CBSE Class 12 Chemistry Question Paper 2017 with Solution PDF-Set 56-1-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) All questions are compulsory.
(ii) Questions number **1** to **5** are very short-answer questions and carry **1** mark each.
(iii) Questions number **6** to **10** are short-answer questions and carry **2** marks each.
(iv) Questions number **11** to **22** are also short-answer questions and carry **3** marks each.
(v) Question number **23** is a value based question and carry **4** marks.
(vi) Questions number **24** to **26** are long-answer questions and carry **5** marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Write the formula of an oxo-anion of Manganese (Mn) in which it shows the oxidation state equal to its group number. [1 mark]

Solution:

Concept:

- Manganese is in group 7 of the modern periodic table, so the required oxidation state is $+7$.
- In an oxo-anion, oxygen normally has oxidation state -2; the sum of oxidation states equals the charge on the ion.

Step 1: Identify the appropriate oxo-anion The permanganate ion contains one manganese atom and four oxygen atoms. Its formula is $\mathrm{MnO_4^-}$, so the charge on the whole ion is -1.

Step 2: Verify the oxidation state Let the oxidation state of Mn be x. Then

$$x + 4(-2) = -1 \quad \Rightarrow \quad x = +7.$$

This equals the group number of Mn. Manganate, $\mathrm{MnO_4^{2-}}$, instead has Mn in the $+6$ state and does not meet the requirement.

Step 3: Conclusion The required oxo-anion is permanganate, $\boxed{\mathrm{MnO_4^-}}$.

Quick Tip to Solve: Check the ion charge: four oxide oxygens require Mn to be $+7$ only when the total charge is -1.

2. Write IUPAC name of the following compound:

$(CH_3CH_2)_2NCH_3$ [1 mark]

Solution:

Concept:

- For an amine, choose a carbon chain bonded to nitrogen as the parent alkanamine; substituents directly attached to nitrogen receive the locant N.
- List different nitrogen substituents alphabetically before the parent name.

Step 1: Choose the parent chain The nitrogen in $(\mathrm{CH_3CH_2})_2\mathrm{NCH_3}$ is bonded to two ethyl groups and one methyl group. Choose one of the two identical ethyl groups as the parent chain. Its two-carbon amine parent is ethanamine.

Step 2: Name the nitrogen substituents After selecting the parent ethyl group, the remaining groups on nitrogen are one ethyl group and one methyl group. Both use the locant N, because they are attached to nitrogen rather than a parent-chain carbon. Place ethyl before methyl in alphabetical order.

Step 3: Conclusion The IUPAC name is $\boxed{N\text{-ethyl-}N\text{-methylethanamine}}$.

Quick Tip to Solve: Expand the brackets first: nitrogen carries ethyl, ethyl and methyl, so one ethyl supplies the parent.

3. For a reaction R $\rightarrow$ P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction? [1 mark]

Solution:

Concept:

- Half-life $t_{1/2}$ is the time required for reactant concentration to fall to half its initial value.
- For a first-order reaction with rate constant k, $t_{1/2} = \ln 2/k$, which does not contain the initial concentration.

Step 1: Apply the first-order integrated rate equation For a first-order reaction,

$$kt = \ln\left(\frac{[R]_0}{[R]}\right),$$

where $[R]_0$ and $[R]$ are the initial and remaining reactant concentrations. At the half-life, $[R] = [R]_0/2$.

Step 2: Check the concentration dependence Substitution gives

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

The initial concentration cancels completely. Thus, at a fixed temperature, equal half-lives occur for different initial concentrations, which is the characteristic first-order behaviour.

Step 3: Conclusion The reaction is $\boxed{\text{first order}}$.

Quick Tip to Solve: An initial-concentration-independent half-life is the direct signature of a first-order rate law.

4. Write the structure of 1-Bromo-4-chlorobut-2-ene. [1 mark]

Solution:

Concept:

- The parent name but-2-ene specifies a four-carbon chain with a double bond between carbons 2 and 3.
- The locants 1-bromo and 4-chloro place Br and Cl on the two terminal carbon atoms respectively.

Step 1: Build the parent carbon chain Number the four-carbon skeleton from 1 to 4 and insert the double bond indicated by the locant 2:

$$\mathrm{C_1 - C_2 = C_3 - C_4}.$$

The internal double-bond carbons each retain one hydrogen when their valence of four is completed.

Step 2: Attach the halogens Attach Br to carbon 1 and Cl to carbon 4. Each terminal carbon then has two hydrogen atoms, one bond to the adjacent carbon and one bond to its halogen. Thus the condensed structure is $\mathrm{BrCH_2 - CH = CH - CH_2Cl}$. The name does not specify a particular geometrical configuration.

Quick Tip to Solve: Write the four-carbon double-bond skeleton before placing the terminal halogens at locants 1 and 4.

Step 3: Conclusion The required structure is $\boxed{BrCH_2 - CH = CH - CH_2Cl}$.

Quick Tip to Solve: Write the four-carbon double-bond skeleton before placing the terminal halogens at locants 1 and 4.

5. Write one similarity between Physisorption and Chemisorption. [1 mark]

Solution:

Concept:

- Physisorption involves weak intermolecular attractions, whereas chemisorption involves chemical bond formation at a surface.
- Both processes can lower the energy of the adsorbent-adsorbate system and therefore release heat.

Step 1: Identify the shared property A suitable similarity is that both physisorption and chemisorption are exothermic processes. In either case, adsorption is accompanied by the release of heat as the adsorbate becomes attached to the surface.

Step 2: Explain why heat is released Attractive interactions between the surface and adsorbate lower the energy of the system. Energy is therefore given out to the surroundings, so the enthalpy change for adsorption is negative, $\Delta H_{ads} < 0$. The magnitude of this heat and the nature of the interactions differ, but the exothermic character is common to both.

Step 3: Conclusion One similarity is that $\boxed{\text{both physisorption and chemisorption are exothermic}}$.

Quick Tip to Solve: Use a shared thermodynamic property: both release heat even though their bonding strengths differ.

6(a). Complete the following reactions:

(i) NH_3 + 3Cl_2 (excess) $\longrightarrow$

(ii) XeF_6 + 2H_2O $\longrightarrow$ [2 marks]

Solution:

Concept:

- With chlorine in excess, ammonia forms nitrogen trichloride; the product depends on which reactant is in excess.
- Partial hydrolysis of xenon hexafluoride replaces pairs of fluorine atoms by oxygen, with hydrogen fluoride released.

Step 1: Complete the reaction with excess chlorine Excess chlorine converts ammonia to nitrogen trichloride rather than leaving ammonia available to give the usual excess-ammonia products. The balanced equation is

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl.$$

There is one N atom, three H atoms and six Cl atoms on each side, confirming the coefficients.

Quick Tip to Solve: Check the excess reactant in ammonia-chlorine reactions; for XeF6, each water replaces two F atoms by one O.

Step 2: Complete the partial hydrolysis of xenon hexafluoride Two molecules of water supply two oxygen atoms. Four fluorine atoms are removed as four molecules of HF, while two remain attached to xenon. Therefore

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF.$$

The product is xenon dioxydifluoride. Atom counts are Xe: 1, F: 6, H: 4 and O: 2 on either side. Complete hydrolysis would require three water molecules and form XeO_3; the stated two water molecules correspond to partial hydrolysis.

Step 3: Conclusion $\boxed{NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl}$

$\boxed{XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF}$

Quick Tip to Solve: Check the excess reactant in ammonia-chlorine reactions; for XeF6, each water replaces two F atoms by one O.

OR

6(b). What happens when

(i) $(NH_4)_2Cr_2O_7$ is heated?

(ii) H_3PO_3 is heated?

Write the equations. [2 marks]

Solution:

Concept:

- Heating ammonium dichromate causes thermal decomposition: nitrogen and steam escape, leaving chromium(III) oxide as a solid residue.
- Phosphorous acid, H_3PO_3, undergoes disproportionation on heating. Phosphorus in oxidation state $+3$ is simultaneously oxidised to $+5$ and reduced to -3.

Step 1: Write the decomposition of ammonium dichromate On heating, orange $(NH_4)_2Cr_2O_7$ decomposes to green Cr_2O_3, nitrogen gas and water vapour:

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4\,H_2O.$$

The equation conserves two nitrogen atoms, eight hydrogen atoms, two chromium atoms and seven oxygen atoms. The escaping gases account for the expansion of the green residue.

Step 2: Write the disproportionation of phosphorous acid Heating H_3PO_3 produces phosphoric acid and phosphine:

$$4\,H_3PO_3 \xrightarrow{\Delta} 3\,H_3PO_4 + PH_3.$$

Three phosphorus atoms increase their oxidation state from $+3$ to $+5$, losing six electrons in total; one changes from $+3$ to -3, gaining six electrons. Thus both atom balance and electron balance support these coefficients.

Step 3: Conclusion (i) $(NH_4)_2Cr_2O_7$ forms green Cr_2O_3, N_2 and steam. (ii) H_3PO_3 forms H_3PO_4 and

Quick Tip to Solve: For heated H_3PO_3, balance phosphorus oxidation states first: three atoms are oxidised for each one reduced, giving the ratio $4 : 3 : 1$.

PH_3, in the balanced equations above.

Quick Tip to Solve: For heated H_3PO_3, balance phosphorus oxidation states first: three atoms are oxidised for each one reduced, giving the ratio $4 : 3 : 1$.

7. Define the following terms:

(i) Colligative properties

(ii) Molality (m) [2 marks]

Solution:

Concept:

- A dilute solution's colligative properties depend on the number of dissolved solute particles relative to the solvent, rather than the chemical nature of the solute particles.
- Molality is a concentration measure based on solvent mass: $m = n_{\text{solute}}/w_{\text{solvent}}$, where n is in moles and w is in kilograms.

Step 1: Define colligative properties Colligative properties are properties of dilute solutions that depend only on the number of solute particles present and not on their nature. Examples are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. When comparing solutions, the actual particle number must include any dissociation or association of the solute.

