skeleton remains unchanged.

Step 1: Write the balanced reaction For acetic acid, the reaction is

$$\mathrm{CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl.}$$

The organic product is acetyl chloride, also called ethanoyl chloride. The equation is balanced: the two oxygen atoms of acetic acid appear one each in acetyl chloride and phosphorus oxychloride; all five chlorine atoms appear in the three products.

Quick Tip to Solve: With PCl5 and a carboxylic acid, replace only the OH in COOH by Cl; leave the adjacent alkyl group unchanged.

Step 2: Distinguish substitution sites The reagent acts on the acid hydroxyl group; it does not replace a hydrogen of the methyl group in this conversion. Thus (A) would involve additional methyl-group chlorination, while (B) and (D) retain the acid group and chlorinate the methyl group. Those structures are not the product of this reaction.

Step 3: Conclusion The product is CH_3COCl, acetyl chloride. Hence, the correct option is (C).

Quick Tip to Solve: With PCl5 and a carboxylic acid, replace only the OH in COOH by Cl; leave the adjacent alkyl group unchanged.

8. The formation of cyanohydrin from an aldehyde is an example of: [1 mark]

(A) nucleophilic addition

(B) electrophilic addition

(C) nucleophilic substitution

(D) electrophilic substitution

Correct Answer: (A) nucleophilic addition

Solution:

Concept:

- The carbonyl bond is polar: its carbon atom is electron deficient and is attacked by a nucleophile.
- In nucleophilic addition, a nucleophile adds across the carbonyl double bond without replacing a leaving group.

Step 1: Identify the attacking species Cyanide ion, CN^-, acts as the nucleophile and attacks the carbonyl carbon of the aldehyde. The carbonyl pi bond opens to give an alkoxide ion.

Step 2: Follow protonation and classify the change The alkoxide takes a proton to form the cyanohydrin:

$$RCHO + HCN \longrightarrow RCH(OH)CN.$$

The aldehyde gains the elements of hydrogen cyanide across its carbonyl bond. No group is displaced, ruling out both substitution options. The initial attack is by CN^-, so it is not electrophilic addition.

Step 3: Conclusion Cyanohydrin formation is a nucleophilic addition reaction. Hence, the correct option is (A).

Quick Tip to Solve: Identify the species that first attacks the carbonyl carbon: cyanide is a nucleophile, and the loss of the pi bond signals addition.

9. 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 $\frac{-E_a}{2.303\,R}$ and intercept is $\log A$.

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

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For a straight line $y = mx + c$, m is the slope and c is the intercept on the vertical axis.

Step 1: Take the common logarithm Here $\log$ denotes the base-10 logarithm. Using $\log e = 1/2.303$, the Arrhenius equation becomes

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

Step 2: Compare with the straight-line equation For $y = \log k$ and $x = 1/T$, the coefficient of x is $-E_a/(2.303R)$, while the constant term is $\log A$. Option (A) gives neither quantity correctly, and (B) mistakes the frequency factor for the slope. In (C), the proposed slope contains the variable T and omits the common-logarithm conversion factor.

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

Quick Tip to Solve: For an Arrhenius plot, first check whether the vertical axis uses log or ln: only the base-10 plot needs the factor 2.303.

10. The reaction of an alkyl halide with sodium alkoxide forming ether is known as: [1 mark]

(A) Wurtz reaction

(B) Reimer-Tiemann reaction

(C) Williamson synthesis

(D) Kolbe reaction

Correct Answer: (C) Williamson synthesis

Solution:

Concept:

- Williamson synthesis prepares ethers by reacting an alkoxide ion with a suitable alkyl halide.
- The alkoxide is the nucleophile and displaces the halide ion through an S_N2 substitution, most effectively with a primary alkyl halide.

Step 1: Identify the bond being formed Sodium alkoxide supplies RO^-, which attacks the alkyl carbon bonded to the halogen. For example,

$$CH_3ONa + C_2H_5Br \longrightarrow CH_3OC_2H_5 + NaBr,$$

sodium methoxide and bromoethane yield methoxyethane, an ether.

Step 2: Distinguish the named reactions This ether-forming substitution is Williamson synthesis. Wurtz reaction couples alkyl halides with sodium to form a carbon–carbon bond. Reimer–Tiemann reaction introduces a formyl group into phenol, while the Kolbe reaction of sodium phenoxide with carbon dioxide introduces a carboxyl group. Neither is the stated ether preparation.

Step 3: Conclusion The reaction is Williamson synthesis. Hence, the correct option is (C).

Quick Tip to Solve: The reagent pair sodium alkoxide plus alkyl halide is the signature of Williamson ether synthesis; look for the new carbon–oxygen bond.

11. The correct order of the ease of dehydration of the following alcohols by the action of conc. H_2SO_4 is: [1 mark]

(A) $(CH_3)_3C–OH > (CH_3)_2CH–OH > CH_3CH_2–OH$

(B) $(CH_3)_2CH–OH > CH_3CH_2–OH > (CH_3)_3C–OH$

(C) $CH_3CH_2–OH > (CH_3)_2CH–OH > (CH_3)_3C–OH$

(D) $(CH_3)_2CH–OH > (CH_3)_3C–OH > CH_3CH_2–OH$

Correct Answer: (A) $(CH_3)_3C–OH > (CH_3)_2CH–OH > CH_3CH_2–OH$

Solution:

Concept:

- Concentrated sulphuric acid catalyses dehydration of alcohols to alkenes by protonating the hydroxyl group so that water can leave.
- The ease of acid-catalysed dehydration follows tertiary alcohol > secondary alcohol > primary

Quick Tip to Solve: Count the alkyl groups attached directly to the carbon bearing OH; for acid dehydration, the order is three, then two, then one.

alcohol, reflecting the stability of developing positive charge on carbon.

Step 1: Classify the three alcohols In $(CH_3)_3COH$, the carbon bearing the hydroxyl group is bonded to three alkyl groups, so the alcohol is tertiary. Similarly, $(CH_3)_2CHOH$ is secondary and CH_3CH_2OH is primary.

Step 2: Compare the ease of water elimination Alkyl groups stabilise positive charge through their electron-releasing effect and hyperconjugation. Tertiary and secondary alcohols therefore dehydrate more readily than the primary alcohol; a free primary carbocation need not be invoked. The order is tertiary $>$ secondary $>$ primary. Options (B) and (C) wrongly place the tertiary alcohol last, and (D) wrongly places the secondary alcohol before the tertiary alcohol.

Step 3: Conclusion $(CH_3)_3COH > (CH_3)_2CHOH > CH_3CH_2OH$ in ease of dehydration. Hence, the correct option is (A).

Quick Tip to Solve: Count the alkyl groups attached directly to the carbon bearing OH; for acid dehydration, the order is three, then two, then one.

12. Which functional groups of glucose interact to form cyclic hemiacetal leading to pyranose structure? [1 mark]

(A) Aldehyde group and hydroxyl group at C–4

(B) Aldehyde group and hydroxyl group at C–5

(C) Ketone group and hydroxyl group at C–4

(D) Ketone group and hydroxyl group at C–5

Correct Answer: (B) Aldehyde group and hydroxyl group at C–5

Solution:

Concept:

- Open-chain glucose is an aldohexose: it contains an aldehyde group at C–1 and hydroxyl groups along its carbon chain.
- An aldehyde reacts with an alcohol group to form a hemiacetal. Intramolecular reaction can close the chain into a ring.

Step 1: Identify the groups forming the ring The hydroxyl group attached to C–5 reacts with the aldehyde group at C–1. The oxygen of this hydroxyl group becomes the ring oxygen, and the original carbonyl oxygen becomes a hydroxyl group at C–1.

Step 2: Count the ring atoms and test the alternatives The resulting ring contains C–1 through C–5 and one oxygen atom, making a six-membered pyranose ring. Reaction with the C–4 hydroxyl group would instead produce a five-membered ring, so (A) fails. Options (C) and (D) incorrectly assign a ketone group to glucose; the open-chain sugar contains an aldehyde group.

Step 3: Conclusion The aldehyde group and the hydroxyl group at C–5 form the cyclic hemiacetal leading to the pyranose structure. Hence, the correct option is (B).

Quick Tip to Solve: Count the ring oxygen as an atom: C–1 to C–5 plus oxygen gives the six-membered pyranose ring.

13. Assertion (A): When NaCl is added to water a depression in freezing point is observed.
Reason (R): NaCl undergoes dissociation in water. [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:

- Depression in freezing point is a colligative property: $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the cryoscopic constant and m the molality.
- Dissociation of an electrolyte increases the number of dissolved particles; in the dilute ideal limit, sodium chloride gives two ions per formula unit.

Step 1: Evaluate the Assertion Dissolving non-volatile sodium chloride in water lowers the freezing point below that of pure water. The dissolved particles lower the chemical potential of liquid water, so equilibrium with ice is reached at a lower temperature. Thus Assertion (A) is true.

Step 2: Evaluate the Reason Sodium chloride dissociates in water according to

$$\mathrm{NaCl} \longrightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-}.$$

Hence Reason (R) is true. Each formula unit supplies two ions, giving i close to 2 in a sufficiently dilute solution.

