

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-2-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This Question Paper contains **35** questions. **All** questions are compulsory.
- (ii) Question Paper is divided into **FIVE** sections – Section **A, B, C, D** and **E**.
- (iii) **In section A** – question number **1 to 18** are Multiple Choice (MCQ) type questions carrying **1** mark each.
- (iv) **In section B** – question number **19 to 25** are Very Short Answer (VSA) type questions carrying **2** marks each.
- (v) **In section C** – question number **26 to 30** are Short Answer (SA) type questions carrying **3** marks each.
- (vi) **In section D** – question number **31 & 32** are case-based questions carrying **4** marks each.
- (vii) **In section E** – question number **33 to 35** are Long Answer (LA) questions carrying **5** marks each.
- (viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section **B**, 2 questions in Section **C**, 2 questions in Section **D** and 2 questions in Section **E**.
- (ix) Use of calculator is **NOT** allowed.

Section A (18 marks)

1. Auto oxidation of chloroform in air and sunlight produces a poisonous gas known as [1 mark]

- (A) Tear gas
- (B) Mustard gas
- (C) Phosgene gas
- (D) Chlorine gas

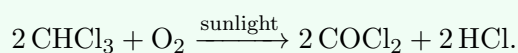
Correct Answer: (C) Phosgene gas

Solution:

Concept:

- Chloroform, CHCl_3 , undergoes slow oxidation by atmospheric oxygen in the presence of light.
- The product carbonyl chloride, COCl_2 , is commonly called phosgene.

Step 1: Write the oxidation reaction The oxygen in air oxidises chloroform under sunlight. The balanced equation is



Both carbon atoms remain in the carbonyl chloride molecules; hydrogen is removed as hydrogen chloride.

Step 2: Compare the gas names Phosgene is the highly poisonous carbonyl chloride gas produced here. Tear gas and mustard gas are different chemical agents and are not the oxidation products in this reaction. Chlorine gas would require formation of Cl_2 ; the balanced reaction instead produces COCl_2 and HCl .

Step 3: Conclusion The poisonous gas is phosgene, COCl_2 . Hence, the correct option is (C).

Quick Tip to Solve: Remember the pair: chloroform plus oxygen in sunlight gives carbonyl chloride, whose common name is phosgene.

2. Which of the following ligands is an ambidentate ligand? [1 mark]

- (A) CO
- (B) NO_2
- (C) NH_3
- (D) H_2O

Correct Answer: (B) NO_2

Solution:

Concept:

- An ambidentate ligand has two alternative donor atoms but attaches through only one of them to a given metal centre.
- The nitrite ligand, NO_2^- , can coordinate through nitrogen or through oxygen.

Quick Tip to Solve: For nitrite, check for N-bound nitro and O-bound nitrito forms; alternative donor atoms signal an ambidentate ligand.

Step 1: Identify the alternative donor sites Option (B) denotes the nitrite ligand in the ligand list. Nitrogen donation produces the nitro form, while oxygen donation produces the nitrito form. These alternative attachment modes give linkage isomerism; they do not mean that both atoms bind simultaneously.

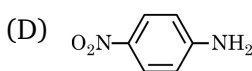
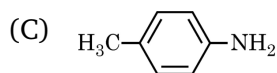
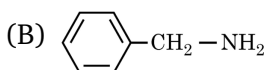
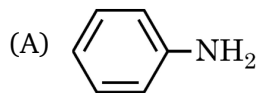
Step 2: Exclude the other ligands CO normally donates through carbon, NH_3 through nitrogen, and H_2O through oxygen in the standard coordination compounds considered here. Each has only one usual donor atom, unlike nitrite, so none of (A), (C), or (D) is the required ambidentate ligand.

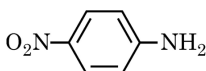
Step 3: Conclusion The nitrite ligand has the two alternative donor atoms required. Hence, the correct option is (B).

Quick Tip to Solve: For nitrite, check for N-bound nitro and O-bound nitrito forms; alternative donor atoms signal an ambidentate ligand.

3. Among the following, which has the highest value of $\text{p}K_b$?

[1 mark]



Correct Answer: (D) 

Solution:

Concept:

- $\text{p}K_b = -\log K_b$; a higher $\text{p}K_b$ means a smaller basicity constant and a weaker base.
- An amine is more basic when the nitrogen lone pair is more available to accept a proton.

Step 1: Compare lone-pair availability In aniline, the nitrogen lone pair is delocalised into the benzene ring. A para nitro group withdraws electron density by both inductive and resonance effects, making the lone pair still less available in p-nitroaniline. This makes it weaker as a base than aniline.

Step 2: Check the remaining substituents The para methyl group of p-toluidine donates electron density and increases basicity relative to aniline. In benzylamine, a saturated CH_2 group separates nitrogen from the ring, so its lone pair is not delocalised directly into the ring and it behaves as an aliphatic amine. Thus neither (B) nor (C), nor unsubstituted aniline (A), is the weakest base of the list.

Step 3: Conclusion p-Nitroaniline is the weakest base and therefore has the highest $\text{p}K_b$. Hence, the correct option is (D).

Quick Tip to Solve: Highest $\text{p}K_b$ means weakest base: select the aromatic amine with the strongest electron-withdrawing substituent.

4. The slope in the plot of $\log \frac{[R]_0}{[R]}$ vs. time for a first order reaction is

[1 mark]

- (A) $\frac{+k}{2.303}$
(B) $+k$
(C) $\frac{-k}{2.303}$
(D) $-k$

Correct Answer: (A) $\frac{+k}{2.303}$

Solution:

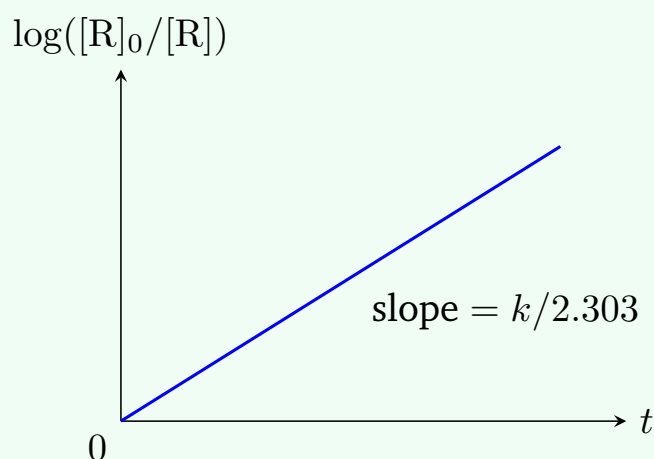
Concept:

- For a first-order reaction, $kt = 2.303 \log([R]_0/[R])$, where k is the rate constant.
- The straight-line form $y = mt + c$ identifies the slope m of a plot of y against time t .

Step 1: Rearrange the integrated rate law With $[R]_0$ the initial reactant concentration and $[R]$ its value at time t ,

$$\log \frac{[R]_0}{[R]} = \frac{k}{2.303}t.$$

This logarithm is base ten; converting a natural logarithm to base ten introduces the factor 2.303.



First-order integrated-rate plot; time is measured in the same units used for the rate constant.

Step 2: Read the slope and reject alternatives The coefficient of time is $+k/2.303$, and the intercept is zero. Reactant concentration decreases as time increases, so the ratio and its logarithm increase; the slope is positive. Options (C) and (D) have the wrong sign. Option (B) would apply to a plot of the natural logarithm of the same ratio, not the common logarithm printed here.

Step 3: Conclusion The slope is $+\frac{k}{2.303}$. Hence, the correct option is (A).

Quick Tip to Solve: Check the logarithm base first: common log gives $k/2.303$, while natural log gives k for this increasing concentration ratio.

5. When D-glucose reacts with HI, it forms

[1 mark]

- (A) Gluconic acid
- (B) n-hexane
- (C) Saccharic acid
- (D) Iodohehexane

Correct Answer: (B) n-hexane

Solution:

Concept:

- Prolonged heating of glucose with hydroiodic acid reduces its oxygen-containing groups and gives a hydrocarbon.
- The product retains all six carbon atoms of glucose in a straight chain.

Step 1: Apply reduction by hydroiodic acid Under the usual prolonged-heating conditions for this reaction, the aldehyde and hydroxyl groups of D-glucose are reduced. The oxygen atoms are removed and the six-carbon skeleton becomes fully saturated. The product has the condensed formula $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$.

Step 2: Identify the hydrocarbon and eliminate other products This straight-chain saturated six-carbon compound is n-hexane. Gluconic acid results from mild oxidation of the aldehyde group, and saccharic acid from stronger oxidation of both terminal groups. HI is used here as a reducing reagent, so neither acid fits. Iodohehexane is not the final product of the prolonged HI treatment of glucose.

Step 3: Conclusion D-Glucose gives n-hexane on prolonged heating with HI. Hence, the correct option is (B).

Quick Tip to Solve: Glucose heated for a long time with HI gives n-hexane; this reaction establishes its straight six-carbon chain.

6. Inversion of configuration occurs in

[1 mark]

- (A) $\text{S}_{\text{N}}2$ reaction
- (B) $\text{S}_{\text{N}}1$ reaction
- (C) Neither $\text{S}_{\text{N}}2$ nor $\text{S}_{\text{N}}1$ reaction
- (D) $\text{S}_{\text{N}}1$ as well as $\text{S}_{\text{N}}2$ reaction

Correct Answer: (A) $\text{S}_{\text{N}}2$ reaction

Solution:

Concept:

- An $\text{S}_{\text{N}}2$ substitution is a concerted process: bond formation and bond breaking occur in one step.
- Backside attack on a stereogenic carbon leads to inversion of its configuration, called Walden inversion.

Step 1: Trace the backside attack The incoming nucleophile approaches the carbon from the side opposite the leaving group. As the new bond forms and the old bond breaks simultaneously, the three

Quick Tip to Solve: Connect backside attack directly with inversion; a planar $\text{S}_{\text{N}}1$ carbocation allows attack from both faces instead.

remaining groups turn over like an umbrella in the wind. The configuration at that carbon is therefore inverted in an S_N2 reaction.

Step 2: Contrast the unimolecular mechanism An S_N1 reaction forms a planar carbocation intermediate. The nucleophile can attack from either face, giving both retained and inverted products and hence racemisation, often with some excess inversion. It does not give the characteristic stereospecific inversion asked here. Thus (B) and (D) do not identify the standard mechanism, while (C) wrongly excludes S_N2 .

Step 3: Conclusion Inversion of configuration is characteristic of the S_N2 reaction. Hence, the correct option is (A).

Quick Tip to Solve: Connect backside attack directly with inversion; a planar S_N1 carbocation allows attack from both faces instead.

7. Solubility of gas in liquid decreases with increase in

[1 mark]

- (A) Pressure
- (B) Temperature
- (C) Volume
- (D) Number of solute molecules

Correct Answer: (B) Temperature

Solution:

Concept:

- For most gases, dissolution in a liquid is exothermic: $\text{gas} + \text{solvent} \rightleftharpoons \text{solution} + \text{heat}$.
- Henry's law, $p = K_H x$, relates gas pressure p to dissolved mole fraction x at fixed temperature.

Step 1: Apply the temperature effect Heating favours the endothermic reverse process, so more dissolved gas escapes from the liquid. At the same gas pressure, the dissolved amount therefore decreases as temperature rises.

Step 2: Compare all four choices Increasing pressure increases gas solubility, so (A) gives the opposite effect. Volume alone is not the temperature dependence of solubility, and the number of solute molecules describes the amount already dissolved rather than the cause of its decrease. Hence (C) and (D) do not give the required effect.

Step 3: Conclusion Increasing temperature decreases the solubility of a gas in a liquid. Hence, the correct option is (B).

Quick Tip to Solve: Recall that warm water loses dissolved gases: heating favours their escape.

8. Which of the following relations is incorrect?

[1 mark]

(A) $R = \frac{1}{k} \left(\frac{l}{a} \right)$

(B) $G = k \left(\frac{a}{l} \right)$

(C) $G = k \left(\frac{l}{a} \right)$

(D) $\Lambda_m = \frac{k}{c}$

Correct Answer: (C) $G = k \left(\frac{l}{a} \right)$

Solution:

Concept:

- Resistance is $R = \rho l/a$, where l is electrode separation, a is cross-sectional area and ρ is resistivity.
- Conductivity $k = 1/\rho$ and conductance $G = 1/R$; molar conductivity is $\Lambda_m = k/c$ when concentration c uses compatible units.

Step 1: Obtain the correct conductance relation Substituting $\rho = 1/k$ gives $R = (1/k)(l/a)$. Taking its reciprocal gives

$$G = k \frac{a}{l}.$$

Thus increasing the cross-sectional area increases conductance, while increasing the length decreases it.