Step 2: Define molality Molality (m) is the number of moles of solute dissolved in one kilogram of solvent:

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}.$$

Its unit is mol kg^{-1}. The denominator is the mass of the solvent alone, rather than the mass or volume of the solution. Because mass does not change with temperature, molality is independent of temperature.

Step 3: Conclusion (i) Colligative properties depend on solute particle number, not solute identity. (ii) Molality is the moles of solute per kilogram of solvent, expressed in mol kg^{-1}.

Quick Tip to Solve: In a molality calculation, convert the solvent mass from grams to kilograms and keep it separate from the total solution mass.

8. Draw the structures of the following:

(i) $H_2S_2O_7$

(ii) XeF_6 [2 marks]

Solution:

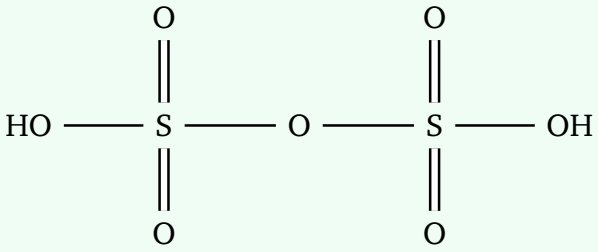
Concept:

- Disulphuric acid, $H_2S_2O_7$, has two tetrahedral sulphur centres linked by an oxygen bridge.

Quick Tip to Solve: Count seven oxygen atoms in $H_2S_2O_7$: four oxo, two hydroxyl and one bridge. For XeF_6, do not omit xenon's lone pair.

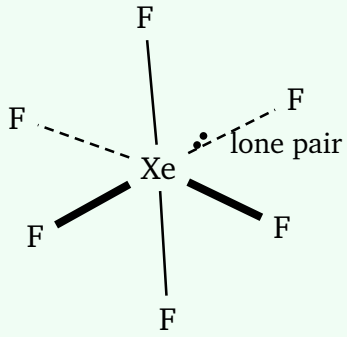
- In XeF_6, xenon has six bonding pairs and one lone pair; lone-pair repulsion produces a distorted octahedral molecular shape.

Step 1: Draw the oxygen bridge in disulphuric acid Draw $HO-S(=O)_2-O-S(=O)_2-OH$: each sulphur has two double-bonded oxygen atoms, one hydroxyl group and the bridging oxygen. The diagram shows bond connectivity; the bonds around each sulphur are tetrahedral in space. Count four oxo, two hydroxyl and one bridging oxygen to verify the formula.



$H_2S_2O_7$: two sulphur centres joined through oxygen.

Step 2: Draw the six xenon–fluorine bonds Six of xenon's eight valence electrons form six Xe–F bonds, leaving one lone pair. Thus AX_6E has a distorted octahedral shape. Dotted bonds recede behind the plane; heavy bonds project towards the observer. The two dots show the xenon lone pair.



XeF_6: distorted octahedral shape.

Step 3: Conclusion (i) $H_2S_2O_7$ has two $SO_2(OH)$ units connected by an oxygen bridge. (ii) XeF_6 has six Xe–F bonds and one xenon lone pair, giving a distorted octahedral molecular shape.

Quick Tip to Solve: Count seven oxygen atoms in $H_2S_2O_7$: four oxo, two hydroxyl and one bridge. For XeF_6, do not omit xenon's lone pair.

9. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.

Given: $\Lambda^\circ(H^+)$ = 349.6 S cm^2 mol^{-1} and $\Lambda^\circ(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1}. [2 marks]

Solution:

Concept:

- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m is its molar conductivity at the given concentration and Λ_m° is its limiting molar conductivity.
- Kohlrausch's law gives the limiting molar conductivity as the sum of the ionic contributions. For CH_3COOH, $\Lambda_m^\circ = \lambda^\circ(H^+) + \lambda^\circ(CH_3COO^-)$.

Step 1: Calculate the limiting molar conductivity Acetic acid dissociates according to $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$. Since each formula unit produces one ion of each kind, add the two given ionic molar conductivities without extra coefficients:

$$\Lambda_m^\circ = 349.6 + 40.9 = 390.5\ \text{S cm}^2\ \text{mol}^{-1}.$$

At infinite dilution, dissociation is effectively complete, so this value represents the conductivity for unit degree of dissociation.

Step 2: Form the conductivity ratio Use the observed molar conductivity $39.05\ \text{S cm}^2\ \text{mol}^{-1}$:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{39.05}{390.5} = 0.1000.$$

Both conductivities use the same units, which cancel in the ratio. The percentage dissociation is therefore $100\alpha = 10.00\%$. Only one tenth of the acid molecules are dissociated at the specified concentration.

Step 3: Conclusion The degree of dissociation of acetic acid is $\boxed{\alpha = 0.1000}$, corresponding to $\boxed{10.00\%}$ dissociation.

Quick Tip to Solve: Add the limiting ionic conductivities first, then divide the observed conductivity by their sum; degree of dissociation is a unitless fraction.

10. Write the equations involved in the following reactions:

(i) Wolff-Kishner reduction

(ii) Etard reaction [2 marks]

Solution:

Concept:

- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine followed by heating with a strong base.
- The Etard reaction selectively oxidises the methyl side chain of toluene to an aldehyde using chromyl chloride, CrO_2Cl_2, followed by hydrolysis.

Quick Tip to Solve: Remember the reagent-product pairs: hydrazine and KOH remove carbonyl oxygen, whereas chromyl chloride converts the benzylic methyl group to an aldehyde.

Step 1: (i) Wolff-Kishner reduction The carbonyl compound first condenses with hydrazine to form a hydrazone. The hydrazone is then heated with potassium hydroxide in a high-boiling solvent such as ethylene glycol, releasing nitrogen and forming the corresponding hydrocarbon:

$$\mathrm{R{-}CO{-}R' + H_2N{-}NH_2 \longrightarrow R{-}C(=N{-}NH_2){-}R' + H_2O},$$
$$\mathrm{R{-}C(=N{-}NH_2){-}R' \xrightarrow[\text{ethylene glycol, heat}]{\text{KOH}} R{-}CH_2{-}R' + N_2}.$$

Here R and $\mathrm{R'}$ are alkyl or aryl groups for a ketone; for an aldehyde, $\mathrm{R'} = \mathrm{H}$. Thus the carbonyl oxygen is removed and the carbonyl carbon is reduced.

Step 2: (ii) Etard reaction Toluene reacts with chromyl chloride in a non-aqueous solvent such as carbon disulphide to form the Etard complex. Hydrolysis of this complex gives benzaldehyde:

$$\mathrm{C_6H_5CH_3} \xrightarrow[\mathrm{CS_2}]{\mathrm{CrO_2Cl_2}} \text{Etard complex} \xrightarrow{\mathrm{H_2O}} \mathrm{C_6H_5CHO}.$$

The controlled oxidation stops at the aldehyde stage, so the product is benzaldehyde rather than benzoic acid.

Step 3: Conclusion Wolff-Kishner reduction gives $\mathrm{R{-}CH_2{-}R'}$ from $\mathrm{R{-}CO{-}R'}$; the Etard reaction gives benzaldehyde, $\mathrm{C_6H_5CHO}$, from toluene.

Quick Tip to Solve: Remember the reagent-product pairs: hydrazine and KOH remove carbonyl oxygen, whereas chromyl chloride converts the benzylic methyl group to an aldehyde.

11. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.

Given: (Molar mass of sucrose = 342 g mol^{-1})

(Molar mass of glucose = 180 g mol^{-1}) [3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = K_f m$ for a non-electrolyte, where K_f is the solvent's molal depression constant and m is the solute molality.
- Sucrose and glucose do not dissociate in water. Therefore their van't Hoff factors are both $i = 1$, and their depressions can be compared directly using their molalities.
- A 10% solution by mass contains $10\,\mathrm{g}$ of solute and $90\,\mathrm{g}$ of water in $100\,\mathrm{g}$ of solution.

Step 1: Obtain the depression for sucrose The freezing point of pure water is $273.15\,\mathrm{K}$, while that of the sucrose solution is $269.15\,\mathrm{K}$. Thus,

$$\Delta T_{f,\mathrm{s}} = 273.15 - 269.15 = 4.00\,\mathrm{K}.$$

On taking $100\,\mathrm{g}$ of each solution, the mass of solvent in each is $90\,\mathrm{g} = 0.090\,\mathrm{kg}$. The solvent mass is not $100\,\mathrm{g}$, since the total solution includes the solute.

Quick Tip to Solve: For equal mass percentages in the same solvent, divide the depressions in the inverse ratio of molar masses, then subtract the new depression from the pure solvent's freezing point.

Step 2: Compare the molalities of the two solutions Using the given molar masses,

$$m_{\mathrm{s}} = \frac{10/342}{0.090} = 0.3249\,\mathrm{mol\,kg^{-1}},$$
$$m_{\mathrm{g}} = \frac{10/180}{0.090} = 0.6173\,\mathrm{mol\,kg^{-1}}.$$

The same solvent gives the same K_f. Because the solute and solvent masses are equal in the two solutions, the ratio simplifies to the inverse ratio of molar masses:

$$\frac{\Delta T_{f,\mathrm{g}}}{\Delta T_{f,\mathrm{s}}} = \frac{m_{\mathrm{g}}}{m_{\mathrm{s}}} = \frac{342}{180} = 1.90.$$

Step 3: Calculate the glucose solution's freezing point The glucose solution therefore has the depression

$$\Delta T_{f,\mathrm{g}} = 4.00 \times 1.90 = 7.60\,\mathrm{K}.$$

Subtract this depression from the freezing point of pure water:

$$T_{f,\mathrm{g}} = 273.15 - 7.60 = 265.55\,\mathrm{K}.$$

This is lower than the sucrose solution's freezing point, as expected: the smaller molar mass of glucose gives more solute particles for the same solute mass.

