CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-4-3

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) Section A : Questions number **1 to 5** are very short answer questions and carry **1 mark** each.

(iii) Section B : Questions number **6 to 12** are short answer questions and carry **2 marks** each.

(iv) Section C : Questions number **13 to 24** are also short answer questions and carry **3 marks** each.

(v) Section D : Questions number **25 to 27** are long answer questions and carry **5 marks** each.

(vi) There is no overall choice. However, an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.

(vii) Use of log tables, if necessary. Use of calculators is **not** allowed.

Section A (5 marks)

1. What would be the nature of solid if there is no energy gap between Valence band and Conduction band? [1 mark]

Solution:

Concept:

- The valence band contains valence electrons; the conduction band provides accessible states in which electrons can move through the solid.
- The energy gap is the separation between these bands. A vanishing gap permits electron motion without overcoming a finite band gap.

Step 1: Interpret the band separation With no energy gap, the valence and conduction bands meet or overlap. Electrons can therefore access nearby conducting states instead of being confined to a filled band separated by a forbidden energy interval.

Step 2: Relate this to electrical behaviour An applied electric field can cause these mobile electrons to move through the crystal and carry current. This is the characteristic band arrangement of a metallic conductor; an insulator has a large gap and a semiconductor has a small finite gap.

Step 3: Conclusion The solid is a conductor (metallic solid).

Quick Tip to Solve: A zero band gap indicates a conductor; distinguish it from the small finite gap of a semiconductor.

2. Write the main reason for the stability of colloidal sols. [1 mark]

Solution:

Concept:

- Colloidal particles of a given sol normally carry the same kind of electrical charge.
- Like charges repel; electrostatic repulsion prevents particles from approaching and aggregating.

Step 1: Identify the common charge Particles within a stable colloidal sol bear charges of the same sign, commonly acquired by selective adsorption of ions. The sign may be positive or negative, but it is alike on the particles of that sol.

Step 2: Explain how aggregation is prevented The resulting electrostatic repulsion opposes close contact between particles. They consequently resist coagulation into larger aggregates that could settle under gravity, and remain dispersed in the medium.

Step 3: Conclusion The main reason for stability is mutual electrostatic repulsion between similarly charged colloidal particles.

Quick Tip to Solve: State both the common charge on the particles and the repulsion that prevents their coagulation.

3(a). When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, two moles of AgCl are precipitated per mole of the compound. What is the structural formula of the coordination compound?

[1 mark]

Solution:

Concept:

- Only ionisable chloride ions outside the coordination sphere readily form AgCl with $\mathrm{AgNO_3}$.
- Chromium(III) has coordination number six here; water is neutral and coordinated chloride has charge -1.

Step 1: Locate the chloride ions Two moles of AgCl per mole of compound mean that two of its three chloride ions are outside the coordination sphere. Thus only one chloride is bonded directly to chromium.

Step 2: Distribute the water molecules The six coordination positions contain one chloride ligand and five water ligands. Of the six water molecules in the formula, the remaining one is water of crystallisation. The complex charge is $+3 - 1 = +2$, balanced by the two external chloride ions.

Step 3: Conclusion The structural formula is $\boxed{[\mathrm{Cr(H_2O)_5Cl}]Cl_2 \cdot H_2O}$.

Quick Tip to Solve: Count precipitated chloride as external chloride; then complete the six coordination positions with water.

OR

3(b). What is the difference between a complex and a double salt? [1 mark]

Solution:

Concept:

- A double salt dissociates completely into its constituent simple ions in aqueous solution.
- A complex salt retains its coordination entity as a complex ion in solution, although its counterions dissociate.

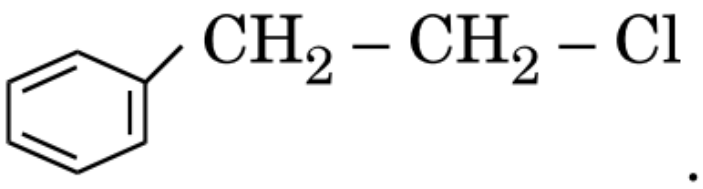
Step 1: Describe a double salt A double salt loses its separate identity on dissolution and gives the tests of its constituent ions. For example, Mohr's salt produces Fe^{2+}, NH_4^+ and SO_4^{2-} ions in water.

Step 2: Describe a complex A complex retains metal-ligand bonding in its coordination entity. For example, $K_4[Fe(CN)_6]$ gives K^+ and $[Fe(CN)_6]^{4-}$, rather than free Fe^{2+} and CN^- ions under ordinary conditions.

