

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-2-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This Question Paper contains **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. The conversion of an alkyl halide into an alkene by alcoholic KOH is classified as [1 mark]

- (A) a substitution reaction
- (B) an addition reaction
- (C) a dehydrohalogenation reaction
- (D) a dehydration reaction

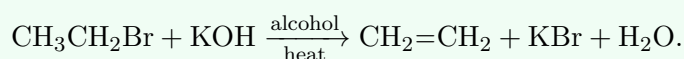
Correct Answer: (C) a dehydrohalogenation reaction

Solution:

Concept:

- Alcoholic KOH promotes elimination of a hydrogen atom and a halogen atom from adjacent carbon atoms of an alkyl halide.
- Removal of the elements of a hydrogen halide, HX, is called dehydrohalogenation; it creates a carbon-carbon double bond.

Step 1: Identify what leaves the substrate The base removes a hydrogen from a carbon adjacent to the carbon carrying the halogen. Loss of the halide forms an alkene. For example,



The net change in the organic molecule is loss of the elements of HBr.

Step 2: Compare the reaction classes Substitution replaces the halogen with another group without producing this double bond. Addition consumes a multiple bond, whereas the reaction here forms one. Dehydration removes the elements of water from an organic substrate, commonly an alcohol; here the substrate loses hydrogen and halogen.

Step 3: Conclusion The conversion is a dehydrohalogenation reaction. Hence, the correct option is (C).

Quick Tip to Solve: Look at the atoms lost by the organic substrate: loss of H and X means dehydrohalogenation, even if water is also a reaction product.

2. The oxidation state of Fe in $[\text{Fe}(\text{CO})_5]$ is

[1 mark]

- (A) +2
- (B) 0
- (C) +3
- (D) +5

Correct Answer: (B) 0

Solution:

Concept:

- The sum of the metal oxidation state and all ligand charges equals the overall charge of the coordination entity.
- Carbon monoxide, CO, is a neutral ligand; each of the five carbonyl ligands contributes zero charge.

Step 1: Write the charge balance Let the oxidation state of iron be x . The complex $[\text{Fe}(\text{CO})_5]$ has no charge written outside its brackets and is therefore neutral. The charge balance is

$$x + 5(0) = 0.$$

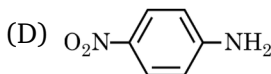
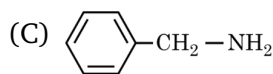
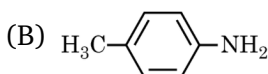
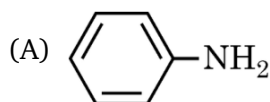
Step 2: Distinguish oxidation state from ligand count The equation gives $x = 0$. The five ligands do not imply an oxidation state of +5, since each ligand is neutral. The familiar iron oxidation states +2 and +3 would give charged complexes with these neutral ligands, contrary to the formula printed here.

Step 3: Conclusion The oxidation state of Fe is 0. Hence, the correct option is (B).

Quick Tip to Solve: Assign ligand charges before counting ligands: neutral carbonyl ligands leave the metal oxidation state equal to the overall complex charge.

3. Among the following, which is the strongest base?

[1 mark]



Correct Answer: (C)

Solution:

Concept:

- Amines act as bases by donating the nitrogen lone pair to a proton. Greater availability of that lone pair generally increases basicity.
- In aniline derivatives the nitrogen lone pair is delocalised into the benzene ring; in benzylamine a saturated CH_2 group interrupts this conjugation.

Quick Tip to Solve: Check whether nitrogen touches the ring directly: an intervening saturated carbon prevents aniline-type resonance of its lone pair.

Step 1: Identify the four structures Option (A) is aniline, (B) is para-methylaniline, (C) is benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, and (D) is para-nitroaniline. In (A), (B) and (D), nitrogen is bonded directly to an aromatic ring.

Step 2: Compare lone-pair availability In benzylamine, the intervening CH_2 group prevents the nitrogen lone pair from delocalising into the ring, making it more available for protonation. The methyl group in (B) increases basicity relative to aniline by donating electron density, but does not remove the lone-pair delocalisation. The nitro group in (D) withdraws electron density and further decreases basicity.

Step 3: Conclusion Benzylamine is the strongest base among the four structures. Hence, the correct option is (C).

Quick Tip to Solve: Check whether nitrogen touches the ring directly: an intervening saturated carbon prevents aniline-type resonance of its lone pair.

4. The slope in the plot of $\ln[R]$ 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: (B) $-k$

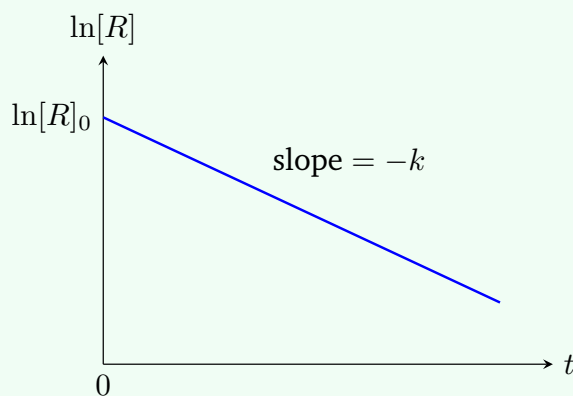
Solution:

Concept:

- For a first-order reaction, the integrated rate law is $\ln[R]_t = \ln[R]_0 - kt$, where $[R]_t$ is reactant concentration at time t , and $k > 0$ is the rate constant.
- A straight line $y = mx + c$ has slope m , the coefficient of the horizontal-axis variable.

Step 1: Compare with the straight-line equation For a plot of $y = \ln[R]_t$ against $x = t$, the integrated rate law identifies the intercept as $\ln[R]_0$ and the coefficient of time as $-k$. The descending line is consistent with reactant concentration decreasing as time increases.

Quick Tip to Solve: First check the log base: a plot using $\ln$ has slope $-k$, while a plot using log base 10 has slope $-k/2.303$.



Schematic first-order plot: its slope is $-k$.

Step 2: Check the logarithm and sign For common logarithms, the law instead reads $\log_{10}[R]_t = \log_{10}[R]_0 - kt/2.303$, giving slope $-k/2.303$. That is option (C), but the question uses natural logarithms. Options (A) and (D) have a positive sign and would incorrectly represent increasing reactant concentration.

Step 3: Conclusion The required slope is $-k$. Hence, the correct option is (B).

Quick Tip to Solve: First check the log base: a plot using $\ln$ has slope $-k$, while a plot using log base 10 has slope $-k/2.303$.

5. An α -helix is a structural feature of

[1 mark]

- (A) Sucrose
- (B) Polypeptides
- (C) Nucleotides
- (D) Starch

Correct Answer: (B) Polypeptides

Solution:

Concept:

- The α -helix is a regular secondary structure of a polypeptide chain, whose amino-acid residues are joined by peptide bonds.
- Hydrogen bonding between backbone $C=O$ and $N-H$ groups stabilises the coiled chain.

Step 1: Connect the helix to peptide bonding In an α -helix, a polypeptide backbone coils into a right-handed helix. Backbone hydrogen bonds form within the same chain, between a carbonyl group and an $N-H$ group four residues farther along, maintaining the regular secondary structure.

Step 2: Eliminate the other biomolecules Sucrose is a disaccharide and has no polypeptide backbone. Nucleotides are the building units of nucleic acids, whose helices are structurally different from a protein α -helix. Starch is a glucose polysaccharide; although amylose can coil, that coil is not the peptide α -helix.

Quick Tip to Solve: Associate protein alpha-helices with peptide-backbone hydrogen bonds; do not confuse them with the different helices of DNA or amylose.

Step 3: Conclusion An α -helix is a structural feature of polypeptides. Hence, the correct option is (B).

Quick Tip to Solve: Associate protein alpha-helices with peptide-backbone hydrogen bonds; do not confuse them with the different helices of DNA or amylose.

6. Racemisation occurs in

[1 mark]

- (A) S_N1 reaction
- (B) S_N2 reaction
- (C) Neither S_N1 nor S_N2 reaction
- (D) S_N2 reaction as well as S_N1 reaction

Correct Answer: (A) S_N1 reaction

Solution:

Concept:

- Racemisation is the formation of both enantiomers from an optically active reactant, causing loss of optical activity when they occur equally.
- An S_N1 reaction proceeds through a planar carbocation; an S_N2 reaction proceeds by concerted backside attack.

Step 1: Examine the carbocation pathway When the leaving group departs in an S_N1 reaction at a chiral centre, a trigonal planar carbocation is formed. A nucleophile can approach either face of this intermediate, producing products with retention or inversion of the original configuration. Thus racemisation can occur; ion-pair effects may make it incomplete in practice.

Step 2: Compare the concerted pathway In an S_N2 reaction, the nucleophile attacks from the side opposite the leaving group while that group departs. This gives inversion of configuration, rather than attack at both faces through a free planar intermediate. Hence the options naming only S_N2 , neither mechanism, or both mechanisms are unsuitable.

Step 3: Conclusion Racemisation is characteristic of the S_N1 reaction. Hence, the correct option is (A).

Quick Tip to Solve: Link a planar carbocation to two-face attack and racemisation; link a single backside attack to inversion in the S_N2 mechanism.

7. Value of Henry's constant K_H :

[1 mark]

- (A) increases with decrease in temperature.
- (B) decreases with increase in temperature.
- (C) increases with increase in temperature.
- (D) remains constant.

Correct Answer: (C) increases with increase in temperature.

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the gas partial pressure and x is its mole fraction dissolved in the liquid.
- For the usual dissolution of a gas in a liquid, increasing temperature decreases its solubility; at a fixed pressure, a larger K_H means a smaller x .

Step 1: Relate the constant to solubility Rearrange Henry's law to obtain $K_H = p/x$. When temperature rises, gas escapes more readily from solution and its equilibrium mole fraction decreases at the same gas pressure.

Step 2: Compare the temperature trends With p fixed, a decrease in x requires an increase in K_H . Thus the trends in (A) and (B) are reversed. Option (D) is incorrect because Henry's constant is constant for a specified gas-solvent pair only at a specified temperature.

Step 3: Conclusion Henry's constant increases with increase in temperature. Hence, the correct option is (C).

Quick Tip to Solve: Use $x = p/K_H$: lower gas solubility at higher temperature means a higher Henry's constant.