Step 4: Conclusion The freezing point of the 10% glucose solution is $\boxed{265.55\,\mathrm{K}}$.

Quick Tip to Solve: For equal mass percentages in the same solvent, divide the depressions in the inverse ratio of molar masses, then subtract the new depression from the pure solvent's freezing point.

12. (a) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $AgNO_3$ for 15 minutes.
(Given: Molar mass of Ag = 108 g mol^{-1}, 1F = 96500 C mol^{-1})
(b) Define fuel cell. [3 marks]

Solution:

Concept:

- Faraday's law gives the deposited mass as $m = \dfrac{MIt}{zF}$, where M is molar mass, I current, t time in seconds, z the electrons needed per ion and F the Faraday constant.
- At the silver cathode, $\mathrm{Ag^+ + e^- \longrightarrow Ag}$; hence one mole of electrons deposits one mole of silver and $z = 1$.
- A fuel cell converts the chemical energy of a fuel and an oxidant directly into electrical energy through electrochemical reactions.

Step 1: (a) Calculate the electric charge passed Convert the time into seconds before using the current in amperes:

$$t = 15 \times 60 = 900\,\mathrm{s}.$$

Quick Tip to Solve: First convert minutes to seconds and read the electron number from the cathode half-reaction; for silver ions, one faraday deposits one mole of silver.

The total charge delivered to the cell is therefore

$$Q = It = (2\,\text{A})(900\,\text{s}) = 1800\,\text{C}.$$

This charge corresponds to Q/F moles of electrons. Since the cathode reaction requires one electron for each silver ion, the moles of silver deposited are also $1800/96500$.

Step 2: (a) Apply Faraday's law to the silver deposit Substitute the given molar mass of silver and Faraday constant, using $z = 1$:

$$\begin{aligned} m &= \frac{MQ}{zF} \\ &= \frac{108 \times 1800}{1 \times 96500}\,\text{g} \\ &= 2.0145\,\text{g} \approx 2.01\,\text{g}. \end{aligned}$$

The silver ion is reduced at the cathode and the neutral silver forms the metallic deposit. No extra factor of two is needed because silver in $AgNO_3$ is monovalent.

Step 3: (b) Define a fuel cell A fuel cell is a galvanic cell that converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy. The fuel is oxidised at the anode and the oxidant is reduced at the cathode; the cell operates while reactants continue to be supplied and products are removed. A hydrogen-oxygen fuel cell is an example, in which hydrogen acts as the fuel, oxygen as the oxidant, and water is the overall reaction product.

Step 4: Conclusion (a) The mass of silver deposited is $\boxed{2.01\,\text{g}}$. (b) A fuel cell is a galvanic cell that directly converts the chemical energy of a continuously supplied fuel and oxidant into electrical energy.

Quick Tip to Solve: First convert minutes to seconds and read the electron number from the cathode half-reaction; for silver ions, one faraday deposits one mole of silver.

13. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?
(ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless? (At. no. of Ni = 28)
(iii) Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]Cl$. [3 marks]

Solution:

Concept:

- Coordination isomerism occurs when ligands are exchanged between the complex cation and complex anion of a coordination compound.
- The colour of a transition-metal complex depends on the splitting of its d orbitals and whether an electronic transition absorbs visible light. Ligand strength affects this splitting.
- In naming a complex, name the ligands before the metal, state the metal oxidation number in Roman numerals, and then name the counter-ion.

Step 1: (i) Identify the isomerism Both ions in $[Co(NH_3)_6][Cr(CN)_6]$ are complexes. Interchanging

Quick Tip to Solve: For the name, use the outer chloride to find the complex charge first; neutral ammonia and carbonate with charge minus two then give cobalt(III).

the ammonia and cyanide ligands between the two metal centres gives $[Cr(NH_3)_6][Co(CN)_6]$, with the same overall composition. This exchange between the complex cation and anion is coordination isomerism.

Step 2: (ii) Explain the difference in colour Nickel has configuration $[Ar]3d^8 4s^2$; hence Ni^{2+} is $3d^8$ in both complexes. Water is a weak-field ligand. The octahedral $[Ni(H_2O)_6]^{2+}$ complex has two unpaired electrons and permits d-d transitions that absorb visible light, so its solution appears green.

Cyanide is a strong-field ligand. It causes pairing and forms square-planar $[Ni(CN)_4]^{2-}$, with dsp^2 hybridisation and no unpaired electrons. Its larger ligand-field energy separation does not give appreciable absorption in the visible region; the relevant absorption is at higher energy. Therefore its solution is colourless. Pairing alone is not a universal test for colour; the transition energy must also be considered.

Step 3: (iii) Determine the oxidation state and name The chloride counter-ion has charge -1, so the complex cation has charge $+1$. Ammonia is neutral and carbonate is CO_3^{2-}. If cobalt has oxidation number x,

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

The ligand names are ammine and carbonato. Five ammine ligands give the prefix pentaammine, and the cationic metal is named cobalt(III). The counter-ion is chloride.

Step 4: Conclusion (i) Coordination isomerism. (ii) The aqua complex absorbs visible light and is green, while the strong-field cyanide complex is colourless. (iii) Pentaamminecarbonatocobalt(III) chloride.

Quick Tip to Solve: For the name, use the outer chloride to find the complex charge first; neutral ammonia and carbonate with charge minus two then give cobalt(III).

14. Write one difference in each of the following:

(i) Lyophobic sol and Lyophilic sol

(ii) Solution and Colloid

(iii) Homogeneous catalysis and Heterogeneous catalysis [3 marks]

Solution:

Concept:

- A sol is a colloidal dispersion of solid particles in a liquid. The terms lyophilic and lyophobic describe the affinity of the dispersed phase for the dispersion medium.
- A true solution contains particles of molecular or ionic size, whereas a colloid has larger dispersed particles that can scatter light.
- Catalysis is classified by comparing the physical phase of the catalyst with the phase of the reactants, rather than by comparing their chemical identities.

Step 1: (i) Compare affinity for the dispersion medium A lyophobic sol has little affinity between its dispersed phase and its dispersion medium. A lyophilic sol has strong affinity between the two. For example, an arsenic sulphide sol in water is lyophobic, whereas a starch sol in water is lyophilic.

Quick Tip to Solve: Keep each comparison on one basis: affinity for sols, light scattering for solution versus colloid, and physical phase for the two types of catalysis.

The prefixes mean solvent-hating and solvent-loving, respectively; this comparison concerns the particle-medium interaction.

Step 2: (ii) Compare light scattering A true solution does not show the Tyndall effect: the path of a beam through it is not visible. A colloid shows the Tyndall effect because its dispersed particles scatter the incident light, making the beam path visible. For example, salt solution does not reveal the light path, whereas a suitable starch sol does. This supplies one direct, observable difference between a true solution and a colloid.

Step 3: (iii) Compare the phases in catalysis In homogeneous catalysis, the catalyst and reactants are in the same phase. In heterogeneous catalysis, the catalyst and reactants are in different phases. For example, gaseous nitric oxide catalysing the oxidation of gaseous sulphur dioxide is homogeneous catalysis. A solid iron catalyst in the reaction of gaseous nitrogen and hydrogen to form ammonia is an example of heterogeneous catalysis: reaction occurs at the solid surface.

Step 4: Conclusion (i) Lyophobic: little affinity for the medium; lyophilic: strong affinity. (ii) True solution: no Tyndall effect; colloid: Tyndall effect. (iii) Homogeneous catalysis: same phase; heterogeneous catalysis: different phases.

Quick Tip to Solve: Keep each comparison on one basis: affinity for sols, light scattering for solution versus colloid, and physical phase for the two types of catalysis.

15. Following data are obtained for the reaction:

$$N_2O_5 \longrightarrow 2NO_2 + \tfrac{1}{2}O_2$$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.

(b) Calculate the half-life.

(Given $\log 2 = 0.3010$**,** $\log 4 = 0.6021$**)** [3 marks]

Solution:

Concept:

- For a first-order reaction, the integrated rate equation is $k = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are the reactant concentrations initially and at time t. The logarithm is to base ten.
- A constant k at different times supports first-order kinetics; its unit here is s^{-1}.
- For first order, $t_{1/2} = 0.693/k$; successive concentration halvings take equal time.

Step 1: (a) Calculate the rate constant at 300 seconds Let $A = N_2O_5$. Substitute the initial and

Quick Tip to Solve: Equal concentration halvings in equal time intervals suggest first order; verify this by obtaining the same rate constant from both nonzero times.

300-second concentrations:

$$k_{300} = \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = \frac{2.303 \times 0.3010}{300} = 2.311 \times 10^{-3}\,\text{s}^{-1}.$$

The concentration ratio is dimensionless, and the time in seconds gives k in s^{-1}.

Step 2: Check the rate constant at 600 seconds At $600\,\text{s}$, the concentration is $0.4 \times 10^{-2}\,\text{mol L}^{-1}$. Taking the same initial concentration,

$$k_{600} = \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = \frac{2.303 \times 0.6021}{600} = 2.311 \times 10^{-3}\,\text{s}^{-1}.$$

The two values agree to the accuracy of the supplied logarithms. Thus the data satisfy the first-order integrated rate equation. Also, the concentration halves in each successive $300\,\text{s}$ interval, as expected for first-order kinetics.

Step 3: (b) Calculate the half-life Substituting the rate constant in the first-order half-life relation gives

$$t_{1/2} = \frac{0.693}{2.311 \times 10^{-3}} \simeq 3.00 \times 10^{2}\,\text{s}.$$

The table confirms this result: the concentration halves in each $300\,\text{s}$ interval.

Step 4: Conclusion (a) The reaction follows first-order kinetics, with $k \simeq 2.31 \times 10^{-3}\,\text{s}^{-1}$. (b) The half-life is $t_{1/2} = 300\,\text{s}$.

Quick Tip to Solve: Equal concentration halvings in equal time intervals suggest first order; verify this by obtaining the same rate constant from both nonzero times.