Step 3: Conclusion A double salt dissociates into all its constituent simple ions, whereas a complex retains its complex ion in aqueous solution.

Quick Tip to Solve: Compare the ions actually present in water: simple constituent ions versus a retained coordination entity.

4. Write the IUPAC name of the following compound: [1 mark]



Solution:

Concept:

- The printed structure is $C_6H_5 - CH_2 - CH_2 - Cl$: the chlorine is on the terminal carbon of a two-carbon side chain.
- When benzene is the parent, number the substituent from its point of attachment to the ring.

Step 1: Identify the parent and substituent The six-carbon benzene ring is the parent. Its substituent is an ethyl group whose first carbon is attached to benzene and whose second carbon carries chlorine.

Step 2: Assign the substituent locant Numbering the side chain away from the ring gives chlorine locant 2, so the substituent is 2-chloroethyl. Enclose this substituted side-chain name in parentheses before the parent name benzene. The chlorine is not directly attached to the aromatic ring.

Step 3: Conclusion The IUPAC name is $\boxed{\text{(2-chloroethyl)benzene}}$ (also named 1-chloro-2-phenylethane).

Quick Tip to Solve: Trace the two-carbon side chain from the ring; chlorine is on its second carbon, not on benzene.

5(a). Write the reaction involved in the Hoffmann bromamide degradation reaction. [1 mark]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide $RCONH_2$ to a primary amine RNH_2.
- Bromine and aqueous alkali remove the carbonyl carbon; the amine contains one fewer carbon atom than the amide.

Step 1: Identify reactants and organic product Treat the primary amide with Br_2 and aqueous $NaOH$ on heating. The group R is retained in the primary amine, while the carbonyl carbon is eliminated as carbonate.

Step 2: Write the balanced reaction

$$RCONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O.$$

The inorganic products account for the carbonyl carbon, bromine and the alkali; no extra carbon is introduced into the amine.

Step 3: Conclusion Hofmann bromamide degradation: $RCONH_2$ gives RNH_2 with bromine and

Quick Tip to Solve: Check that the amine has one carbon fewer and that the balanced equation uses four equivalents of NaOH.

aqueous alkali, as in the balanced equation above.

Quick Tip to Solve: Check that the amine has one carbon fewer and that the balanced equation uses four equivalents of NaOH.

OR

5(b). Propanamine and N,N-dimethylmethanamine contain the same number of carbon atoms, even though Propanamine has higher boiling point than N,N-dimethylmethanamine. Why? [1 mark]

Solution:

Concept:

- Boiling requires molecules to overcome intermolecular attractions; stronger attractions raise the boiling point.
- Intermolecular hydrogen bonding between amine molecules requires an N-H bond as a hydrogen donor and a nitrogen lone pair as an acceptor.

Step 1: Examine propanamine Propanamine, $CH_3CH_2CH_2NH_2$, is a primary amine with N-H bonds and a nitrogen lone pair. Its molecules can form intermolecular hydrogen bonds, increasing the energy required to separate them during boiling.

Step 2: Examine the tertiary isomer N,N-Dimethylmethanamine, $(CH_3)_3N$, is a tertiary amine without any N-H bond. Although nitrogen has a lone pair, its molecules cannot donate hydrogen to form such hydrogen bonds with one another. Equal carbon counts therefore do not imply equal intermolecular attractions.

Step 3: Conclusion Propanamine has the higher boiling point because it forms intermolecular hydrogen bonds, while N,N-dimethylmethanamine cannot form them between its own molecules.

Quick Tip to Solve: For boiling points of isomeric amines, look for N-H bonds; a lone pair alone does not supply a hydrogen donor.

Section B (14 marks)

6(a). When dilute ferrous sulphate solution is added to an aqueous solution containing nitrate ion followed by careful addition of concentrated sulphuric acid along the sides of test tube, a brown ring is formed at the interface between the solution and sulphuric acid layers. Which anion is confirmed by the appearance of brown ring? What is the composition of the brown ring? [2 marks]

Solution:

Concept:

- The brown-ring test detects nitrate ions, NO_3^-, through reduction to nitric oxide in an acidic medium.
- Nitric oxide coordinates to ferrous ions to form the brown nitrosyl complex; water supplies the remaining five ligands.

Quick Tip to Solve: Remember the brown-ring formula as five water ligands plus one NO ligand around iron.