8. Which of the following solutions of KCl will have the highest value of molar conductivity? [1 mark]

- (A) 0.01 M
- (B) 1 M
- (C) 0.5 M
- (D) 0.1 M

Correct Answer: (A) 0.01 M

Solution:

Concept:

- Molar conductivity Λ_m is the conductivity contribution per mole of an electrolyte; for conductivity κ in S cm^{-1} and concentration c in mol L^{-1} , $\Lambda_m = 1000\kappa/c$.
- For a strong electrolyte such as KCl, molar conductivity increases on dilution because interionic attractions decrease and ionic mobility increases.

Step 1: Compare the concentrations The concentrations in increasing order are $0.01 < 0.1 < 0.5 < 1$ M. Therefore, the 0.01 M solution is the most dilute among the four choices.

Quick Tip to Solve: For the same strong electrolyte, select the lowest concentration when the question asks for the highest molar conductivity.

Step 2: Distinguish molar conductivity from conductivity The most dilute solution has the highest molar conductivity. The 0.1, 0.5 and 1 M solutions all have stronger interionic interactions and hence smaller Λ_m . Although conductivity per unit volume generally decreases on dilution, the question asks for conductivity per mole.

Step 3: Conclusion The 0.01 M solution of KCl has the highest molar conductivity. Hence, the correct option is (A).

Quick Tip to Solve: For the same strong electrolyte, select the lowest concentration when the question asks for the highest molar conductivity.

9. Which of the following reactions are feasible?

[1 mark]

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

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

Solution:

Concept:

- Williamson ether synthesis involves nucleophilic substitution of an alkyl halide by an alkoxide ion through the $\text{S}_{\text{N}}2$ mechanism.
- A primary alkyl halide favours this substitution. A tertiary alkyl halide is too crowded for backside attack and gives elimination with a strongly basic alkoxide.

Step 1: Examine reaction (a) In (a), the carbon bonded to bromine in $\text{CH}_3\text{CH}_2\text{Br}$ is primary. The tert-butoxide ion can attack this relatively unhindered carbon and displace bromide, giving ethyl tert-butyl ether. Thus (a) is the feasible Williamson route to the stated ether.

Step 2: Examine reaction (b) and the combined choices In (b), $(\text{CH}_3)_3\text{CCl}$ is a tertiary halide, so the ethoxide ion acts predominantly as a base and promotes elimination to $\text{CH}_2=\text{C}(\text{CH}_3)_2$, rather than the stated ether formation. Consequently (b) is unsuitable; both reactions are not feasible, and the choice that neither is feasible is also excluded.

Step 3: Conclusion Reaction (a) is the feasible synthesis of the ether shown. Hence, the correct option is (A).

Quick Tip to Solve: For an unsymmetrical ether, place the halogen on the less hindered alkyl group; avoid tertiary alkyl halides in Williamson synthesis.

10. Which of the following is most reactive in nucleophilic addition reactions?

[1 mark]

- (A) HCHO
- (B) CH_3CHO
- (C) CH_3COCH_3
- (D) $\text{CH}_3\text{COC}_2\text{H}_5$

Correct Answer: (A) HCHO

Solution:

Concept:

- In nucleophilic addition to a carbonyl compound, a nucleophile attacks the electron-deficient carbon atom of the $\text{C}=\text{O}$ group.
- Alkyl groups lower carbonyl reactivity by donating electron density through their positive inductive effect and by hindering the approaching nucleophile.

Step 1: Compare the groups around the carbonyl carbon Methanal, HCHO , has two hydrogen atoms and no electron-donating alkyl group attached to its carbonyl carbon. Ethanal has one methyl group, whereas acetone and butan-2-one each have two alkyl groups.

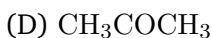
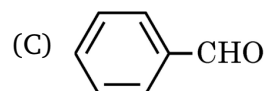
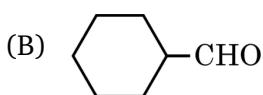
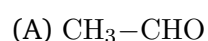
Step 2: Apply electronic and steric effects Methanal therefore has the least steric obstruction and a strongly electrophilic carbonyl carbon. Ethanal is less reactive because of its methyl group. Both ketones have greater alkyl electron donation and crowding, making them still less susceptible to nucleophilic attack than methanal.

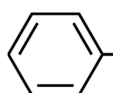
Step 3: Conclusion HCHO is the most reactive compound towards nucleophilic addition. Hence, the correct option is (A).

Quick Tip to Solve: For simple aliphatic carbonyl compounds, use the reactivity order: methanal, then other aldehydes, then ketones.

11. Which of the following does not give aldol condensation reaction?

[1 mark]



Correct Answer: (C) 

Solution:

Concept:

- Aldol condensation requires an aldehyde or ketone to have at least one α -hydrogen, a hydrogen on the carbon directly adjacent to the carbonyl carbon.

Quick Tip to Solve: Count hydrogens on the carbon next to the carbonyl; never count the aldehydic hydrogen as an α -hydrogen.

- A base removes an α -hydrogen to form an enolate, which attacks another carbonyl molecule; without an α -hydrogen, a compound cannot undergo self-aldol condensation.

Step 1: Check the compounds that contain alpha-hydrogen Acetaldehyde in (A) has three α -hydrogens on its methyl group. The saturated ring carbon bonded to the $-\text{CHO}$ group in (B), cyclohexanecarbaldehyde, bears one α -hydrogen. Acetone in (D) has α -hydrogens on both methyl groups. Each can form an enolate and undergo aldol condensation.

Step 2: Inspect benzaldehyde In (C), $\text{C}_6\text{H}_5\text{CHO}$, the aromatic ring carbon directly attached to the aldehyde group has no hydrogen. The hydrogen on $-\text{CHO}$ is attached to the carbonyl carbon itself and is not an α -hydrogen. Benzaldehyde therefore cannot form the required enolate for self-aldol condensation.

Step 3: Conclusion Benzaldehyde does not give aldol condensation on its own. Hence, the correct option is (C).

Quick Tip to Solve: Count hydrogens on the carbon next to the carbonyl; never count the aldehydic hydrogen as an alpha-hydrogen.

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

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

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

Solution:

Concept:

- For $3A \rightarrow 2B$, the stoichiometrically normalised reaction rate is $r = -\frac{1}{3} \frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$, where square brackets denote concentration.
- Reactant concentration decreases, so $d[A]/dt < 0$; product concentration increases, so $d[B]/dt > 0$.

Step 1: Relate the concentration changes For every three units of A consumed, two units of B form. At constant volume their concentration changes obey $d[B] = -(2/3)d[A]$. Dividing by the same time interval relates their rates of change.

Step 2: Isolate the rate of formation requested Multiply the normalised rate equation by two:

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

Option (A) reverses the stoichiometric ratio. Option (C) gives the normalised reaction rate r , rather

Quick Tip to Solve: To find a product's formation rate, multiply the reactant's disappearance rate by product coefficient divided by reactant coefficient.

than the rate of formation of B. Option (D) has the wrong sign and coefficient.

Step 3: Conclusion The requested rate is $+d[B]/dt = -\frac{2}{3}d[A]/dt$. Hence, the correct option is (B).

Quick Tip to Solve: To find a product's formation rate, multiply the reactant's disappearance rate by product coefficient divided by reactant coefficient.

13. Which of the following characteristics of transition metals is associated with their catalytic activity? [1 mark]

- (A) Paramagnetic nature
- (B) Colour of hydrated ions
- (C) High enthalpy of atomisation
- (D) Variable oxidation states

Correct Answer: (D) Variable oxidation states

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with a lower activation energy and is regenerated during the reaction.
- Transition metals exhibit variable oxidation states because their outer ns and $(n-1)d$ electrons have comparable energies and can participate in bonding.

Step 1: Connect oxidation states with a catalytic cycle By changing oxidation state, a transition metal can accept electrons in one step and transfer them in another. It can form intermediate compounds and return to its initial state, providing an easier pathway for the overall reaction.

Step 2: Eliminate the other properties Paramagnetism arises from unpaired electrons, while the colour of many hydrated ions is associated with electronic transitions between split d levels. High enthalpy of atomisation reflects strong metallic bonding. These properties do not provide the direct explanation for catalytic electron-transfer cycles that variable oxidation states do.

Step 3: Conclusion Variable oxidation states are associated with the catalytic activity of transition metals. Hence, the correct option is (D).

Quick Tip to Solve: For transition-metal catalysis, connect easy changes in oxidation state with intermediate formation and regeneration of the catalyst.

14. The formula of the complex dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate is [1 mark]

- (A) $[\text{Pt Cl}_2(\text{en})_2(\text{NO}_3)_2]$
(B) $[\text{Pt Cl}_2(\text{en})_2](\text{NO}_3)_2$
(C) $[\text{Pt Cl}_2(\text{en})_2(\text{NO}_3)]\text{NO}_3$
(D) $[\text{Pt}(\text{en})_2(\text{NO}_3)_2]\text{Cl}_2$

Correct Answer: (B) $[\text{Pt Cl}_2(\text{en})_2](\text{NO}_3)_2$

Solution:

Concept:

- The ligands named before the metal belong inside the coordination sphere. Chlorido is Cl^- ; ethane-1,2-diamine (en) is a neutral bidentate ligand.
- The oxidation state of platinum is +4. Counterions outside the square brackets balance the charge of the complex ion.

Step 1: Identify the coordinated ligands Dichlorido specifies two chloride ligands and bis(ethane-1,2-diamine) specifies two neutral en ligands. Thus the coordination sphere is $[\text{PtCl}_2(\text{en})_2]$. The two chlorides provide two donor atoms and the two en ligands provide four, giving coordination number six.

Step 2: Balance the ionic charge and compare the options The charge of the complex is $+4 + 2(-1) + 2(0) = +2$. Therefore two nitrate anions must remain outside the brackets to give an electrically neutral salt. Option (A) puts both nitrates inside the sphere, (C) puts one nitrate inside, and (D) coordinates nitrate instead of chloride. None of these matches the stated ligand names.

Step 3: Conclusion The formula is $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$. Hence, the correct option is (B).

Quick Tip to Solve: First put only the named ligands inside brackets; then use the metal oxidation state to count the counterions.

15. Assertion (A): Osmotic pressure is a colligative property.

Reason (R): Osmotic pressure is proportional to the molality.

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:

- A colligative property depends on the number of solute particles in a specified amount of solution or solvent, rather than their chemical identity.
- For a dilute ideal solution, osmotic pressure is $\Pi = (n/V)RT = CRT$, where C is molarity, R is

Quick Tip to Solve: In osmotic pressure, the volume in n/V identifies molarity; reserve molality for freezing-point depression and boiling-point elevation.

the gas constant and T is absolute temperature.

Step 1: Evaluate the assertion At a fixed temperature, solutions with the same number concentration of solute particles exert the same osmotic pressure. Thus osmotic pressure is a colligative property and assertion (A) is true.