16. Following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-elimination reaction. [3 marks]

Solution:

Concept:

- In an S_N2 reaction, a nucleophile attacks the carbon bearing the halogen from the back side. Increasing alkyl substitution obstructs this attack: primary halides react faster than secondary and tertiary halides.
- A chiral carbon bears four different groups; an individual enantiomer containing such a centre rotates plane-polarised light.
- In β-elimination, a hydrogen from a carbon adjacent to the halogen-bearing carbon and the halogen

Quick Tip to Solve: Classify the bromine-bearing carbon first: primary favours back-side substitution, tertiary favours elimination; test for four different groups to find chirality.

are removed to form an alkene. The usual reactivity order for the given bromides is tertiary greater than secondary greater than primary.

Step 1: (i) Compare steric hindrance to substitution The carbon bearing bromine is primary in 1-bromopentane, secondary in 2-bromopentane and tertiary in 2-bromo-2-methylbutane. Thus 1-bromopentane, $CH_3CH_2CH_2CH_2CH_2Br$, offers the least steric hindrance to the incoming nucleophile and is most reactive towards S_N2. The bulky tertiary substrate strongly obstructs the required back-side attack.

Step 2: (ii) Identify the asymmetric carbon In 2-bromopentane, $CH_3CH(Br)CH_2CH_2CH_3$, carbon 2 is bonded to H, Br, CH_3 and $CH_2CH_2CH_3$, four different groups. Hence 2-bromopentane is capable of optical activity. In 1-bromopentane the bromine-bearing carbon has two hydrogen atoms, while in 2-bromo-2-methylbutane it has two identical methyl groups; neither is chiral. An equal mixture of the two enantiomers of 2-bromopentane would be optically inactive.

Step 3: (iii) Compare elimination reactivity 2-Bromo-2-methylbutane, $CH_3C(Br)(CH_3)CH_2CH_3$, is the tertiary alkyl bromide. Alkyl substitution favours elimination and formation of a more substituted, more stable alkene. It is therefore most reactive towards β-elimination among these three compounds. Under usual conditions with a small base, its major elimination product is 2-methylbut-2-ene.

Step 4: Conclusion (i) Most reactive towards S_N2: **1-bromopentane**. (ii) Optically active compound: **2-bromopentane**. (iii) Most reactive towards β-elimination: **2-bromo-2-methylbutane**.

Quick Tip to Solve: Classify the bromine-bearing carbon first: primary favours back-side substitution, tertiary favours elimination; test for four different groups to find chirality.

17. (a) Write the principle of method used for the refining of germanium.

(b) Out of PbS and $PbCO_3$ (ores of lead), which one is concentrated by froth floatation process preferably?

(c) What is the significance of leaching in the extraction of aluminium? [3 marks]

Solution:

Concept:

- Zone refining exploits the unequal solubility of impurities in solid and molten metal: impurities are more soluble in the molten region.
- Froth flotation concentrates sulphide ores by their preferential wetting by oil, while gangue is wetted by water.
- Leaching selectively dissolves a useful ore constituent in a suitable reagent, separating it from insoluble impurities.

Step 1: (a) State the principle of germanium refining Germanium is refined by **zone refining**, based on the principle that impurities are more soluble in the melt than in the solid metal. A narrow molten zone is produced in a germanium rod and moved slowly along it. As the region behind the heater solidifies, comparatively pure germanium is deposited and impurities remain in the melt. Repeated movement carries the impurities towards one end, which is cut off, leaving highly pure germanium

Quick Tip to Solve: Link each operation to its selective property: melt solubility for zone refining, oil wetting for sulphides, and NaOH dissolution for alumina.

suitable for semiconductor applications.

Step 2: (b) Choose the lead ore for froth flotation PbS, galena, is the preferred ore because it is a sulphide ore. Its particles are preferentially wetted by the collector oil and attach to air bubbles. They rise with the froth, which is skimmed off, while water-wetted gangue remains behind. $PbCO_3$, cerussite, is a carbonate ore and is not the preferred choice for the conventional froth flotation process.

Step 3: (c) Explain the significance of leaching aluminium ore Leaching purifies bauxite by separating its alumina from impurities, particularly insoluble iron oxide. Treatment with hot concentrated sodium hydroxide dissolves the amphoteric alumina as soluble sodium aluminate:

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4].$$

Insoluble impurities are filtered off. Aluminium hydroxide is subsequently precipitated from the purified solution and heated to obtain alumina:

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O.$$

This yields purified alumina for electrolytic extraction of aluminium. Leaching is a purification step; it does not itself reduce alumina to aluminium metal.

Step 4: Conclusion (a) Zone refining: impurities are more soluble in molten germanium than in solid germanium. (b) $\boxed{PbS}$ is preferred for froth flotation. (c) Leaching separates alumina from bauxite impurities and provides purified Al_2O_3 for extraction.

Quick Tip to Solve: Link each operation to its selective property: melt solubility for zone refining, oil wetting for sulphides, and NaOH dissolution for alumina.

18(a). Write structures of compounds A, B and C in each of the following reactions:

(i) $C_6H_5Br \xrightarrow{Mg/\text{dry ether}} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_{2(g)}} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$ [3 marks]

Solution:

Concept:

- An aryl bromide reacts with magnesium in dry ether to form a Grignard reagent. Reaction with CO_2, followed by acidic hydrolysis, gives a carboxylic acid with one additional carbon atom.
- PCl_5 converts a carboxylic acid into its acyl chloride by replacing the hydroxyl group with chlorine.
- Stephen reduction converts a nitrile into an aldehyde using $SnCl_2/HCl$ followed by hydrolysis. An aldehyde having an α-hydrogen undergoes aldol addition in dilute base and the aldol loses water on heating.

Step 1: (i) Identify the Grignard reagent and benzoic acid Magnesium inserts into the carbon-bromine bond of bromobenzene in dry ether. Thus A is phenylmagnesium bromide, $C_6H_5{-}MgBr$. Carbon

Quick Tip to Solve: Track carbon counts: Grignard carboxylation adds one carbon; ethanal aldol addition doubles two carbons to four, and heating then removes only water.

dioxide supplies the new carboxyl carbon, and acidic hydrolysis gives B, benzoic acid:

$$C_6H_5Br + Mg \xrightarrow{\text{dry ether}} C_6H_5MgBr,$$
$$C_6H_5MgBr + CO_2 \longrightarrow C_6H_5COOMgBr,$$
$$C_6H_5COOMgBr \xrightarrow{H_3O^+} C_6H_5{-}C(=O){-}OH.$$

Step 2: (i) Convert benzoic acid into the acyl chloride Phosphorus pentachloride replaces the acid hydroxyl group with chlorine. Therefore C is benzoyl chloride, $C_6H_5{-}C(=O){-}Cl$:

$$C_6H_5COOH + PCl_5 \longrightarrow C_6H_5COCl + POCl_3 + HCl.$$

Step 3: (ii) Identify the aldehyde and the aldol product Stephen reduction of ethanenitrile, CH_3CN, followed by hydrolysis yields ethanal. Hence A is $CH_3{-}C(=O){-}H$. Ethanal contains α-hydrogens and two molecules undergo aldol addition in dilute sodium hydroxide. The product B is 3-hydroxybutanal:

$$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3{-}CH(OH){-}CH_2{-}CHO.$$

The product has four carbon atoms and retains one aldehyde group.

Step 4: (ii) Dehydrate the aldol on heating Heating removes the hydroxyl group on carbon 3 and a hydrogen from carbon 2 as water. C is the conjugated aldehyde but-2-enal (crotonaldehyde):

$$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3{-}CH{=}CH{-}CHO + H_2O.$$

Step 5: Conclusion (i) $A = C_6H_5{-}MgBr$, $B = C_6H_5{-}C(=O){-}OH$, $C = C_6H_5{-}C(=O){-}Cl$.
(ii) $A = CH_3{-}CHO$, $B = CH_3{-}CH(OH){-}CH_2{-}CHO$, $C = CH_3{-}CH{=}CH{-}CHO$.

Quick Tip to Solve: Track carbon counts: Grignard carboxylation adds one carbon; ethanal aldol addition doubles two carbons to four, and heating then removes only water.

OR

18(b). Do the following conversions in not more than two steps:

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic acid

(iii) Propanone to Propene [3 marks]

Solution:

Concept:

- An acid chloride is selectively reduced to an aldehyde by Rosenmund reduction using hydrogen and poisoned palladium supported on barium sulphate.
- Hot alkaline potassium permanganate oxidises an alkyl side chain containing a benzylic hydrogen to a carboxylate group. Acidification then gives the carboxylic acid.

Quick Tip to Solve: For acid to aldehyde, use the acid chloride and Rosenmund reduction; for ketone to alkene, reduce to an alcohol before dehydrating.

- Reduction converts a ketone to a secondary alcohol; dehydration of that alcohol gives an alkene without changing the carbon skeleton.

Step 1: (i) Convert benzoic acid into benzaldehyde First treat benzoic acid with thionyl chloride to form benzoyl chloride. Then carry out Rosenmund reduction. The poisoned catalyst prevents further reduction of the aldehyde to an alcohol.

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$$
$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$$

This two-step route retains the acid carbonyl carbon.

Step 2: (ii) Oxidise ethylbenzene to benzoic acid Heat ethylbenzene with alkaline $KMnO_4$; the side chain is oxidised to potassium benzoate. Acidify the product with dilute acid to obtain benzoic acid:

$$C_6H_5CH_2CH_3 \xrightarrow{\text{hot alkaline } KMnO_4} C_6H_5COOK \xrightarrow{H_3O^+} C_6H_5COOH$$

Ethylbenzene has benzylic hydrogens, permitting oxidation. The carbon attached to the ring becomes the carboxyl carbon; the other side-chain carbon is oxidised further.