Step 2: Check each printed expression Option (A) is the correct resistance expression and (B) is its reciprocal. Option (C) reverses the geometry factor and incorrectly uses l/a for conductance. Option (D) is the definition of molar conductivity with consistent concentration and conductivity units; any numerical unit-conversion factor depends on the units chosen.

Step 3: Conclusion The incorrect relation is $G = k(l/a)$. Hence, the correct option is (C).

Quick Tip to Solve: First write resistance using length/area, then invert the entire relation for conductance.

9. The reagent that can be used to distinguish acetophenone and benzophenone is

[1 mark]

(A) 2,4-dinitrophenyl hydrazine

(B) aqueous NaHSO_3

(C) Fehling solution

(D) I_2 and NaOH

Correct Answer: Both (B), aqueous sodium bisulphite, and (D), iodine and sodium hydroxide, can distinguish the ketones; (D) is the standard iodoform test.

Solution:

Concept:

- The iodoform test uses I_2/NaOH and gives yellow CHI_3 with a methyl ketone, RCOCH_3 .
- Acetophenone is $\text{C}_6\text{H}_5\text{COCH}_3$; benzophenone is $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$.

Quick Tip to Solve: Spot the carbonyl methyl group: acetophenone has it, benzophenone does not.

Step 1: Identify the diagnostic group Acetophenone contains the $-\text{COCH}_3$ group, so it forms yellow iodoform. Benzophenone has two phenyl groups attached to its carbonyl carbon and no carbonyl methyl group, so it gives a negative iodoform test.

Step 2: Compare the reagents Both are ketones, so 2,4-dinitrophenylhydrazine gives a carbonyl derivative with either and Fehling solution is negative with either. I_2/NaOH gives the clear positive-versus-negative iodoform distinction. Aqueous bisulphite can also form an addition compound with acetophenone, whereas benzophenone is sterically hindered and does not readily form one; consequently (B) can also be used under suitable conditions. The printed choices therefore are not strictly exclusive.

Step 3: Conclusion Both (B) and (D) are chemically valid distinctions. In the standard iodoform test, I_2/NaOH , acetophenone gives yellow CHI_3 and benzophenone does not. Aqueous sodium bisulphite can distinguish them by addition-compound formation. The printed question therefore has more than one defensible choice.

Quick Tip to Solve: Spot the carbonyl methyl group: acetophenone has it, benzophenone does not.

10. Which of the following reactions are feasible?

[1 mark]

- (A) $\text{CH}_3\text{CH}_2\text{Br} + \text{Na}^+ \text{ } ^-\text{OC}(\text{CH}_3)_3 \rightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_3$
(B) $(\text{CH}_3)_3\text{C} - \text{Cl} + \text{Na}^+ \text{ } ^-\text{OCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_3$
(C) Both (a) and (b)
(D) Neither (a) nor (b)

Correct Answer: (A) $\text{CH}_3\text{CH}_2\text{Br} + \text{Na}^+ \text{ } ^-\text{OC}(\text{CH}_3)_3 \rightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_3$

Solution:

Concept:

- Williamson ether synthesis is an $\text{S}_\text{N}2$ reaction of an alkoxide with a suitable alkyl halide.
- Primary alkyl halides allow backside displacement; tertiary halides favour elimination with a strong alkoxide base.

Step 1: Examine reaction (a) Ethyl bromide, $\text{CH}_3\text{CH}_2\text{Br}$, is a primary halide. The tert-butoxide ion attacks its primary carbon and displaces bromide in the Williamson substitution, forming ethyl tert-butyl ether. The bulky group is on the alkoxide side, not on the carbon bearing the leaving group.

Step 2: Examine reaction (b) Tert-butyl chloride has a tertiary carbon bearing chlorine, so steric crowding prevents the required $\text{S}_\text{N}2$ displacement. Ethoxide instead abstracts a beta hydrogen and promotes elimination to 2-methylpropene. It therefore does not give the ether by the displayed Williamson route. Thus (B), (C) and (D) do not represent the feasible ether-forming reaction.

Step 3: Conclusion Only the reaction printed in option (A) is feasible for the displayed ether synthesis. Hence, the correct option is (A).

Quick Tip to Solve: To prepare an unsymmetrical ether, put the less hindered group on the alkyl-halide side.

11. Which of the following compounds will undergo self-condensation in the presence of dilute NaOH solution? [1 mark]

- (A) $\text{C}_6\text{H}_5\text{CHO}$
(B) $\text{CH}_3\text{CH}_2\text{CHO}$
(C) $(\text{CH}_3)_3\text{C-CHO}$
(D) H-CHO

Correct Answer: (B) $\text{CH}_3\text{CH}_2\text{CHO}$

Solution:

Concept:

- Aldol self-condensation requires an aldehyde or ketone with at least one alpha hydrogen, on the carbon adjacent to $\text{C}=\text{O}$.
- Dilute NaOH removes an alpha hydrogen to produce the enolate nucleophile that attacks another carbonyl molecule.

Step 1: Identify the compound with alpha hydrogen Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, has an alpha CH_2 group containing two hydrogens. It can form an enolate and undergo aldol self-condensation, initially producing a beta-hydroxy aldehyde.

Step 2: Exclude the remaining compounds In benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, the adjacent aromatic carbon has no alpha hydrogen. In $(\text{CH}_3)_3\text{CCHO}$, the alpha carbon is bonded to three methyl groups and the aldehyde carbon, so it has no hydrogen. Formaldehyde, HCHO , has no alpha carbon at all. These cannot undergo the required aldol self-condensation.

Step 3: Conclusion $\text{CH}_3\text{CH}_2\text{CHO}$ undergoes self-condensation in dilute NaOH. Hence, the correct option is (B).

Quick Tip to Solve: Count hydrogens on the carbon immediately next to the carbonyl, not on the aldehyde carbon.

12. For the reaction $3\text{A} \rightarrow 2\text{B}$, rate of reaction $-\frac{d[\text{A}]}{dt}$ is equal to [1 mark]

- (A) $\frac{+3}{2} \frac{d[\text{B}]}{dt}$
(B) $\frac{+2}{3} \frac{d[\text{B}]}{dt}$
(C) $\frac{+1}{3} \frac{d[\text{B}]}{dt}$
(D) $\frac{+1}{2} \frac{d[\text{B}]}{dt}$

Correct Answer: (A) $\frac{+3}{2} \frac{d[\text{B}]}{dt}$

Solution:

Concept:

- For $3\text{A} \rightarrow 2\text{B}$, the normalised rate is $r = -\frac{1}{3} \frac{d[\text{A}]}{dt} = \frac{1}{2} \frac{d[\text{B}]}{dt}$.

Quick Tip to Solve: Use consumption/formation = 3/2; do not confuse disappearance rate with normalised reaction rate.

- The negative sign makes the rate of reactant disappearance positive; product concentration increases with time.

Step 1: Relate the concentration changes Every three moles of A consumed produce two moles of B. At constant volume, the magnitude of the decrease in [A] is therefore 3/2 times the increase in [B].

Step 2: Isolate the expression requested Multiplying the normalised-rate relation by 3 gives

$$-\frac{d[A]}{dt} = \frac{3}{2} \frac{d[B]}{dt}.$$

The printed expression asks for the unnormalised disappearance rate of A. The factor 2/3 in (B) would apply to the inverse relation; 1/3 and 1/2 in (C) and (D) omit the required stoichiometric ratio.

Step 3: Conclusion $-d[A]/dt = +(3/2)d[B]/dt$. Hence, the correct option is (A).

Quick Tip to Solve: Use consumption/formation = 3/2; do not confuse disappearance rate with normalised reaction rate.

13. Which of the following transition metals shows +1 and +2 oxidation states?

[1 mark]

- (A) Mn
- (B) Zn
- (C) Sc
- (D) Cu

Correct Answer: (D) Cu

Solution:

Concept:

- Copper has electronic configuration $[Ar] 3d^{10}4s^1$ and commonly shows +1 and +2 oxidation states.
- Electrons are removed from the outer 4s orbital before the 3d orbitals on forming these metal ions.

Step 1: Find the two copper ions Loss of the 4s electron gives Cu^+ , with $3d^{10}$ configuration. Loss of one further electron gives Cu^{2+} , with $3d^9$ configuration. Both oxidation states are characteristic of copper compounds.

Step 2: Compare the other choices Manganese commonly shows +2, +3, +4, +6 and +7 in the standard CBSE treatment, rather than the characteristic +1, +2 pair asked here. Zinc predominantly forms Zn^{2+} , and scandium predominantly forms Sc^{3+} . Thus neither (A), (B) nor (C) matches the pair as directly as copper.

Step 3: Conclusion Copper, Cu, shows +1 and +2 oxidation states. Hence, the correct option is (D).

Quick Tip to Solve: Recall cuprous = copper(I) and cupric = copper(II), the two familiar oxidation states.

14. The formula of the complex Iron(III) hexacyanidoferrate(II) is:

[1 mark]

- (A) $\text{Fe}_2[\text{Fe}(\text{CN})_6]_3$
- (B) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- (C) $\text{Fe}[\text{Fe}(\text{CN})_6]$
- (D) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$

Correct Answer: (B) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

Solution:

Concept:

- Iron(III) outside the coordination sphere is the cation Fe^{3+} .
- Each cyanido ligand, CN^- , has charge -1 ; the Roman numeral (II) refers to the oxidation state of the central iron.

Step 1: Determine the complex ion charge Hexacyanidoferrate(II) contains six cyanido ligands coordinated to iron in oxidation state $+2$. Thus its charge is

$$+2 + 6(-1) = -4.$$

The anion is therefore $[\text{Fe}(\text{CN})_6]^{4-}$, rather than a neutral species.

Step 2: Balance the ionic charges A neutral salt requires equal total positive and negative charges. The lowest common multiple of 3 and 4 is 12: four Fe^{3+} cations give $+12$, and three complex anions give -12 . Option (A) instead has net charge -6 , option (C) has net charge -1 , and option (D) has net charge $+1$, so none is neutral for the specified oxidation states.

Step 3: Conclusion The formula is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. Hence, the correct option is (B).

Quick Tip to Solve: Find the complex anion charge first, then use the smallest cation-to-anion ratio that makes the salt electrically neutral.

15. Assertion (A): The enthalpy of mixing $\Delta_{\text{mix}}H$ is equal to zero for an ideal solution.

Reason (R): For an ideal solution the interaction between solute and solvent molecules is stronger than the interactions between solute-solute or solvent-solvent molecules.

Select the most appropriate answer from the options given below:

[1 mark]

- (A) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (B) Both (A) and (R) are true, but (R) is not the correct explanation of (A).
- (C) (A) is true, but (R) is false.
- (D) (A) is false, but (R) is true.

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

Solution:

Concept:

- An ideal solution obeys Raoult's law at all compositions and has $\Delta_{\text{mix}}H = 0$.

Quick Tip to Solve: For an ideal solution remember equal interaction strengths, zero heat of mixing and zero volume change on mixing.

- Ideal mixing requires similar intermolecular interactions: solute-solvent attractions are approximately equal to solute-solute and solvent-solvent attractions.

Step 1: Evaluate the assertion During ideal mixing, the energy needed to separate like molecules is balanced by the energy released when unlike molecules interact. No net heat is absorbed or evolved, so the enthalpy of mixing is zero. Assertion (A) is true.

Step 2: Evaluate the reason Reason (R) says that unlike molecules interact more strongly than like molecules. That describes a tendency towards negative deviation from Raoult's law, with heat evolved on mixing, rather than an ideal solution. For ideal behaviour the strengths must be approximately equal. Reason (R) is false.

Step 3: Check the explanatory link The stated stronger interaction cannot explain zero enthalpy of mixing; comparable interactions explain it. Options (A) and (B) both incorrectly accept the reason, and option (D) incorrectly rejects the assertion.

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

Quick Tip to Solve: For an ideal solution remember equal interaction strengths, zero heat of mixing and zero volume change on mixing.

16. Assertion (A): Molar conductivity decreases with increase in concentration.

Reason (R): When concentration approaches zero, the molar conductivity is known as limiting molar conductivity.

Select the most appropriate answer from the options given below:

[1 mark]

- (A) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (B) Both (A) and (R) are true, but (R) is not the correct explanation of (A).
- (C) (A) is true, but (R) is false.
- (D) (A) is false, but (R) is true.

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

Solution:

Concept:

- Molar conductivity Λ_m is the conductance associated with the volume of solution containing one mole of electrolyte.
- Limiting molar conductivity is $\Lambda_m^\circ = \lim_{c \rightarrow 0} \Lambda_m$, where c is the electrolyte concentration.

Step 1: Evaluate the assertion Molar conductivity increases on dilution, so it decreases as concentration increases. For strong electrolytes, stronger interionic interactions at higher concentration hinder ionic movement. For weak electrolytes, increasing concentration also reduces the degree of ionisation. Assertion (A) is true.