Step 2: Evaluate the reason The concentration in $\Pi = CRT$ is moles per litre of solution, namely molarity. Molality instead measures moles per kilogram of solvent. Therefore the stated proportionality to molality is not the osmotic-pressure law, and reason (R) is false.

Step 3: Test the explanation and option combinations A false reason cannot explain the true assertion. Options (A) and (B) incorrectly call the reason true, while (D) incorrectly calls the assertion false. Only the true-assertion, false-reason combination applies.

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

Quick Tip to Solve: In osmotic pressure, the volume in n/V identifies molarity; reserve molality for freezing-point depression and boiling-point elevation.

16. Assertion (A): Conductivity decreases with decrease in concentration of electrolyte.

Reason (R): Number of ions per unit volume that carry the current in a solution decreases on dilution.

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:

- Conductivity κ measures the conducting ability of a solution and depends on the number of mobile ions per unit volume as well as their mobility.
- Dilution increases solution volume and reduces the concentration of charge carriers. Conductivity must be distinguished from molar conductivity, which refers to one mole of electrolyte.

Step 1: Evaluate the assertion On decreasing electrolyte concentration by dilution, the number of ions available to carry current in a given volume decreases. Consequently conductivity decreases. Assertion (A) is therefore true.

Step 2: Evaluate the reason Dilution spreads the electrolyte through a larger volume. Even though ionisation of a weak electrolyte may increase, the number of ions per unit volume decreases. Reason (R) correctly identifies this reduction of charge-carrier concentration and is true.

Step 3: Link the reason to the assertion Fewer mobile ions per unit volume account directly for the decrease in conductivity. Thus the reason explains the assertion; option (B) wrongly denies the explanation, while (C) and (D) wrongly declare one of the statements false. The increase of molar

Quick Tip to Solve: On dilution, conductivity falls but molar conductivity rises; check which of these two quantities the question names.

conductivity on dilution does not contradict this result.

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

Quick Tip to Solve: On dilution, conductivity falls but molar conductivity rises; check which of these two quantities the question names.

17. Assertion (A): Copper is a non-transition element.

Reason (R): Copper has completely filled d-orbitals in its ground state.

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: (D) (A) is false, but (R) is true.

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its ions.
- Copper has ground-state configuration $[\text{Ar}] 3d^{10}4s^1$, whereas Cu^{2+} has configuration $[\text{Ar}] 3d^9$.

Step 1: Evaluate the assertion Copper forms Cu^{2+} , whose d subshell is incomplete. This satisfies the definition of a transition element even though the neutral atom has a full d subshell. Therefore copper is a transition element and assertion (A) is false.

Step 2: Evaluate the reason In the ground state of a neutral copper atom the d configuration is $3d^{10}$. All five d orbitals are fully occupied by two electrons each. Hence the statement about completely filled d orbitals is correct, so reason (R) is true.

Step 3: Test the implication The neutral atom alone does not determine transition character: the configurations of its ions must also be considered. Thus the true reason does not support the false assertion. Options (A), (B) and (C) all incorrectly treat the assertion as true.

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

Quick Tip to Solve: Before excluding a d-block metal from the transition elements, check its common ions; copper(II) has an incomplete $3d^9$ subshell.

18. Assertion (A): Nucleophilic substitution of iodoethane is easier than chloroethane.

Reason (R): Bond enthalpy of C-I bond is less than that of C-Cl bond.

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:

- Nucleophilic substitution replaces the halogen of a haloalkane with a nucleophile and involves cleavage of the carbon-halogen bond.
- For the same alkyl group under comparable conditions, iodoalkanes react more readily than chloroalkanes because the carbon-iodine bond is weaker and iodide is a better leaving group.

Step 1: Evaluate the assertion Both compounds contain the same ethyl group, so the comparison isolates the halogen effect. Iodoethane undergoes nucleophilic substitution more easily than chloroethane under comparable conditions. Assertion (A) is true.

Step 2: Evaluate the reason The larger iodine atom forms a longer, weaker bond to carbon than chlorine does. Therefore the bond enthalpy of the carbon-iodine bond is lower than that of the carbon-chlorine bond. Reason (R) is true.

Step 3: Connect bond cleavage to substitution Easier cleavage of the weaker carbon-iodine bond facilitates displacement of iodide by the nucleophile. The reason directly explains the greater substitution reactivity of iodoethane. Option (B) wrongly denies this link; (C) and (D) wrongly classify a true statement as false.

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

Quick Tip to Solve: Compare haloalkanes with the same alkyl group using leaving-group ability: iodide leaves more readily than chloride.

Section B (14 marks)

19. 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 solution of two volatile liquids, Raoult's law gives each partial pressure as $p_i = x_i p_i^\circ$, where x_i is its liquid-phase mole fraction and p_i° its pure-liquid vapour pressure at the same temperature.
- The total vapour pressure is the sum of the partial pressures: $P = p_X + p_Y = x_X p_X^\circ + x_Y p_Y^\circ$.

Step 1: Determine the mole fractions Let the amount of each liquid mixed be n moles. Equal moles, rather than equal masses or volumes, imply equal mole fractions:

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

These fractions add to unity, as required for the binary liquid mixture.

Step 2: Calculate the partial pressures at the stated temperature Using the pure-liquid vapour pressures at 25 °C, Raoult's law gives

$$p_X = \frac{1}{2}(120) = 60 \text{ mm Hg}, \quad p_Y = \frac{1}{2}(160) = 80 \text{ mm Hg}.$$

Both liquids are volatile, so both partial pressures must contribute. No temperature conversion is needed because the supplied vapour pressures already correspond to the mixture temperature.

Step 3: Add the vapour contributions Applying Dalton's law to the vapour above the ideal liquid solution,

$$P = p_X + p_Y = 60 + 80 = 140 \text{ mm Hg}.$$

This value lies between the pure-liquid pressures and is their arithmetic mean, as expected for equal mole fractions.

Step 4: Conclusion The vapour pressure of the ideal solution at 25 °C is 140 mm Hg.

Quick Tip to Solve: When equal moles of two volatile liquids form an ideal solution, average their pure-liquid vapour pressures at the same temperature.

20(a). Give reasons:

(i) Mercury cell delivers a constant potential during its life time.

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

[2 marks]

Solution:

Concept:

- The Nernst equation relates cell potential to the reaction quotient: $E = E^\circ - \frac{RT}{nF} \ln Q$. At fixed temperature, a constant Q gives a constant potential.
- Conductance measurements must measure the resistance of the original electrolyte without changing its composition or polarising the electrodes.

Step 1: (i) Examine the overall mercury-cell reaction In the mercury cell, zinc amalgam is oxidised and mercury(II) oxide is reduced. The overall reaction is



The hydroxide ions participating in the electrode reactions cancel from this net equation. No electrolyte ion occurs in the overall reaction, so its concentration does not change as the cell operates. The activities of the condensed phases remain effectively constant during useful operation; hence the reaction quotient and cell potential remain practically constant throughout its life.

Step 2: (ii) Explain the problem with direct current Direct current drives sustained electrolysis at the electrodes. This changes the electrolyte composition near them and produces electrode polarisation, which introduces an opposing potential. The resulting current therefore does not give the true resistance of the unchanged electrolyte. Alternating current is used instead: its frequent reversal minimises electrolysis and polarisation during measurement.

Step 3: Conclusion (i) Mercury cells have a constant potential because the net reaction causes no change in electrolyte-ion concentration. (ii) DC is avoided because electrolysis and electrode polarisation interfere with conductance measurement; AC is used.

Quick Tip to Solve: For a constant cell potential, first cancel the electrode reactions and check whether dissolved ions remain in the net reaction.

OR

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

[2 marks]

Solution:

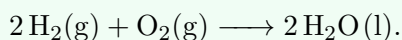
Concept:

- A fuel cell is a galvanic cell that converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy.
- A primary cell uses a finite stock of reactants and cannot normally be recharged; a secondary cell

Quick Tip to Solve: Contrast externally supplied fuel with the finite reactants stored in a battery; this explains why continuous operation is possible.

stores energy chemically and needs electrical recharging after discharge.

Step 1: Define a fuel cell and give an example In a fuel cell, the fuel and oxidant are fed continuously to suitable electrodes, where oxidation and reduction produce an electric current. For example, the hydrogen–oxygen fuel cell uses hydrogen as fuel and oxygen as oxidant. Its overall reaction is



Hydrogen loses electrons at the anode, and oxygen gains electrons at the cathode; the electrons pass through the external circuit to do electrical work.

Step 2: Compare operation with ordinary batteries A fuel cell can supply electricity continuously as long as fuel and oxidant are supplied and products are removed. It therefore avoids the replacement required after a primary cell is exhausted and the charging interruptions needed by a secondary battery. Fuel cells provide efficient direct conversion of chemical energy into electrical energy. The hydrogen–oxygen cell is also clean at the point of operation because its product is water, rather than polluting exhaust gases.

Step 3: Conclusion A fuel cell, such as the hydrogen–oxygen cell, directly converts continuously supplied fuel into electrical energy. Its advantages include continuous operation without battery recharging, high efficiency and, for the hydrogen–oxygen cell, water as the product.

Quick Tip to Solve: Contrast externally supplied fuel with the finite reactants stored in a battery; this explains why continuous operation is possible.

21. (a) The conversion of molecule A to B followed second order kinetics. If concentration of A 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 reaction that is second order in A, the rate of formation of B is $r = k[A]^2$, where k is the rate constant at the given temperature.
- A pseudo-first-order reaction has a higher-order rate law but behaves as first order when the concentrations of other reactants remain effectively constant, usually because they are in large excess.

Step 1: (a) Compare the new and original rates Let the initial concentration of A be a . At the same temperature, k remains unchanged. The original and new rates are therefore

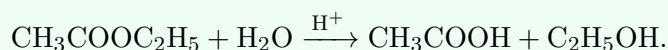
$$r_1 = ka^2, \quad r_2 = k(3a)^2 = 9ka^2, \quad \frac{r_2}{r_1} = 9.$$

The second-order exponent acts on the entire concentration factor, so tripling the concentration increases the rate of formation of B ninefold.

Step 2: (b) Explain pseudo-first-order behaviour with an example Acid-catalysed hydrolysis of ethyl

Quick Tip to Solve: Raise the concentration multiplier to the order: tripling a second-order reactant multiplies its rate by 3^2 , not by 3.

acetate in excess water is a standard example:



At a fixed acid concentration, the rate may be written $r = k[\text{ester}][\text{water}]$. Since water is the solvent and is present in large excess, its concentration changes negligibly during reaction. Thus

$$r = k'[\text{ester}], \quad k' = k[\text{water}] \approx \text{constant}.$$

The observed rate is consequently first order in ester, although the original concentration dependence includes water as well.