Step 3: Relate dissociation to the observed depression The ions produced by dissociation act as solute particles and depress the freezing point. Their increased number enhances this colligative effect, as shown by $\Delta T_f = iK_f m$. Thus the reason explains the assertion. It does not imply that dissociation is required for every solute to lower the freezing point; a non-electrolyte also causes depression with $i = 1$.

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

Quick Tip to Solve: For dissolved sodium chloride, count both sodium and chloride ions when applying the freezing-point depression formula.

14. Assertion (A): Separation of Zr and Hf is difficult.

Reason (R): Zr and Hf have similar radii due to lanthanoid contraction. [1 mark]

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

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

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series, arising from the poor shielding of nuclear charge by 4f electrons.
- Zirconium and hafnium lie in the same group. Their very similar sizes and usual oxidation state of $+4$ give them closely similar chemical properties.

Step 1: Evaluate the Assertion Zirconium and hafnium show very similar chemical behaviour and commonly occur together in minerals. Their compounds respond similarly to many chemical separation methods, making their separation difficult. Therefore Assertion (A) is true.

Step 2: Evaluate the Reason Hafnium follows the lanthanoids in the sixth period. Poor shielding by the added 4f electrons increases effective nuclear attraction and contracts its size. This largely offsets the expected increase in radius from zirconium to hafnium, so their radii are nearly equal. Therefore Reason (R) is true.

Step 3: Link the size similarity to separation Nearly equal radii, together with the same common oxidation state, give the two elements similar charge density and compound formation. Since chemical separation depends on differences in properties, this close similarity directly accounts for the difficulty of separating them. Thus the reason correctly explains the assertion, ruling out option (B); options (C) and (D) each incorrectly call a true statement false.

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

Quick Tip to Solve: When comparing zirconium with hafnium, connect lanthanoid contraction to nearly equal radii and then to similar chemical behaviour.

15. Assertion (A): The pK_a of ethanoic acid is lower than that of Cl–CH_2–COOH.

Reason (R): Chlorine shows electron withdrawing (-I) effect which increases the acidic character of Cl–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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- Acid strength increases with the dissociation constant K_a, while $pK_a = -\log K_a$. A stronger acid therefore has a lower pK_a.
- An electron-withdrawing substituent stabilises the carboxylate conjugate base through its negative inductive effect and increases acidity.

Step 1: Judge the assertion Chloroacetic acid, $\mathrm{ClCH_2COOH}$, is stronger than ethanoic acid, $\mathrm{CH_3COOH}$. Consequently,

$$pK_a(\mathrm{ClCH_2COOH}) < pK_a(\mathrm{CH_3COOH}).$$

The assertion reverses this order and is false.

Step 2: Judge the reason Chlorine withdraws electron density through sigma bonds by its $-I$ effect. This stabilises the negative charge of $\mathrm{ClCH_2COO^-}$ and favours loss of $\mathrm{H^+}$. Thus the reason is true.

Step 3: Check the explanatory relation The reason explains why chloroacetic acid has the lower pK_a; it contradicts the asserted ordering. Options (A) and (B) require a true assertion, and option (C) requires a false reason, so none fits.

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

Quick Tip to Solve: First rank acid strength using the inductive effect, then reverse that order for pK_a.

16. 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 lone pair. Greater availability of the nitrogen lone pair generally favours protonation.
- In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring by resonance; in ammonia, NH_3, it is localised on nitrogen.

Step 1: Judge the assertion The localised lone pair in ammonia is more available to bond to H^+ than the delocalised lone pair in aniline. Therefore aniline is a weaker base than ammonia, so the assertion is false.

Step 2: Judge the reason Resonance involves overlap of the nitrogen lone pair with the aromatic pi system. The pair is consequently less available for protonation. The stated reason correctly describes this effect and is true.

Step 3: Check the explanatory relation The reason explains aniline's weaker basicity, the opposite of the assertion. Thus (A) and (B), which require both statements to be true, are excluded. Option (C) reverses the actual truth values.

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

Quick Tip to Solve: Before comparing basicity, check whether nitrogen's lone pair is localised or shared with an aromatic ring.

Section B (10 marks)

17. 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 a reduction half-cell, the Nernst equation at 298 K is $E = E^{\circ} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Pure solid iron has unit activity. For a dilute solution, the activity of Fe^{2+} is approximated by its molar concentration divided by $1\ \text{mol L}^{-1}$.

Step 1: Write the reduction half-reaction The given standard potential is a reduction potential, so use

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

Two electrons are transferred, hence $n = 2$. Since iron is a pure solid,

$$Q = \frac{1}{a(\text{Fe}^{2+})} = \frac{1}{0.01} = 100.$$

Step 2: Substitute in the Nernst equation With $E^{\circ} = -0.45\,\text{V}$ and $\log 100 = 2\log 10 = 2$,

$$\begin{aligned} E &= -0.45 - \frac{0.0591}{2}\log 100 \\ &= -0.45 - 0.0591 \\ &= -0.5091\,\text{V}. \end{aligned}$$

Dilution lowers the tendency of the ions to undergo reduction, consistently making the potential more negative than its standard value.

Step 3: Conclusion The iron electrode potential at the stated concentration is $\boxed{-0.5091\,\text{V}}$, approximately $-0.51\,\text{V}$, relative to the standard hydrogen electrode.

Quick Tip to Solve: For a metal-ion/metal reduction, use $E = E^{\circ} + (0.0591/n)\log[\text{metal ion}]$; a concentration below unity lowers E.

18. Define molecularity of the reaction. State any one condition in which a bimolecular reaction may be kinetically of first order. [2 marks]

Solution:

Concept:

- Molecularity counts the reacting species participating together in one elementary reaction step. It is a positive integer and is defined for an elementary step.

Quick Tip to Solve: For pseudo-first-order kinetics, identify the excess reactant and absorb its almost constant concentration into k_{obs}.

- Reaction order describes the concentration dependence of the measured rate. A nearly constant reactant concentration can be absorbed into the observed rate constant.

Step 1: Define molecularity Molecularity is the number of reacting species (atoms, ions or molecules) that collide or participate simultaneously in an elementary reaction to bring about chemical change. For an elementary bimolecular step involving one molecule each of reactants A and B, two species participate and the rate law is $r = k[\mathrm{A}][\mathrm{B}]$.

Step 2: State the condition for apparent first-order kinetics Take one reactant, say B, in a very large excess so that its concentration changes negligibly during the reaction. Then

$$r = k[\mathrm{B}][\mathrm{A}] = k_{\mathrm{obs}}[\mathrm{A}], \qquad k_{\mathrm{obs}} = k[\mathrm{B}] \approx \text{constant}.$$

The measured rate now depends effectively only on the first power of the concentration of A. This is called a pseudo-first-order reaction; the excess reactant still participates chemically.

Step 3: Conclusion Molecularity is the number of reacting species involved in one elementary step. A bimolecular reaction may show first-order kinetics when one reactant is present in large excess and its concentration remains practically constant.

Quick Tip to Solve: For pseudo-first-order kinetics, identify the excess reactant and absorb its almost constant concentration into k_{obs}.

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

(a) HI

(b) Conc. HNO_3 [2 marks]

Solution:

Concept:

- Open-chain D-glucose contains an aldehyde group at one end and a primary alcohol group at the other: $\mathrm{CHO}-(\mathrm{CHOH})_4-\mathrm{CH_2OH}$.
- Prolonged heating with HI reduces glucose to its corresponding straight-chain hydrocarbon. Strong oxidation with concentrated $\mathrm{HNO_3}$ converts both terminal groups to carboxyl groups.

Step 1: Treat glucose with hydrogen iodide On prolonged heating with HI, D-glucose is reduced to n-hexane. Its oxygen-containing groups are removed while the chain of six carbon atoms remains intact. The net reaction can be written as

$$\mathrm{C_6H_{12}O_6} + 14\,\mathrm{HI} \xrightarrow{\text{heat}} \mathrm{CH_3(CH_2)_4CH_3} + 6\,\mathrm{H_2O} + 7\,\mathrm{I_2}.$$

Formation of the unbranched hydrocarbon supports the straight-chain arrangement of all six carbon atoms in glucose.

Step 2: Oxidise glucose with concentrated nitric acid Concentrated $\mathrm{HNO_3}$ oxidises both the aldehyde group $-\mathrm{CHO}$ and the terminal primary alcohol group $-\mathrm{CH_2OH}$ to $-\mathrm{COOH}$. The product is saccharic

Quick Tip to Solve: Track the two ends of glucose: strong nitric-acid oxidation changes both ends to $-\mathrm{COOH}$, whereas hot HI gives the six-carbon alkane.

acid, also called D-glucaric acid:

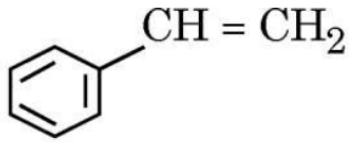
$$\mathrm{CHO{-}(CHOH)_4{-}CH_2OH + 3\,[O] \longrightarrow HOOC{-}(CHOH)_4{-}COOH + H_2O.}$$

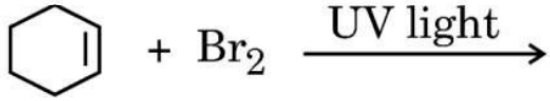
Here [O] represents an oxygen equivalent supplied by the oxidising reagent. The product is a dicarboxylic acid.