Step 1: Identify the anion The appearance of a brown ring in the stated test confirms the nitrate ion, NO_3^-. Ferrous ions reduce nitrate to nitric oxide in the acidified solution, as shown by the balanced ionic equation:

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O.$$

Thus, nitrate is the anion identified, while nitric oxide is the intermediate responsible for forming the coloured complex.

Step 2: State the composition of the ring The nitric oxide produced combines with hydrated ferrous ions:

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O.$$

The brown ring consists of nitrosyl ferrous sulphate, $[Fe(H_2O)_5(NO)]SO_4$. Its complex ion contains five water ligands and one nitric oxide ligand; sulphate is the counter-ion. The colour is seen at the interface where the two layers meet.

Step 3: Conclusion The anion is $\boxed{NO_3^-}$, and the brown ring is $\boxed{[Fe(H_2O)_5(NO)]SO_4}$, nitrosyl ferrous sulphate.

Quick Tip to Solve: Remember the brown-ring formula as five water ligands plus one NO ligand around iron.

OR

6(b). How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only. [2 marks]

Solution:

Concept:

- $2Cl^- \longrightarrow Cl_2 + 2e^-$, $\quad MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$
- $H_2 \longrightarrow 2H^+ + 2e^-$, $\quad Cl_2 + 2e^- \longrightarrow 2Cl^-$

Step 1: $HCl \longrightarrow Cl_2$

$$MnO_2 + 4HCl(\text{conc.}) \xrightarrow{\Delta} MnCl_2 + Cl_2 \uparrow + 2H_2O.$$

$$2Cl^- \longrightarrow Cl_2 + 2e^-,$$
$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O.$$

Step 2: $Cl_2 \longrightarrow HCl$

$$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl.$$

$$H_2 \longrightarrow 2H^+ + 2e^-,$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^-.$$

Step 3: Conclusion

$$MnO_2 + 4HCl(\text{conc.}) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O,$$
$$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl.$$

Quick Tip to Solve: Use hot concentrated HCl with MnO2, then combine chlorine with hydrogen in sunlight.

7. Using the E° values of X and Y, predict which is better for coating the surface of iron to prevent rust and why?

Given: $E^\circ_{(Fe^{2+}/Fe)} = -0.44$ V; $E^\circ_{(X^{2+}/X)} = -2.36$ V; $E^\circ_{(Y^{2+}/Y)} = -0.14$ V [2 marks]

Solution:

Concept:

- A more negative standard reduction potential means a metal loses electrons more readily and is a stronger reducing agent.
- A sacrificial coating must oxidise preferentially to iron so that iron remains the cathode, even at a scratch in the coating.

Step 1: Compare the reduction potentials The given values are $E^\circ_{X^{2+}/X} = -2.36\,V$, $E^\circ_{Fe^{2+}/Fe} = -0.44\,V$ and $E^\circ_{Y^{2+}/Y} = -0.14\,V$. Since X has a much more negative reduction potential than iron, X oxidises more readily:

$$X \longrightarrow X^{2+} + 2e^-.$$

The electrons supplied by X protect iron against oxidation.

Step 2: Explain the protection and reject Y X acts as the sacrificial anode and iron as the cathode. The relative driving force is

$$E^\circ_{cell} = E^\circ_{Fe^{2+}/Fe} - E^\circ_{X^{2+}/X} = -0.44 - (-2.36) = 1.92\,V.$$

Hence oxidation of X is favoured. Y has a less negative reduction potential than iron. If a Y coating is damaged and both metals contact the electrolyte, iron becomes the anode and corrodes; Y therefore does not provide the same sacrificial protection.

Step 3: Conclusion $\boxed{X}$ is the better coating because it oxidises preferentially and protects iron as a sacrificial anode.

Quick Tip to Solve: Choose the coating metal whose reduction potential is more negative than that of iron.

8(a). Give reasons for the following:

(a) Aquatic species are more comfortable in cold water than warm water.

(b) At higher altitudes people suffer from anoxia resulting in inability to think. [2 marks]

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the partial pressure of the gas, x its mole fraction in solution and K_H the Henry's law constant.
- For oxygen in water, increasing temperature decreases solubility; decreasing oxygen partial pressure also decreases the amount dissolved.

Step 1: (a) Oxygen in cold water At the same oxygen partial pressure, cold water dissolves more oxygen than warm water. Gas dissolution is generally exothermic, so raising the temperature favours escape of dissolved oxygen. Equivalently, the Henry's law constant for oxygen is smaller at lower temperature, and $x = p/K_H$ is therefore larger. Aquatic species have more dissolved oxygen available

Quick Tip to Solve: For Henry's law questions, distinguish a temperature change from a gas-pressure change.

for respiration in cold water, making them more comfortable.