Step 3: Conclusion (a) The rate becomes nine times its original value. (b) A pseudo-first-order reaction behaves as first order because another reactant's concentration is effectively constant; hydrolysis of ethyl acetate in excess water is an example.

Quick Tip to Solve: Raise the concentration multiplier to the order: tripling a second-order reactant multiplies its rate by 3^2 , not by 3.

22(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 before the metal, in alphabetical order ignoring multiplicative prefixes. The metal oxidation state is written as a Roman numeral in parentheses.
- A complex anion takes the metal suffix -ate. The ambidentate nitrite ligand is named nitrito-O when oxygen is the donor atom, as shown by ONO.

Step 1: (i) Name the cobalt complex cation In $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$, ammonia is a neutral ligand called ammine, while ONO^- has charge -1 . If cobalt has oxidation state x ,

$$x + 5(0) - 1 = +2 \Rightarrow x = +3.$$

There are five ammine ligands and one oxygen-bound nitrito ligand. Ammine precedes nitrito alphabetically. As the complex is a cation, the metal retains the name cobalt. Its name is **pentaammine(nitrito-O)cobalt(III) ion**.

Step 2: (ii) Name the potassium salt The two K^+ ions show that the coordination entity is $[\text{NiCl}_4]^{2-}$. Each chlorido ligand has charge -1 , so the nickel oxidation state follows from

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

Name the cation potassium first. Four chlorido ligands give tetrachlorido, and the anionic complex requires nickelate rather than nickel. The complete name is **potassium tetrachloridonickelate(II)**.

Quick Tip to Solve: Use the displayed donor order: ONO means O-bound nitrito. Then balance ligand charges to obtain the metal's Roman numeral.

Step 3: Conclusion (i) Pentaammine(nitrito-O)cobalt(III) ion.
(ii) Potassium tetrachloridonickelate(II).

Quick Tip to Solve: Use the displayed donor order: ONO means O-bound nitrito. Then balance ligand charges to obtain the metal's Roman numeral.

OR

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

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

[2 marks]

Solution:

Concept:

- Denticity is the number of donor atoms through which one ligand attaches to a metal ion. A bidentate or polydentate ligand can bind at two or more sites.
- Chelation describes ring formation by a multidentate ligand; heteroleptic describes the presence of more than one kind of ligand in the same coordination entity.

Step 1: (i) Define a chelate complex with an example A chelate complex is formed when a bidentate or polydentate ligand coordinates to the same 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. Here en is ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$. Each en molecule attaches through both nitrogen atoms and forms a five-membered ring with cobalt; three en ligands supply six donor atoms in total.

Step 2: (ii) Define a heteroleptic complex with an example A heteroleptic complex contains a metal bonded to more than one type of ligand. For example, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has two kinds of ligands: neutral ammine ligands and negatively charged chlorido ligands. Four ammine ligands and two chlorido ligands surround cobalt, so this coordination entity is heteroleptic. The term refers to the different ligand identities, not to different oxidation states of the central metal.

Step 3: Conclusion (i) Chelate complexes contain rings formed by multidentate ligands, for example $[\text{Co}(\text{en})_3]^{3+}$. (ii) Heteroleptic complexes contain more than one kind of ligand, for example $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

Quick Tip to Solve: For chelation, check whether one ligand forms a ring with the metal; for heteroleptic character, count distinct ligand types.

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

(a) Reimer-Tiemann reaction

(b) Acetylation of Salicylic acid

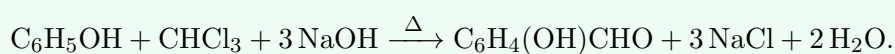
[2 marks]

Solution:

Concept:

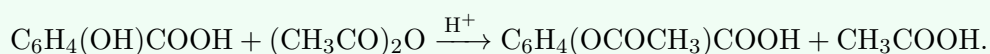
- Reimer-Tiemann formylation introduces a $-\text{CHO}$ group mainly ortho to the hydroxyl group of phenol using chloroform and aqueous alkali, followed by acidification.
- Acetylation replaces the hydrogen of a phenolic $-\text{OH}$ group by CH_3CO^- , forming an ester; the carboxyl group of salicylic acid remains unchanged.

Step 1: (a) Write the Reimer-Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify the reaction mixture. The principal product is salicylaldehyde (2-hydroxybenzaldehyde). A balanced overall equation, with the product shown after acid work-up, is



In the product, $-\text{OH}$ and $-\text{CHO}$ are at adjacent (1,2) positions. The ortho product predominates; a small amount of the para product may also form.

Step 2: (b) Acetylate the phenolic hydroxyl group Treat salicylic acid (2-hydroxybenzoic acid) with acetic anhydride in the presence of an acid catalyst:



The adjacent substituents are retained. The product is acetylsalicylic acid, commonly called aspirin, and acetic acid is the by-product.

Step 3: Conclusion Reimer-Tiemann reaction gives mainly ortho-hydroxybenzaldehyde; acetylation of salicylic acid gives acetylsalicylic acid (aspirin).

Quick Tip to Solve: In Reimer-Tiemann formylation add an ortho $-\text{CHO}$; in aspirin formation acetylate the phenolic $-\text{OH}$, leaving $-\text{COOH}$ intact.

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

(a) CH_3CN to $\text{CH}_3\text{-CO-CH}_3$

(b)

[2 marks]

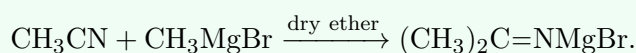


Solution:

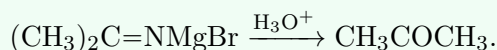
Concept:

- A nitrile reacts with one equivalent of a Grignard reagent to form an imine magnesium salt; subsequent acidic hydrolysis gives a ketone.
- Soda-lime decarboxylation of a sodium carboxylate replaces the $-\text{COONa}$ group by hydrogen, shortening the carbon skeleton by one carbon atom.

Step 1: (a) Convert ethanenitrile into propanone First add methylmagnesium bromide in dry ether. The methyl group adds to the electrophilic carbon of the nitrile:



Second, hydrolyse the intermediate using dilute aqueous acid:

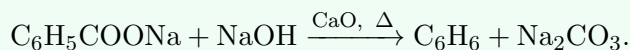


The original nitrile carbon becomes the carbonyl carbon. The original methyl group and the added methyl group become the two groups bonded to it, giving the required acetone. Acid is introduced only after the Grignard addition is complete.

Step 2: (b) Convert benzoic acid into benzene First neutralise benzoic acid with sodium hydroxide to form sodium benzoate:



Isolate and dry the salt. Second, heat it with soda lime (a mixture of NaOH and CaO):



Decarboxylation removes the carboxyl carbon while retaining the benzene ring. Both conversions therefore use no more than two reaction steps.

Step 3: Conclusion (a) Use CH_3MgBr /dry ether, then acidic hydrolysis. (b) Form sodium benzoate with NaOH , then heat with soda lime to obtain benzene.

Quick Tip to Solve: To get a ketone from a nitrile, add the Grignard group missing from the target; to remove $-\text{COOH}$, decarboxylate its dry sodium salt.

25. Write two differences between DNA and RNA.

[2 marks]

Solution:**Concept:**

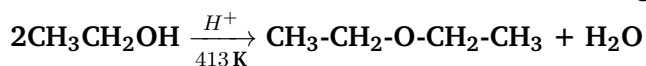
- DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) are polynucleotides. Each nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group.
- Their characteristic chemical differences lie in the sugar and one of the pyrimidine bases; both contain the bases adenine, guanine and cytosine.

Step 1: Compare the pentose sugars DNA contains 2-deoxy-D-ribose, whereas RNA contains D-ribose. At the 2' carbon of the sugar, DNA has a hydrogen atom in place of the hydroxyl group present in RNA. The prime distinguishes sugar-carbon numbering from the numbering of atoms in the nitrogenous base. Thus the word “deoxy” indicates one fewer oxygen atom in the sugar, rather than an absence of oxygen throughout DNA.

Step 2: Compare the nitrogenous bases DNA contains adenine (A), guanine (G), cytosine (C) and thymine (T). RNA contains adenine (A), guanine (G), cytosine (C) and uracil (U). Therefore thymine is the characteristic base in DNA and uracil replaces it in RNA. Adenine, guanine and cytosine do not distinguish the two because they occur in both.

Step 3: Conclusion The two differences are: DNA has 2-deoxyribose and thymine, whereas RNA has ribose and uracil.

Quick Tip to Solve: Pair DNA with deoxyribose and T; pair RNA with ribose and U. State each difference as a direct comparison of both molecules.

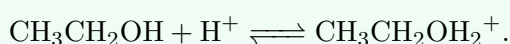
Section C (15 marks)**26(a). (i) Write the mechanism of the following reaction:****(ii) Why ortho-nitrophenol is steam volatile while para-nitrophenol is not?**

[3 marks]

Solution:**Concept:**

- At 413 K, acid-catalysed intermolecular dehydration of ethanol gives ethoxyethane. Protonation converts the poor leaving group –OH into the good leaving group water.
- A primary alcohol forms the ether by nucleophilic substitution: an unprotonated alcohol attacks the primary carbon of the protonated alcohol, without a free primary carbocation.
- Intramolecular hydrogen bonding occurs within one molecule; intermolecular hydrogen bonding associates different molecules and reduces their volatility.

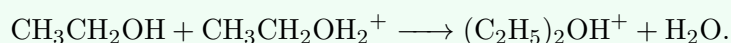
Step 1: (i) Protonate ethanol A lone pair on the oxygen of ethanol accepts a proton from the acid. This produces the ethyloxonium ion:



Quick Tip to Solve: For ethanol at 413 K, show an attacking second ethanol molecule, not a primary carbocation; remember ortho means hydrogen bonding within one nitrophenol molecule.

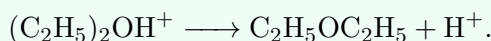
The oxygen now bears a positive charge, and water can leave during the next step.

Step 2: Form the carbon–oxygen bond by substitution The oxygen lone pair of a second, unprotonated ethanol molecule attacks the carbon bonded to OH_2^+ . Simultaneously, the carbon–oxygen bond to the leaving water molecule breaks, with its electron pair going to oxygen:

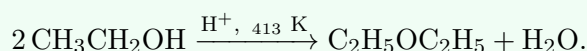


This is an $\text{S}_\text{N}2$ step and gives protonated diethyl ether. A free ethyl carbocation is not an intermediate.