Step 2: Evaluate the reason As concentration approaches zero, ions become increasingly separated and the molar conductivity approaches its limiting value, called limiting molar conductivity. This is precisely the definition of Λ_m° , so Reason (R) is true.

Quick Tip to Solve: Separate a definition of the infinite-dilution limit from the physical explanation of how concentration affects ionic mobility.

Step 3: Check the explanatory link The reason names the limiting value; it does not give the physical cause of the decrease on increasing concentration. Interionic interactions, and for weak electrolytes reduced ionisation, explain that trend. Thus option (A) incorrectly claims an explanation, while (C) and (D) incorrectly declare a true statement false.

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

Quick Tip to Solve: Separate a definition of the infinite-dilution limit from the physical explanation of how concentration affects ionic mobility.

17. Assertion (A): Transition metals show their highest oxidation state with oxygen.

Reason (R): The ability of oxygen to form multiple bonds to metals.

Select the most appropriate answer from the options given below:

[1 mark]

- (A) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (B) Both (A) and (R) are true, but (R) is not the correct explanation of (A).
- (C) (A) is true, but (R) is false.
- (D) (A) is false, but (R) is true.

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

Solution:

Concept:

- Oxygen stabilises high oxidation states of transition metals through strong metal-oxygen bonding.
- Oxygen can form multiple bonds with metals; this helps stabilise high oxidation states in oxides and oxoanions.

Step 1: Evaluate the assertion Transition metals attain their highest oxidation states in compounds with oxygen. For example, manganese has oxidation state +7 in Mn_2O_7 , since the seven oxygen atoms contribute a total of -14 . Assertion (A) expresses this standard trend and is true.

Step 2: Evaluate the reason Oxygen can form strong multiple bonds to a metal centre. The resulting strong bonding stabilises compounds in which the metal has a high positive oxidation state. Reason (R) is therefore true.

Step 3: Check the explanatory link The multiple-bond-forming ability of oxygen is the stated reason for the stability of the highest oxidation states with oxygen. It therefore explains the assertion. Option (B) wrongly denies this connection, while options (C) and (D) incorrectly classify one of the true statements as false.

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

Quick Tip to Solve: Associate the highest transition-metal oxidation states in oxides with oxygen's ability to form strong multiple bonds.

18. Assertion (A): Chlorobenzene is resistant to nucleophilic substitution reaction at room temperature.

Reason (R): C-Cl bond gets weaker due to resonance.

Select the most appropriate answer from the options given below:

[1 mark]

- (A) Both (A) and (R) are true and (R) is the correct explanation of (A).
(B) Both (A) and (R) are true, but (R) is not the correct explanation of (A).
(C) (A) is true, but (R) is false.
(D) (A) is false, but (R) is true.

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

Solution:

Concept:

- In chlorobenzene, a lone pair on chlorine is delocalised into the benzene ring by resonance.
- Resonance gives the carbon-chlorine bond partial double-bond character, making it shorter and stronger than the corresponding bond in a haloalkane.

Step 1: Evaluate the assertion Chlorobenzene resists nucleophilic substitution at room temperature because its carbon-chlorine bond is difficult to break. The bonded ring carbon is sp^2 -hybridised, and resonance further strengthens the bond. Assertion (A) is true.

Step 2: Evaluate the reason The reason states that resonance makes the carbon-chlorine bond weaker. This reverses the actual effect: delocalisation imparts partial double-bond character and strengthens the bond. Therefore Reason (R) is false.

Step 3: Check the explanatory link A weaker bond would favour bond cleavage and would not explain the resistance observed here. The correct explanation uses the stronger bond arising from resonance. Options (A) and (B) incorrectly treat the reason as true, and (D) incorrectly treats the assertion as false.

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

Quick Tip to Solve: In chlorobenzene, resonance strengthens the carbon-chlorine bond; never confuse delocalisation with easier bond cleavage.

Section B (14 marks)

19. What are nucleic acids? Why two strands in DNA are not identical but are complementary?

[2 marks]

Solution:

Concept:

- Nucleic acids are polynucleotides: long chains of repeating nucleotide units joined by phosphodiester linkages.
- Complementary base pairing in DNA is specific: adenine pairs with thymine, and guanine pairs with cytosine.

Quick Tip to Solve: To find a complementary DNA sequence, replace A with T and G with C, and reverse the strand direction labels.

Step 1: Define nucleic acids Nucleic acids are biological macromolecules made of nucleotide units. Each nucleotide contains a pentose sugar, a phosphate group and a nitrogenous base. The two main types are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). They are involved in the storage and expression of genetic information; DNA provides the hereditary information that is transmitted during reproduction.

Step 2: Explain complementary DNA strands DNA contains two strands held together by hydrogen bonds between specific pairs of bases. Adenine (A) on one strand pairs with thymine (T) on the other through two hydrogen bonds, while guanine (G) pairs with cytosine (C) through three hydrogen bonds. Thus a base on one strand requires its partner base, rather than an identical base, opposite it on the other strand. For example, a strand read as 5'-ATGC-3' pairs with 3'-TACG-5'. The strands run in opposite directions, and knowledge of one strand determines the sequence of the other through these pairing rules.

Step 3: Conclusion Nucleic acids are nucleotide polymers, chiefly DNA and RNA. The two DNA strands are complementary because A pairs specifically with T and G with C, so the sequence of one strand determines the paired sequence of the other.

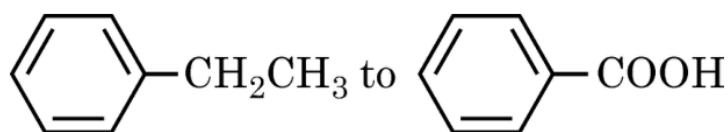
Quick Tip to Solve: To find a complementary DNA sequence, replace A with T and G with C, and reverse the strand direction labels.

20. Do the following conversions in not more than two steps:

(a) CH_3COOH to CH_3COCH_3

(b)

[2 marks]

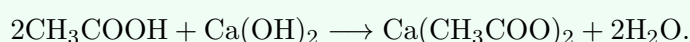


Solution:

Concept:

- Dry distillation of a calcium carboxylate gives a ketone: calcium acetate gives acetone, CH_3COCH_3 .
- Hot alkaline potassium permanganate oxidises an alkylbenzene having a benzylic hydrogen to a benzoate salt; acidification then gives benzoic acid.

Step 1: (a) Convert ethanoic acid to calcium acetate Treat ethanoic acid with calcium hydroxide to form its calcium salt. Remove water to obtain dry calcium acetate:



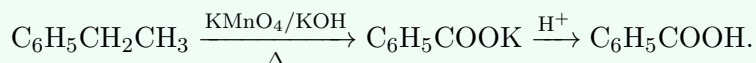
Step 2: (a) Heat the dry calcium salt Dry distillation converts calcium acetate into acetone, with calcium carbonate as the inorganic product:



Quick Tip to Solve: For acid-to-ketone conversion, use dry calcium acetate; for an alkylbenzene, check for a benzylic hydrogen before using hot alkaline permanganate.

Thus the requested conversion is completed in two reaction steps.

Step 3: (b) Oxidise the ethyl side chain and acidify Heat ethylbenzene with alkaline KMnO_4 , then acidify the resulting potassium benzoate:



The carbon attached directly to the ring becomes the carboxyl carbon. The remaining side-chain carbon is further oxidised; the benzene ring is retained.

Step 4: Conclusion (a) Ethanoic acid $\rightarrow$ calcium acetate $\rightarrow$ acetone. (b) Ethylbenzene $\rightarrow$ potassium benzoate $\rightarrow$ benzoic acid.

Quick Tip to Solve: For acid-to-ketone conversion, use dry calcium acetate; for an alkylbenzene, check for a benzylic hydrogen before using hot alkaline permanganate.

21. Write the chemical equation involved in the following reactions:

(a) Reimer-Tiemann reaction

(b) Acetylation of Salicylic acid

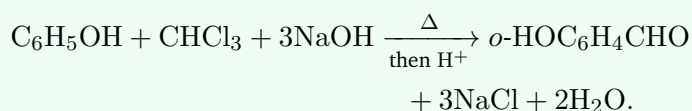
[2 marks]

Solution:

Concept:

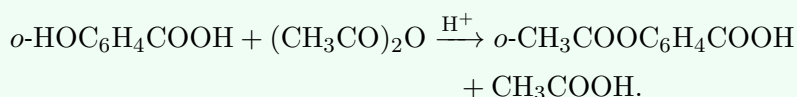
- The Reimer-Tiemann reaction introduces a $-\text{CHO}$ group mainly at the ortho position of phenol using chloroform and aqueous alkali, followed by acidification.
- Acetylation replaces the hydrogen of the phenolic hydroxyl group by CH_3CO ; the carboxyl group of salicylic acid remains unchanged.

Step 1: (a) Reimer-Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide, and the mixture is then acidified. The net equation after work-up is:



The major organic product is 2-hydroxybenzaldehyde (salicylaldehyde). The ortho prefix specifies that the hydroxyl and aldehyde groups are on adjacent ring carbons.

Step 2: (b) Acetylation of salicylic acid Treat salicylic acid with acetic anhydride in the presence of an acid catalyst:



The product is acetylsalicylic acid (aspirin). Its phenolic oxygen forms the acetate ester, whereas the $-\text{COOH}$ group is retained.

Step 3: Conclusion Reimer-Tiemann reaction gives salicylaldehyde as the major product; acetylation

Quick Tip to Solve: Keep the ortho positions explicit: Reimer-Tiemann adds CHO beside OH; aspirin formation acetylates the phenolic OH and leaves COOH intact.

of salicylic acid gives acetylsalicylic acid (aspirin).

Quick Tip to Solve: Keep the ortho positions explicit: Reimer–Tiemann adds CHO beside OH; aspirin formation acetylates the phenolic OH and leaves COOH intact.

22. (a) The conversion of molecule A to B follows second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B?

(b) Define Pseudo first order reaction with an example.

[2 marks]

Solution:

Concept:

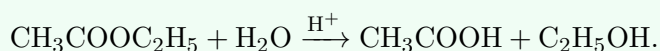
- For a second-order conversion involving only reactant A, the rate law is $r = k[A]^2$, where k is the rate constant at a fixed temperature.
- A pseudo first-order reaction has a higher actual order but follows apparent first-order kinetics because one reactant is present in large excess and its concentration remains nearly constant.

Step 1: (a) Compare the initial and final rates Let the original concentration of A be a . Then $r_1 = ka^2$. On making the concentration three times its original value, while keeping temperature unchanged,

$$r_2 = k(3a)^2 = 9ka^2, \quad \frac{r_2}{r_1} = 9.$$

Because the conversion is A to B, the rate of formation of B follows this same rate law.

Step 2: (b) Explain pseudo first-order behaviour with an example Consider hydrolysis of ethyl acetate in excess water, with acid catalyst concentration kept fixed:



The rate expression can be written as $r = k[\text{ester}][\text{H}_2\text{O}]$. Since water is in large excess, its concentration changes negligibly. Combining the constant factors gives

$$k' = k[\text{H}_2\text{O}], \quad r = k'[\text{ester}].$$

Thus the observed reaction is first order with respect to ester, even though the underlying expression involves both ester and water.

Step 3: Conclusion (a) The rate of formation of B becomes nine times the original rate. (b) Hydrolysis of ethyl acetate in excess water is a pseudo first-order reaction.

Quick Tip to Solve: Raise the concentration multiplier to the reaction order: for second order, tripling concentration multiplies the rate by 3 squared, not by 3.

23. The vapour pressure of pure liquid X and pure liquid Y at 25°C are 120 mm Hg and 160 mm Hg respectively. If equal moles of X and Y are mixed to form an ideal solution, calculate the vapour pressure of the solution. [2 marks]

Solution:

Concept:

- For an ideal binary solution, Raoult's law gives $p_X = x_X p_X^\circ$ and $p_Y = x_Y p_Y^\circ$, where x denotes the liquid mole fraction and p° denotes the pure-liquid vapour pressure.
- The total vapour pressure is the sum of the two partial pressures: $P = p_X + p_Y$, with $x_X + x_Y = 1$.

Step 1: Find the mole fractions The solution contains equal moles of X and Y. If each contributes n moles, the total is $2n$, so

$$x_X = \frac{n}{2n} = \frac{1}{2}, \quad x_Y = \frac{n}{2n} = \frac{1}{2}.$$

Equal moles, rather than equal masses or volumes, therefore give equal mole fractions.