Step 2: (b) Anoxia at higher altitudes Atmospheric pressure decreases with increasing altitude. Although the fraction of oxygen in air is approximately unchanged, its partial pressure decreases. By Henry's law, lower oxygen partial pressure leads to less oxygen dissolving in blood. This reduces the oxygen supply to the tissues and brain. The resulting oxygen deficiency, called anoxia in the question, causes difficulty in thinking and other effects of inadequate oxygenation.

Step 3: Conclusion (a) Cold water contains more dissolved oxygen for aquatic respiration. (b) Lower oxygen partial pressure at high altitude reduces oxygen uptake into blood and causes oxygen deficiency.

Quick Tip to Solve: For Henry's law questions, distinguish a temperature change from a gas-pressure change.

OR

8(b). What type of azeotropic mixture will be formed by a solution of acetone and chloroform? Justify on the basis of strength of intermolecular interactions that develop in the solution. [2 marks]

Solution:

Concept:

- Raoult's law for an ideal solution is $p_i = x_i p_i^\circ$; negative deviation means each component escapes less readily than predicted.
- Stronger attractions between unlike molecules lower total vapour pressure and may produce a maximum-boiling azeotrope.

Step 1: Identify the intermolecular attraction In a mixture of acetone, $(CH_3)_2CO$, and chloroform, $CHCl_3$, the hydrogen of chloroform forms a hydrogen bond with the oxygen of the carbonyl group of acetone:

$$(CH_3)_2C{=}O \cdots H{-}CCl_3.$$

The electron-withdrawing chlorine atoms make the hydrogen of chloroform sufficiently positive to interact strongly with the oxygen atom. These acetone-chloroform attractions are stronger than the corresponding attractions between like molecules in the pure liquids.

Step 2: Relate attraction to the azeotrope The stronger unlike-molecule attractions hold molecules in the liquid and reduce their tendency to enter the vapour phase. Consequently, the solution shows negative deviation from Raoult's law and has a lower total vapour pressure than the ideal prediction. A higher temperature is then needed for its vapour pressure to equal atmospheric pressure. The mixture therefore forms a maximum-boiling azeotrope, whose liquid and vapour have the same composition at the azeotropic point.

Step 3: Conclusion Acetone and chloroform form a $\boxed{\text{maximum-boiling azeotrope}}$ because strong hydrogen bonding produces negative deviation from Raoult's law.

Quick Tip to Solve: Stronger unlike-molecule attractions imply lower vapour pressure and a maximum-boiling azeotrope.

9. Write the name of monomers and their structures for the following polymers:

(a) Neoprene

(b) Nylon-6 [2 marks]

Solution:

Concept:

- A monomer is the small molecule that supplies the repeating units of a polymer. Identify the starting molecule, rather than writing only the polymer repeat unit.
- Neoprene is formed by addition polymerisation of a substituted conjugated diene; nylon-6 is obtained by ring-opening polymerisation of a cyclic amide.

Step 1: (a) Monomer of neoprene The monomer is chloroprene, whose systematic name is 2-chlorobuta-1,3-diene. Its structure is

$$CH_2 = C(Cl) - CH = CH_2.$$

The chlorine substituent is on carbon 2 of the four-carbon conjugated diene. During polymerisation the diene units join to give neoprene; chlorine remains attached to the carbon chain.

Step 2: (b) Monomer of nylon-6 The monomer is ε-caprolactam, a seven-membered cyclic amide. Its structure can be written explicitly as

$$\begin{array}{ccc} & C(=O) & \\ / & & \backslash \\ NH & & CH_2 \\ | & & | \\ CH_2 & & CH_2 \\ \backslash & & / \\ & CH_2 - CH_2 & \end{array}$$

The ring contains five methylene groups, one carbonyl carbon and one nitrogen. Ring opening produces the nylon-6 repeat unit $[-NH-(CH_2)_5-CO-]_n$.

Step 3: Conclusion Neoprene: chloroprene, $CH_2 = C(Cl) - CH = CH_2$. Nylon-6: ε-caprolactam, the cyclic amide with ring sequence $-NH-(CH_2)_5-C(=O)-$, closed back to nitrogen.

Quick Tip to Solve: For nylon-6, count six carbons in caprolactam: five methylene carbons and one carbonyl carbon.