Step 3: Regenerate the acid catalyst The protonated ether loses a proton; the oxygen–hydrogen bond pair returns to oxygen:



Adding the steps cancels the catalyst and intermediates, giving



Step 4: (ii) Compare hydrogen bonding in the nitrophenols In ortho-nitrophenol, the adjacent $-\text{OH}$ and $-\text{NO}_2$ groups form an intramolecular hydrogen bond. Consequently, intermolecular association is reduced and the compound is sufficiently volatile to distil with steam. In para-nitrophenol, the groups are too far apart for this intramolecular bond. Instead, the molecules form intermolecular hydrogen bonds, causing greater association and stronger attraction between molecules. More energy is needed to separate them; its volatility is lower and it is not steam volatile under the usual conditions.

Step 5: Conclusion (i) Protonation, bimolecular substitution and deprotonation produce ethoxyethane while regenerating H^+ . (ii) Intramolecular hydrogen bonding makes ortho-nitrophenol steam volatile, whereas intermolecular association makes para-nitrophenol non-steam-volatile.

Quick Tip to Solve: For ethanol at 413 K, show an attacking second ethanol molecule, not a primary carbocation; remember ortho means hydrogen bonding within one nitrophenol molecule.

OR

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

Write chemical equation in support of your answer.

[3 marks]

Solution:

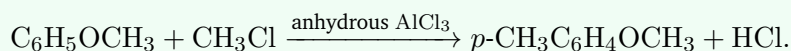
Concept:

- The methoxy group of anisole donates electron density to its benzene ring by resonance and directs electrophilic substitution mainly to the ortho and para positions.
- Strong oxidation converts phenol into a quinone. A tertiary alcohol lacks a hydrogen on the carbon

Quick Tip to Solve: For an alcohol over hot copper, first check for a hydrogen on the hydroxyl-bearing carbon: its absence in a tertiary alcohol points to dehydration.

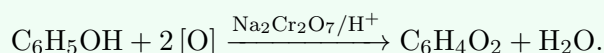
bearing the hydroxyl group and therefore cannot undergo ordinary dehydrogenation.

Step 1: (i) Methylate the anisole ring Anisole undergoes Friedel–Crafts alkylation with CH_3Cl and anhydrous AlCl_3 . A methyl group replaces a ring hydrogen at an ortho or para position relative to $-\text{OCH}_3$. The para product predominates because it is less sterically crowded. The two substitution pathways are



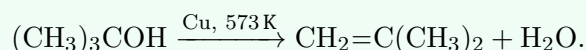
These products are 2-methylanisole and 4-methylanisole, respectively.

Step 2: (ii) Oxidise phenol Acidified sodium dichromate oxidises phenol to benzoquinone, specifically 1,4-benzoquinone. Representing oxygen supplied by the oxidising agent as $[\text{O}]$, the balanced equation is



The product has two carbonyl groups at opposite positions of the six-membered ring.

Step 3: (iii) Heat the tertiary alcohol over copper The alcohol $(\text{CH}_3)_3\text{COH}$ is 2-methylpropan-2-ol. Its hydroxyl-bearing carbon has no hydrogen, so carbonyl formation by loss of hydrogen is not possible. Over heated copper at 573 K, it undergoes dehydration: the hydroxyl group and a hydrogen from an adjacent methyl group are removed as water.



The alkene formed is 2-methylpropene.

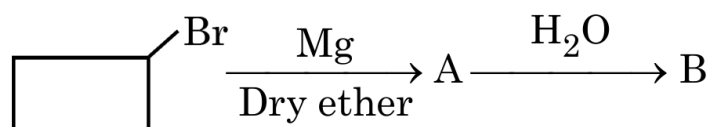
Step 4: Conclusion (i) Anisole gives ortho- and para-methylanisole, with the para product major; (ii) phenol gives 1,4-benzoquinone; (iii) the tertiary alcohol gives 2-methylpropene by dehydration.

Quick Tip to Solve: For an alcohol over hot copper, first check for a hydrogen on the hydroxyl-bearing carbon: its absence in a tertiary alcohol points to dehydration.

27. 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]

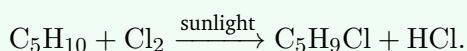


Solution:

Concept:

- Equivalent hydrogen positions give a single monochlorination product. Steric crowding hinders backside attack in S_N2 reactions.
- Symmetry aids crystal packing. Magnesium in dry ether forms a Grignard reagent; water converts it to a hydrocarbon.

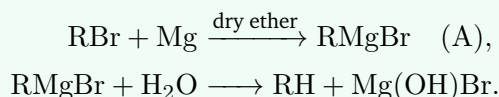
Step 1: (a) Identify equivalent positions Cyclopentane (C_5H_{10}) has equivalent ring carbons. Substituting any one hydrogen gives the same constitutional product, chlorocyclopentane. Radical substitution in sunlight is



Step 2: (b) Compare steric hindrance The bromine-bearing carbon is tertiary, secondary and primary in 2-bromo-2-methylbutane, 2-bromopentane and 1-bromopentane, respectively. Backside attack becomes easier as crowding decreases. Increasing S_N2 reactivity is therefore: 2-bromo-2-methylbutane < 2-bromopentane < 1-bromopentane.

Step 3: (c) Explain the melting point Para-dichlorobenzene is more symmetrical than its ortho and meta isomers and packs more efficiently in a crystal. Its more stable lattice requires more thermal energy to disrupt, explaining its higher melting point.

Step 4: (d) Form and hydrolyse the Grignard reagent Magnesium inserts into the carbon–bromine bond of bromocyclobutane. With R denoting the cyclobutyl group C_4H_7 ,



A is cyclobutylmagnesium bromide. Water replaces $-MgBr$ with hydrogen to give B, cyclobutane (C_4H_8). The four-membered ring stays intact; dry ether prevents premature hydrolysis of A.

Step 5: Conclusion (a) Cyclopentane; (b) tertiary < secondary < primary bromide, in the order stated; (c) efficient crystal packing; (d) A: cyclobutylmagnesium bromide, B: cyclobutane.

Quick Tip to Solve: Count the ring vertices in (d): the four-membered ring stays intact as $-Br$ becomes $-MgBr$ and then hydrogen.

28. 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 its half-life, $t_{1/2} = 0.693/k$, where k is the rate constant.
- The two-temperature Arrhenius equation is $\log(k_2/k_1) = \frac{E_a}{2.303R}(1/T_1 - 1/T_2)$, where E_a is activation energy, R is the gas constant and temperatures are in kelvin.

Step 1: Convert the half-lives into a rate-constant ratio Since 50% of the reactant has reacted, each stated time is a half-life. At $T_1 = 300 \text{ K}$, $t_{1/2,1} = 30 \text{ min}$; at $T_2 = 320 \text{ K}$, $t_{1/2,2} = 10 \text{ min}$. Hence

$$\begin{aligned}k_1 &= \frac{0.693}{30} = 0.0231 \text{ min}^{-1}, \\k_2 &= \frac{0.693}{10} = 0.0693 \text{ min}^{-1}, \\ \frac{k_2}{k_1} &= \frac{30}{10} = 3.\end{aligned}$$

The ratio is dimensionless, so conversion of both half-lives to seconds is unnecessary.

Step 2: Substitute in the Arrhenius equation Rearranging the two-temperature equation gives

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

The temperature term is positive because $T_2 > T_1$:

$$\frac{1}{300} - \frac{1}{320} = \frac{20}{96000} = \frac{1}{4800} \text{ K}^{-1}.$$

Using $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and the supplied $\log 3 = 0.4771$,

$$\begin{aligned}E_a &= 2.303(8.314)(0.4771)(4800) \text{ J mol}^{-1} \\ &\approx 4.385 \times 10^4 \text{ J mol}^{-1} \\ &\approx 43.85 \text{ kJ mol}^{-1}.\end{aligned}$$

The positive value agrees with the observed increase in reaction rate on heating.

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

Quick Tip to Solve: For first-order half-life data, use $k_2/k_1 = t_{1/2,1}/t_{1/2,2}$: the rate-constant ratio is the inverse of the half-life ratio.

29. When 19.5 g of F-CH₂-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 F-CH₂-COOH.

[Given: K_f for water = 1.86 K kg mol⁻¹]

[3 marks]

Solution:

Concept:

- Freezing-point depression obeys $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f is the molal depression constant and m is the molality based on the amount of acid added.
- A monoprotic acid dissociates into two ions. If a fraction α dissociates, one initial mole gives $(1 - \alpha) + \alpha + \alpha = 1 + \alpha$ moles of particles; hence $i = 1 + \alpha$.

Step 1: Calculate the initial molality Use the molar mass of the acid to convert its mass into moles, and use the mass of water in kilograms as the denominator:

$$n = \frac{19.5}{78} = 0.25 \text{ mol}, \quad m = \frac{0.25}{0.500} = 0.500 \text{ mol kg}^{-1}.$$

Molality uses solvent mass, so the acid mass is not added to the denominator.

Step 2: Obtain the van't Hoff factor from the observed depression A temperature difference of 1 °C equals 1 K. Without dissociation the calculated depression would be $K_fm = 1.86 \times 0.500 = 0.930$ K. Thus

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

The observed depression is larger because dissociation increases the number of dissolved particles.

Step 3: Relate the particle increase to dissociation The ionisation is $\text{FCH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{FCH}_2\text{COO}^-$. Each dissociated molecule produces two ions, so

$$\alpha = i - 1 = 1.07527 - 1 = 0.07527, \quad 100\alpha = 7.527\%.$$

Step 4: Conclusion The degree of dissociation of FCH₂COOH is $\alpha \approx 0.0753$, corresponding to approximately 7.53% dissociation.

Quick Tip to Solve: For this monoprotic acid, calculate $\Delta T_f / (K_fm)$ first, then subtract one to obtain the fraction dissociated; multiply by 100 only for the percentage.

30. (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]

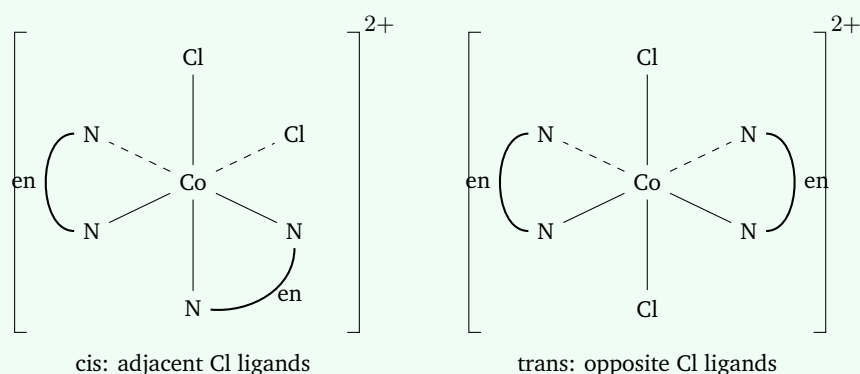
[3 marks]

Solution:

Concept:

- Ethane-1,2-diamine (en) is bidentate, binding through two adjacent nitrogen donors. Two en and two chlorido ligands form an octahedral complex with cis and trans isomers.
- Optical activity requires chirality. An isomer with a plane of symmetry is superimposable on its mirror image and is optically inactive.