Step 2: Calculate both partial pressures and add At the stated temperature, $p_X^\circ = 120$ mm Hg and $p_Y^\circ = 160$ mm Hg. Applying Raoult's law,

$$\begin{aligned} p_X &= \frac{1}{2}(120) = 60 \text{ mm Hg}, \\ p_Y &= \frac{1}{2}(160) = 80 \text{ mm Hg}, \\ P &= 60 + 80 = 140 \text{ mm Hg}. \end{aligned}$$

Both components are volatile, so both partial pressures must be included. The result lies between the pure-liquid vapour pressures, as expected for an ideal solution.

Step 3: Conclusion The vapour pressure of the ideal solution at 25°C is 140 mm Hg.

Quick Tip to Solve: For equal moles of two volatile liquids in an ideal solution, the total vapour pressure is the arithmetic mean of their pure-liquid vapour pressures.

24(a). Give reasons:

- Mercury cell delivers a constant potential during its lifetime.
- In the experimental determination of electrolytic conductance, Direct Current (DC) is not used.

[2 marks]

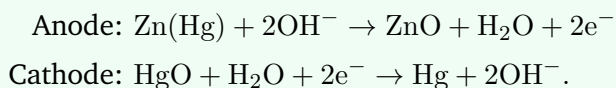
Solution:

Concept:

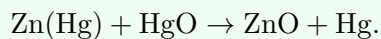
- Electrode potential depends on the reaction quotient through the Nernst equation, $E = E^\circ - (RT/nF) \ln Q$, where Q describes the activities of reacting species.
- A conductance measurement should measure ionic conduction without changing the solution or polarising the electrodes.

Quick Tip to Solve: Add the mercury-cell half-reactions first: cancellation of OH^- reveals why the electrolyte concentration stays constant.

Step 1: (i) Examine the overall mercury-cell reaction The two half-reactions are



Adding them gives



The hydroxide ions cancel: the net reaction does not involve an electrolyte ion whose concentration changes as the cell operates. The activities of the solid phases remain effectively constant, so the reaction quotient, and therefore the cell potential, stays essentially constant during its useful lifetime.

Step 2: (ii) Explain the difficulty with direct current Direct current causes electrolysis and sustained accumulation or discharge of ions at the electrodes. This changes the local ion concentration and can produce gas films, leading to electrode polarisation and an opposing potential. The measured resistance would then include these effects instead of representing only the electrolyte's resistance. Alternating current is used because rapid reversal of the current minimises net electrolysis and polarisation.

Step 3: Conclusion (i) The mercury cell has a nearly constant reaction quotient because its net reaction does not change electrolyte-ion concentrations. (ii) DC is avoided because electrolysis and electrode polarisation distort conductance measurements; AC minimises these effects.

Quick Tip to Solve: Add the mercury-cell half-reactions first: cancellation of OH^- reveals why the electrolyte concentration stays constant.

OR

24(b). Define fuel cell with an example. What advantages do the fuel cells have over primary and secondary batteries?

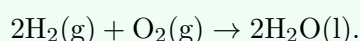
[2 marks]

Solution:

Concept:

- A galvanic cell converts the chemical energy of a spontaneous oxidation-reduction reaction directly into electrical energy.
- Fuel cells receive reactants continuously from an external supply, whereas ordinary batteries contain a finite store of their active materials.

Step 1: Define a fuel cell and give an example A fuel cell is a galvanic cell in which the chemical energy of a fuel's combustion is converted directly into electrical energy, with fuel and oxidant continuously supplied to the electrodes. An example is the hydrogen-oxygen fuel cell. Hydrogen is oxidised and oxygen is reduced; their overall reaction is



Thus the reaction provides electric current while water is produced, rather than first producing heat

Quick Tip to Solve: Compare the source of reactants: batteries store them internally, while a fuel cell keeps receiving them from outside.

to drive a mechanical generator.

Step 2: Compare its operation with ordinary batteries A fuel cell can operate continuously as long as fuel and oxidant are supplied and products are removed. Unlike a primary battery, it is not discarded merely because its initially stored reactants are exhausted. Unlike a secondary battery, it does not need to stop operation for electrical recharging; replenishing the reactant supply sustains its operation. Fuel cells also offer high energy-conversion efficiency. The hydrogen-oxygen cell is particularly clean at the point of use because its reaction product is water, avoiding polluting combustion exhaust.

Step 3: Conclusion A fuel cell continuously converts supplied fuel and oxidant into electrical energy; the hydrogen-oxygen cell is an example. Its advantages include continuous operation without periodic electrical recharging, high conversion efficiency, and clean water production in the hydrogen-oxygen cell.

Quick Tip to Solve: Compare the source of reactants: batteries store them internally, while a fuel cell keeps receiving them from outside.

25(a). Write the IUPAC names of the following:

(i) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

(ii) $\text{K}_2[\text{NiCl}_4]$

[2 marks]

Solution:

Concept:

- Name ligands alphabetically, using prefixes such as penta- and tetra- for their numbers. Ammine denotes NH_3 , and chlorido denotes Cl^- .
- The metal oxidation state follows from the complex charge and ligand charges. An anionic complex uses a metal name ending in -ate.

Step 1: (i) Identify the ligands and cobalt oxidation state In $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$, the five ammine ligands are neutral and the O-bonded nitrite ligand, ONO^- , has charge -1 . If cobalt has oxidation state x , then $x + 5(0) - 1 = +2$, so $x = +3$. The O-bonded ligand is named nitrito-O, distinguishing it from N-bonded nitrite. Ammine precedes nitrito alphabetically; five ammines require the prefix penta-. Since the complex is cationic, the metal retains the name cobalt. Its name is therefore pentaammine(nitrito-O)cobalt(III) ion.

Step 2: (ii) Name the cation and the complex anion In $\text{K}_2[\text{NiCl}_4]$, two K^+ ions balance a complex ion of charge -2 . Each chlorido ligand has charge -1 ; thus $x + 4(-1) = -2$, giving nickel oxidation state $+2$. Four chlorido ligands are named tetrachlorido. Because the coordination entity is an anion, nickel becomes nickellate. Name the potassium cation first, followed by the anion: potassium tetrachloridonickelate(II).

Step 3: Conclusion (i) Pentaammine(nitrito-O)cobalt(III) ion.

(ii) Potassium tetrachloridonickelate(II).

Quick Tip to Solve: Read ONO from its first atom: oxygen is the donor, so specify nitrito-O before naming the metal.

25(b). (i) What is a chelate complex? Give one example.

(ii) What are heteroleptic complexes? Give one example.

[2 marks]

Solution:

Concept:

- A ligand donates an electron pair to a central metal ion. A polydentate ligand can coordinate through two or more donor atoms.
- Chelation describes ring formation by a ligand, whereas heteroleptic describes the presence of different types of ligands in one complex.

Step 1: (i) Define and illustrate a chelate complex A chelate complex is a coordination complex in which a bidentate or polydentate ligand attaches to the same central metal ion through two or more donor atoms, forming one or more rings that include the metal. For example, $[\text{Co}(\text{en})_3]^{3+}$ is a chelate complex, where en denotes ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$. Each en ligand binds through both nitrogen atoms, forming a five-membered ring with cobalt. Thus the example satisfies the ring-forming requirement, rather than merely containing several separate monodentate ligands.

Step 2: (ii) Define and illustrate a heteroleptic complex A heteroleptic complex is a coordination complex in which the central metal is bonded to more than one type of ligand. An example is $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, containing neutral ammine ligands and negatively charged chlorido ligands around the same cobalt ion. There are two ligand types even though there are six coordinated ligands in total. By contrast, a complex containing only one ligand type is homoleptic; the number of ligands alone does not determine this classification.

Step 3: Conclusion (i) Chelate complexes contain metal-ligand rings formed by multidentate ligands; an example is $[\text{Co}(\text{en})_3]^{3+}$.

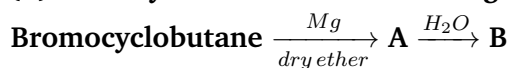
(ii) Heteroleptic complexes contain more than one ligand type; an example is $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

Quick Tip to Solve: For chelation check that one ligand binds through multiple donor atoms; for heteroleptic character count distinct ligand types.

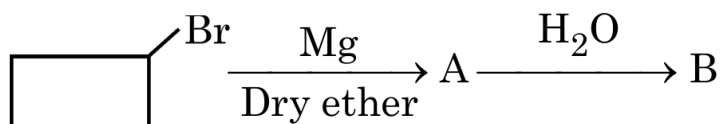
Section C (15 marks)

26. Answer any 3 of the following:

- (a) Which isomer of C_5H_{10} gives a single monochloro compound C_5H_9Cl in bright sunlight?
- (b) Arrange the following compounds in increasing order of reactivity towards S_N2 reaction:
2-Bromopentane, 1-Bromopentane, 2-Bromo-2-methylbutane
- (c) Why *p*-dichlorobenzene has higher melting point than those of ortho- and meta-isomers?
- (d) Identify A and B in the following:



[3 marks]



Solution:

Concept:

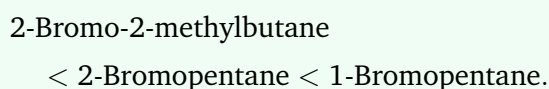
- Free-radical chlorination in sunlight replaces a hydrogen atom by chlorine. Equivalent hydrogen positions give the same constitutional monochloro product.
- An S_N2 reaction requires backside attack at the carbon bearing the leaving group; steric hindrance decreases its rate.
- Molecular symmetry favours efficient crystal packing. A Grignard reagent $RMgBr$ gives RH on reaction with water.

Step 1: (a) Identify the symmetric cyclic isomer Cyclopentane, C_5H_{10} , has equivalent ring-carbon positions. Replacing one hydrogen at any of these positions therefore gives the same constitutional product, chlorocyclopentane:



An alkene of this molecular formula would not provide the required simple substitution pattern. The ring symmetry of cyclopentane is the key to obtaining a single monochloro compound.

Step 2: (b) Compare steric hindrance for backside attack The carbon bearing bromine is tertiary in 2-bromo-2-methylbutane, secondary in 2-bromopentane and primary in 1-bromopentane. Since the entering nucleophile must approach this carbon from the side opposite bromine, branching obstructs the approach. Thus the increasing order is

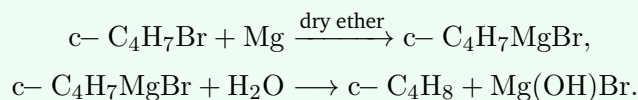


Step 3: (c) Explain the higher melting point of the para isomer *p*-Dichlorobenzene is more symmetrical than the ortho and meta isomers. Its molecules pack more efficiently in the crystal lattice, giving stronger overall intermolecular cohesion in the solid. More thermal energy is required to disrupt this

Quick Tip to Solve: For an S_N2 order, classify the carbon attached to bromine first; for Grignard hydrolysis, replace the $MgBr$ group by hydrogen without changing the carbon skeleton.

lattice, so its melting point is higher. This explanation concerns packing in the solid, rather than an increase in molecular mass, which is identical for all three isomers.

Step 4: (d) Identify the Grignard reagent and its hydrolysis product Magnesium inserts into the carbon–bromine bond of bromocyclobutane in dry ether. Thus *A* is cyclobutylmagnesium bromide, $c-C_4H_7MgBr$. Water protonates the carbon bonded to magnesium, so *B* is cyclobutane:

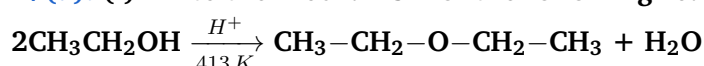


Here $c-$ denotes the cyclic carbon skeleton; the four-membered ring is retained throughout.

Step 5: Conclusion (a) Cyclopentane. (b) 2-Bromo-2-methylbutane < 2-bromopentane < 1-bromopentane. (c) Better crystal packing due to greater symmetry. (d) *A*: cyclobutylmagnesium bromide; *B*: cyclobutane. Any three parts may be attempted.

Quick Tip to Solve: For an S_N2 order, classify the carbon attached to bromine first; for Grignard hydrolysis, replace the $MgBr$ group by hydrogen without changing the carbon skeleton.

27(a). (i) Write the mechanism of the following reaction:



(ii) Why ortho-nitrophenol is steam volatile while para-nitrophenol is not?

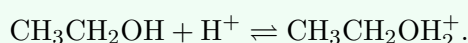
[3 marks]

Solution:

Concept:

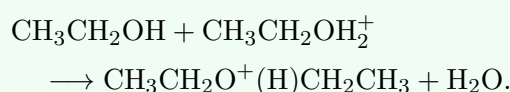
- At 413 K, acid-catalysed intermolecular dehydration of ethanol produces ethoxyethane (diethyl ether). Protonation converts the poor leaving group $-OH$ into water.
- Hydrogen bonding within one molecule reduces intermolecular association; hydrogen bonding between different molecules increases association and lowers volatility.