10. Classify the following as addition and condensation polymers giving reason:

(a) Teflon

(b) PHBV [2 marks]

Solution:

Concept:

- Addition polymers form by joining unsaturated monomers without eliminating small molecules. The double bond opens to form the polymer backbone.
- Condensation polymers form through reactions of functional groups, typically eliminating small molecules such as water and creating links such as ester or amide bonds.

Step 1: (a) Classify Teflon Teflon is an addition polymer of tetrafluoroethene, $CF_2 = CF_2$. Its formation is represented by

$$n\,CF_2 = CF_2 \longrightarrow [-CF_2 - CF_2-]_n.$$

The carbon-carbon double bonds open and link the monomers into a chain. No water, hydrogen chloride or other small molecule is eliminated; all atoms of each monomer remain in the polymer.

Step 2: (b) Classify PHBV PHBV is a condensation copolymer formed from 3-hydroxybutanoic acid, $CH_3 - CH(OH) - CH_2 - COOH$, and 3-hydroxypentanoic acid, $CH_3CH_2 - CH(OH) - CH_2 - COOH$. The hydroxyl group of one molecule reacts with the carboxyl group of another. Ester links, $-CO - O-$, form with elimination of water. Because two different hydroxy-acid monomers participate, PHBV is also a copolymer and a biodegradable polyester.

Step 3: Conclusion Teflon is an addition polymer: unsaturated monomers join without loss of a small molecule. PHBV is a condensation polymer: ester links form between hydroxy-acid monomers with elimination of water.

Quick Tip to Solve: Check the bond formed: opening C=C without by-products indicates addition; ester formation with water loss indicates condensation.

11. Use the data to answer the following and also justify giving reason:

	Cr	Mn	Fe	Co
$E^\circ_{M^{2+}/M}$ (V)	−0.91	−1.18	−0.44	−0.28
$E^\circ_{M^{3+}/M^{2+}}$ (V)	−0.41	+1.57	+0.77	+1.97

(a) Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?

(b) Which is the most stable ion in +2 oxidation and why? [2 marks]

Solution:

Concept:

- The supplied $E^\circ_{M^{3+}/M^{2+}}$ values refer to reduction: $M^{3+} + e^- \longrightarrow M^{2+}$. Reverse their signs to compare oxidation of M^{2+}.

Quick Tip to Solve: Reverse the supplied M(III)/M(II) reduction potential before comparing M(II) as a reducing agent.

- A stronger reducing agent loses an electron more readily. Stability of an oxidation state also depends on electronic configuration and resistance to both oxidation and reduction.

Step 1: (a) Compare the reducing agents For chromium, $E^{\circ}_{Cr^{3+}/Cr^{2+}} = -0.41\,V$, whereas for iron it is $+0.77\,V$. Hence the oxidation potentials for $Cr^{2+} \rightarrow Cr^{3+} + e^-$ and $Fe^{2+} \rightarrow Fe^{3+} + e^-$ are $+0.41\,V$ and $-0.77\,V$, respectively. Chromium(II) therefore loses an electron more readily. Its oxidation gives Cr^{3+}, with the relatively stable $3d^3$ configuration.

Step 2: (b) Identify the stable +2 ion Mn^{2+} is the most stable +2 ion in the given series because it has the particularly stable half-filled $3d^5$ configuration. The strongly negative $E^{\circ}_{Mn^{2+}/Mn} = -1.18\,V$ shows that its reduction to manganese metal is difficult. The large positive $E^{\circ}_{Mn^{3+}/Mn^{2+}} = +1.57\,V$ shows that the reverse oxidation of Mn^{2+} to Mn^{3+} is also unfavourable under standard conditions. Together these data support its stability in the +2 state.

Step 3: Conclusion (a) Cr^{2+} is the stronger reducing agent. (b) Mn^{2+} is the most stable +2 ion, owing to its half-filled $3d^5$ configuration and resistance to reduction and oxidation.

Quick Tip to Solve: Reverse the supplied M(III)/M(II) reduction potential before comparing M(II) as a reducing agent.

12. What happens when

(a) Phenol reacts with Conc. HNO_3?

(b) Ethyl chloride reacts with $NaOC_2H_5$?

Write the chemical equations involved in the above reactions. [2 marks]

Solution:

Concept:

- The hydroxyl group activates the benzene ring of phenol and directs electrophilic substitution to its ortho and para positions.
- Williamson ether synthesis is the nucleophilic substitution of a primary alkyl halide by an alkoxide ion, forming an ether and a halide salt.