Step 3: (iii) Reduce propanone and dehydrate the alcohol Reduce propanone with $NaBH_4$ to propan-2-ol, then heat the alcohol with concentrated sulphuric acid at approximately $443\,K$. Dehydration removes water and forms propene:

$$CH_3COCH_3 + 2\,[H] \xrightarrow{NaBH_4} CH_3CH(OH)CH_3$$
$$CH_3CH(OH)CH_3 \xrightarrow[443\,K]{\text{conc} \cdot H_2SO_4} CH_3CH{=}CH_2 + H_2O$$

Reduction provides the alcohol needed for elimination; direct ketone reduction alone would not produce the alkene.

Step 4: Conclusion The two-step routes give benzaldehyde via benzoyl chloride, benzoic acid via potassium benzoate, and propene via propan-2-ol.

Quick Tip to Solve: For acid to aldehyde, use the acid chloride and Rosenmund reduction; for ketone to alkene, reduce to an alcohol before dehydrating.

19. Write the structures of the monomers used for getting the following polymers:

(i) Dacron

(ii) Melamine - formaldehyde polymer

(iii) Buna-N [3 marks]

Solution:

Concept:

- Monomers join repeatedly to form polymers through their functional groups or double bonds.
- Dacron is a condensation polyester, melamine-formaldehyde is a condensation resin, and Buna-N

Quick Tip to Solve: Remember the N in Buna-N through the nitrile group, and place Dacron's two acid groups opposite one another on the benzene ring.

is an addition copolymer of two unsaturated monomers.

Step 1: (i) Write the two monomers of Dacron Dacron is prepared from ethylene glycol (ethane-1,2-diol) and terephthalic acid (benzene-1,4-dicarboxylic acid). Their condensed structural formulae are

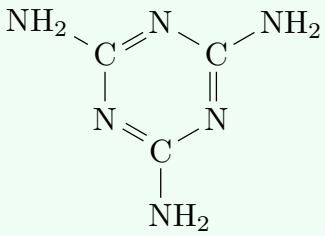
$$\underbrace{\mathrm{HO{-}CH_2{-}CH_2{-}OH}}_{\text{ethylene glycol}} \qquad \underbrace{\mathrm{HOOC{-}C_6H_4{-}COOH}}_{\text{terephthalic acid; para groups}}.$$

The two carboxyl groups of terephthalic acid occupy the 1 and 4 positions on the benzene ring. The diol and diacid form ester links by eliminating water.

Step 2: (ii) Write the monomers of melamine-formaldehyde polymer The monomers are melamine and formaldehyde (methanal). Melamine is 2,4,6-triamino-1,3,5-triazine: its six-membered ring contains alternating carbon and nitrogen atoms, with an amino group attached to each carbon. Its structure is shown below. Formaldehyde has the structural formula

$$\mathrm{H{-}C(=O){-}H}.$$

Condensation of melamine with formaldehyde produces a cross-linked resin.



Melamine: 2,4,6-triamino-1,3,5-triazine

Step 3: (iii) Write the two monomers of Buna-N Buna-N is obtained by copolymerising buta-1,3-diene and acrylonitrile (prop-2-enenitrile). Their structural formulae are

$$\underbrace{\mathrm{CH_2{=}CH{-}CH{=}CH_2}}_{\text{buta-1,3-diene}} \qquad \underbrace{\mathrm{CH_2{=}CH{-}C{\equiv}N}}_{\text{acrylonitrile}}.$$

The double bonds permit addition polymerisation. Acrylonitrile supplies nitrile groups; replacing it with styrene would give Buna-S.

Step 4: Conclusion Dacron uses ethylene glycol and terephthalic acid; melamine-formaldehyde polymer uses melamine and methanal; Buna-N uses buta-1,3-diene and acrylonitrile.

Quick Tip to Solve: Remember the N in Buna-N through the nitrile group, and place Dacron's two acid groups opposite one another on the benzene ring.

20. Define the following:

(i) Anionic detergents

(ii) Broad spectrum antibiotics

(iii) Antiseptic [3 marks]

Solution:

Concept:

- A detergent molecule contains a hydrophobic hydrocarbon chain and a hydrophilic head. Detergents are classified by the charge on the cleansing-active part of the molecule.
- Antibiotics act against microorganisms, while antiseptics are antimicrobial substances suitable for application to living tissues. The range of bacteria affected defines an antibiotic's spectrum.

Step 1: (i) Define anionic detergents Anionic detergents are detergents in which the cleansing-active portion is a negatively charged ion. They are commonly sodium salts of sulphonated long-chain hydrocarbons or sulphated long-chain alcohols. For example, sodium lauryl sulphate has the structure

$$CH_3(CH_2)_{11}-O-SO_3^- Na^+.$$

Its long hydrocarbon tail is hydrophobic and its negatively charged sulphate head is hydrophilic. The anionic portion assists cleansing, while Na^+ is the counter-ion; the name therefore refers to the active part rather than to the whole electrically neutral salt.

Step 2: (ii) Define broad spectrum antibiotics Broad spectrum antibiotics are antibiotics that kill or inhibit a wide range of both Gram-positive and Gram-negative bacteria. For example, chloramphenicol is a broad spectrum antibiotic.

The term describes activity across different bacterial groups; it does not mean activity against every microorganism. An antibiotic effective only against a limited group of bacteria has a narrow spectrum.

Step 3: (iii) Define antiseptics Antiseptics are chemical substances that kill microorganisms or prevent their growth and can be applied to living tissues such as wounds, cuts, ulcers and diseased skin. They are used to prevent infection and must be suitable for use on tissue at the employed concentration.

For example, tincture of iodine is an antiseptic. Antiseptics are distinguished from disinfectants by their application to living tissue; disinfectants are used on non-living objects such as floors and instruments. The suitability of a substance also depends on its concentration.

Step 4: Conclusion Anionic detergents have a negatively charged cleansing-active ion; broad spectrum antibiotics act against many Gram-positive and Gram-negative bacteria; antiseptics kill or inhibit microorganisms on living tissues.

Quick Tip to Solve: Identify the defining feature of each term: charge for the detergent, bacterial range for the antibiotic, and living tissue for the antiseptic.

21. Give reasons:

(i) Thermal stability decreases from H_2O to H_2Te.

(ii) Fluoride ion has higher hydration enthalpy than chloride ion.

(iii) Nitrogen does not form pentahalide. [3 marks]

Solution:

Concept:

- The thermal stability of a hydride depends on its bond strength: a stronger $\mathrm{E-H}$ bond needs more energy to break, where E is the group 16 atom.
- Hydration enthalpy is the enthalpy change when gaseous ions become hydrated in water. For ions of the same charge, smaller radius gives greater charge density and stronger attraction to water molecules.
- Nitrogen has valence-shell configuration $2s^2 2p^3$. As a second-period element, it cannot expand its octet to accommodate five covalent bonds.

Step 1: (i) Compare the strengths of the hydride bonds Atomic size increases from oxygen to tellurium. Consequently the $\mathrm{E-H}$ bond becomes longer, and overlap of the larger valence orbital of E with the hydrogen $1s$ orbital becomes less effective. The bond dissociation enthalpy decreases down the group. Less heat is therefore needed to break these bonds, so the hydrides become less thermally stable in the order

$$\mathrm{H_2O > H_2S > H_2Se > H_2Te.}$$

Step 2: (ii) Compare hydration of fluoride and chloride Both $\mathrm{F^-}$ and $\mathrm{Cl^-}$ carry the same negative charge, but $\mathrm{F^-}$ is smaller. Its greater charge density produces stronger ion-dipole attraction to the positive hydrogen ends of water molecules. More energy is released on hydration of fluoride. Thus its hydration enthalpy has a greater magnitude, meaning it is more negative than that of chloride; this is the sense of higher hydration enthalpy in the question.

Step 3: (iii) Apply the octet restriction to nitrogen A neutral nitrogen pentahalide would require nitrogen to form five bonds and have ten electrons around it. Nitrogen has only the $2s$ and $2p$ valence orbitals and no vacant d orbitals in its valence shell. It cannot expand its octet and therefore does not form a pentahalide, unlike the heavier group 15 elements such as phosphorus.

Step 4: Conclusion (i) Increasing atomic size weakens the $\mathrm{E-H}$ bond, decreasing thermal stability. (ii) Smaller $\mathrm{F^-}$ has stronger hydration and a more negative hydration enthalpy. (iii) Nitrogen cannot expand its octet to form five covalent bonds.

Quick Tip to Solve: For these three reasons, connect hydride stability to bond length, hydration to ionic size at equal charge, and pentahalide formation to the valence-shell octet.

22. Give reasons:

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Although -NH_2 is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline. [3 marks]

Solution:

Concept:

- The nitrogen lone pair in aniline can donate electron density into the benzene ring by resonance, activating the ring towards electrophilic substitution.
- Basicity depends on the availability of the nitrogen lone pair to accept a proton. Electron donation increases this availability, whereas delocalisation into an aromatic ring reduces it.
- An amino group $-NH_2$ directs electrophilic substitution to ortho and para positions, but its protonated form $-NH_3^+$ is deactivating and meta directing.

Step 1: (i) Explain the effect of acetylation Acetylation converts aniline, $C_6H_5NH_2$, into acetanilide, $C_6H_5NHCOCH_3$. The nitrogen lone pair now participates in resonance with the carbonyl group of the acetyl substituent. It is consequently less available for donation into the benzene ring. The electron density supplied to the ring decreases, so the acetylamino group activates the ring less strongly than the amino group. It remains ortho/para directing, but its reduced activation helps control substitution.

Step 2: (ii) Compare methylamine and aniline as bases In methylamine, CH_3NH_2, the methyl group exerts a positive inductive effect and increases the electron density on nitrogen. Its lone pair is localised and readily accepts a proton. In aniline, $C_6H_5NH_2$, the lone pair is delocalised into the benzene ring by resonance and is less readily available for protonation. Therefore methylamine is more basic than aniline.