Step 3: Conclusion (a) Prolonged heating with HI gives n-hexane, $\mathrm{CH_3(CH_2)_4CH_3}$. (b) Concentrated $\mathrm{HNO_3}$ gives saccharic acid, $\mathrm{HOOC{-}(CHOH)_4{-}COOH}$.

Quick Tip to Solve: Track the two ends of glucose: strong nitric-acid oxidation changes both ends to $-\mathrm{COOH}$, whereas hot HI gives the six-carbon alkane.

20(a). Draw the structures of major monohalo products in each of the following reactions: [2 marks]

(i) 

(ii) 

Solution:

Concept:

- Addition of HBr to styrene in the absence of peroxide follows Markovnikov's rule: protonation produces the more stable benzylic carbocation.
- Under UV light, bromine undergoes homolytic cleavage. Allylic substitution replaces a hydrogen next to a carbon–carbon double bond while retaining the double bond in the monohalo product.

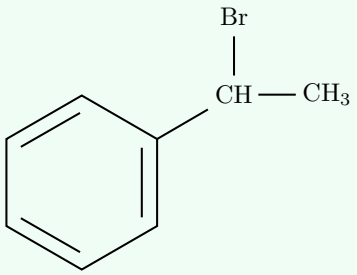
Step 1: Add hydrogen bromide to styrene In (i), the reactant is $\mathrm{C_6H_5CH{=}CH_2}$. Hydrogen adds to the terminal carbon, so the positive charge is on the carbon adjacent to the benzene ring. This benzylic carbocation is stabilised by resonance. Attack by $\mathrm{Br^-}$ then places bromine on that carbon:

$$\mathrm{C_6H_5CH{=}CH_2 + HBr \longrightarrow C_6H_5CH(Br)CH_3.}$$

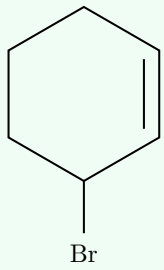
The benzene ring remains unchanged.

Step 2: Brominate the allylic position of cyclohexene In (ii), $\mathrm{Br_2}$ and UV light favour the free-radical pathway required for the monobromo product. An allylic hydrogen is abstracted, forming a resonance-stabilised allylic radical. Reaction with bromine gives 3-bromocyclohex-1-ene and HBr. Equivalent allylic positions give the same product. Bromine is bonded to the saturated carbon next to the retained double bond.

Quick Tip to Solve: Check the conditions first: plain HBr adds across the side-chain double bond, whereas $\mathrm{Br_2}$/UV gives the allylic monobromo product here.



(i)



(ii)

Major monohalo products of (i) and (ii)

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

Quick Tip to Solve: Check the conditions first: plain HBr adds across the side-chain double bond, whereas Br_2/UV gives the allylic monobromo product here.

OR

20(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:

- The carbon–magnesium bond in a Grignard reagent, RMgX, is strongly polar. Its carbon behaves as a powerful base and reacts with compounds containing an acidic hydrogen.
- Hydroxide can act as a nucleophile in substitution or as a base in elimination. The solvent and reaction conditions influence which pathway predominates.

Step 1: Explain why moisture must be excluded In (i), even traces of water destroy the Grignard reagent by protonating its carbon atom. Instead of obtaining the required organomagnesium reagent, an alkane is formed:

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

Here R is an alkyl group and X is a halogen. Hence the apparatus and ether solvent must be dry, and the preparation must be carried out under anhydrous conditions.

Step 2: Compare aqueous and alcoholic potassium hydroxide In (ii), aqueous KOH supplies hydroxide ions that act mainly as nucleophiles, replacing the halogen and producing an alcohol. For example:

$$CH_3CH_2Br + KOH\,(aq) \longrightarrow CH_3CH_2OH + KBr.$$

In alcoholic KOH, the basic medium favours removal of a hydrogen from a carbon adjacent to the

Quick Tip to Solve: For KOH, read the solvent: aqueous means replace the halogen with OH; alcoholic means remove a neighbouring hydrogen and form a double bond.

carbon bearing the halogen, especially on heating. Loss of hydrogen and halide forms a double bond by β-elimination:

$$CH_3CH_2Br + KOH \xrightarrow{\text{alcohol, heat}} CH_2{=}CH_2 + KBr + H_2O.$$

An alkyl halide must possess a suitable β-hydrogen for this elimination.

Step 3: Conclusion Grignard reagents require dry conditions because water converts them to hydrocarbons. Aqueous KOH favours nucleophilic substitution to alcohols, while alcoholic KOH favours elimination to alkenes.

Quick Tip to Solve: For KOH, read the solvent: aqueous means replace the halogen with OH; alcoholic means remove a neighbouring hydrogen and form a double bond.

21. Write the chemical equation when:

(a) Butan-2-one is treated with Zn(Hg) and conc. HCl.

(b) Two molecules of benzaldehyde are treated with conc. NaOH. [2 marks]

Solution:

Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- Aldehydes without an α-hydrogen undergo the Cannizzaro reaction in concentrated alkali: one molecule is reduced to an alcohol and another is oxidised to a carboxylate salt.

Step 1: Reduce butan-2-one by the Clemmensen method In (a), zinc amalgam, $Zn(Hg)$, with concentrated HCl reduces the ketonic $C{=}O$ group to CH_2, retaining the four-carbon skeleton. The equation is:

$$CH_3COCH_2CH_3 + 4\,[H] \xrightarrow{Zn(Hg),\ conc\cdot\ HCl} CH_3CH_2CH_2CH_3 + H_2O.$$

The product is butane. Here $[H]$ denotes a reducing-hydrogen equivalent; four such equivalents remove the oxygen as water and supply the two new carbon–hydrogen bonds. Reduction under these conditions proceeds to the hydrocarbon.

Step 2: Disproportionate benzaldehyde in concentrated alkali In (b), benzaldehyde, C_6H_5CHO, has no α-hydrogen, so it undergoes the Cannizzaro reaction rather than aldol condensation. Two molecules react with concentrated $NaOH$:

$$2\,C_6H_5CHO + NaOH \xrightarrow{conc\cdot} C_6H_5CH_2OH + C_6H_5COONa.$$

One molecule accepts hydrogen and is reduced to benzyl alcohol; the other is oxidised to sodium benzoate. The oxidation product remains a sodium salt because the reaction medium is strongly alkaline. Benzoic acid would require a subsequent acidification step.

Step 3: Conclusion (a) Butan-2-one gives butane by Clemmensen reduction. (b) Two molecules of benzaldehyde give one molecule each of benzyl alcohol and sodium benzoate by the Cannizzaro

Quick Tip to Solve: Recognise $Zn(Hg)/HCl$ as carbonyl-to-methylene reduction; with benzaldehyde and concentrated alkali, write both the alcohol and carboxylate salt.

reaction.

Quick Tip to Solve: Recognise $\mathrm{Zn(Hg)/HCl}$ as carbonyl-to-methylene reduction; with benzaldehyde and concentrated alkali, write both the alcohol and carboxylate salt.

Section C (21 marks)

22. 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:

- Conductance is the reciprocal of resistance: $G = 1/R$, where R is measured in ohms and G in Ω^{-1}.
- Conductivity is $\kappa = G(l/A) = (l/A)/R$. The cell constant l/A depends on the electrode geometry and is unchanged when the same cell is filled with another solution.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity is in $\Omega^{-1}\,\mathrm{cm}^{-1}$ and concentration c is in mol L^{-1}. The factor 1000 converts litres to cubic centimetres.

Step 1: Calibrate the cell using the potassium chloride solution For the reference KCl solution, $R = 100\,\Omega$ and $\kappa = 1.35 \times 10^{-2}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. Rearranging the conductivity relation gives

$$\frac{l}{A} = \kappa R = (1.35 \times 10^{-2})(100) = 1.35\,\mathrm{cm}^{-1}.$$

The reference concentration identifies the solution whose known conductivity is supplied; it is not the concentration used in calculating the silver nitrate molar conductivity.

Step 2: Calculate the conductivity of silver nitrate Use the same cell constant with the resistance $90\,\Omega$ of the $AgNO_3$ solution:

$$\kappa_{\mathrm{AgNO_3}} = \frac{l/A}{R} = \frac{1.35}{90} = 1.50 \times 10^{-2}\,\Omega^{-1}\,\mathrm{cm}^{-1}.$$

Its smaller resistance implies a larger conductivity than the reference solution in this fixed cell, consistent with this value.

Step 3: Convert conductivity to molar conductivity The silver nitrate concentration is $c = 0.02\,\mathrm{mol\ L}^{-1}$. Substitution gives

$$\Lambda_m = \frac{1000(1.50 \times 10^{-2})}{0.02} = 750\,\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}.$$

This calculation uses the conductivity and concentration of the same solution.