Step 1: (a) Phenol with concentrated nitric acid Phenol undergoes nitration at both ortho positions and at the para position. Concentrated nitric acid gives 2,4,6-trinitrophenol, commonly called picric acid. The balanced equation is

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{conc.}} C_6H_2(NO_2)_3OH + 3H_2O.$$

The three nitro groups occupy positions 2, 4 and 6 relative to the hydroxyl group. Each substituted ring hydrogen combines with the hydroxyl portion of nitric acid to form water.

Step 2: (b) Ethyl chloride with sodium ethoxide The ethoxide ion, $C_2H_5O^-$, attacks the primary carbon bonded to chlorine in ethyl chloride and displaces chloride by an S_N2 substitution. Diethyl ether (ethoxyethane) is formed by Williamson synthesis:

$$C_2H_5Cl + NaOC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaCl.$$

Quick Tip to Solve: Use three HNO3 molecules for picric acid; in Williamson synthesis place oxygen between the alkyl group and the alkoxide alkyl group.

One ethyl group comes from the halide and the other from sodium ethoxide. The oxygen remains between the two ethyl groups; the reaction forms an ether rather than an alcohol.

Step 3: Conclusion (a) Phenol gives 2,4,6-trinitrophenol (picric acid). (b) Ethyl chloride and sodium ethoxide give diethyl ether (ethoxyethane), with sodium chloride as the by-product.

Quick Tip to Solve: Use three HNO3 molecules for picric acid; in Williamson synthesis place oxygen between the alkyl group and the alkoxide alkyl group.

Section C (36 marks)

13. At 300 K, 30 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of a glucose solution is 1.52 bar at the same temperature, what would be its concentration? [3 marks]

Solution:

Concept:

- For a dilute solution, osmotic pressure obeys $\pi = CRT$, where $C = n/V$ is molar concentration, R is the gas constant and T is absolute temperature.
- Glucose is a non-electrolyte and does not dissociate. At fixed temperature its osmotic pressure is directly proportional to concentration, in molarity or grams per litre.

Step 1: Relate the two solutions Let the mass concentrations be c_1 and c_2. For glucose of molar mass M, $C = c/M$, so $\pi = (c/M)RT$. Both solutions contain glucose at $300\,\text{K}$; thus M, R and T cancel upon division:

$$\frac{\pi_2}{\pi_1} = \frac{c_2}{c_1}.$$

The given values are $c_1 = 30\,\text{g L}^{-1}$, $\pi_1 = 4.98\,\text{bar}$ and $\pi_2 = 1.52\,\text{bar}$. Since both pressures have the same unit, their ratio is dimensionless.

Step 2: Calculate the concentration Rearranging the proportionality and substituting gives

$$c_2 = c_1\frac{\pi_2}{\pi_1} = 30 \times \frac{1.52}{4.98} = 9.1566\,\text{g L}^{-1}.$$

In molar units, the glucose molar mass is $180\,\text{g mol}^{-1}$, hence

$$C_2 = \frac{9.1566}{180} = 0.05087\,\text{mol L}^{-1}.$$

The concentration falls to approximately 0.3052 of its original value, just as the pressure does. This checks the direction of the change.

Step 3: Conclusion The concentration is $\boxed{9.16\,\text{g L}^{-1}}$, equivalently approximately $\boxed{0.0509\,\text{mol L}^{-1}}$.

Quick Tip to Solve: For the same solute at the same temperature, multiply the known concentration by the new-to-old pressure ratio; the gas constant cancels.

14. Chromium crystallises in bcc structure. If its edge length is 300 pm, find its density. Atomic mass of chromium is 52 u. [$N_A = 6.022 \times 10^{23}$ mol^{-1}] [3 marks]

Solution:

Concept:

- A body-centred cubic (bcc) unit cell contains $Z = 2$ atoms: eight corner atoms contribute $8 \times \frac{1}{8} = 1$ atom, and the body-centre atom contributes one more.
- Crystal density is $\rho = ZM/(N_A a^3)$, where M is molar mass, N_A is Avogadro's constant and a is unit-cell edge length.

Step 1: Calculate the mass and volume of a unit cell The atomic mass 52 u corresponds to molar mass $M = 52\,\text{g mol}^{-1}$. With two chromium atoms per bcc cell, its mass is

$$m_{\text{cell}} = \frac{2 \times 52}{6.022 \times 10^{23}}\,\text{g}.$$

Convert the edge to centimetres before calculating volume. Since $1\,\text{pm} = 10^{-10}\,\text{cm}$,

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

Step 2: Divide mass by volume Density is the mass of one unit cell divided by its volume:

$$\rho = \frac{2 \times 52}{(6.022 \times 10^{23})(2.70 \times 10^{-23})} = \frac{104}{16.2594} = 6.396\,\text{g cm}^{-3}.$$

The powers of ten cancel in the denominator. The units reduce to grams per cubic centimetre because the molar mass divided by Avogadro's constant gives the mass of one atom. In SI units this is approximately $6.40 \times 10^3\,\text{kg m}^{-3}$.