Step 1: Draw the cis and trans arrangements in part (a) In the cis isomer the two chlorido ligands occupy adjacent sites, with a 90° angle at cobalt. In the trans isomer they occupy opposite sites, with a 180° angle. In the sketches, each curved link joins the two nitrogen donors of one en ligand. Solid and dashed bonds distinguish the front and rear equatorial sites; the vertical bonds are axial.



Octahedral cis and trans isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$; each curved en link represents one bidentate ligand.

Step 2: Identify the optically inactive isomer The trans isomer has a plane of symmetry through cobalt and the four equatorial nitrogen donors. The plane exchanges the axial chlorido ligands. The mirror image is superimposable, so the trans isomer is optically inactive. The cis arrangement lacks this symmetry and exists as a pair of non-superimposable mirror images, each of which is optically active.

Step 3: Determine the electronic configuration in part (b) For $[\text{CoF}_6]^{3-}$, write the oxidation-state equation $x + 6(-1) = -3$, giving $x = +3$. Neutral cobalt is $[\text{Ar}] 3d^7 4s^2$; removing the two $4s$ electrons and one $3d$ electron gives Co^{3+} with $3d^6$.

Step 4: Establish hybridisation and magnetic behaviour Since F^- is a weak-field ligand, the complex is high spin. The octahedral occupancy is $t_{2g}^4 e_g^2$, with four unpaired electrons. Two inner $3d$ orbitals are not available for hybridisation, so one $4s$, three $4p$ and two $4d$ orbitals form sp^3d^2 hybrids. Thus it is an outer-orbital octahedral complex. Its four unpaired electrons make it paramagnetic.

Step 5: Conclusion (a) The trans isomer is optically inactive due to its symmetry plane. (b) $[\text{CoF}_6]^{3-}$ has sp^3d^2 hybridisation and is paramagnetic with four unpaired electrons.

Quick Tip to Solve: Compare the chlorido positions for cis/trans; then treat the fluoride complex separately by finding cobalt's oxidation state before counting unpaired electrons.

Section D (8 marks)

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

31. 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.

Answer the following:

[4 marks]

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

[1 mark]

Solution:

Concept:

- Acid-catalysed addition of an alcohol to an aldehyde first produces a hemiacetal, having one hydroxyl and one alkoxy group on the same carbon.
- With excess alcohol and dry HCl, the hemiacetal reacts further to give an acetal with two alkoxy groups on that carbon.

Step 1: Recognise the first addition product The acid activates the carbonyl group for attack by alcohol. For example, addition of one ethanol molecule gives RCH(OH)(OC₂H₅), a hemiacetal. This is the intermediate, since the question specifies excess alcohol.

Step 2: Replace the hydroxyl group with a second alkoxy group The hemiacetal reacts with another alcohol molecule under acidic conditions, eliminating water. Using ethanol as the alcohol, the overall reaction is



The two alkoxy groups are attached to the former carbonyl carbon, which still bears its aldehydic hydrogen.

Step 3: Conclusion The product is an **acetal**; with ethanol it is RCH(OC₂H₅)₂.

Quick Tip to Solve: The words excess alcohol identify the acetal; stop at the hemiacetal only when one alcohol addition is being considered.

31(b). Why carboxylic acid is a stronger acid than phenol?

[1 mark]

Solution:

Concept:

- Acid strength increases with the stability of the conjugate base formed by loss of a proton.
- Resonance delocalisation is especially effective when equivalent contributors place negative charge

Quick Tip to Solve: Compare where the negative charge resides: sharing it between two oxygen atoms stabilises a conjugate base better than spreading it onto ring carbons.

on electronegative oxygen atoms.

Step 1: Compare the conjugate bases A carboxylic acid loses a proton to form a carboxylate ion, RCOO^- . Its two equivalent principal resonance contributors share the negative charge between two oxygen atoms, strongly stabilising the ion.

Step 2: Examine phenoxide resonance Phenol forms the phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$. Its resonance contributors are not equivalent: some place negative charge on the less electronegative ring carbon atoms. Thus its resonance stabilisation is less effective than that of a carboxylate ion.

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

Quick Tip to Solve: Compare where the negative charge resides: sharing it between two oxygen atoms stabilises a conjugate base better than spreading it onto ring carbons.

31(c). (i) Arrange the following compounds in increasing order of their reactivity towards CH_3MgBr : CH_3CHO , $(\text{CH}_3)_3\text{C-CO-CH}_3$, $\text{CH}_3\text{-CO-CH}_3$

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

[2 marks]

Solution:

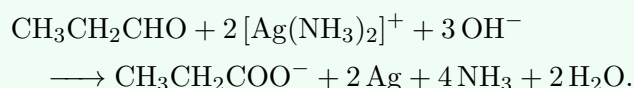
Concept:

- Grignard reagents add to the electrophilic carbonyl carbon. Alkyl groups reduce its electrophilicity by their electron-releasing effect and obstruct nucleophilic attack through steric hindrance.
- Tollens' reagent oxidises an aldehyde to a carboxylate ion while silver(I) is reduced to metallic silver. An ordinary ketone does not give this test.

Step 1: (i) Compare electronic and steric effects Ethanal, CH_3CHO , has only one alkyl group attached to its carbonyl carbon and is more reactive than either ketone. Of the ketones, $(\text{CH}_3)_3\text{C-CO-CH}_3$ contains a bulky tert-butyl group, which hinders attack much more than a methyl group in propanone. The increasing order is



Step 2: (ii) Apply Tollens' test Warm separate samples with freshly prepared Tollens' reagent. Propanal gives a silver mirror on the inner wall of the test tube, whereas propanone gives no silver mirror. The oxidation-reduction equation is

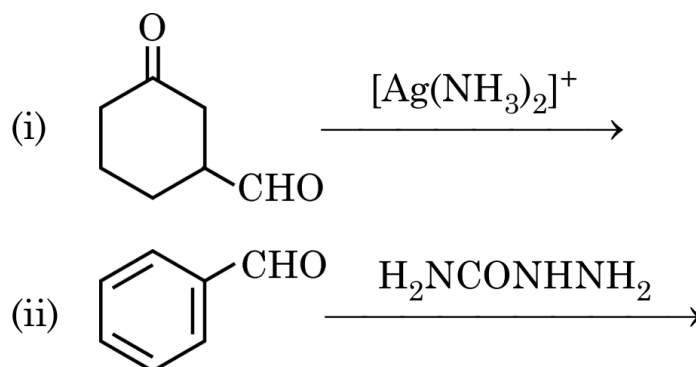


Step 3: Conclusion (i) Increasing reactivity: $(\text{CH}_3)_3\text{C-CO-CH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO}$. (ii) Propanal gives a positive silver-mirror test with Tollens' reagent; propanone does not.

Quick Tip to Solve: For carbonyl addition, first place aldehydes above ketones, then compare crowding among the ketones; use Tollens' reagent to identify the aldehyde.

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

[2 marks]



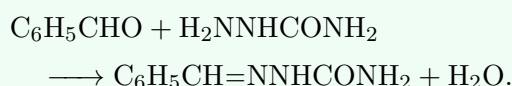
Solution:

Concept:

- Tollens' reagent, $[\text{Ag}(\text{NH}_3)_2]^+$ in alkaline solution, selectively oxidises an aldehyde group to a carboxylate group; an ordinary ketone group remains unchanged.
- Semicarbazide, $\text{H}_2\text{N}-\text{NH}-\text{CO}-\text{NH}_2$, condenses through its terminal hydrazino $-\text{NH}_2$ group with a carbonyl compound, eliminating water and forming a semicarbazone.

Step 1: (i) Oxidise only the aldehyde group The ring contains a ketone group and an aldehyde substituent. Tollens' reagent changes the $-\text{CHO}$ substituent into $-\text{COO}^-$, while preserving the ring ketone and all carbon-carbon bonds. The organic product in the alkaline reagent is 3-oxocyclohexane-1-carboxylate. On acidification, this gives 3-oxocyclohexane-1-carboxylic acid: the same cyclohexanone ring with $-\text{COOH}$ replacing $-\text{CHO}$ at its original position. Silver metal is also deposited.

Step 2: (ii) Form the benzaldehyde semicarbazone Benzaldehyde reacts with the terminal hydrazino amino group of semicarbazide. Its carbonyl oxygen is removed as water and a carbon-nitrogen double bond is formed:



The amide $-\text{CONH}_2$ group remains unchanged because its nitrogen lone pair is delocalised into its own carbonyl group.

Step 3: Conclusion (i) The aldehyde becomes a carboxylate, giving 3-oxocyclohexane-1-carboxylate (3-oxocyclohexane-1-carboxylic acid after acidification); the ring ketone is unchanged. (ii) The product is benzaldehyde semicarbazone, $\text{C}_6\text{H}_5\text{CH}=\text{NNHCONH}_2$.

Quick Tip to Solve: With Tollens' reagent, replace only the aldehyde group; with semicarbazide, replace carbonyl oxygen by $=\text{NNHCONH}_2$ while retaining the carbon skeleton.

32. 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.

Answer the following:

[4 marks]

32(a). The penta-acetate of glucose does not react with Hydroxylamine. What does it indicate?

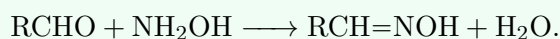
[1 mark]

Solution:

Concept:

- Hydroxylamine, NH_2OH , reacts with a free aldehyde or ketone carbonyl group to produce an oxime.
- In cyclic glucose penta-acetate, acetylation of the anomeric hydroxyl group locks the cyclic acetal structure, so a free aldehyde group is unavailable.

Step 1: Identify what hydroxylamine detects A free aldehyde would undergo condensation with hydroxylamine:



Thus oxime formation requires an available carbonyl group.

Step 2: Interpret the negative reaction Glucose penta-acetate does not form an oxime. This shows that it has no free aldehydic carbonyl group. Its aldehydic carbon is incorporated in the cyclic acetal structure, supporting the cyclic structure of glucose.