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

Quick Tip to Solve: First find κR from KCl; divide it by the new resistance, then use only the $AgNO_3$ concentration in $1000\kappa/c$.

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

$$2\,NO\,(g) + Br_2(g) \longrightarrow 2\,NOBr\,(g)$$

Expt. No.	$[NO]$/mol L^{-1}	$[Br_2]$/mol L^{-1}	Initial Rate (mol L^{-1} s^{-1})
1	0.05	0.05	1.0×10^{-3}
2	0.05	0.15	3.0×10^{-3}
3	0.15	0.05	9.0×10^{-3}

(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]

Solution:

Concept:

- Write the experimental rate law as $r = k[NO]^m[Br_2]^n$, where m and n are the respective reaction orders and k is the rate constant.
- Compare experiments with one concentration unchanged to determine the order in the other reactant. Orders are experimental, not inferred from stoichiometry.

Step 1: (a) Determine the order with respect to each reactant In experiments 1 and 2, NO is fixed; tripling Br_2 triples the initial rate:

$$\frac{3.0 \times 10^{-3}}{1.0 \times 10^{-3}} = \left(\frac{0.15}{0.05}\right)^n, \qquad 3 = 3^n \Rightarrow n = 1.$$

In experiments 1 and 3, Br_2 is fixed; tripling NO makes the rate nine times as large:

$$\frac{9.0 \times 10^{-3}}{1.0 \times 10^{-3}} = \left(\frac{0.15}{0.05}\right)^m, \qquad 9 = 3^m \Rightarrow m = 2.$$

Thus the reaction is second order in NO, first order in Br_2, and third order overall.

Step 2: (b) Calculate the rate constant The rate law is $r = k[NO]^2[Br_2]$. Using experiment 1,

$$k = \frac{1.0 \times 10^{-3}}{(0.05)^2(0.05)} = \frac{1.0 \times 10^{-3}}{1.25 \times 10^{-4}} = 8.0\,L^2\,mol^{-2}\,s^{-1}.$$

The units follow by dividing rate units by concentration cubed.

Step 3: (c) Substitute the new concentrations At the same temperature, k remains unchanged. With $[NO] = 0.4$ M and $[Br_2] = 0.2$ M,

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

Step 4: Conclusion (a) Orders: NO, 2; Br_2, 1. (b) $k = 8.0\,L^2\,mol^{-2}\,s^{-1}$. (c) Rate $= 0.256$ mol L^{-1} s^{-1}.

Quick Tip to Solve: Use experiments 1 and 2 for Br_2, then 1 and 3 for NO; each pair holds the other reactant fixed, so its concentration cancels from the ratio.

24. (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:

- The charge on a coordination entity equals the oxidation state of the metal plus the sum of ligand charges. Counterions balance this charge to form a neutral compound.
- In comparable dilute solutions, a complex yielding more ions generally has greater conductivity. Ligands within square brackets remain coordinated; counterions outside the brackets dissociate.
- An ambidentate ligand can bind through either of two different donor atoms, giving linkage isomerism. Non-superimposable mirror-image complexes show optical isomerism.

Step 1: (a) Balance the charges to write the formula Zinc(II) has oxidation state $+2$, and each of the four hydroxido ligands, OH^-, has charge -1. Therefore,

$$q\big([Zn(OH)_4]\big) = +2 + 4(-1) = -2.$$

Two potassium ions, K^+, are required to balance one $[Zn(OH)_4]^{2-}$ ion. The formula is $K_2[Zn(OH)_4]$.

Step 2: (b) Compare the number of ions released in solution The neutral entity $[Cr(NH_3)_3Cl_3]$ has no counterions outside its coordination sphere and gives no ions by simple dissociation. The other two compounds dissociate as follows:

$$[Cr(NH_3)_5Cl]Cl_2 \longrightarrow [Cr(NH_3)_5Cl]^{2+} + 2\,Cl^-,$$
$$[Cr(NH_3)_6]Cl_3 \longrightarrow [Cr(NH_3)_6]^{3+} + 3\,Cl^-.$$

They yield three and four ions per formula unit, respectively. Hence the increasing conductivity order, for comparable concentrations and conditions, is

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

Coordinated chloride is not counted as a free chloride ion.

Step 3: (c) Identify the isomerism in each complex (i) $[Co(NH_3)_5NO_2]^{2+}$ shows **linkage isomerism**. The ambidentate NO_2^- ligand can coordinate through nitrogen as nitro or through oxygen as nitrito. The corresponding linkage forms are $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$.

(ii) $[Co(en)_3]Cl_3$ shows **optical isomerism**. Here en is the neutral bidentate ethane-1,2-diamine ligand. Three such ligands form an octahedral $[Co(en)_3]^{3+}$ ion with two non-superimposable mirror-image arrangements, denoted Δ and Λ.

Step 4: Conclusion (a) $K_2[Zn(OH)_4]$. (b) $[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]Cl_2 < [Cr(NH_3)_6]Cl_3$. (c) (i) Linkage isomerism; (ii) optical isomerism.

Quick Tip to Solve: Count the charged complex as one ion plus its counterions; coordinated ligands stay bound. Ambidentate NO_2^- gives linkage isomers, and three en ligands give optical isomers.

25. (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 its halogen on an sp^3-hybridised carbon adjacent to a carbon-carbon double bond; a vinylic halide has it directly on a double-bonded carbon.
- Electron-withdrawing nitro groups at ortho and para positions activate an aryl halide towards nucleophilic substitution by stabilising the negatively charged intermediate.
- Among isomeric haloalkanes, increased branching generally lowers the boiling point by reducing molecular surface contact and London dispersion forces.

Step 1: (a) Locate the carbon bonded to bromine In (i), $CH_3-CH=CH-Br$, bromine is attached directly to an sp^2 carbon of the double bond, so this is a vinylic halide. In (ii), $CH_2=CH-CH(Br)-CH_3$, the carbon bearing bromine is saturated and immediately next to the double bond. Thus, compound (ii) is the allylic halide.

Step 2: (b) Compare stabilisation during nucleophilic attack In 2,4,6-trinitrochlorobenzene, two NO_2 groups are ortho and one is para to the chlorine-bearing carbon. Their electron-withdrawing effects facilitate attack by a nucleophile and delocalise the negative charge of the resulting addition intermediate. Subsequent loss of Cl^- restores aromaticity. Chlorobenzene lacks these stabilising groups and its carbon-chlorine bond has partial double-bond character owing to resonance. Therefore, 2,4,6-trinitrochlorobenzene is much more reactive towards nucleophilic substitution.

Step 3: (c) Select the most compact isomer The most highly branched isomer of C_4H_9Cl is tert-butyl chloride, $(CH_3)_3CCl$, whose IUPAC name is 2-chloro-2-methylpropane. Its compact shape reduces intermolecular surface contact compared with the less branched isomers, giving weaker dispersion attractions and the lowest boiling point.

Step 4: Conclusion (a) Compound (ii), $CH_2=CH-CH(Br)-CH_3$, is allylic.

(b) 2,4,6-Trinitrochlorobenzene is more reactive because its ortho/para nitro groups stabilise the substitution intermediate.

(c) tert-Butyl chloride, 2-chloro-2-methylpropane, has the lowest boiling point.

Quick Tip to Solve: First locate the halogen-bearing carbon: adjacent to a double bond means allylic, while on the double bond means vinylic. For boiling points of these isomers, identify the most branched structure.

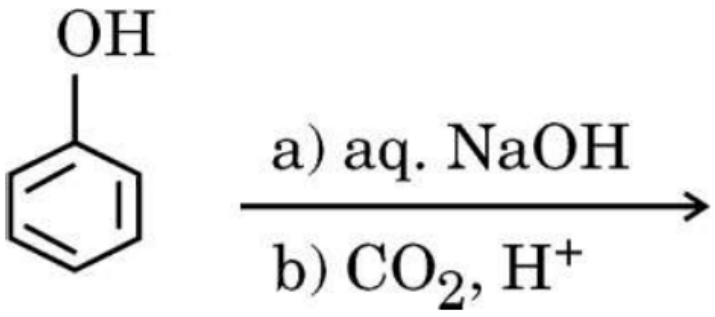
26. (a) Write the mechanism of the following reaction:

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

(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 to form an alkene. Protonation converts the poor leaving group OH into the good leaving group H_2O, and the acid catalyst is regenerated.
- Hydroboration followed by oxidation gives anti-Markovnikov hydration: the hydroxyl group is introduced at the less substituted carbon of the original double bond.
- In the Kolbe reaction, sodium phenoxide reacts with CO_2, and acidification gives predominantly an ortho-hydroxy aromatic carboxylic acid.

Step 1: (a) Protonate the ethanol oxygen The oxygen lone pair accepts a proton from the acid to form the protonated alcohol (an oxonium ion):

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

Protonation is essential because neutral water can leave much more readily than a hydroxide ion.