Step 3: (iii) Identify the species present during nitration The strongly acidic nitrating mixture protonates a significant proportion of aniline to the anilinium ion:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3^+.$$

The $-NH_3^+$ group has no available nitrogen lone pair for resonance donation into the ring and withdraws electron density. It is meta directing. Nitration of this protonated species therefore forms a significant amount of m-nitroaniline after work-up. Unprotonated aniline still directs substitution to ortho and para positions, accounting for the mixture of products.

Step 4: Conclusion (i) Acetylation draws the nitrogen lone pair into resonance with the carbonyl group, reducing ring activation. (ii) Methylamine has a more available lone pair and is more basic. (iii) Acidic nitration produces meta-directing anilinium ions, giving significant m-nitroaniline.

Quick Tip to Solve: Track the nitrogen lone pair: acetylation shares it with a carbonyl, aniline shares it with the ring, and protonation removes its ability to donate into the ring.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Ritu a class XII student decided to aware others about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contractor to stop selling sandwiches, pizza, burgers and other bakery products to the students. Principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins rich food like fruits, salads, sprouts etc. The decision was welcomed by the parents and students.

After reading the above passage, answer the following questions:

(i) What are the values (at least two) displayed by Ritu?

(ii) Which polysaccharide component of carbohydrates is commonly present in bread?

(iii) Write the two types of secondary structure of proteins.

(iv) Give two examples of water soluble vitamins. [4 marks]

Solution:

Concept:

- Social responsibility means acting constructively for the welfare of others; the values in a passage should be supported by the person's actions.
- Starch is a plant storage polysaccharide made of glucose units. Protein secondary structure describes the local arrangement of the polypeptide backbone.
- The B-group vitamins and vitamin C are water-soluble; vitamins A, D, E and K are fat-soluble.

Step 1: (i) Values displayed by Ritu Ritu displays **health awareness and concern for others**: she recognises a possible food-related health problem and wants to protect fellow students. She also shows **social responsibility and initiative**, approaching the principal to seek a practical change in the canteen. Any two of these values, supported by her actions, answer this part.

Step 2: (ii) Polysaccharide commonly present in bread The polysaccharide is **starch**, the major carbohydrate in cereal flour used to make bread. It is composed of α-D-glucose units and contains amylose and amylopectin. Glucose itself is a monosaccharide, so it is not the polysaccharide asked for here.

Step 3: (iii) Secondary structures of proteins The two types are the **α-helix** and the **β-pleated sheet**. The helix is a coiled arrangement of the polypeptide chain; the sheet consists of extended segments lying alongside one another. Both are stabilised by hydrogen bonds involving peptide groups. These are local backbone arrangements, whereas primary structure is the amino-acid sequence.

Step 4: (iv) Examples of water-soluble vitamins Two examples are **vitamin B_1 (thiamine)** and **vitamin C (ascorbic acid)**. Vitamin B_1 belongs to the water-soluble B-group, and vitamin C is also water-soluble. Vitamins A or D would be unsuitable because they are fat-soluble.

Step 5: Conclusion (i) Health awareness and social responsibility. (ii) **Starch**. (iii) **α-helix and β-pleated sheet**. (iv) **Vitamin B_1 and vitamin C**.

Quick Tip to Solve: Associate bread with starch, protein secondary structure with helix and sheet, and water-soluble vitamins with the B-group and C.

24(a). Account for the following:

(i) Transition metals form large number of complex compounds.

(ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(iii) E° value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

[5 marks]

Solution:

Concept:

- Complex formation is favoured by the small size and high charge density of transition-metal ions, together with suitable vacant orbitals that accept lone pairs from ligands.
- Increasing the oxidation state of a metal generally increases the covalent character and acidity of its oxides. Low-oxidation-state oxides have more ionic character and are basic.
- A positive standard reduction potential favours reduction under standard conditions. Particularly stable electronic configurations influence the relative stability of the two oxidation states.
- Lanthanoids involve progressive filling of the $4f$ subshell, whereas actinoids involve the $5f$ subshell; both commonly form compounds in the $+3$ oxidation state.

Step 1: (a)(i) Explain the large number of complex compounds Transition-metal ions generally have small ionic radii and appreciable positive charges, giving them high charge density. They therefore attract ligands strongly. They also have suitable vacant orbitals into which ligands can donate electron pairs to form coordinate bonds. Their variable oxidation states permit different metal-ion charges and a wide variety of coordination compounds. For example, Fe^{3+} forms $[Fe(CN)_6]^{3-}$, in which cyanide ligands donate lone pairs to the metal ion.

Step 2: (a)(ii) Relate oxide nature to oxidation state In a low oxidation state, the metal has a smaller polarising power and its oxide is predominantly ionic. The oxide ions accept protons, so such an oxide behaves as a base; for example,

$$MnO + 2H^+ \longrightarrow Mn^{2+} + H_2O.$$

As the oxidation state rises, the metal's polarising power increases and the metal–oxygen bonds become more covalent. The oxide then becomes amphoteric or acidic. A high-oxidation-state oxide such as Mn_2O_7 is acidic and is the anhydride of permanganic acid:

$$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4.$$

Thus, basic character decreases and acidic character increases with oxidation state.

Step 3: (a)(iii) Compare the manganese and chromium reduction couples The relevant manganese reduction is

$$Mn^{3+}(3d^4) + e^- \longrightarrow Mn^{2+}(3d^5).$$

The product Mn^{2+} has an especially stable half-filled $3d^5$ configuration. Reduction of Mn^{3+} to this stable state is consequently strongly favoured, explaining its highly positive $E^\circ = +1.57\,V$. In contrast, Cr^{3+} has a stable $3d^3$ configuration (a half-filled t_{2g} set in an octahedral environment), while Cr^{2+} is

Quick Tip to Solve: Write the d-electron configurations on both sides of each reduction couple before comparing their stability and reduction potentials.

$3d^4$:

$$\mathrm{Cr^{3+}(3d^3) + e^- \longrightarrow Cr^{2+}(3d^4)}.$$

Reduction therefore removes the relative stability of $\mathrm{Cr^{3+}}$, and its reduction potential is much less positive than that of the manganese couple.

Step 4: (b) State one similarity and one difference **Similarity:** Both lanthanoids and actinoids commonly exhibit the $+3$ oxidation state and show a gradual decrease in ionic radii across their respective series (lanthanoid and actinoid contraction).

Difference: Lanthanoids predominantly show the $+3$ oxidation state, with only a few elements also exhibiting $+2$ or $+4$. Actinoids exhibit a wider range of oxidation states because the energies of their $5f$, $6d$ and $7s$ orbitals are relatively close, allowing different numbers of electrons to participate in bonding.

Step 5: Conclusion Transition metals form complexes because of high charge density and available acceptor orbitals; their oxides become more acidic as oxidation state increases. The stable $3d^5$ configuration of $\mathrm{Mn^{2+}}$ accounts for the highly positive manganese reduction potential. Both f-block series commonly show $+3$, but actinoids exhibit a wider range of oxidation states.

Quick Tip to Solve: Write the d-electron configurations on both sides of each reduction couple before comparing their stability and reduction potentials.

OR

24(b). (a) (i) How is the variability in oxidation states of transition metals different from that of the p-block elements?

(ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why?

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?

(b) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons. [5 marks]

Solution:

Concept:

- Transition-metal oxidation states involve electrons from both the $(n-1)d$ and ns subshells, whose energies are comparable. Their successive common oxidation states often differ by one unit.
- Stability of an ion in aqueous solution depends on the overall energy change, including hydration of the ion; gaseous electronic configuration alone is insufficient.
- Chromate and dichromate ions are related by an acid-base equilibrium. An alkali removes $\mathrm{H^+}$, shifting the equilibrium towards yellow chromate.
- Actinoid chemistry involves the closely spaced $5f$, $6d$ and $7s$ energy levels, as well as the radioactive nature of the elements.

Step 1: (a)(i) Compare the oxidation-state patterns In transition metals, the ns and $(n-1)d$ electrons have comparable energies and can participate in bonding. Consequently, a transition metal commonly exhibits several oxidation states differing by one unit. For example, manganese exhibits $+2, +3, +4, +5, +6$ and $+7$ states. In contrast, common oxidation states of a p-block element generally

Quick Tip to Solve: For copper ions, consider hydration as well as electronic configuration; for the chromium colour change, check the pH before proposing a redox reaction.

differ by two units, as illustrated by $+2, +4$ for tin and $+3, +5$ for phosphorus. Thus, the characteristic distinction is one-unit variation for transition metals versus two-unit variation for p-block elements.

Step 2: (a)(ii) Explain the instability of the copper(I) ion Cu^{+} is unstable in aqueous solution and undergoes disproportionation: one copper(I) ion is oxidised to copper(II), while another is reduced to copper metal.

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

Although converting gaseous Cu^{+} to Cu^{2+} requires the second ionisation energy, the much more negative hydration enthalpy of Cu^{2+} provides sufficient energetic compensation to favour the disproportionation in water. The higher charge of Cu^{2+} produces stronger attraction to water molecules. Therefore, the filled $3d^{10}$ configuration of Cu^{+} does not by itself make that ion stable in aqueous solution.

Step 3: (a)(iii) Explain the orange-to-yellow colour change Orange dichromate ions and yellow chromate ions interconvert according to

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

On adding alkali, OH^{-} consumes H^{+}. By Le Chatelier's principle the equilibrium shifts towards chromate. The net conversion is

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

Formation of yellow CrO_4^{2-} explains the observed colour change. Chromium remains in the $+6$ oxidation state, so this conversion is not a redox reaction.

Step 4: (b) Give two reasons for the more complicated chemistry of actinoids First, actinoids exhibit a wider range of oxidation states than lanthanoids. The energies of their $5f$, $6d$ and $7s$ orbitals are comparable, so different numbers of electrons can participate in bonding. Lanthanoids, by comparison, predominantly exhibit the $+3$ state, with only a few important exceptions.