Step 3: Conclusion The non-reaction indicates the absence of a free $-\text{CHO}$ group in glucose penta-acetate and supports a cyclic structure for glucose.

Quick Tip to Solve: Hydroxylamine tests for an available carbonyl group; acetylation at the anomeric centre prevents glucose penta-acetate from exposing an aldehyde group.

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

[1 mark]

Solution:

Concept:

- Vitamins are classified as water-soluble or fat-soluble according to their solubility.
- Vitamin C is water-soluble; an excess is readily eliminated from the body in urine instead of being stored as a substantial long-term reserve.

Step 1: Identify vitamin C's solubility Vitamin C, also called ascorbic acid, belongs to the water-soluble group of vitamins. It dissolves in the aqueous fluids of the body and does not build up in fatty tissues as fat-soluble vitamins can.

Step 2: Relate solubility to excretion The excess dissolved vitamin is excreted through urine. Conse-

Quick Tip to Solve: Link the answer in order: vitamin C is water-soluble, excess leaves in urine, and therefore regular dietary intake is needed.

quently, the body cannot retain an adequate long-term store of vitamin C, and it must be supplied regularly through the diet.

Step 3: Conclusion Vitamin C cannot be stored as a substantial long-term reserve because it is water-soluble and its excess is readily excreted in urine.

Quick Tip to Solve: Link the answer in order: vitamin C is water-soluble, excess leaves in urine, and therefore regular dietary intake is needed.

32(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 covalent peptide bonds.
- A protein's biological activity depends on its specific three-dimensional structure, maintained by interactions between its amino acid residues.

Step 1: Define peptide linkage A peptide linkage is the amide linkage $-\text{CO}-\text{NH}-$ formed when the carboxyl group of one amino acid reacts with the amino group of another amino acid, with elimination of one molecule of water. Repetition of this condensation joins amino acids into a polypeptide chain.

Step 2: Define denaturation Denaturation is the loss of a protein's native conformation and biological activity under the action of heat, a change in pH or other denaturing agents. The interactions maintaining its secondary and tertiary structures are disrupted, while its primary structure, namely the amino acid sequence linked by peptide bonds, remains intact. Coagulation of egg white on boiling is an example.

Step 3: Conclusion Peptide linkage is the $-\text{CO}-\text{NH}-$ bond connecting amino acid residues; denaturation is loss of native protein structure and activity without breaking its primary peptide chain.

Quick Tip to Solve: Distinguish denaturation from hydrolysis: denaturation changes folding, whereas hydrolysis breaks peptide bonds.

32(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 the anomeric carbon, allowing two configurations at this centre.
- Monosaccharide units can join through an oxygen atom by condensation, with elimination of water.

Step 1: Define anomers Anomers are cyclic stereoisomers of the same sugar that differ only in the configuration at the anomeric carbon. For glucose this is carbon 1, the carbon derived from the aldehyde group. Thus α -D-glucose and β -D-glucose are anomers; they differ in the orientation of the hydroxyl group attached to carbon 1, while the other stereocentres retain the same configuration.

Step 2: Define glycosidic linkage A glycosidic linkage is the oxygen bridge joining two monosaccharide units through condensation of hydroxyl groups, with loss of a water molecule. It involves the anomeric carbon of at least one sugar unit. For example, maltose contains an $\alpha(1 \rightarrow 4)$ glycosidic linkage connecting carbon 1 of one glucose unit to carbon 4 of the other through oxygen.

Step 3: Conclusion Anomers differ only at the anomeric carbon, whereas a glycosidic linkage is the oxygen bridge connecting monosaccharide units in a carbohydrate.

Quick Tip to Solve: For glucose anomers, compare carbon 1 only; in a glycosidic linkage, identify the two carbon numbers joined through oxygen.

Section E (15 marks)

33(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 indicates a greater tendency to accept electrons. Relative electronic stability helps explain this trend.
- Colour in aqueous transition-metal ions commonly arises from d-d transitions; variable oxidation states arise from participation of different numbers of valence electrons.

Step 1: (I)(i) Compare electronic stability Reduction changes Mn^{3+} , $3d^4$, into Mn^{2+} , with the especially stable half-filled $3d^5$ configuration. This gain in stability favours electron acceptance. In

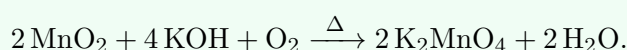
Quick Tip to Solve: Compare d-electron counts first; for permanganate preparation, track manganese through $+4 \rightarrow +6 \rightarrow +7$.

contrast, aqueous Cr^{3+} already has the stable $3d^3$ configuration, with three electrons in the lower-energy t_{2g} orbitals. Its reduction to Cr^{2+} , $3d^4$, is less favourable. Thus E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is much more positive than for $\text{Cr}^{3+}/\text{Cr}^{2+}$.

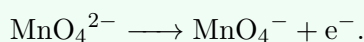
Step 2: (I)(ii) Explain the colour difference Sc^{3+} has configuration $[\text{Ar}]3d^0$, so it has no d electron for a d-d transition and is colourless. Ti^{3+} has configuration $[\text{Ar}]3d^1$. Water ligands split its d orbitals into groups of different energies. Absorption of visible light promotes its electron to a higher-energy d orbital, making the aqueous ion coloured.

Step 3: (I)(iii) Explain actinoid oxidation states The $5f$, $6d$ and $7s$ subshells have comparable energies. Different numbers of electrons from these subshells can therefore participate in bonding or be removed. This produces a wide range of oxidation states, particularly among the early actinoids.

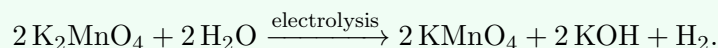
Step 4: (II) Form potassium manganate Fuse MnO_2 with potassium hydroxide in air or oxygen. Manganese is oxidised from +4 to +6, producing green potassium manganate:



Step 5: Oxidise manganate to permanganate Electrolytic oxidation of alkaline potassium manganate solution gives purple potassium permanganate. Manganese changes from +6 to +7 at the anode:



With reduction of water at the cathode, the overall equation is



Step 6: Conclusion Electronic stability explains the reduction potentials; d^0 and d^1 configurations explain the colours. Closely spaced actinoid valence subshells allow variable oxidation states. Oxidative fusion and electrolysis convert MnO_2 into KMnO_4 .

Quick Tip to Solve: Compare d-electron counts first; for permanganate preparation, track manganese through $+4 \rightarrow +6 \rightarrow +7$.

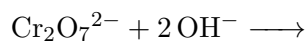
33(b). (I) Account for the following:

(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]

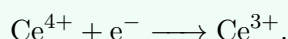
Solution:

Concept:

- An alloy is a metallic mixture, often a solid solution in which atoms of one metal replace atoms of another in its crystal lattice.
- An oxidising agent accepts electrons and is reduced. The tendency of Ce^{4+} to accept an electron is described by the $\text{Ce}^{4+}/\text{Ce}^{3+}$ reduction potential.
- Lanthanoids and actinoids are inner-transition series with progressive filling of the $4f$ and $5f$ subshells, respectively.
- Chromate and dichromate interconvert with a change of pH; chromium remains in oxidation state +6 in both ions.

Step 1: (I)(i) Explain alloy formation Transition metals have similar atomic radii and often similar crystal structures. Hence atoms of one transition metal can substitute for atoms of another in the metallic lattice without greatly disturbing it. Metallic bonding is retained, allowing the formation of solid solutions or alloys. For example, copper and nickel form alloys because their atoms have comparable sizes.

Step 2: (I)(ii) Explain the oxidising action of cerium(IV) The +3 state is the more stable common oxidation state of cerium in aqueous solution. Although Ce^{4+} has a $4f^0$ configuration, it readily accepts one electron to form Ce^{3+} :

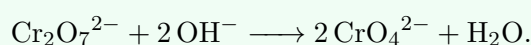


The standard reduction potential of this couple is highly positive. Thus, Ce^{4+} has a strong tendency to undergo reduction and oxidises other species by accepting their electrons.

Step 3: (II) Compare the two inner-transition series Similarity: Both lanthanoids and actinoids commonly show the +3 oxidation state. In each series, the two outer s electrons and one additional electron can be removed to form tripositive ions.

Difference: Lanthanoids predominantly show +3, with only a few ions in +2 or +4. Actinoids show a much wider range of oxidation states, particularly among the early members. Their $5f$, $6d$ and $7s$ orbitals have comparable energies, so different numbers of electrons can participate in bonding.

Step 4: (III) Complete and check the ionic equation Addition of hydroxide changes orange dichromate ions into yellow chromate ions:



Quick Tip to Solve: For dichromate in alkali, put two chromate ions on the product side, then use water to balance hydrogen and oxygen and check the net charge.

There are two chromium atoms, nine oxygen atoms and two hydrogen atoms on each side. The total charge is -4 on both sides. No electron transfer occurs: this is the alkaline shift of the chromate–dichromate equilibrium, not a redox reaction.

Step 5: Conclusion Similar atomic sizes favour alloy formation; Ce^{4+} strongly oxidises by reduction to Ce^{3+} . Both inner-transition series commonly form $+3$ ions, but actinoids show more varied oxidation states. The missing products are $2\text{CrO}_4^{2-} + \text{H}_2\text{O}$.

Quick Tip to Solve: For dichromate in alkali, put two chromate ions on the product side, then use water to balance hydrogen and oxygen and check the net charge.

34(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) Carbyl amine test

(ii) Gabriel phthalimide synthesis

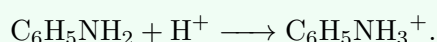
[5 marks]

Solution:

Concept:

- The directing influence of an amino group changes on protonation: $-\text{NH}_2$ donates electron density by resonance, whereas $-\text{NH}_3^+$ withdraws electron density.
- Aqueous basicity depends on the electron-donating effect of alkyl groups and the hydration and steric accessibility of the amine and its conjugate acid.
- Primary amines undergo the carbylamine test; Gabriel synthesis uses the phthalimide anion to obtain primary alkylamines without repeated alkylation.

Step 1: (I)(i) Explain meta substitution during nitration The nitrating mixture of concentrated nitric and sulphuric acids is strongly acidic. It protonates much of the aniline to form the anilinium ion:



In aniline, the nitrogen lone pair donates into the ring, making $-\text{NH}_2$ ortho/para directing. In the anilinium ion that lone pair is no longer available for resonance donation. The positively charged $-\text{NH}_3^+$ group is strongly deactivating and meta directing. Consequently, direct nitration gives a substantial amount of meta-nitroaniline after work-up, alongside the ortho and para products formed from unprotonated aniline.