Step 2: Show dehydration and regeneration of the acid In the standard textbook mechanism, the protonated alcohol loses water, followed by removal of a proton from the adjacent carbon:

$$CH_3CH_2OH_2{}^+ \longrightarrow CH_3CH_2{}^+ + H_2O$$

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

The electrons of the carbon-hydrogen bond form the carbon-carbon double bond. The net reaction at 443 K is

$$CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O.$$

The regenerated H^+ explains the catalytic role of the acid.

Step 3: (b)(i) Place the hydroxyl group at the terminal carbon Diborane adds across the double bond of but-1-ene with boron on the less substituted, terminal carbon. Oxidation with alkaline H_2O_2 replaces

Quick Tip to Solve: For diborane followed by alkaline peroxide, put OH on the less substituted alkene carbon. Phenol followed by alkali, CO_2 and acid gives an ortho COOH group.

the carbon-boron bond by a carbon-oxygen bond. The product is therefore $CH_3CH_2CH_2CH_2OH$, butan-1-ol, rather than butan-2-ol.

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

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

Carboxylation by CO_2 introduces a carboxyl group predominantly ortho to the oxygen substituent. Acidification gives 2-HOC_6H_4COOH, 2-hydroxybenzoic acid (salicylic acid), with the OH and COOH groups on adjacent ring carbons.

Step 5: Conclusion (a) Ethanol forms ethene by acid-catalysed dehydration through protonation, loss of water and proton elimination. (b)(i) The product is butan-1-ol, $CH_3CH_2CH_2CH_2OH$. (b)(ii) The main product is salicylic acid, 2-HOC_6H_4COOH.

Quick Tip to Solve: For diborane followed by alkaline peroxide, put OH on the less substituted alkene carbon. Phenol followed by alkali, CO_2 and acid gives an ortho COOH group.

27. 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:

- Proteins contain amino-acid residues joined by peptide (amide) linkages, formed through condensation of an amino group and a carboxyl group.
- Complementary bases on opposite DNA strands form hydrogen bonds. Carbohydrates are classified by the number of monosaccharide units they contain.
- Vitamins are classified by their solubility: the B group and vitamin C are water-soluble, whereas vitamins A, D, E and K are fat-soluble.

Step 1: (a) Identify the peptide linkage A peptide linkage is the $-CO-NH-$ amide bond formed between the carboxyl group of one amino acid and the amino group of another, with elimination of one water molecule. For example, the reacting groups combine as

$$H_2NCH_2COOH + H_2NCH_2COOH \longrightarrow H_2NCH_2CONHCH_2COOH + H_2O.$$

Repetition of such linkages joins amino-acid residues into a polypeptide chain.

Step 2: (b) Identify the bonds between the DNA strands Hydrogen bonds between complementary nitrogenous bases hold the two strands of the DNA double helix together: adenine pairs with thymine through two hydrogen bonds, while guanine pairs with cytosine through three. The phosphodiester

Quick Tip to Solve: Distinguish bonds between DNA strands (hydrogen bonds) from the backbone bonds within a strand (phosphodiester bonds). Recall A, D, E and K as the fat-soluble vitamin group.

bonds belong to the sugar-phosphate backbone within each strand; they are not the base-pair links between the two strands.

Step 3: (c) Classify the given carbohydrates Starch is the polysaccharide: it is built from many glucose units joined by glycosidic linkages. Glucose and fructose are monosaccharides, each consisting of a single sugar unit, whereas sucrose is a disaccharide made from glucose and fructose. Thus the other three choices are not polysaccharides.

Step 4: (d) Give one vitamin from each solubility class Vitamin C (ascorbic acid) is a water-soluble vitamin. Vitamin A (retinol) is a fat-soluble vitamin. These examples belong to the two distinct solubility classes requested; the question permits any three parts, and all four answers are supplied for completeness.

Step 5: Conclusion (a) Peptide linkage: $-CO-NH-$, formed by condensation of two amino acids. (b) Hydrogen bonds between complementary bases. (c) Starch. (d) Water-soluble: vitamin C; fat-soluble: vitamin A.

Quick Tip to Solve: Distinguish bonds between DNA strands (hydrogen bonds) from the backbone bonds within a strand (phosphodiester bonds). Recall A, D, E and K as the fat-soluble vitamin group.

28. 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:

- Reduction of an ester with $LiAlH_4$, followed by hydrolysis, produces two alcohols: $RCOOR' \longrightarrow RCH_2OH + R'OH$. The alcohol from the acyl group has the same number of carbon atoms as the acid part.
- PCC oxidises a primary alcohol to an aldehyde. Aldehydes with an alpha hydrogen undergo aldol addition in dilute $NaOH$; heating the aldol eliminates water to form an unsaturated aldehyde.

Step 1: Work backwards from the acid The monobasic acid (F), of molecular mass 60, is ethanoic acid, CH_3COOH, since $2(12) + 4(1) + 2(16) = 60$. Its aldehyde precursor (D) is therefore ethanal, CH_3CHO. The primary alcohol (B) which produces ethanal on oxidation with PCC must be ethanol:

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

Step 2: Follow the aldol condensation and hydrogenation Two molecules of ethanal first form 3-hydroxybutanal in dilute alkali. Heating removes water to give (E), but-2-enal (crotonaldehyde):

$$2\,CH_3CHO \xrightarrow{dil\cdot NaOH} CH_3CH(OH)CH_2CHO$$

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

Quick Tip to Solve: Start with the acid of molecular mass 60, trace back to ethanal and ethanol, then use aldol condensation to determine the four-carbon alcohol and assemble the ester.

Complete catalytic hydrogenation reduces both the carbon–carbon double bond and the aldehyde group. Thus (C) is butan-1-ol, rather than butanal:

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

Step 3: Reconstruct and check the ester The acid-derived alcohol is ethanol, so the ester has an ethanoate group. The other alcohol is butan-1-ol, so its alkoxy group is the straight-chain butyl group. Hence the starting ester is butyl ethanoate:

$$CH_3COOCH_2CH_2CH_2CH_3 + 4\,[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + CH_3CH_2CH_2CH_2OH.$$

Hydrolytic work-up releases these alcohols from the reduction products. Counting atoms in the ester gives six carbons, twelve hydrogens and two oxygens, agreeing with $C_6H_{12}O_2$. Both product alcohols and every subsequent transformation are therefore consistent with the starting formula.

Step 4: Conclusion (A) Butyl ethanoate, $CH_3COOCH_2CH_2CH_2CH_3$; (B) ethanol, CH_3CH_2OH; (C) butan-1-ol, $CH_3CH_2CH_2CH_2OH$; (D) ethanal, CH_3CHO; (E) but-2-enal, $CH_3CH{=}CHCHO$; and (F) ethanoic acid, CH_3COOH.

Quick Tip to Solve: Start with the acid of molecular mass 60, trace back to ethanal and ethanol, then use aldol condensation to determine the four-carbon alcohol and assemble the ester.

Section D (8 marks)

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

29. 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]

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

Solution:

Concept:

- A galvanic cell supplies electrical energy through a spontaneous chemical reaction during discharge.
- Rechargeability depends on whether an external electrical supply can reverse the discharge reaction and restore the active electrode materials.

Step 1: Identify the behaviour of a primary battery In a primary battery, the discharge reaction is not

Quick Tip to Solve: Distinguish these batteries by reversibility and rechargeability, not by their size or voltage.

practically reversible. Once its reactants have been used up, the battery becomes dead and cannot be recharged for repeated use. A dry cell is a familiar example.

Step 2: Identify the behaviour of a secondary battery In a secondary battery, the discharge reaction can be reversed by passing an external current in the opposite direction. This regenerates the active materials, so the battery can be charged and used again. A lead storage battery is an example.

Step 3: Conclusion Primary batteries are non-rechargeable and are used only until their reactants are exhausted; secondary batteries are rechargeable and can undergo repeated charge–discharge cycles.

Quick Tip to Solve: Distinguish these batteries by reversibility and rechargeability, not by their size or voltage.

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

[1 mark]

Solution:

Concept:

- The cell potential depends on the reaction quotient through the Nernst equation, $E = E^\circ - (RT/nF)\ln Q$, where Q is the reaction quotient and n is the number of electrons transferred.
- Pure solids and pure liquids have constant unit activity; changing their amounts does not introduce a concentration term into Q.

Step 1: Write the overall mercury-cell reaction Adding the zinc-anode and mercury(II)-oxide cathode reactions cancels the hydroxide ions and water. The overall discharge reaction is

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

Here $\mathrm{Zn(Hg)}$ denotes zinc amalgam, and HgO is reduced to mercury.

Step 2: Examine the concentration dependence The net reaction contains no ions in solution whose concentration changes during discharge. Consequently the electrolyte concentration does not change through the overall cell reaction, and no changing ionic concentration enters its reaction quotient. The electrode potential difference therefore remains nearly constant during the useful life of the cell.

Step 3: Conclusion The mercury cell maintains about $1.35\,\mathrm{V}$ because its overall reaction involves no dissolved ions whose concentration changes during use.

Quick Tip to Solve: Add the mercury-cell half-reactions first: the cancellation of hydroxide ions explains its constant voltage.