Step 1: (i) Protonate the oxygen of ethanol The oxygen lone pair of ethanol accepts a proton from the acid, producing protonated ethanol, an oxonium ion:



This activation is essential because water can leave much more readily than a hydroxide ion. The carbon skeleton remains unchanged, and the carbon bonded to oxygen is primary.

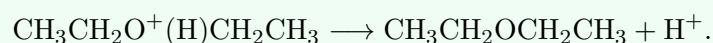
Step 2: (i) Form the carbon–oxygen bond by nucleophilic substitution A lone pair on the oxygen of a second ethanol molecule attacks the primary carbon of protonated ethanol. At the same time, the carbon–oxygen bond to OH_2^+ breaks, releasing water. This is an S_N2 step, without formation of a primary carbocation:



Quick Tip to Solve: In the ether mechanism, show water leaving from protonated ethanol; do not introduce a primary ethyl carbocation. For nitrophenols, distinguish hydrogen bonding within a molecule from bonding between molecules.

The attacking ethanol oxygen becomes the oxygen atom joining the two ethyl groups in the protonated ether.

Step 3: (i) Regenerate the acid catalyst Loss of the proton from the protonated ether produces neutral diethyl ether and regenerates the acid:



Adding these steps gives the stated overall reaction of two ethanol molecules, with one water molecule eliminated. The temperature 413 K favours ether formation for this primary alcohol.

Step 4: (ii) Compare hydrogen bonding and steam volatility In ortho-nitrophenol, the $-\text{OH}$ group and the neighbouring $-\text{NO}_2$ group are close enough for intramolecular hydrogen bonding between the phenolic hydrogen and a nitro oxygen. This reduces hydrogen bonding between separate molecules and hence reduces association. Its greater volatility allows it to distil with steam. In para-nitrophenol, the groups are too far apart for this intramolecular bond. It instead forms intermolecular hydrogen bonds and associated molecular aggregates. Stronger attraction between its molecules lowers its volatility, so it is not steam volatile under the same conditions.

Step 5: Conclusion (i) Ether formation proceeds through protonation of ethanol, attack by a second ethanol molecule with loss of water, and deprotonation. (ii) Ortho-nitrophenol is steam volatile owing to intramolecular hydrogen bonding; para-nitrophenol is less volatile owing to intermolecular association.

Quick Tip to Solve: In the ether mechanism, show water leaving from protonated ethanol; do not introduce a primary ethyl carbocation. For nitrophenols, distinguish hydrogen bonding within a molecule from bonding between molecules.

OR

27(b). What happens when:

(i) Anisole is treated with $\text{CH}_3\text{Cl}/\text{anhydrous AlCl}_3$?

(ii) Phenol is oxidised with $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$?

(iii) $(\text{CH}_3)_3\text{C}-\text{OH}$ is heated with $\text{Cu}/573\text{ K}$?

Write chemical equation in support of your answer.

[3 marks]

Solution:

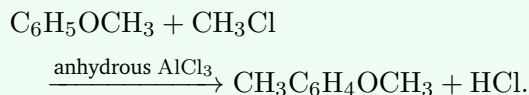
Concept:

- The methoxy group of anisole activates the benzene ring by resonance and directs electrophilic substitution mainly to the ortho and para positions.
- Acidified dichromate oxidises phenol to a quinone. Alcohols with no hydrogen on the carbon bearing $-\text{OH}$ cannot undergo ordinary dehydrogenation to a carbonyl compound.

Step 1: (i) Friedel-Crafts alkylation of anisole Anisole reacts with methyl chloride in the presence of anhydrous aluminium chloride to give a mixture of 2-methylanisole and 4-methylanisole. The para product is the major product because the para position is less sterically hindered. Aluminium chloride

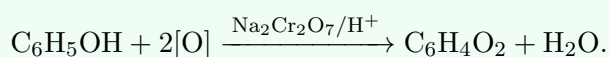
Quick Tip to Solve: Before applying the hot-copper alcohol test, check for a hydrogen on the hydroxyl-bearing carbon: a tertiary alcohol lacks it and forms an alkene by dehydration.

assists formation of the methyl electrophile, while the methoxy group directs its attack to ortho and para positions:



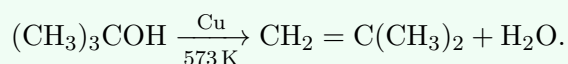
Here $\text{CH}_3\text{C}_6\text{H}_4\text{OCH}_3$ represents the ortho and para positional isomers; the methyl group occupies position 2 or position 4 relative to $-\text{OCH}_3$.

Step 2: (ii) Oxidation of phenol Acidified sodium dichromate oxidises phenol to *p*-benzoquinone, also called 1,4-benzoquinone. Its ring contains carbonyl groups at opposite positions:



In this equation, $\text{C}_6\text{H}_4\text{O}_2$ specifically denotes 1,4-benzoquinone and $[\text{O}]$ denotes oxygen supplied by the oxidising agent. The equation balances carbon, hydrogen and oxygen and shows oxidation rather than substitution on the aromatic ring.

Step 3: (iii) Heat the tertiary alcohol over copper The given alcohol, $(\text{CH}_3)_3\text{COH}$, is 2-methylpropan-2-ol, a tertiary alcohol. Its hydroxyl-bearing carbon has no hydrogen, so it cannot lose hydrogen by the usual dehydrogenation route to an aldehyde or ketone. Under the stated conditions it undergoes dehydration to 2-methylpropene:



The hydrogen removed from a neighbouring methyl group and the hydroxyl group together form water; a carbon-carbon double bond appears between that neighbouring carbon and the original hydroxyl-bearing carbon.

Step 4: Conclusion (i) Ortho- and para-methylanisole are formed, with the para isomer predominant. (ii) Phenol gives 1,4-benzoquinone. (iii) 2-Methylpropan-2-ol gives 2-methylpropene by dehydration.

Quick Tip to Solve: Before applying the hot-copper alcohol test, check for a hydrogen on the hydroxyl-bearing carbon: a tertiary alcohol lacks it and forms an alkene by dehydration.

28. (a) Draw the geometrical isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$. Which geometrical isomer of $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$ is not optically active and why?

(b) Write the hybridisation and magnetic behaviour of $[\text{CoF}_6]^{3-}$.

[Given: Atomic number of Co = 27]

[3 marks]

Solution:

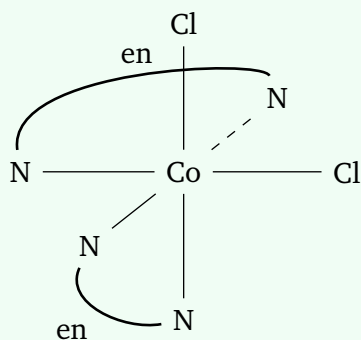
Concept:

- Ethane-1,2-diamine (en) is bidentate: its two N donors occupy adjacent octahedral positions. Two en and two chloride ligands give coordination number six.
- Geometrical isomers differ in the relative positions of ligands. In the cis form the two chlorides are adjacent, at 90° ; in the trans form they are opposite, at 180° .

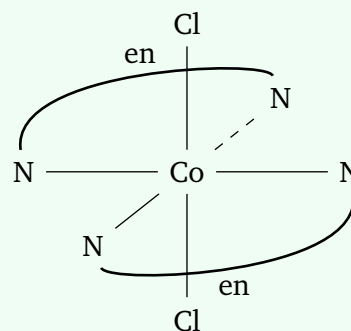
Quick Tip to Solve: Draw the two chlorides first: adjacent gives cis, opposite gives trans. For the fluoride complex, find the oxidation state before counting d electrons.

- Optical activity requires a chiral structure. In valence-bond theory, a weak-field ligand gives an outer-orbital octahedral complex; unpaired electrons produce paramagnetism.

Step 1: (a) Construct the cis and trans geometrical isomers The drawings place the six donor atoms at the octahedral vertices. In cis, the chlorides occupy adjacent positions; in trans, they occupy opposite positions. Each en arc joins two adjacent N donors belonging to one chelate ligand. Dashed bonds show positions behind the metal.



cis: $\text{Cl-Co-Cl} = 90^\circ$



trans: $\text{Cl-Co-Cl} = 180^\circ$

Octahedral cis and trans isomers; each en arc joins two nitrogen donors.

Step 2: (a) Identify the optically inactive isomer The trans isomer has a plane of symmetry through the four nitrogen donors, perpendicular to the axial Cl–Co–Cl line. Reflection interchanges the identical chlorides and preserves the equatorial chelates. Its mirror image is superimposable, so trans is optically inactive. The cis form gives a pair of non-superimposable mirror images; each member is optically active.

Step 3: (b) Determine hybridisation and magnetic behaviour For $[\text{CoF}_6]^{3-}$, let the oxidation state of Co be x . Then $x + 6(-1) = -3$, hence $x = +3$. Cobalt (atomic number 27) has configuration $[\text{Ar}]3d^74s^2$; thus Co^{3+} is $3d^6$. Fluoride is a weak-field ligand and does not force pairing of the $3d$ electrons. The high-spin octahedral distribution is $t_{2g}^4e_g^2$, with four unpaired electrons. The complex uses one $4s$, three $4p$ and two $4d$ orbitals for sp^3d^2 hybridisation and is paramagnetic.

Step 4: Conclusion (a) The geometrical isomers are cis and trans; the trans isomer is optically inactive because it has a plane of symmetry. (b) $[\text{CoF}_6]^{3-}$ has sp^3d^2 hybridisation and is paramagnetic with four unpaired electrons.

Quick Tip to Solve: Draw the two chlorides first: adjacent gives cis, opposite gives trans. For the fluoride complex, find the oxidation state before counting d electrons.

29. A first order reaction is 50% complete in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate activation energy (E_a) for the reaction. [$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

[Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$]

[3 marks]

Solution:

Concept:

- For a first-order reaction, the time for 50% completion is the half-life: $t_{1/2} = 0.693/k$, where k is the rate constant.
- The two-temperature Arrhenius equation is $\log(k_2/k_1) = \frac{E_a}{2.303R}(1/T_1 - 1/T_2)$. Here E_a is activation energy, R is the gas constant and temperatures must be in kelvin.

Step 1: Convert the completion times into rate constants Since 50% of the reactant has reacted, the given times are half-lives, not arbitrary reaction times. At $T_1 = 300 \text{ K}$ and $T_2 = 320 \text{ K}$,

$$k_1 = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}, \quad k_2 = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}.$$

Thus $k_2/k_1 = 30/10 = 3$. Both constants use the same time unit, which cancels in their ratio, so conversion of minutes to seconds is unnecessary here. The shorter half-life at the higher temperature correctly gives the larger rate constant.

Step 2: Apply the Arrhenius equation and substitute the values Rearranging the two-temperature expression gives

$$E_a = \frac{2.303R \log(k_2/k_1)}{1/T_1 - 1/T_2}.$$

Using the supplied common logarithm $\log 3 = 0.4771$,

$$\begin{aligned} E_a &= \frac{2.303(8.314)(0.4771)}{1/300 - 1/320} \\ &= 2.303(8.314)(0.4771) \frac{300 \times 320}{20} \\ &\approx 4.385 \times 10^4 \text{ J mol}^{-1}. \end{aligned}$$

The reciprocal-temperature difference is positive because $T_2 > T_1$; together with $\log(k_2/k_1) > 0$, this gives a positive activation energy. Dividing the numerical value in joules by 1000 expresses the energy in kilojoules per mole.

Step 3: Conclusion The activation energy of the reaction is $E_a \approx 43.85 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: At 50% completion, use half-lives directly: the rate-constant ratio is the inverse time ratio, so here it is $30/10 = 3$.

30. When 19.5 g of $\text{F}-\text{CH}_2-\text{COOH}$ (Molar mass = 78 g mol^{-1}), is dissolved in 500 g of water, the depression in freezing point is observed to be 1°C . Calculate the degree of dissociation of $\text{F}-\text{CH}_2-\text{COOH}$.

[Given: K_f for water = $1.86 \text{ K kg mol}^{-1}$]

[3 marks]

Solution:

Concept:

- The freezing-point depression is $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f is the solvent's molal depression constant and m is the molality calculated from the initial amount of solute.
- For a solute that dissociates into two particles, $i = 1 + \alpha$, where α is the fraction of the initial solute that dissociates. A temperature interval of 1°C equals 1 K.

Step 1: Calculate the initial molality of fluoroacetic acid The amount of acid present is

$$n = \frac{19.5 \text{ g}}{78 \text{ g mol}^{-1}} = 0.250 \text{ mol.}$$

The mass of water, the solvent, is $500 \text{ g} = 0.500 \text{ kg}$. Therefore,

$$m = \frac{0.250}{0.500} = 0.500 \text{ mol kg}^{-1}.$$

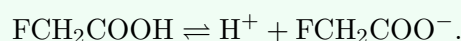
Use the solvent mass, not the total solution mass, in the denominator. This initial molality describes the acid added before allowing for the increase in particles caused by ionisation.