Second, all actinoids are radioactive. Their radioactive decay and the short half-lives of many of their isotopes make the preparation, handling and experimental study of their compounds difficult. Together, the numerous oxidation states and radioactivity make actinoid chemistry more complicated than lanthanoid chemistry.

Step 5: Conclusion (a)(i) Transition-metal oxidation states commonly differ by one unit, whereas those of p-block elements generally differ by two. (ii) Cu^{+} is unstable in water and disproportionates because hydration strongly stabilises Cu^{2+}. (iii) Alkali converts orange dichromate into yellow chromate. (b) Actinoids have a wider range of oxidation states and are all radioactive.

Quick Tip to Solve: For copper ions, consider hydration as well as electronic configuration; for the chromium colour change, check the pH before proposing a redox reaction.

25(a). An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell.

(b) Write any two differences between amorphous solids and crystalline solids. [5 marks]

Solution:

Concept:

- The mass of one unit cell is ZM/N_{A}, where Z is the number of atoms per unit cell, M is the molar mass and N_{A} is Avogadro's constant. For a cubic unit cell of edge a, its volume is a^3, so $\rho = ZM/(a^3 N_{\mathrm{A}})$.
- The atom counts for simple cubic, body-centred cubic and face-centred cubic unit cells are respectively 1, 2 and 4. Crystalline solids have long-range order, whereas amorphous solids have only short-range order.

Step 1: (a) Convert the edge length into centimetres Since the density is expressed in g cm^{-3}, the edge length must be in centimetres. Using $1\,\mathrm{pm} = 10^{-10}\,\mathrm{cm}$,

$$a = 300 \times 10^{-10} = 3.00 \times 10^{-8}\,\mathrm{cm}, \qquad a^3 = 2.70 \times 10^{-23}\,\mathrm{cm}^3.$$

The given molar mass is $M = 93\,\mathrm{g\ mol^{-1}}$ and the density is $\rho = 11.5\,\mathrm{g\ cm^{-3}}$.

Step 2: (a) Determine the number of atoms per unit cell Rearrange the density relation and substitute $N_{\mathrm{A}} = 6.022 \times 10^{23}\,\mathrm{mol^{-1}}$:

$$\begin{aligned} Z &= \frac{\rho a^3 N_{\mathrm{A}}}{M} \\ &= \frac{11.5 \times 2.70 \times 10^{-23} \times 6.022 \times 10^{23}}{93} \\ &= 2.01 \simeq 2. \end{aligned}$$

The count must be an integer; the small difference from 2 results from the rounded experimental data. A body-centred cubic cell has eight corner atoms, each shared by eight cells, and one complete atom at its body centre. Its effective atom count is therefore $8 \times \frac{1}{8} + 1 = 2$, consistent with the calculation.

Step 3: (b) First difference: arrangement of constituent particles In a crystalline solid, constituent particles are arranged in a regular pattern that repeats over large distances; this is long-range order. In an amorphous solid, there is no such extended periodic arrangement. Neighbouring particles can show short-range order, but the regularity does not continue throughout the solid.

Step 4: (b) Second difference: behaviour on heating A crystalline solid has a sharp, definite melting point because of its ordered structure. An amorphous solid softens gradually over a range of temperatures and has no sharp melting point. Thus particle arrangement and melting behaviour provide two independent differences between these classes of solids.

Step 5: Conclusion (a) $Z \simeq 2$, so the element has a $\boxed{\text{body-centred cubic (bcc) unit cell}}$. (b) Crystalline solids have long-range order and a sharp melting point; amorphous solids have only short-range order and soften over a temperature range.

Quick Tip to Solve: Convert pm to cm before cubing the edge; then compare the calculated atom count with 1, 2 and 4 to identify the cubic cell.

OR

25(b). (a) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a f.c.c. structure. (Atomic mass of Al = 27 g mol^{-1})

(b) Give reasons:

(i) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.

(ii) Silicon on doping with Phosphorus forms n-type semiconductor.

(iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances. [5 marks]

Solution:

Concept:

- The number of atoms in a sample is $N = (m/M)N_{\mathrm{A}}$, where m is the sample mass, M is its molar mass and $N_{\mathrm{A}} = 6.022 \times 10^{23}\,\mathrm{mol}^{-1}$ is Avogadro's constant. A face-centred cubic (f.c.c.) unit cell contains four atoms.
- Schottky defects consist of equal numbers of cation and anion vacancies; Frenkel defects involve a smaller ion leaving its lattice site and occupying an interstitial site. Both preserve stoichiometry and electrical neutrality.
- Donor doping supplies extra mobile electrons to a semiconductor. In magnetic solids, the net magnetic moment depends on whether oppositely aligned magnetic moments cancel completely or only partly.

Step 1: (a) Count the aluminium atoms Convert the given mass into moles using the molar mass of aluminium:

$$n = \frac{8.1\,\mathrm{g}}{27\,\mathrm{g\ mol}^{-1}} = 0.30\,\mathrm{mol}.$$

Thus the total number of aluminium atoms in the sample is

$$N = 0.30 \times 6.022 \times 10^{23} = 1.8066 \times 10^{23}.$$

Step 2: (a) Convert the atom count into the unit-cell count An f.c.c. cell has eight corner atoms, each shared among eight cells, and six face-centred atoms, each shared between two cells. Hence its effective atom count is

$$Z = 8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4.$$

Dividing the total atom count by four gives

$$N_{\mathrm{cells}} = \frac{1.8066 \times 10^{23}}{4} = 4.5165 \times 10^{22} \approx 4.52 \times 10^{22}.$$

No edge length or density is needed, because the mass already determines the atom count.

Step 3: (b)(i) Explain the defect in sodium chloride In NaCl, the cation and anion sizes are sufficiently comparable, and the crystal has a high coordination number. A Na^{+} ion cannot readily fit into an interstitial position, so Frenkel displacement is unfavourable. Instead, equal numbers of Na^{+} and Cl^{-} ions are missing from their normal lattice sites, producing Schottky defects. Equal vacancies preserve

Quick Tip to Solve: For f.c.c. aluminium, first find atoms using $(m/M)N_{\mathrm{A}}$, then divide by four. For the reasons, compare ion sizes, count the dopant's extra electron, and check whether opposing magnetic moments fully cancel.

the $1:1$ composition and electrical neutrality, while lowering the crystal density.

Step 4: (b)(ii) Explain phosphorus doping of silicon Silicon has four valence electrons and forms four covalent bonds with neighbouring silicon atoms. Phosphorus has five valence electrons. When a phosphorus atom replaces silicon in the lattice, four of its electrons participate in these bonds, leaving the fifth weakly bound. This extra electron can become mobile and conduct electricity. Electrons are therefore the majority charge carriers, so phosphorus-doped silicon is an n-type semiconductor. The letter n refers to the negative charge of the mobile carriers; the crystal as a whole remains electrically neutral.

Step 5: (b)(iii) Compare ferrimagnetism and antiferromagnetism In an antiferromagnetic substance, neighbouring magnetic moments align in opposite directions with equal magnitudes. They cancel, giving zero resultant magnetic moment in the ideal ordered state. In a ferrimagnetic substance, the oppositely aligned sets of moments have unequal magnitudes. Cancellation is incomplete, leaving a net magnetic moment. This nonzero resultant moment explains why ferrimagnetic substances show stronger magnetism than antiferromagnetic substances.

Step 6: Conclusion (a) The sample contains approximately $\boxed{4.52 \times 10^{22}}$ f.c.c. unit cells. (b)(i) NaCl favours paired ionic vacancies rather than interstitial displacement; (ii) phosphorus supplies extra mobile electrons, giving n-type conduction; (iii) unequal opposing moments in ferrimagnetic solids leave a net moment, whereas equal opposing moments in antiferromagnetic solids cancel.

Quick Tip to Solve: For f.c.c. aluminium, first find atoms using $(m/M)N_A$, then divide by four. For the reasons, compare ion sizes, count the dopant's extra electron, and check whether opposing magnetic moments fully cancel.

26(a). Write the product(s) in the following reactions:

(i) The reaction shown in the figure.

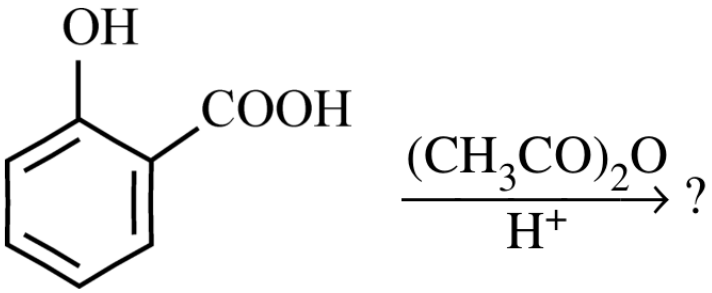
(ii) $CH_3 - CH(CH_3) - O - CH_2 - CH_3 \xrightarrow{HI}$ **? + ?**

(iii) $CH_3 - CH = CH - CH_2 - OH \xrightarrow{PCC}$ **?**

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol [5 marks]



Solution:

Concept:

- Acetylation replaces the hydrogen of the phenolic $-OH$ group by an acetyl group, CH_3CO^-, forming an ester. In salicylic acid, the carboxyl group remains unchanged.
- Hydrogen iodide cleaves an unsymmetrical alkyl ether after protonation of oxygen. With primary and secondary alkyl groups, iodide attacks the less hindered primary carbon by an S_N2 reaction.
- Pyridinium chlorochromate (PCC) oxidises a primary alcohol to an aldehyde without oxidising an isolated carbon-carbon double bond under the usual conditions.
- A distinguishing test must give different observations for the two compounds. Neutral ferric chloride detects phenols; Lucas reagent distinguishes primary and tertiary alcohols by the rate of formation of an insoluble alkyl chloride.