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

Solution:

Concept:

- Recharging a secondary battery uses external electrical energy to reverse its spontaneous discharge reaction.
- During discharge of a lead storage battery, both electrodes become coated with $PbSO_4$. Charging restores Pb at the negative electrode, PbO_2 at the positive electrode, and sulphuric acid in the electrolyte.

Step 1: Write reduction at the negative electrode The external supply delivers electrons to the negative plate. Lead(II) sulphate gains electrons and is converted back into metallic lead:

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

This plate is the cathode during charging because reduction takes place there, although it acts as the anode during discharge.

Step 2: Write oxidation at the positive electrode At the positive plate, lead(II) sulphate is oxidised to lead(IV) oxide. The balanced charging half-reaction is

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

This plate is the anode during charging. The two electrons released here balance the two consumed at the negative plate.

Step 3: Add the charging half-reactions On cancelling the electrons, the sulphate and hydrogen ions regenerate sulphuric acid. Thus the electrolyte's acid concentration increases during charging, reversing the dilution that occurs during discharge.

Step 4: Conclusion The overall recharging reaction is

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

The external supply restores the lead and lead dioxide electrodes and regenerates sulphuric acid.

Quick Tip to Solve: Reverse the discharge equations to obtain charging equations; label electrodes by their charging reactions to avoid interchanging anode and cathode.

OR

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

Solution:

Concept:

- A fuel cell is a galvanic cell in which fuel and oxidant are supplied continuously from outside the cell; their chemical energy is converted directly into electrical energy.

Quick Tip to Solve: Link fuel-cell advantages to its external reactant supply and to water as the hydrogen–oxygen cell's product.

- In the hydrogen–oxygen fuel cell, the overall reaction is $2\,H_2 + O_2 \longrightarrow 2\,H_2O$. The product determines an important environmental advantage of this cell.

Step 1: Explain continuous operation A fuel cell keeps producing electricity as long as fuel and oxidant are supplied and products are removed. It is therefore not limited to a fixed stock of reactants stored inside the cell. In contrast, an ordinary primary galvanic cell stops working when its reactants are exhausted; a secondary cell then requires recharging.

Step 2: Explain cleaner operation A hydrogen–oxygen fuel cell produces water as its reaction product. Its operation avoids the toxic metal-containing spent electrode materials associated with cells such as mercury and lead batteries. Thus this fuel cell supplies electricity with very little pollution at the point of use.

Step 3: Conclusion Two advantages are continuous electricity generation while reactants are supplied, and clean operation, exemplified by the hydrogen–oxygen fuel cell whose product is water.

Quick Tip to Solve: Link fuel-cell advantages to its external reactant supply and to water as the hydrogen–oxygen cell's product.

30. 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]

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

Solution:

Concept:

- In a free metal ion, the five d orbitals are degenerate: they have equal energy.
- Ligands create an electrostatic field that interacts unequally with orbitals of different orientations, splitting them into groups with different energies.

Step 1: Identify the two orbital sets In an octahedral ligand field, the d_{xy}, d_{yz} and d_{xz} orbitals form the lower-energy t_{2g} set. The $d_{x^2-y^2}$ and d_{z^2} orbitals form the higher-energy e_g set because they point directly towards the ligands.

Step 2: Express the energy separation The separation between these two energy levels is denoted by Δ_o for an octahedral complex:

$$\Delta_o = E(e_g) - E(t_{2g}).$$

It represents an energy difference, rather than the energy of either individual orbital set.

Step 3: Conclusion Crystal field splitting energy is the energy difference between the sets of d orbitals produced by the ligand field; in an octahedral complex it is Δ_o, the separation between t_{2g} and e_g.

Quick Tip to Solve: Define splitting energy as the gap between orbital sets, not merely as the splitting process itself.

30(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:

- The colour of a coordination compound can arise from absorption of visible light that promotes a d electron between crystal-field-split energy levels.
- Absorption occurs when photon energy $h\nu$ equals the orbital energy gap, where h is Planck's constant and ν is the light frequency.

Step 1: Find the electron arrangement Water is neutral, so titanium is in the $+3$ oxidation state in $[Ti(H_2O)_6]^{3+}$. The Ti^{3+} ion has a $3d^1$ configuration. In the octahedral field of six water ligands, its single d electron occupies the lower-energy t_{2g} set.

Step 2: Connect absorption with the observed colour The electron absorbs visible light in the green-yellow region and is promoted from t_{2g} to e_g: a d-d transition. The absorbed photon satisfies $h\nu = \Delta_o$. The light remaining after this selective absorption gives the complex its complementary violet appearance.

Step 3: Conclusion $[Ti(H_2O)_6]^{3+}$ is violet because its $3d^1$ electron undergoes a visible-light-induced $t_{2g} \rightarrow e_g$ transition, selectively absorbing the complementary region of light.

Quick Tip to Solve: For colour questions, first find the metal's oxidation state and d-electron count, then identify the d-d transition.

30(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:

- A complex with unpaired electrons is paramagnetic; a complex with all electrons paired is diamagnetic.
- Determine the metal ion's oxidation state and d-electron configuration before applying the ligand-field or valence-bond description of its geometry and pairing.

Step 1: Count unpaired electrons in the chromium complex Since NH_3 is neutral, chromium is $+3$ in $[Cr(NH_3)_6]^{3+}$. Chromium has atomic configuration $[Ar]3d^5 4s^1$; removing three electrons gives Cr^{3+} the configuration $[Ar]3d^3$. Its six-coordinate octahedral complex has the arrangement $t_{2g}^3 e_g^0$. The three lower orbitals each contain one electron, so there are three unpaired electrons.

Step 2: Account for pairing in the nickel complex Each CN^- ligand carries charge -1. Thus $x + 4(-1) = -2$ gives nickel the oxidation state $+2$. Nickel is $[Ar]3d^8 4s^2$, so Ni^{2+} is $3d^8$. Cyanide is a strong-field ligand. In the valence-bond description it causes the eight $3d$ electrons to pair in four orbitals, leaving one $3d$ orbital available for dsp^2 hybridisation. The resulting square-planar complex has no unpaired electrons.

Quick Tip to Solve: A d^3 octahedral ion has three unpaired electrons; for d^8 nickel, check whether strong-field ligands produce a square-planar complex.

Step 3: Conclusion $[Cr(NH_3)_6]^{3+}$ is paramagnetic because its $3d^3$ metal ion has three unpaired electrons. Square-planar $[Ni(CN)_4]^{2-}$ is diamagnetic because all its $3d^8$ electrons are paired.

Quick Tip to Solve: A d^3 octahedral ion has three unpaired electrons; for d^8 nickel, check whether strong-field ligands produce a square-planar complex.

OR

30(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:

- In valence bond theory, an octahedral complex uses six hybrid orbitals. Inner-orbital complexes use d^2sp^3 hybridisation, whereas outer-orbital complexes use sp^3d^2 hybridisation.
- Strong-field ligands can cause pairing of the metal's $3d$ electrons; weak-field ligands leave the high-spin arrangement unchanged.

Step 1: Find the electronic configuration of the metal ion In both complexes, iron is in the $+3$ oxidation state. For atomic number 26, the ground-state configuration of Fe is $[Ar]3d^64s^2$. Removing the two $4s$ electrons and one $3d$ electron gives Fe^{3+} the configuration $[Ar]3d^5$.

Step 2: Compare the effect of the two ligands In $[Fe(CN)_6]^{3-}$, CN^- is a strong-field ligand. It pairs the five $3d$ electrons into three orbitals, leaving two $3d$ orbitals vacant. These two inner $3d$ orbitals, one $4s$ and three $4p$ orbitals form six d^2sp^3 hybrid orbitals for ligand bonding.

In $[Fe(H_2O)_6]^{3+}$, H_2O is a weak-field ligand and does not cause pairing. Each of the five $3d$ orbitals remains singly occupied, so two vacant $3d$ orbitals are unavailable. One $4s$, three $4p$ and two outer $4d$ orbitals instead undergo sp^3d^2 hybridisation.

Step 3: Conclusion $[Fe(CN)_6]^{3-}$ is an inner-orbital d^2sp^3 complex because it uses $3d$ orbitals; $[Fe(H_2O)_6]^{3+}$ is an outer-orbital sp^3d^2 complex because it uses $4d$ orbitals. Both are octahedral.

Quick Tip to Solve: For Fe^{3+} complexes, start with $3d^5$: CN^- creates two vacant inner orbitals by pairing, while H_2O does not.

Section E (15 marks)

31(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 gas partial pressure, x dissolved gas mole fraction and K_H Henry's law constant. At fixed pressure and temperature, larger K_H means lower solubility.
- Osmosis moves water through a semipermeable membrane towards the more concentrated solution. Blood cells are isotonic with approximately 0.9% (mass/volume) aqueous NaCl.
- Boiling-point elevation is $\Delta T_b = iK_b m$, with molality m, molal elevation constant K_b and van't Hoff factor i. For ionisation degree α into ν ions, $i = 1 + (\nu - 1)\alpha$.