Step 3: Conclusion The density of chromium is $\boxed{6.40\,\text{g cm}^{-3}}$.

Quick Tip to Solve: For a bcc density calculation use two atoms per unit cell, and convert picometres to centimetres before cubing the edge length.

15. Define the following terms with a suitable example of each:

(a) Sol

(b) Aerosol

(c) Hydrosol [3 marks]

Solution:

Concept:

- A colloid consists of a dispersed phase, the particles distributed through the mixture, and a dispersion medium, the continuous phase in which those particles are dispersed.
- Colloids are classified by the physical states of these two phases. The term hydrosol further

Quick Tip to Solve: Identify both phases for each example: fog has liquid droplets in gas, while the prefix hydro specifies water as the medium of a sol.

identifies water as the liquid dispersion medium of a sol.

Step 1: (a) Define sol and give an example A sol is a colloidal system in which the dispersed phase is a solid and the dispersion medium is a liquid. The solid particles remain dispersed through the liquid rather than forming a molecular solution. For example, gold sol consists of colloidal particles of solid gold dispersed in water. Thus gold is the dispersed phase and water is the dispersion medium.

Step 2: (b) Define aerosol and give an example An aerosol is a colloidal system in which a solid or a liquid forms the dispersed phase and a gas forms the dispersion medium. For example, fog contains tiny liquid water droplets dispersed in air: water is the liquid dispersed phase and air is the gaseous dispersion medium. Smoke, with solid particles in air, is another aerosol; the gas medium is the defining feature.

Step 3: (c) Define hydrosol and give an example A hydrosol is a sol whose dispersion medium is water; its dispersed phase is solid. For example, a starch sol in water is a hydrosol, with colloidal starch as the dispersed phase and water as the dispersion medium. A hydrosol therefore belongs to the broader class of sols, but specifying water distinguishes it from sols made with other liquid media.

Step 4: Conclusion Sol: solid in liquid, e.g. gold sol. Aerosol: solid or liquid in gas, e.g. fog. Hydrosol: solid in water, e.g. starch sol in water.

Quick Tip to Solve: Identify both phases for each example: fog has liquid droplets in gas, while the prefix hydro specifies water as the medium of a sol.

16(a). Calculate $\Delta_r G^\circ$ and log K_c for the following reaction:

$Cd^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cd(s)$

Given: $E^\circ_{Cd^{2+}/Cd} = -0.403$ V; $E^\circ_{Zn^{2+}/Zn} = -0.763$ V [3 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, where both tabulated potentials are reduction potentials.
- The relations $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$ and $\Delta_r G^\circ = -2.303RT \log K_c$ connect electrical work, standard Gibbs energy and equilibrium; n is electrons transferred and $F = 96500\,\text{C mol}^{-1}$.

Step 1: Identify the electrodes and electron transfer In the printed reaction, zinc is oxidised and cadmium ions are reduced. The balanced half-reactions are

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

Hence zinc is the anode, cadmium is the cathode and $n = 2$. The electron number refers to the reaction as written; the two half-reactions exchange the same two electrons.

Step 2: Calculate the cell potential and Gibbs energy Using the supplied reduction potentials,

$$E^\circ_{\text{cell}} = (-0.403) - (-0.763) = 0.360\,\text{V}.$$

Quick Tip to Solve: Use both values as reduction potentials: subtract the zinc value from the cadmium value, then use two electrons for both calculations.

Therefore,

$$\Delta_r G^\circ = -2(96500)(0.360) = -69480\,\text{J mol}^{-1} = -69.48\,\text{kJ mol}^{-1}.$$

The positive standard cell potential gives a negative standard Gibbs energy, so the forward reaction is thermodynamically favourable under standard conditions.

Step 3: Calculate the equilibrium constant logarithm At the standard temperature $T = 298\,\text{K}$, the usual CBSE relation is $E^\circ_{\text{cell}} = (0.0591/n)\log K_c$, with log denoting base ten. Thus

$$\log K_c = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{2(0.360)}{0.0591} \approx 12.18.$$

Here the pure solids have unit activity; the concentration form of the reaction quotient involves $[\text{Zn}^{2+}]/[\text{Cd}^{2+}]$. The large positive logarithm agrees with the negative Gibbs energy.