Step 2: Obtain the van't Hoff factor from the observed depression Without dissociation, the expected depression would be $K_fm = (1.86)(0.500) = 0.930 \text{ K}$. The actual depression is 1.00 K , which is larger because ionisation produces additional solute particles. Thus,

$$i = \frac{\Delta T_f}{K_fm} = \frac{1.00}{1.86 \times 0.500} = \frac{1.00}{0.930} = 1.07527.$$

The factor is dimensionless: the units in the observed and calculated temperature depressions cancel.

Step 3: Relate particle count to the degree of dissociation Fluoroacetic acid dissociates as



Starting with one mole of acid, dissociation of a fraction α leaves $1 - \alpha$ mole of acid and forms α mole of each ion. The total is $(1 - \alpha) + \alpha + \alpha = 1 + \alpha$ mole of particles, so $i = 1 + \alpha$. Hence $\alpha = i - 1 = 1.07527 - 1 = 0.07527$. Multiplying this fraction by 100 converts it to percentage dissociation.

Step 4: Conclusion The degree of dissociation is $\alpha \approx 0.0753$, or approximately 7.53%.

Quick Tip to Solve: Fluoroacetic acid gives two ions, so subtract 1 from the measured van't Hoff factor to obtain the dissociated fraction.

Section D (8 marks)

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

31(i). Case Study: The carbon-oxygen double bond is polarised in aldehydes and ketones due to higher electronegativity of oxygen relative to carbon. Therefore they undergo nucleophilic addition reactions with a number of nucleophiles such as HCN, NaHSO₃, alcohols, ammonia derivatives and Grignard reagents. Aldehydes are easily oxidised by mild oxidising agents as compared to ketones. The carbonyl group of carboxylic acid does not give reactions of aldehydes and ketones. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

(a) Write the name of the product when an aldehyde reacts with excess alcohol in presence of dry HCl. [1 mark]

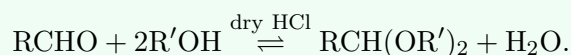
Solution:

Concept:

- An aldehyde undergoes acid-catalysed nucleophilic addition with an alcohol, giving a hemiacetal initially.
- With excess alcohol, the hemiacetal is converted into an acetal; dry HCl acts as the acid catalyst.

Step 1: Identify the initial addition product The alcohol attacks the aldehyde carbonyl group. After proton transfers, a hemiacetal is formed, with one hydroxyl group and one alkoxy group on the original carbonyl carbon: RCH(OH)(OR').

Step 2: Account for excess alcohol A second molecule of alcohol replaces the hydroxyl group under acidic conditions. The overall reaction is



Thus the carbon originally present in the carbonyl group now carries two alkoxy groups.

Step 3: Conclusion The product is an **acetal**, RCH(OR')₂.

Quick Tip to Solve: Excess alcohol with an aldehyde and dry HCl points to an acetal; one alcohol molecule gives the intermediate hemiacetal.

31(ii). (b) Why carboxylic acid is a stronger acid than phenol? [1 mark]

Solution:

Concept:

- Acid strength increases when the conjugate base formed by loss of H⁺ is more stable.
- A carboxylate ion has two equivalent resonance contributors, with the negative charge shared by two electronegative oxygen atoms.

Step 1: Compare the carboxylate ion Loss of a proton from RCOOH gives RCOO⁻. Its two equivalent resonance structures distribute the negative charge equally over the two oxygen atoms, providing

Quick Tip to Solve: Compare where the negative charge resides: two equivalent oxygen sites stabilise carboxylate better than oxygen and ring carbon sites stabilise phenoxide.

strong stabilisation of the conjugate base.

Step 2: Compare the phenoxide ion Phenol gives the phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$. Although this ion is also resonance-stabilised, its resonance contributors are not equivalent: some place negative charge on the less electronegative carbon atoms of the aromatic ring. This stabilisation is less effective than that of carboxylate.

Step 3: Conclusion Carboxylic acid is stronger than phenol because its carboxylate conjugate base is more effectively resonance-stabilised than phenoxide.

Quick Tip to Solve: Compare where the negative charge resides: two equivalent oxygen sites stabilise carboxylate better than oxygen and ring carbon sites stabilise phenoxide.

31(iii). (c) (i) Arrange the following compounds in increasing order of their reactivity towards CH_3MgBr :

CH_3CHO , $(\text{CH}_3)_3\text{C}-\text{CO}-\text{CH}_3$, $\text{CH}_3-\text{CO}-\text{CH}_3$

(ii) Write a chemical test to distinguish between propanal and propanone.

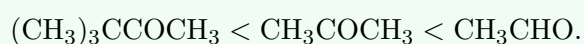
[2 marks]

Solution:

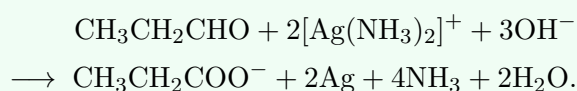
Concept:

- CH_3MgBr supplies a nucleophilic methyl group that attacks the electrophilic carbonyl carbon.
- Alkyl groups reduce carbonyl electrophilicity by their electron-releasing effect and hinder nucleophilic attack sterically.
- Tollens' reagent oxidises an aldehyde to a carboxylate ion while silver ions are reduced to metallic silver; ordinary ketones do not give this test.

Step 1: (i) Compare the carbonyl compounds Ethanal, CH_3CHO , has one alkyl group and one hydrogen attached to its carbonyl carbon, so it is least hindered and most electrophilic. Propanone has two methyl groups, so it is less reactive. In $(\text{CH}_3)_3\text{CCOCH}_3$, the bulky tert-butyl group further obstructs approach of the nucleophile. Hence increasing reactivity is



Step 2: (ii) Apply Tollens' test Warm separate samples with freshly prepared Tollens' reagent. Propanal produces a silver mirror as it is oxidised to propanoate; propanone does not produce a silver mirror. The propanal reaction is



The deposited silver provides a clear positive observation for the aldehyde.

Step 3: Conclusion (i) $(\text{CH}_3)_3\text{CCOCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO}$. (ii) Propanal gives a silver mirror with Tollens' reagent; propanone does not.

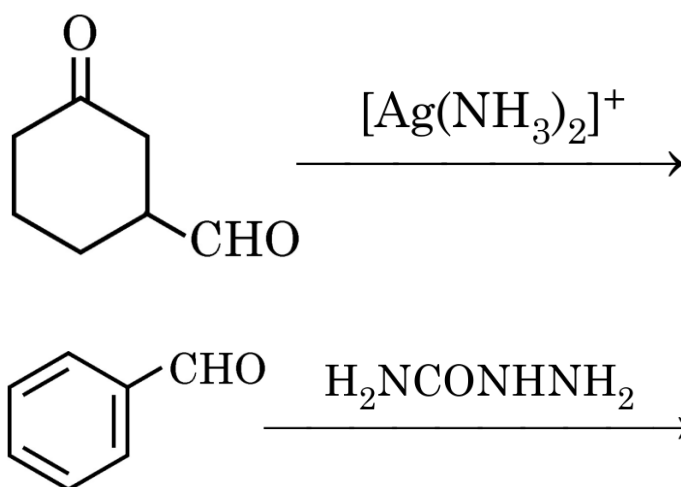
Quick Tip to Solve: For Grignard addition, compare carbonyl crowding first; for an aldehyde versus an ordinary ketone, use the silver-mirror test.

31(iii). (c) Write the main product in the following:

(i) The reaction shown in the first figure.

(ii) The reaction shown in the second figure.

[2 marks]



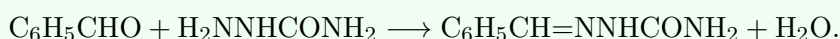
Solution:

Concept:

- Tollens' reagent selectively oxidises an aldehyde group, $-CHO$, to $-COO^-$ in its alkaline medium; a ketone carbonyl remains unchanged.
- Semicarbazide, $H_2NCONHNH_2$, reacts through its terminal $-NH_2$ group to form a semicarbazone with loss of water.

Step 1: (i) Oxidise the formyl group selectively The first substrate is a cyclohexanone ring bearing a formyl group at its third carbon relative to the ring ketone. Tollens' reagent oxidises only the side-chain $-CHO$; the ring $C=O$ is retained. The product therefore has the same six-membered ring with its ketone group and a $-COO^-$ substituent in place of $-CHO$. It is **3-oxocyclohexane-1-carboxylate** in the alkaline reaction mixture. On acidification it gives **3-oxocyclohexane-1-carboxylic acid**, with $-COOH$ at the same site. Silver metal is deposited during oxidation.

Step 2: (ii) Form the benzaldehyde semicarbazone The second substrate is benzaldehyde, C_6H_5CHO . Its carbonyl group condenses with the terminal amino group of semicarbazide. Elimination of water produces



The product is benzaldehyde semicarbazone. The nitrogen directly bonded to CO is not the attacking amino nitrogen because its lone pair participates in resonance with the carbonyl group.

Step 3: Conclusion (i) **3-Oxocyclohexane-1-carboxylate** (the corresponding $-COOH$ product after acidification), with the ring ketone intact. (ii) **Benzaldehyde semicarbazone**, $C_6H_5CH=NNHCONH_2$.

Quick Tip to Solve: In the first structure change only CHO to carboxylate; in the second replace the aldehyde oxygen by the group $NNHCONH_2$.

32(i). Case Study: Carbohydrates are optically active polyhydroxy aldehydes and ketones. They are also called saccharides. All those carbohydrates which reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars. Glucose, the most important source of energy for mammals, is obtained by the hydrolysis of starch. Vitamins are accessory food factors required in the diet. Proteins are the polymers of α -amino acids and perform various structural and dynamic functions in the organisms. Deficiency of vitamins leads to many diseases.

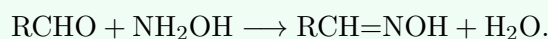
(a) The penta-acetate of glucose does not react with Hydroxylamine. What does it indicate? [1 mark]

Solution:

Concept:

- Hydroxylamine, NH_2OH , reacts with a free aldehyde or ketone carbonyl group to form an oxime.
- The penta-acetate of glucose retains a cyclic structure in which the aldehyde carbon is part of an acetal arrangement.

Step 1: Use the hydroxylamine test A free aldehyde group would undergo condensation with hydroxylamine:



Therefore the absence of this reaction means that an accessible aldehyde carbonyl group is absent.

Step 2: Interpret the glucose derivative In cyclic glucose, the aldehyde group is involved in intramolecular hemiacetal formation. Acetylation of all five hydroxyl groups, including the anomeric hydroxyl group, gives the cyclic penta-acetate. The anomeric centre is then an acetal and does not supply a free aldehyde group for oxime formation.

Step 3: Conclusion It indicates the **absence of a free aldehyde group** in glucose penta-acetate and supports the cyclic structure of glucose.

Quick Tip to Solve: Failure to form an oxime signals no free carbonyl: glucose penta-acetate has its aldehyde carbon locked in the cyclic acetal form.

32(ii). (b) Why cannot vitamin C be stored in our body?

[1 mark]

Solution:

Concept:

- Vitamin C is a water-soluble vitamin, unlike the fat-soluble vitamins A, D, E and K.
- Excess water-soluble vitamin C is eliminated from the body in urine, so it does not build up as a lasting store.

Step 1: Identify the solubility class Vitamin C, also called ascorbic acid, contains several polar hydroxyl groups and is soluble in water. It is consequently transported in the aqueous body fluids and is not stored in fatty tissues in the manner of fat-soluble vitamins.

Step 2: Relate solubility to excretion The body uses the vitamin C it needs, while excess amounts are excreted in urine. It therefore cannot maintain a substantial long-term reserve of this vitamin. A regular dietary supply is needed to replace what is used or lost and to avoid deficiency.

Quick Tip to Solve: Recall the water-soluble pair B and C: their excess is generally removed in urine, so a regular dietary supply is needed.

Step 3: Conclusion Vitamin C cannot be stored to any appreciable extent because it is **water-soluble** and excess vitamin C is **excreted in urine**.

Quick Tip to Solve: Recall the water-soluble pair B and C: their excess is generally removed in urine, so a regular dietary supply is needed.

32(iii). (c) Define the following as related to proteins:

(i) Peptide linkage

(ii) Denaturation

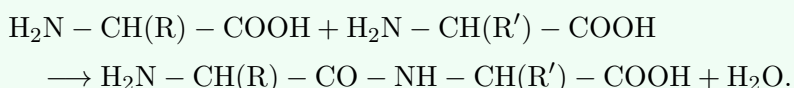
[2 marks]

Solution:

Concept:

- Proteins are polymers of α -amino acids joined by amide bonds called peptide linkages.
- A protein's biological function depends on its characteristic secondary and tertiary structures, as well as its amino-acid sequence.