Step 1: (i) Compare Henry's law constants At a common gas pressure and the same temperature, $K_H = p/x$. Since CO_2 is more soluble, its dissolved mole fraction is larger and its K_H is smaller. Hence O_2, being less soluble, has the higher K_H:

$$K_H(\mathrm{O_2}) > K_H(\mathrm{CO_2}).$$

Step 2: (ii) Determine the change in cell size The external solution containing more than 0.9% (mass/volume) NaCl is hypertonic relative to blood cells. Water moves out through their semipermeable membranes by exosmosis. The cells lose water and shrink.

Step 3: (iii) Calculate the van't Hoff factor Each ionised formula unit of A_2B_3 gives two ions of A and three ions of B, hence $\nu = 5$. For one mole initially, 0.40 mol remains unionised and 0.60 mol ionises. The total particle amount is $0.40 + 5(0.60) = 3.40$ mol. Thus,

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

Step 4: Calculate the solution's boiling point Using $m = 1\,\text{mol kg}^{-1}$ and $K_b = 0.52\,\text{K kg mol}^{-1}$,

$$\Delta T_b = 3.40 \times 0.52 \times 1 = 1.768\,\text{K}.$$

At normal atmospheric pressure, water boils at $100\,^\circ$C. Since a kelvin interval equals a Celsius degree interval,

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

Step 5: Conclusion (i) O_2 has the higher K_H. (ii) The blood cells shrink due to exosmosis. (iii) The solution boils at approximately $\boxed{101.77\,^\circ\text{C}}$, with $i = 3.40$.

Quick Tip to Solve: Count all five ions from A_2B_3, but apply the 60% ionisation: use $i = 1 + 4\alpha$, then add the elevation to $100\,^\circ$C.

OR

31(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:

- Raoult's law for an ideal solution 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's vapour pressure at the same temperature.
- Dalton's law gives the vapour-phase mole fraction $y_B = p_B/(p_A + p_B)$. Liquid and vapour compositions need not be identical.
- Colligative properties depend on the number of solute particles relative to solvent particles, rather than the chemical identity of the solute.
- For a dilute solution, osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is the molar concentration, R is the gas constant and T is absolute temperature.

Step 1: (i) Find both partial vapour pressures The liquid mixture contains only A and B, so its mole fractions add to unity:

$$x_B = 1 - x_A = 1 - 0.4 = 0.6.$$

Apply Raoult's law to each component using the pure vapour pressures at 25°C:

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

Component A has the larger pure vapour pressure and contributes more strongly to the vapour despite its smaller liquid mole fraction.

Step 2: (i) Relate vapour composition to partial pressure By Dalton's law, B's fraction of the vapour equals its fraction of the total pressure. Hence the required calculation is

$$y_B = \frac{p_B}{p_{\text{total}}} = \frac{15}{45} = \frac{1}{3}.$$

The mole fraction is dimensionless. Its value is less than the liquid-phase fraction 0.6, as expected because B is the less volatile component.

Step 3: (ii) Define a colligative property and select the method A colligative property is a property of a dilute solution that depends on the number of solute particles present relative to the number of solvent particles and not on the nature of the solute particles. Osmotic pressure is preferred for determining the molar masses of macromolecules such as proteins and polymers.

Their very large molar masses produce small numbers of particles for a given dissolved mass. Con-

Quick Tip to Solve: For vapour composition, first calculate both partial pressures and divide by their sum. For isotonicity, compare iC, not just the stated molarity.

sequently, boiling-point elevation and freezing-point depression are often too small to measure accurately. Osmotic pressure remains appreciable even in very dilute solutions and can be measured at room temperature, avoiding decomposition of heat-sensitive macromolecules. For a non-electrolyte of mass w, molar mass M and solution volume V,

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

Step 4: (iii) Compare the numbers of dissolved particles Isotonic solutions have equal osmotic pressures at the same temperature. Sodium chloride dissociates in water:

$$\mathrm{NaCl(aq)} \longrightarrow \mathrm{Na^+(aq) + Cl^-(aq)}.$$

Glucose, $\mathrm{C_6H_{12}O_6}$, is a non-electrolyte and remains as molecules. Thus, at equal molar concentrations and temperature, sodium chloride supplies more dissolved particles than glucose. Its van't Hoff factor is approximately 2 in the dilute limit, whereas glucose has $i = 1$. Since $\pi = iCRT$, their osmotic pressures differ even though their molar concentrations are equal.

Step 5: Conclusion (i) The mole fraction of B in the vapour is $\boxed{y_B = \frac{1}{3} \approx 0.333}$. (ii) Colligative properties depend on particle number rather than solute identity; osmotic pressure is preferred for molar-mass determination of macromolecules. (iii) Equimolar sodium chloride and glucose solutions are not isotonic because dissociation makes the osmotic pressure of sodium chloride higher at the same temperature.

Quick Tip to Solve: For vapour composition, first calculate both partial pressures and divide by their sum. For isotonicity, compare iC, not just the stated molarity.

32. Answer any five questions of the following:

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

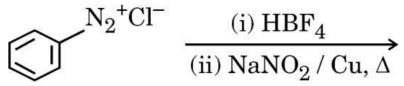
(b) Aniline does not undergo Friedel-Crafts reaction. Why?

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

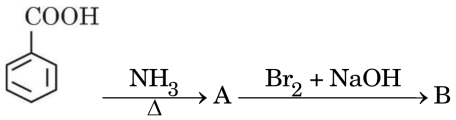
(d) Write the chemical reaction involved in Gabriel phthalimide synthesis.

(e) How will you convert aniline to p-bromoaniline? [5 marks]

(f) Complete the following reaction :



(g) Write the structures of A and B in the following reaction :



Solution:

Concept:

- A sulphonamide dissolves in alkali only if it contains an acidic hydrogen on nitrogen, which can be removed to form a soluble salt.
- The amino group activates an aromatic ring, but its lone pair also forms a salt or complex with the Lewis acid catalyst used in Friedel-Crafts reactions.
- Gabriel synthesis gives primary alkylamines by alkylation of phthalimide followed by hydrolysis. Hofmann bromamide degradation converts $\mathrm{RCONH_2}$ into $\mathrm{RNH_2}$, losing the carbonyl carbon.
- Protecting aniline as acetanilide controls bromination; diazonium salts allow replacement of the diazonium group with evolution of $\mathrm{N_2}$.

Step 1: (a) Check the nitrogen substituents The structure of N,N-diethyl-benzenesulphonamide is $\mathrm{C_6H_5SO_2N(C_2H_5)_2}$. Both hydrogens of the original sulphonamide nitrogen have been replaced by ethyl groups, so there is no $\mathrm{N-H}$ bond. Alkali cannot remove an acidic hydrogen from nitrogen to form an ionic, water-soluble salt. Hence this sulphonamide is insoluble in alkali.

Step 2: (b) Examine the interaction with the catalyst Aniline is a Lewis base because nitrogen has a lone pair. It reacts with the Lewis acid catalyst $\mathrm{AlCl_3}$ to form a salt/complex. Nitrogen then acquires positive character, and the amino group can no longer donate its lone pair freely to the ring. The ring becomes strongly deactivated towards electrophilic substitution, so aniline does not undergo the usual Friedel-Crafts alkylation or acylation.

Step 3: (c) Use the bromine-water test Add bromine water to separate aqueous samples. Aniline produces a white precipitate of 2,4,6-tribromoaniline, while methylamine does not produce this white precipitate. The observation distinguishes the aromatic primary amine from the aliphatic primary amine.

$$\mathrm{C_6H_5NH_2 + 3\,Br_2 \longrightarrow C_6H_2Br_3NH_2\downarrow + 3\,HBr}$$

Bromination occurs at both ortho positions and the para position because the unprotected amino group strongly activates the benzene ring.

Step 4: (d) Write the stages of Gabriel phthalimide synthesis Treat phthalimide with alcoholic potassium hydroxide to obtain potassium phthalimide. Its nitrogen anion then displaces halide from an alkyl halide $\mathrm{R-X}$, where R is an alkyl group and X is a halogen. Hydrolysis of the N-alkyl derivative gives the primary amine. The two carbonyl groups in the formula below belong to the cyclic phthalimide group attached at adjacent positions of the benzene ring.

$$\mathrm{C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK + H_2O}$$

$$\mathrm{C_6H_4(CO)_2NK + R-X \longrightarrow C_6H_4(CO)_2NR + KX}$$

$$\mathrm{C_6H_4(CO)_2NR + 2\,NaOH \longrightarrow C_6H_4(COONa)_2 + RNH_2}$$

This method prepares primary alkylamines; aryl halides do not undergo the required nucleophilic substitution readily.

Step 5: (e) Protect, brominate and deprotect aniline First acetylate aniline using acetic anhydride. Brominate the resulting acetanilide with bromine in acetic acid, then hydrolyse the isolated para

Quick Tip to Solve: For selective para bromination, protect aniline first. In part (f), read both reagent stages: sodium nitrite with copper replaces the diazonium group by a nitro group.

product to remove the acetyl protecting group.