Step 1: (a)(i) Acetylation of salicylic acid Salicylic acid is 2-hydroxybenzoic acid: its phenolic hydroxyl and carboxyl groups are adjacent on the benzene ring. Acetic anhydride in the presence of acid acetylates the phenolic hydroxyl group. The organic product is acetylsalicylic acid, also called aspirin or 2-acetoxybenzoic acid. Acetic acid is the coproduct:

$$o\text{-}HO-C_6H_4-COOH + (CH_3CO)_2O \xrightarrow{H^+} o\text{-}CH_3COO-C_6H_4-COOH + CH_3COOH.$$

Here o- specifies the adjacent ring substituents. The ester linkage is formed through the phenolic oxygen; the $-COOH$ group is retained.

Step 2: (a)(ii) Cleavage of ethyl isopropyl ether Protonation makes the ether susceptible to cleavage. The ethyl carbon bonded to oxygen is primary, whereas the isopropyl carbon is secondary. Iodide therefore attacks the ethyl group, where steric hindrance is smaller, and gives iodoethane and propan-2-ol:

$$CH_3CH(CH_3)OCH_2CH_3 + HI \longrightarrow CH_3CH(OH)CH_3 + CH_3CH_2I.$$

These are the products of the cleavage shown. Further conversion of the alcohol to an iodide would require the additional treatment with excess HI, which is not specified here.

Step 3: (a)(iii) Oxidation with PCC The terminal $-CH_2OH$ group of but-2-en-1-ol is a primary alcohol group. PCC converts it into $-CHO$, while the carbon-carbon double bond remains in the same position:

$$CH_3CH{=}CHCH_2OH \xrightarrow{PCC} CH_3CH{=}CHCHO.$$

Thus the product is but-2-enal (crotonaldehyde), an unsaturated aldehyde, rather than the corresponding carboxylic acid.

Step 4: (b)(i) Distinguish ethanol from phenol Add a few drops of neutral aqueous ferric chloride solution to separate samples. Phenol gives a violet colour owing to formation of a coloured iron(III)-phenol complex. Ethanol does not give this violet colour. The appearance of the violet colour therefore identifies phenol; its absence distinguishes ethanol under the same test conditions. Use neutral ferric chloride, since strongly acidic conditions can interfere with the characteristic phenol test.

Quick Tip to Solve: For cleavage of a primary-secondary ether by HI, place iodine on the less hindered primary group and OH on the other group; for PCC, replace CH2OH by CHO without moving the double bond.

Step 5: (b)(ii) Distinguish propanol from 2-methylpropan-2-ol Add Lucas reagent, a mixture of concentrated hydrochloric acid and anhydrous zinc chloride, to separate samples at room temperature. Propanol (propan-1-ol) is a primary alcohol and shows no turbidity at room temperature during the ordinary test period. In contrast, 2-methylpropan-2-ol is a tertiary alcohol and gives immediate turbidity because insoluble tert-butyl chloride forms rapidly:

$$(CH_3)_3COH + HCl \xrightarrow{ZnCl_2} (CH_3)_3CCl + H_2O.$$

The tertiary alcohol reacts readily through a stable tertiary carbocation. Comparing the time at which turbidity appears is the essential observation.

Step 6: Conclusion (a) The products are (i) acetylsalicylic acid (aspirin) and acetic acid, (ii) propan-2-ol and iodoethane, and (iii) but-2-enal. (b) Neutral $FeCl_3$ gives a violet colour with phenol but not ethanol; Lucas reagent gives immediate turbidity with 2-methylpropan-2-ol and no turbidity at room temperature with propan-1-ol.

Quick Tip to Solve: For cleavage of a primary-secondary ether by HI, place iodine on the less hindered primary group and OH on the other group; for PCC, replace CH2OH by CHO without moving the double bond.

OR

26(b). (a) Write the formula of reagents used in the following reactions:

(i) Bromination of phenol to 2,4,6-tribromophenol

(ii) Hydroboration of propene and then oxidation to propanol.

(b) Arrange the following compound groups in the increasing order of their property indicated:

(i) p-nitrophenol, ethanol, phenol (acidic character)

(ii) Propanol, Propane, Propanal (boiling point)

(c) Write the mechanism (using curved arrow notation) of the following reaction:

$$CH_3CH_2OH_2^+ \xrightarrow{CH_3CH_2OH} CH_3CH_2O^+(H)CH_2CH_3 + H_2O.$$

[5 marks]

Solution:

Concept:

- The hydroxyl group strongly activates the phenol ring towards electrophilic substitution at its two ortho positions and its para position. Bromine water therefore gives the tribromo derivative.
- Hydroboration followed by alkaline peroxide oxidation adds water across an alkene in the anti-Markovnikov orientation: the hydroxyl group appears at the less substituted carbon.
- Acidity increases with stability of the conjugate base. Intermolecular hydrogen bonding produces a greater boiling point than ordinary dipole-dipole attractions or dispersion forces for these similarly sized molecules.
- In a substitution mechanism, a curved arrow starts at an electron pair or a bond and ends at the

Quick Tip to Solve: For the mechanism, start both curved arrows at electron pairs: one at the attacking oxygen lone pair, the other at the carbon-oxygen bond that breaks.

atom receiving that electron pair. Protonation converts the poor leaving group hydroxide into water.

Step 1: (a)(i) Reagent for bromination of phenol Use bromine water, $Br_2(aq)$. With aqueous bromine, activation by the hydroxyl group is sufficiently strong for all three available ortho and para positions to undergo substitution, giving a white precipitate of 2,4,6-tribromophenol:

$$C_6H_5OH + 3Br_2(aq) \longrightarrow C_6H_2Br_3OH + 3HBr.$$

Bromine in a nonpolar solvent would favour controlled monobromination and is therefore not the reagent for the specified tribromo product.

Step 2: (a)(ii) Reagents for hydroboration and oxidation First use diborane, B_2H_6, equivalently BH_3 in tetrahydrofuran (THF). Then oxidise with hydrogen peroxide in alkaline medium, H_2O_2/OH^-, for example $H_2O_2/NaOH$.

$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2/OH^-]{1.\ BH_3/THF} CH_3CH_2CH_2OH.$$

Boron attaches to the less substituted terminal carbon during hydroboration; oxidation replaces the carbon-boron bond by a carbon-oxygen bond. Thus the alcohol is propan-1-ol.

Step 3: (b)(i) Increasing acidic character The required order is

$$\text{ethanol} < \text{phenol} < p\text{-nitrophenol}.$$

Ethoxide lacks resonance delocalisation, and the electron-releasing ethyl group destabilises its negative charge. Phenoxide is stabilised by delocalisation of the negative charge over the aromatic ring. The para nitro group further stabilises the conjugate base by electron withdrawal through inductive and resonance effects. Consequently removal of the hydroxyl proton becomes easier along the stated order.

Step 4: (b)(ii) Increasing boiling point The required order is

$$\text{propane} < \text{propanal} < \text{propanol}.$$

Propane is nonpolar and its molecules attract each other mainly through weak dispersion forces. Propanal has a polar carbonyl group, so dipole-dipole attractions increase the energy required for vaporisation. Propanol molecules form intermolecular hydrogen bonds through their hydroxyl groups; these stronger attractions give the greatest boiling point among the three compounds.

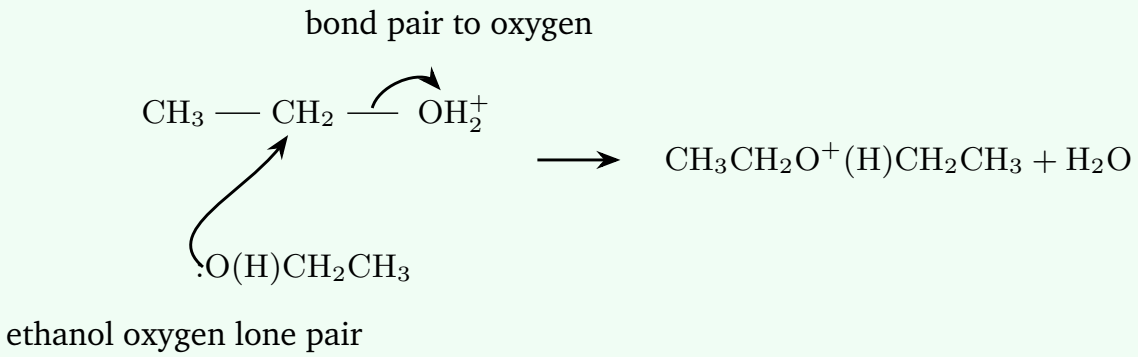
Step 5: (c) Curved-arrow mechanism of the printed reaction The starting species is already protonated ethanol, $CH_3CH_2OH_2^+$. The oxygen lone pair of a second, neutral ethanol molecule attacks its primary carbon bearing OH_2^+. At the same time the carbon-oxygen bond of the protonated alcohol breaks, with its electron pair moving to the leaving oxygen. This concerted S_N2 displacement releases neutral water and produces protonated diethyl ether:

$$CH_3CH_2OH_2^+ + HOCH_2CH_3 \longrightarrow CH_3CH_2O^+(H)CH_2CH_3 + H_2O.$$

The attacking oxygen now has three bonds and bears the positive charge. The curved arrows below

Quick Tip to Solve: For the mechanism, start both curved arrows at electron pairs: one at the attacking oxygen lone pair, the other at the carbon-oxygen bond that breaks.

show the two electron-pair movements in this substitution. The protonated ether is exactly the product in the given equation. In the overall acid-catalysed preparation of ether, a subsequent deprotonation gives neutral diethyl ether and regenerates the acid.



Curved arrows for attack by ethanol and simultaneous departure of water.

Step 6: Conclusion Reagents: $Br_2(aq)$; B_2H_6 then H_2O_2/OH^-. Orders: ethanol $<$ phenol $<$ p-nitrophenol; propane $<$ propanal $<$ propanol. The substitution produces protonated diethyl ether and water.

Quick Tip to Solve: For the mechanism, start both curved arrows at electron pairs: one at the attacking oxygen lone pair, the other at the carbon-oxygen bond that breaks.