Step 1: (i) Define peptide linkage A peptide linkage is the amide bond $-\text{CO} - \text{NH}-$ formed when the carboxyl group of one amino acid reacts with the amino group of another, with elimination of a water molecule. For example,



Here R and R' are the side chains of the amino acids; the newly formed $-\text{CO} - \text{NH}-$ group connects the two residues.

Step 2: (ii) Define denaturation Denaturation is the loss of a protein's native conformation and biological activity when physical or chemical conditions, such as heating or a change in pH, disrupt the interactions maintaining its folded structure. The secondary and tertiary structures are altered, while its primary structure, including the peptide bonds and amino-acid sequence, remains intact. Coagulation of egg white on heating is a familiar example.

Step 3: Conclusion Peptide linkage is the $-\text{CO} - \text{NH}-$ bond joining amino-acid residues. Denaturation destroys the native folded structure and biological activity of a protein without breaking its primary peptide chain.

Quick Tip to Solve: In denaturation, distinguish loss of folding from hydrolysis: the peptide bonds and amino-acid sequence remain unchanged.

32(iii). (c) Define the following as related to carbohydrates:

(i) Anomers

(ii) Glycosidic linkage

[2 marks]

Solution:

Concept:

- Cyclisation of a monosaccharide converts its carbonyl carbon into an anomeric carbon, whose configuration distinguishes the α and β forms.
- A glycosidic linkage is an oxygen-containing bond joining monosaccharide units through condensation with loss of water.

Step 1: (i) Define anomers Anomers are cyclic stereoisomers of a sugar that differ only in the configuration at the anomeric carbon. This carbon was the carbonyl carbon in the open-chain form: C-1 in glucose and C-2 in fructose. For example, α -D-glucose and β -D-glucose are anomers because they differ only in the orientation of the hydroxyl group attached to C-1. In the usual Haworth representation of D-glucose, the anomeric hydroxyl group lies opposite to the CH_2OH group in the α form and on the same side in the β form.

Step 2: (ii) Define glycosidic linkage A glycosidic linkage is the $\text{C} - \text{O} - \text{C}$ bond that joins two monosaccharide units through an oxygen atom, formed by condensation of hydroxyl groups with elimination of water. At least one of the participating groups is the anomeric hydroxyl group of a sugar. For example, maltose contains an $\alpha(1 \rightarrow 4)$ glycosidic linkage between C-1 of one glucose unit and C-4 of the other glucose unit. Hydrolysis of this bond releases the component monosaccharides.

Step 3: Conclusion Anomers differ only at the anomeric carbon of a cyclic sugar. A glycosidic linkage is the oxygen bridge joining monosaccharide units, as in the $\alpha(1 \rightarrow 4)$ bond of maltose.

Quick Tip to Solve: Identify the former carbonyl carbon to locate the anomeric centre; use the two connected carbon numbers to name a glycosidic linkage.

Section E (15 marks)

33(a). (I) Give reasons:

(i) Aniline on nitration gives good amount of m-nitroaniline, though $-\text{NH}_2$ group is o/p directing in electrophilic substitution reactions.

(ii) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

(iii) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

(II) Write the reaction involved in the following:

(i) Carbylamine test

(ii) Gabriel phthalimide synthesis

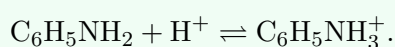
[5 marks]

Solution:

Concept:

- An amine accepts a proton through the nitrogen lone pair. Its basicity in water depends on the electron-releasing effect of alkyl groups and the hydration of its conjugate acid.
- Protonation changes the directing influence of aniline: $-\text{NH}_2$ is ortho/para directing, whereas $-\text{NH}_3^+$ is meta directing.
- Primary amines undergo the carbylamine reaction. Gabriel synthesis uses alkylation of potassium phthalimide followed by hydrolysis to prepare a primary aliphatic amine.

Step 1: (I)(i) Explain formation of meta-nitroaniline Nitration takes place in a strongly acidic mixture of concentrated nitric and sulphuric acids. Under these conditions aniline is protonated:



In the anilinium ion, nitrogen no longer has a free lone pair to donate into the benzene ring. The positively charged $-\text{NH}_3^+$ group strongly withdraws electron density and is meta directing. Nitration of this protonated species therefore gives a substantial amount of the meta product, recovered as m-nitroaniline after work-up. The unprotonated $-\text{NH}_2$ group remains ortho/para directing; its usual directing effect does not describe the protonated species.

Step 2: (I)(ii) Compare basicity in aqueous solution Alkyl groups increase electron density on nitrogen by their positive inductive effect. However, aqueous basicity also depends on how well water stabilises the protonated amine. The dimethylammonium ion, $(\text{CH}_3)_2\text{NH}_2^+$, is better hydrated than the trimethylammonium ion, $(\text{CH}_3)_3\text{NH}^+$: it has more N-H bonds available for hydrogen bonding and less steric shielding around the charged nitrogen. This greater hydration outweighs the additional electron-releasing effect of the third methyl group. Consequently, $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in water.

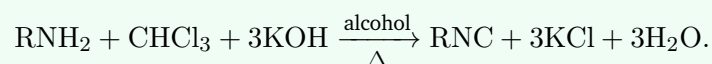
Step 3: (I)(iii) Explain the limitation of ammonolysis Ammonia initially reacts with an alkyl halide to produce a primary amine, but that amine also acts as a nucleophile and reacts further with the alkyl halide. Successive alkylation therefore occurs:



Quick Tip to Solve: For basicity in water compare the hydrated conjugate acids; for nitration first check whether the amino group has been protonated.

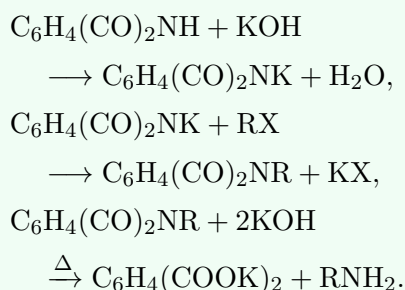
Here R denotes an alkyl group and X a halogen. The product is a mixture of primary, secondary and tertiary amines together with a quaternary ammonium salt, which is difficult to separate. Excess ammonia favours the primary amine but does not make ammonolysis a reliable method for preparing it pure.

Step 4: (II)(i) Write the carbylamine-test reaction A primary amine is heated with chloroform and alcoholic potassium hydroxide to give an isocyanide, which has an offensive smell:



Both aliphatic and aromatic primary amines give this test; secondary and tertiary amines do not. The product $R - N \equiv C$ is an isocyanide, with the organic group bonded to nitrogen.

Step 5: (II)(ii) Write Gabriel phthalimide synthesis Phthalimide is treated with alcoholic KOH to form potassium phthalimide. This salt reacts with a suitable alkyl halide, RX , to give N-alkylphthalimide. Subsequent alkaline hydrolysis liberates the primary amine:

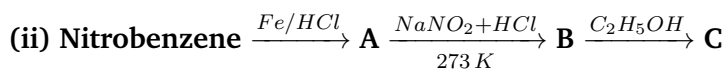
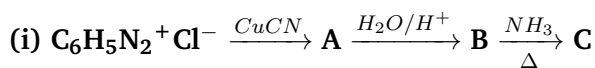


In this notation the two adjacent carbonyl groups of phthalimide share the imide nitrogen; hydrolysis opens the ring to form dipotassium phthalate. Gabriel synthesis gives a primary aliphatic amine without successive alkylation. Aryl halides do not undergo the required nucleophilic substitution, so this route does not prepare aromatic primary amines.

Step 6: Conclusion Acidic nitration protonates aniline to a meta-directing anilinium ion; stronger hydration makes dimethylamine more basic than trimethylamine in water; repeated alkylation makes ammonolysis give a mixture. The carbylamine test converts a primary amine to an isocyanide, while Gabriel synthesis releases a primary aliphatic amine by hydrolysis of N-alkylphthalimide.

Quick Tip to Solve: For basicity in water compare the hydrated conjugate acids; for nitration first check whether the amino group has been protonated.

33(b). (I) Write the structures of A, B and C in the following reactions:

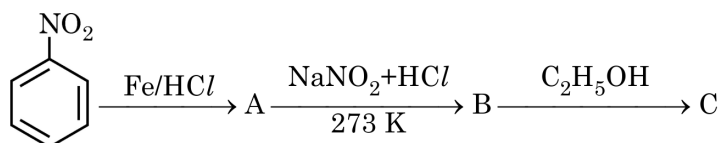
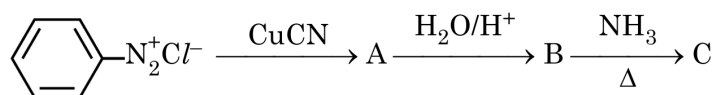


(II) Why aniline does not undergo Friedel-Crafts reaction?

(III) Arrange the following in increasing order of their boiling point:



[5 marks]

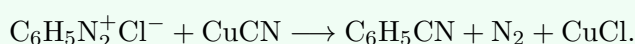


Solution:

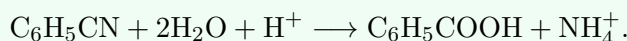
Concept:

- In a Sandmeyer reaction, the diazonium group is replaced by cyanide using CuCN; acidic hydrolysis converts a nitrile into a carboxylic acid.
- A carboxylic acid forms an ammonium carboxylate with ammonia. Heating this salt eliminates water to form an amide.
- Reduction converts an aromatic nitro group into an amino group; diazotisation with NaNO₂/HCl at 273 K forms a diazonium salt. Ethanol replaces its diazonium group by hydrogen.
- Boiling point depends on intermolecular hydrogen bonding as well as molecular size and dispersion forces. The amino lone pair also reacts with the Lewis acid catalyst AlCl₃.

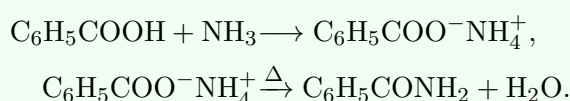
Step 1: (I)(i) Identify the nitrile, acid and amide Copper(I) cyanide replaces the diazonium group, with liberation of nitrogen:



Hence A is benzonitrile, $\text{C}_6\text{H}_5-\text{C} \equiv \text{N}$. Acidic hydrolysis of its nitrile group gives B, benzoic acid, $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{OH}$:



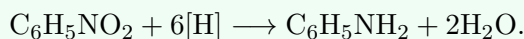
Benzoic acid first reacts with ammonia to form ammonium benzoate. On heating, this salt loses water:



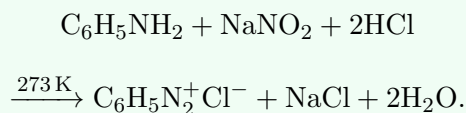
Thus C is benzamide, with structure $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}_2$. The carbon atom introduced by cyanide remains the carbonyl carbon in B and C.

Quick Tip to Solve: Track the extra carbon added by CN in sequence (i); for boiling points, compare molecular size as well as the ability to form hydrogen bonds.

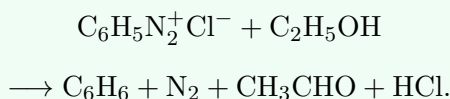
Step 2: (I)(ii) Follow reduction, diazotisation and deamination Iron and hydrochloric acid reduce nitrobenzene to aniline (obtained as the free amine after work-up):



Therefore A is aniline, $\text{C}_6\text{H}_5-\text{NH}_2$. Sodium nitrite and hydrochloric acid generate nitrous acid, which diazotises aniline at the stated low temperature:



B is benzenediazonium chloride, $\text{C}_6\text{H}_5-\text{N} \equiv \text{N}^+\text{Cl}^-$. Ethanol reduces the diazonium salt to benzene and is itself oxidised to ethanal:



C is benzene, C_6H_6 , an aromatic six-membered carbon ring bearing one hydrogen on every carbon.

Step 3: (II) Explain the failure of the Friedel–Crafts reaction Aniline's nitrogen lone pair binds strongly to the Lewis acid catalyst AlCl_3 , forming a salt or coordination complex. The nitrogen consequently becomes electron deficient and can no longer donate its lone pair into the benzene ring. This strongly deactivates the ring toward electrophilic substitution and also ties up the catalyst. Hence aniline does not undergo the usual Friedel–Crafts alkylation or acylation.

Step 4: (III) Compare the boiling points Ethylamine has intermolecular N–H hydrogen bonding, but this is weaker than the O–H hydrogen bonding in ethanol because oxygen is more electronegative than nitrogen. Their molecular masses are similar, so ethanol boils at a higher temperature than ethylamine. Triethylamine has no N–H bond and cannot hydrogen bond with itself. However, its substantially greater molecular mass and larger electron cloud produce stronger dispersion forces, making its boiling point higher than that of ethanol. Thus the absence of self hydrogen bonding alone cannot determine the order when molecular sizes differ greatly.