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

$$C_6H_5NHCOCH_3 + Br_2 \xrightarrow{CH_3COOH} \text{p-}BrC_6H_4NHCOCH_3 + HBr$$

$$\text{p-}BrC_6H_4NHCOCH_3 + NaOH \xrightarrow{\text{heat}} \text{p-}BrC_6H_4NH_2 + CH_3COONa$$

Acetylation decreases the activating effect of nitrogen while retaining ortho/para direction. The para product predominates because it is less sterically hindered. Direct bromination of aniline with bromine water would instead give the tribromo compound.

Step 6: (f) Replace the diazonium group with a nitro group Fluoroboric acid first converts benzenediazonium chloride into benzenediazonium tetrafluoroborate. On heating this salt with aqueous sodium nitrite in the presence of copper, the diazonium group is replaced by NO_2, giving nitrobenzene.

$$C_6H_5N_2Cl + HBF_4 \longrightarrow C_6H_5N_2BF_4 + HCl$$

$$C_6H_5N_2BF_4 + NaNO_2 \xrightarrow{Cu,\ \Delta} C_6H_5NO_2 + N_2\uparrow + NaBF_4$$

The printed second-stage reagent $NaNO_2/Cu$ is essential: the product here is nitrobenzene.

Step 7: (g) Identify the amide and its degradation product Benzoic acid reacts with ammonia to form ammonium benzoate; heating removes water to give benzamide. Thus A has the condensed structural formula $C_6H_5{-}C(=O){-}NH_2$.

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COO^-\ NH_4^+$$

$$C_6H_5COO^-\ NH_4^+ \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O$$

Bromine and sodium hydroxide cause Hofmann bromamide degradation. The carbonyl carbon is removed and the phenyl group remains attached to nitrogen, so B is aniline, $C_6H_5{-}NH_2$.

$$C_6H_5CONH_2 + Br_2 + 4\,NaOH \longrightarrow C_6H_5NH_2 + 2\,NaBr + Na_2CO_3 + 2\,H_2O$$

Step 8: Conclusion (a) No acidic $N{-}H$ hydrogen is present. (b) Reaction with $AlCl_3$ deactivates the ring. (c) Only aniline gives a white tribromoaniline precipitate with bromine water. (d) Gabriel synthesis gives RNH_2. (e) Acetylation, bromination and hydrolysis give p-bromoaniline. (f) The product is nitrobenzene, $C_6H_5NO_2$. (g) A is benzamide, $C_6H_5CONH_2$, and B is aniline, $C_6H_5NH_2$.

Quick Tip to Solve: For selective para bromination, protect aniline first. In part (f), read both reagent stages: sodium nitrite with copper replaces the diazonium group by a nitro group.

33(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 and enthalpy of atomisation depend on the participation of valence electrons. Filled d subshells contribute little to strong metallic bonding in the zinc group.
- Oxidation and reduction tendencies depend on the relative stability of the electronic configurations before and after electron transfer. A half-filled d^5 configuration is particularly stable.
- The standard electrode potential reflects the overall energy change, including atomisation, ionisation and hydration. Redox equations must conserve both atoms and total charge.

Step 1: (i)(1) Relate the low melting and boiling points to bonding Zn, Cd and Hg have the valence configuration $(n-1)d^{10}ns^2$, with completely filled d subshells. Their d electrons do not contribute effectively to the strong metallic bonding found in many other transition-series metals. Their metal–metal bonding is relatively weak and their enthalpies of atomisation are low. Consequently, less energy is needed to overcome these attractions, explaining their low melting and boiling points.

Step 2: (i)(2) Compare the configurations reached by electron transfer Both Cr^{2+} and Mn^{3+} are $3d^4$ species, but they attain greater stability by different changes. Cr^{2+} readily loses an electron to form Cr^{3+}, which has the stable $3d^3$ configuration (t_{2g}^3 in an octahedral aqueous complex):

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

By donating an electron it reduces another species, so Cr^{2+} is strongly reducing. In contrast, Mn^{3+} readily gains an electron to form Mn^{2+} with the particularly stable half-filled $3d^5$ configuration:

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

By accepting an electron it oxidises another species, so Mn^{3+} is strongly oxidising.

Step 3: (i)(3) Explain the positive copper electrode potential The reduction half-reaction is

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu\,(s), \qquad E^\circ = +0.34\,V.$$

Formation of $Cu^{2+}(aq)$ from Cu (s) requires atomisation of the metal followed by the first and second ionisations. Copper has a high enthalpy of atomisation and high ionisation-energy requirements, especially the second ionisation because Cu^+ has a filled $3d^{10}$ configuration. The hydration enthalpy released on forming $Cu^{2+}(aq)$ does not compensate sufficiently for these energy requirements. Thus copper resists oxidation relative to hydrogen, and the standard reduction potential of the Cu^{2+}/Cu couple is positive.

Quick Tip to Solve: For the two d^4 ions, compare the configurations after losing or gaining one electron. In the dichromate equation, use six electrons and check the final charge of $+6$ on each side.

Step 4: (ii)(1) Balance the thermal decomposition of permanganate On heating, potassium permanganate produces potassium manganate, manganese dioxide and oxygen:

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

The two sides each contain two potassium atoms, two manganese atoms and eight oxygen atoms. The products contain manganese in the $+6$ and $+4$ oxidation states, compared with $+7$ in the reactant.

Step 5: (ii)(2) Balance the dichromate–iodide reaction in acid Dichromate is reduced to Cr^{3+}, while iodide is oxidised to iodine. The half-reactions are

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

Adding them cancels the six transferred electrons:

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

The net charge is $+6$ on each side, and chromium, iodine, oxygen and hydrogen atoms are all conserved.

Step 6: Conclusion The zinc-group metals have weak metallic bonding; Cr^{2+} is reducing because it forms stable Cr^{3+}, whereas Mn^{3+} is oxidising because it forms half-filled Mn^{2+}. Copper's atomisation and ionisation energy requirements account for its positive standard reduction potential. The balanced reactions give $K_2MnO_4 + MnO_2 + O_2$ from $2\,KMnO_4$, and $2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$ from the printed acidic dichromate–iodide reactants.

Quick Tip to Solve: For the two d^4 ions, compare the configurations after losing or gaining one electron. In the dichromate equation, use six electrons and check the final charge of $+6$ on each side.

OR

33(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:

- Stability in water depends on hydration as well as electronic configuration; the large hydration enthalpy of Cu^{2+} favours it over Cu^+.
- In f-block elements the differentiating electron enters the $(n-2)f$ subshell, where n is the outermost

Quick Tip to Solve: For aqueous ion questions, first write the ionic d configuration, but compare hydration energies when judging stability; a filled subshell alone does not guarantee stability in water.

principal quantum number.

- A partially filled d subshell can permit absorption of visible light by a hydrated ion. Empty and completely filled d subshells do not allow d–d transitions.
- Acidification converts chromate to dichromate; a less soluble salt can then be isolated by crystallisation. Variable oxidation states and adsorption help transition-metal catalysts provide a lower-activation-energy pathway.

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

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

Thus a filled $3d^{10}$ configuration of Cu^{+} alone does not establish aqueous stability.

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

$$[\text{noble-gas core}]\,(n-2)f^{1-14}(n-1)d^{0-1}ns^2.$$

Here $n = 6$ for the lanthanoids and $n = 7$ for the actinoids. The f subshell is progressively filled, with at most one electron generally shown in the adjacent d subshell.

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

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

Fe^{3+} is coloured in aqueous solution and has a partially filled d subshell. Sc^{3+} and Zn^{2+} are colourless: their empty and completely filled d subshells, respectively, do not permit d–d transitions. Thus only the iron(III) ion among the given ions is coloured.

Step 4: (iv) Convert sodium chromate into potassium dichromate First acidify the aqueous sodium chromate solution with dilute sulphuric acid. Yellow chromate is converted into orange dichromate:

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

Then treat the sodium dichromate solution with potassium chloride:

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

On concentrating and cooling, $K_2Cr_2O_7$ crystallises because it is less soluble than sodium dichromate. Separate these orange crystals from the solution.

Step 5: (v) Explain catalytic activity Transition metals and their compounds can adopt different oxidation states and form intermediate complexes with reactants. These intermediates allow an alternative reaction pathway of lower activation energy, while the catalyst is regenerated. Solid transition metals also adsorb reactants on their surfaces, bringing them together and weakening bonds

Quick Tip to Solve: For aqueous ion questions, first write the ionic d configuration, but compare hydration energies when judging stability; a filled subshell alone does not guarantee stability in water.

so that reaction becomes easier. For example, finely divided iron catalyses ammonia synthesis.

Step 6: Conclusion (i) $CuCl_2$ is more stable in water due to stronger hydration of Cu^{2+}. (ii) The f-block configuration is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ beyond the noble-gas core. (iii) Only Fe^{3+} is coloured. (iv) Acidify Na_2CrO_4, add KCl, and crystallise $K_2Cr_2O_7$. (v) Variable oxidation states, intermediate formation and surface adsorption explain catalytic activity.

Quick Tip to Solve: For aqueous ion questions, first write the ionic d configuration, but compare hydration energies when judging stability; a filled subshell alone does not guarantee stability in water.