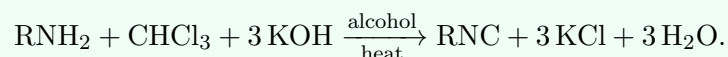
Step 2: (I)(ii) Compare basicity in water Methyl groups increase nitrogen's electron density by their positive inductive effect, which favours proton acceptance. However, hydration also stabilises the protonated amine in water. The conjugate acid $(\text{CH}_3)_2\text{NH}_2^+$ has less steric crowding and is better hydrated than $(\text{CH}_3)_3\text{NH}^+$. This hydration advantage outweighs the extra inductive effect of the third

Quick Tip to Solve: Before predicting directing effects, check whether nitrogen is protonated. In aqueous basicity comparisons, include hydration as well as the alkyl groups' inductive effect.

methyl group. Hence dimethylamine is more basic than trimethylamine in aqueous solution.

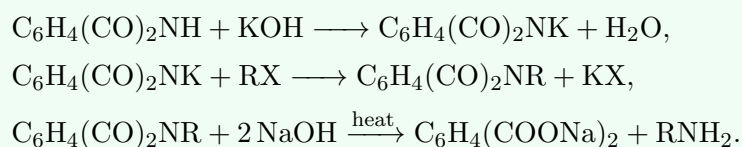
Step 3: (I)(iii) Explain why ammonolysis gives a mixture Ammonia first reacts with an alkyl halide to produce a primary amine. The primary amine still has a lone pair and is itself a nucleophile; it reacts further with the alkyl halide. Successive alkylations produce secondary and tertiary amines and finally a quaternary ammonium salt. The reaction therefore gives a mixture that is difficult to separate, rather than a pure primary amine. A large excess of ammonia favours the primary product but does not make the method completely selective.

Step 4: (II)(i) Write the carbylamine reaction A primary aliphatic or aromatic amine is heated with chloroform and alcoholic potassium hydroxide. It gives an isocyanide with an extremely unpleasant smell:



Here R is an alkyl or aryl group and RNC is the isocyanide. Secondary and tertiary amines do not give this test because they do not possess the required primary amino group.

Step 5: (II)(ii) Write the Gabriel synthesis sequence Phthalimide reacts with ethanolic potassium hydroxide to form potassium phthalimide. Its nitrogen anion then displaces halide from a primary alkyl halide RX , producing an N -alkylphthalimide. Hydrolysis releases the primary amine:



The two carbonyl groups shown in each phthalimide formula belong to its cyclic imide group; the product $\text{C}_6\text{H}_4(\text{COONa})_2$ is disodium phthalate. Alkylation occurs once at nitrogen before hydrolysis, so a primary amine is obtained without secondary or tertiary amine contamination. Aryl halides do not undergo the required nucleophilic substitution readily, so this method does not prepare aniline.

Step 6: Conclusion Anilinium formation explains the meta nitration product; better hydration makes dimethylamine more basic in water; repeated alkylation makes ammonolysis unselective. The carbylamine test forms RNC , whereas Gabriel synthesis releases a primary alkylamine, RNH_2 , by hydrolysis.

Quick Tip to Solve: Before predicting directing effects, check whether nitrogen is protonated. In aqueous basicity comparisons, include hydration as well as the alkyl groups' inductive effect.

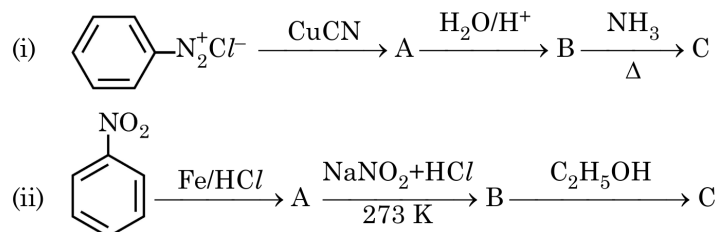
34(b). (I) Write the structures of A, B and C in the following reactions (i) and (ii):

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

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

C_2H_5OH , $C_2H_5NH_2$, $(C_2H_5)_3N$

[5 marks]



Solution:

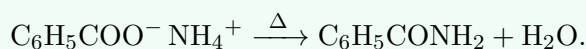
Concept:

- A diazonium group can be replaced by $-CN$ using $CuCN$; acidic hydrolysis converts a nitrile into a carboxylic acid, which forms an amide on heating with ammonia.
- Reduction converts $-NO_2$ into $-NH_2$. Diazotisation with $NaNO_2/HCl$ at 273 K gives a diazonium salt; ethanol then replaces the diazonium group by hydrogen.
- A Lewis-acid catalyst can bind the nitrogen lone pair of aniline. Boiling points depend jointly on hydrogen bonding, molecular size and dispersion forces.

Step 1: (I)(i) Follow cyanation, hydrolysis and amide formation $CuCN$ replaces the diazonium group with a carbon-bonded cyanide group, releasing nitrogen. Thus A is benzonitrile, $C_6H_5-C\equiv N$. Hydrolysis of its nitrile group gives B, benzoic acid, $C_6H_5-C(=O)-OH$:

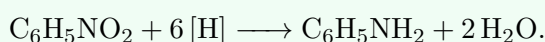


Benzoic acid first reacts with ammonia to give ammonium benzoate. Heating removes water from this salt and produces C, benzamide, $C_6H_5-C(=O)-NH_2$:



The additional carbon introduced by cyanation remains the carbonyl carbon in B and C.

Step 2: (I)(ii) Follow reduction, diazotisation and deamination Iron and hydrochloric acid reduce nitrobenzene to A, aniline, $C_6H_5-NH_2$. Treatment with nitrous acid generated from $NaNO_2$ and HCl at 273 K gives B, benzenediazonium chloride, $C_6H_5-N\equiv N^+ Cl^-$:



Ethanol acts as a reducing agent, replacing the diazonium group by H. C is therefore benzene, C_6H_6 ,

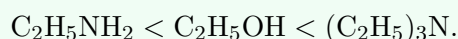
Quick Tip to Solve: Track the carbon introduced by $CuCN$: it becomes the acid and then the amide carbonyl. Compare molecular size as well as hydrogen bonding when ranking triethylamine.

while ethanol is oxidised to ethanal:



Step 3: (II) Explain why the Friedel-Crafts reaction fails Aniline is a Lewis base because its nitrogen has a lone pair. It reacts with the Lewis-acid catalyst AlCl_3 to form a salt-like coordination complex. Nitrogen consequently acquires positive character and its lone pair becomes unavailable for donation into the benzene ring. The complex strongly deactivates the ring towards electrophilic substitution and also ties up the catalyst, so aniline does not undergo the usual Friedel-Crafts alkylation or acylation.

Step 4: (III) Compare the intermolecular attractions Ethylamine has weaker intermolecular hydrogen bonding than ethanol because nitrogen is less electronegative than oxygen; ethylamine therefore boils below ethanol. Triethylamine has no N–H bond and cannot hydrogen-bond to itself, but its much larger molecular size and electron cloud give substantially stronger dispersion forces. For these particular compounds that size effect makes its boiling point exceed that of ethanol. Thus the increasing order is

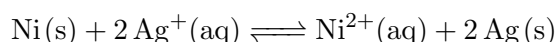


Step 5: Conclusion (I)(i) $\text{A} = \text{C}_6\text{H}_5\text{CN}$, $\text{B} = \text{C}_6\text{H}_5\text{COOH}$, $\text{C} = \text{C}_6\text{H}_5\text{CONH}_2$; (ii) $\text{A} = \text{C}_6\text{H}_5\text{NH}_2$, $\text{B} = \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, $\text{C} = \text{C}_6\text{H}_6$. (II) Aniline complexes with AlCl_3 , deactivating its ring. (III) $\text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH} < (\text{C}_2\text{H}_5)_3\text{N}$.

Quick Tip to Solve: Track the carbon introduced by CuCN : it becomes the acid and then the amide carbonyl. Compare molecular size as well as hydrogen bonding when ranking triethylamine.

35. (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 the $\Delta_r G^\circ$ and $\log K_c$ for the given reaction at 298 K:



Given: $E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}$, $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$.

$1F = 96500 \text{ C mol}^{-1}$.

[5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} . For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.
- The standard cell potential is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using reduction potentials for both electrodes. The standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons transferred and F is the Faraday constant.
- The equilibrium constant satisfies $\Delta_r G^\circ = -2.303RT \log K_c$. At 298 K, this gives $\log K_c = nE_{\text{cell}}^\circ/0.0591$, where the logarithm is to base ten and the potential is in volts.

Quick Tip to Solve: Keep the factor 1000 in the conductivity formula. For the cell, count two electrons and subtract the negative nickel reduction potential; do not double the silver electrode potential.

Step 1: (a) Calculate the molar conductivity Substitute $\kappa = 8 \times 10^{-5} \text{ S cm}^{-1}$ and $c = 2 \times 10^{-3} \text{ mol L}^{-1}$. The factor 1000 converts the litre-based concentration to the cubic-centimetre convention needed for the given conductivity:

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

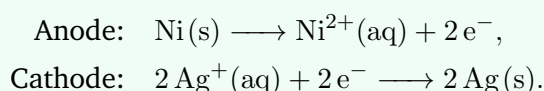
This is the conductivity contribution per mole at the stated concentration, rather than the limiting value at infinite dilution.

Step 2: (a) Obtain the fraction dissociated Methanoic acid is a weak electrolyte. At infinite dilution it approaches complete dissociation; the ratio of its molar conductivity at the given concentration to its limiting value estimates 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 $100\alpha = 9.90\%$; the remaining acid is predominantly undissociated.

Step 3: (b) Identify the electrodes and electron transfer Nickel loses two electrons, whereas each silver ion gains one electron:



Thus $n = 2$. Silver has the higher reduction potential and is reduced. Using the given reduction potentials without multiplying either potential by its stoichiometric coefficient,

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

Step 4: (b) Calculate the standard Gibbs energy and equilibrium constant Apply the Gibbs-energy relation with $F = 96500 \text{ C mol}^{-1}$:

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

At 298 K, the Nernst equilibrium relation gives

$$\log K_c = \frac{2(1.05)}{0.0591} \approx 35.53.$$

The negative Gibbs energy and the very large positive logarithm agree: the forward reaction is thermodynamically favourable under standard conditions and its equilibrium lies strongly towards products. Using a more precise thermal factor gives about 35.52, equivalent at the stated precision.

Step 5: 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 $\log K_c \approx 35.53$ at 298 K.

Quick Tip to Solve: Keep the factor 1000 in the conductivity formula. For the cell, count two electrons and subtract the negative nickel reduction potential; do not double the silver electrode potential.