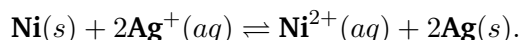
Step 5: Conclusion (I)(i) A: $\text{C}_6\text{H}_5-\text{C} \equiv \text{N}$, B: $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{OH}$, C: $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}_2$. (I)(ii) A: $\text{C}_6\text{H}_5\text{NH}_2$, B: $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, C: benzene, C_6H_6 . (II) Aniline complexes with AlCl_3 , deactivating its ring. (III) Increasing boiling point:



Quick Tip to Solve: Track the extra carbon added by CN in sequence (i); for boiling points, compare molecular size as well as the ability to form hydrogen bonds.

34. (a) Conductivity of $2 \times 10^{-3} \text{ M}$ methanoic acid is $8 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation if Λ_m° for methanoic acid is $404 \text{ S cm}^2 \text{ mol}^{-1}$.

(b) Calculate $\Delta_r G^\circ$ and $\log K_c$ for the given reaction at 298 K :



Given: $E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}$, $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$; $1 \text{ F} = 96500 \text{ C mol}^{-1}$.

[5 marks]

Solution:

Concept:

- Molar conductivity is the conductivity of the volume of solution containing one mole of electrolyte: $\Lambda_m = 1000\kappa/c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} .
- For a weak electrolyte such as methanoic acid, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m° is its molar conductivity at infinite dilution.
- The standard cell potential is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using reduction potentials for both electrodes. Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$, with n the number of electrons transferred and F the Faraday constant.
- The equilibrium relation $\Delta_r G^\circ = -RT \ln K_c$ gives $\log K_c = nFE_{\text{cell}}^\circ/(2.303RT)$. Here $\log$ is base ten, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and T is the absolute temperature.

Step 1: (a) Calculate the molar conductivity The given solution has $\kappa = 8 \times 10^{-5} \text{ S cm}^{-1}$ and $c = 2 \times 10^{-3} \text{ mol L}^{-1}$. The factor of 1000 converts the concentration basis from litres to cubic centimetres. Therefore,

$$\Lambda_m = \frac{1000(8 \times 10^{-5})}{2 \times 10^{-3}} = 40 \text{ S cm}^2 \text{ mol}^{-1}.$$

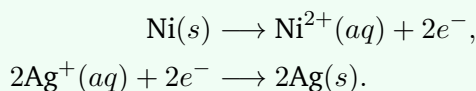
This is smaller than the limiting molar conductivity, as expected for a weak acid that is only partly ionised at this concentration.

Step 2: (a) Calculate the degree of dissociation Methanoic acid dissociates as $\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$. At infinite dilution its dissociation is effectively complete. The ratio of the observed molar conductivity to the limiting value measures the fraction dissociated:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{40}{404} = 0.0990.$$

The degree of dissociation is dimensionless. Expressed as a percentage, it is $100\alpha = 9.90\%$; approximately one tenth of the acid molecules are dissociated.

Step 3: (b) Identify the electrodes and the electron transfer Nickel is oxidised at the anode, while silver ions are reduced at the cathode:



Thus the balanced reaction transfers $n = 2$ electrons. Both supplied electrode potentials are reduction potentials, so

$$E_{\text{cell}}^\circ = 0.80 - (-0.25) = 1.05 \text{ V}.$$

Quick Tip to Solve: Use the factor 1000 in the molar-conductivity formula for concentration in mol per litre. For the cell, count two transferred electrons and subtract the negative nickel reduction potential.

Multiplying a half-reaction by two balances electrons; it does not multiply its electrode potential.

Step 4: (b) Calculate the standard Gibbs energy change Substitution into the electrochemical relation gives

$$\begin{aligned}\Delta_r G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -2(96500)(1.05) \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1}.\end{aligned}$$

The energy is per mole of the reaction as written. Its negative sign agrees with the positive standard cell potential and indicates that the forward reaction is thermodynamically favourable under standard conditions.

Step 5: (b) Calculate the logarithm of the equilibrium constant Use $T = 298 \text{ K}$, retaining the energy in joules to match the units of R :

$$\begin{aligned}\log K_c &= \frac{-\Delta_r G^\circ}{2.303RT} \\ &= \frac{202650}{2.303(8.314)(298)} \\ &\simeq 35.5.\end{aligned}$$

Pure solid nickel and silver have unit activity and do not appear in the equilibrium expression. The very large positive logarithm means that the equilibrium strongly favours the products, consistent with the sign of $\Delta_r G^\circ$.

Step 6: Conclusion (a) $\Lambda_m = 40 \text{ S cm}^2 \text{ mol}^{-1}$ and $\alpha = 0.0990$, or 9.90%. (b) $\Delta_r G^\circ = -202.65 \text{ kJ mol}^{-1}$ and $\log K_c \simeq 35.5$.

Quick Tip to Solve: Use the factor 1000 in the molar-conductivity formula for concentration in mol per litre. For the cell, count two transferred electrons and subtract the negative nickel reduction potential.

35(a). (I) Account for the following:

(i) E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$.

(ii) Sc^{3+} is colourless whereas Ti^{3+} is coloured in an aqueous solution.

(iii) Actinoids show wide range of oxidation states.

(II) Write the chemical equations for the preparation of KMnO_4 from MnO_2 .

[5 marks]

Solution:

Concept:

- A more positive standard reduction potential, E° , indicates a greater tendency of the oxidised ion to accept an electron. The relative stability of the electronic configurations of both ions helps explain the trend.
- In an aqueous transition-metal ion, the ligand field splits the d orbitals. Absorption of visible light for a $d-d$ transition can produce colour when a d electron is present.

Quick Tip to Solve: Write the ion configurations before explaining colour or reduction potentials; for permanganate preparation track manganese as $+4 \rightarrow +6 \rightarrow +7$.

- Actinoids can use electrons from the $5f$, $6d$ and $7s$ subshells in bonding because their energies are comparable. Potassium permanganate is prepared by oxidising manganese from +4 to +6, then from +6 to +7.

Step 1: (I)(i) Compare the stability of the manganese and chromium ions The reductions under consideration are

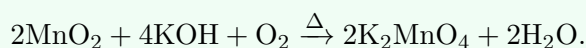


Mn^{3+} has the configuration $[\text{Ar}] 3d^4$, whereas Mn^{2+} has the particularly stable half-filled configuration $[\text{Ar}] 3d^5$. Reduction to Mn^{2+} is therefore strongly favoured. By contrast, Cr^{3+} has the stable $[\text{Ar}] 3d^3$ configuration; in an octahedral aqueous complex its three electrons occupy the lower-energy t_{2g} orbitals. Reduction gives Cr^{2+} , with $[\text{Ar}] 3d^4$, and loses this relative stability. Thus reduction of Cr^{3+} is less favourable, so the E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is much more positive.

Step 2: (I)(ii) Explain the colours of the aqueous ions Scandium has the configuration $[\text{Ar}] 3d^1 4s^2$, so Sc^{3+} is $[\text{Ar}] 3d^0$. With no d electron, it cannot undergo a $d-d$ transition and its aqueous solution is colourless. Titanium has the configuration $[\text{Ar}] 3d^2 4s^2$, so Ti^{3+} is $[\text{Ar}] 3d^1$. In its aqueous complex, the electron can absorb visible light and move from a lower-energy to a higher-energy split d orbital. The remaining transmitted light gives the solution its colour.

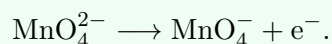
Step 3: (I)(iii) Explain the range of actinoid oxidation states The $5f$, $6d$ and $7s$ subshells of actinoids have similar energies. Consequently, varying numbers of electrons from these subshells can participate in bond formation, producing a wide range of oxidation states. The $5f$ electrons are less deeply buried than the $4f$ electrons of lanthanoids and can participate more readily in bonding, especially in the early actinoids.

Step 4: (II) Prepare potassium manganate from manganese dioxide Fuse MnO_2 with potassium hydroxide in the presence of air or oxygen. Manganese is oxidised from +4 to +6, forming green potassium manganate:

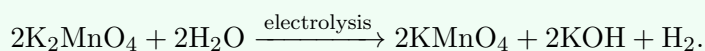


The equation conserves manganese, potassium, hydrogen and oxygen atoms.

Step 5: (II) Oxidise manganate to potassium permanganate The manganate solution is then electrolytically oxidised to permanganate. At the anode, manganese changes from +6 to +7:



Including the cathodic liberation of hydrogen, the overall preparation equation is



Thus the green manganate is converted into purple potassium permanganate.

Step 6: Conclusion Mn^{2+} is stabilised by its half-filled $3d^5$ configuration, while Cr^{3+} is relatively stable as $3d^3$, explaining the reduction-potential difference. Sc^{3+} is d^0 and colourless; Ti^{3+} is d^1 and coloured. Comparable $5f$, $6d$ and $7s$ energies give actinoids variable oxidation states. Preparation follows $\text{MnO}_2 \longrightarrow \text{K}_2\text{MnO}_4 \longrightarrow \text{KMnO}_4$ using alkaline fusion followed by electrolytic oxidation.

Quick Tip to Solve: Write the ion configurations before explaining colour or reduction potentials; for permanganate preparation track manganese as $+4 \rightarrow +6 \rightarrow +7$.

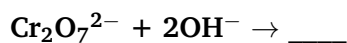
35(b). (I) Account for the following:

(i) Transition metals form alloys.

(ii) Ce^{4+} is a strong oxidising agent.

(II) Write one similarity and one difference between chemistry of Lanthanoids and Actinoids.

(III) Complete the following ionic equation:



[5 marks]

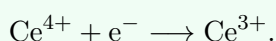
Solution:

Concept:

- Alloy formation is favoured when constituent metals have comparable atomic sizes and compatible crystal structures, permitting substitution in a metallic lattice.
- An oxidising agent accepts electrons and is itself reduced. The stability of the reduced oxidation state helps explain the oxidising power of a metal ion.
- Lanthanoids and actinoids involve filling the $4f$ and $5f$ subshells respectively; both commonly show the +3 oxidation state.
- The chromate–dichromate equilibrium depends on acidity: adding hydroxide favours chromate ions, CrO_4^{2-} .

Step 1: (I)(i) Explain alloy formation Transition metals have similar atomic radii, and many have similar metallic crystal structures. An atom of one transition metal can therefore replace an atom of another in its lattice without greatly disturbing that lattice. The resulting solid mixture retains metallic bonding and is an alloy. For example, chromium and nickel form alloys with iron. Comparable atomic sizes, rather than identical oxidation states, are the principal reason for this ready substitution.

Step 2: (I)(ii) Explain the oxidising power of cerium(IV) Cerium shows both the +3 and +4 oxidation states, but +3 is the characteristic stable oxidation state of lanthanoids. Thus Ce^{4+} readily accepts an electron and is reduced to Ce^{3+} :



The standard reduction potential for the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple is highly positive, about +1.74 V. Consequently, Ce^{4+} can accept electrons from other substances and oxidise them; it is a strong oxidising agent.

Step 3: (II) Compare lanthanoids and actinoids Similarity: Both series commonly exhibit the +3 oxidation state in their compounds. In each series, increasing nuclear charge with poor shielding by the added f electrons also produces a progressive decrease in ionic size, called lanthanoid or actinoid contraction.

Difference: Actinoids exhibit a much wider range of oxidation states than lanthanoids. The $5f$, $6d$ and $7s$ orbitals of actinoids are close enough in energy that differing numbers of electrons can participate in bonding. Lanthanoids predominantly show +3, with only a few exceptions such as Ce^{4+} and Eu^{2+} .

Step 4: (III) Complete and check the ionic equation Hydroxide converts orange dichromate ions into yellow chromate ions by shifting the equilibrium towards the alkaline form. Each dichromate ion

Quick Tip to Solve: In alkaline medium, write two chromate ions for one dichromate ion, then add water and check that the total charge is equal on both sides.

contains two chromium atoms, so it produces two chromate ions:



There are two chromium atoms, nine oxygen atoms and two hydrogen atoms on each side. The total charge is -4 on each side. Chromium remains in the $+6$ oxidation state, so this is an acid–base equilibrium conversion, not a redox reaction.

Step 5: Conclusion Transition metals form alloys because their similar atomic sizes allow substitution in metallic lattices. Ce^{4+} is strongly oxidising because it readily reduces to Ce^{3+} . Both lanthanoids and actinoids commonly show $+3$, but actinoids show more oxidation states. The required products are $2\text{CrO}_4^{2-} + \text{H}_2\text{O}$.

Quick Tip to Solve: In alkaline medium, write two chromate ions for one dichromate ion, then add water and check that the total charge is equal on both sides.