Step 4: Conclusion $\boxed{\Delta_r G^\circ = -69.48\,\text{kJ mol}^{-1}, \quad \log K_c \approx 12.18}$ at 298 K.

Quick Tip to Solve: Use both values as reduction potentials: subtract the zinc value from the cadmium value, then use two electrons for both calculations.

OR

16(b). Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation:

$CrO_3(aq) + 6H^+ + 6e^- \rightarrow Cr(s) + 3H_2O$

Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?

[Atomic mass of Cr = 52 g mol^{-1}, 1 F = 96500 C mol^{-1}] [3 marks]

Solution:

Concept:

- Faraday's law gives $m = MQ/(nF)$, where m is deposited mass, M is molar mass, Q is charge and n is electrons required per atom deposited.
- For constant current, $Q = It$, where I is measured in amperes and t in seconds. One mole of electrons carries $F = 96500\,\text{C mol}^{-1}$.

Step 1: Determine the electron requirement The given cathode reaction is

$$\text{CrO}_3(\text{aq}) + 6\text{H}^+ + 6e^- \longrightarrow \text{Cr(s)} + 3\text{H}_2\text{O}.$$

Chromium in CrO_3 has oxidation state $+6$ and the deposited metal has oxidation state zero. Each chromium atom therefore requires six electrons. Hence $n = 6$, and $6F$ of charge deposits one mole, or 52 g, of chromium.

Step 2: Find the mass deposited by the specified charge For $Q = 24000\,\text{C}$, the number of moles of electrons is Q/F, so the number of moles of chromium deposited is $Q/(6F)$. Multiplying by the molar

Quick Tip to Solve: Read the electron coefficient from the balanced deposition equation first; here six faradays deposit one mole of chromium.

mass gives

$$m = \frac{52 \times 24000}{6 \times 96500}\,\text{g} = 2.1554\,\text{g} \approx 2.16\,\text{g}.$$

This calculation uses the stoichiometric electron coefficient of six, rather than the charge on an imagined chromium ion.

Step 3: Find the time required for the second deposition To deposit $1.5\,\text{g}$, the required charge is

$$Q = \frac{mnF}{M} = \frac{1.5 \times 6 \times 96500}{52}\,\text{C} = 16701.9\,\text{C}.$$

With $I = 12.5\,\text{A} = 12.5\,\text{C s}^{-1}$,

$$t = \frac{Q}{I} = \frac{16701.9}{12.5}\,\text{s} = 1336.15\,\text{s} \approx 22.27\,\text{min}.$$

The mass in this part is the separately specified $1.5\,\text{g}$; the charge from the first part must not be reused.

Step 4: Conclusion $\boxed{m \approx 2.16\,\text{g}, \quad t \approx 1.34 \times 10^3\,\text{s}\ (22.3\,\text{min})}$.

Quick Tip to Solve: Read the electron coefficient from the balanced deposition equation first; here six faradays deposit one mole of chromium.

17. Write the hybridization and magnetic character of the following complexes:

(i) $[Fe(H_2O)_6]^{2+}$

(ii) $[Ni(CN)_4]^{2-}$

[Atomic number: Fe = 26, Ni = 28] [3 marks]

Solution:

Concept:

- The metal oxidation state is found from ligand charges and overall complex charge. Remove the $4s$ electrons before the $3d$ electrons when forming transition-metal ions.
- In valence bond theory, weak-field ligands retain unpaired electrons, while strong-field ligands can cause pairing. A complex with unpaired electrons is paramagnetic; one with all electrons paired is diamagnetic.

Step 1: Analyse the iron aqua complex Water is neutral, so iron in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ has oxidation state $+2$. Neutral iron is $[\text{Ar}]3d^6 4s^2$, hence Fe^{2+} is $[\text{Ar}]3d^6$. Water is a weak-field ligand and does not cause the pairing needed to free two inner $3d$ orbitals. The six ligands use the outer-orbital combination of one $4s$, three $4p$ and two $4d$ orbitals, producing sp^3d^2 hybridisation and octahedral geometry. The high-spin d^6 arrangement has four unpaired electrons, so this complex is paramagnetic.

Step 2: Analyse the nickel cyanide complex Each cyanide ligand has charge -1. If nickel has oxidation state x, then $x + 4(-1) = -2$, giving $x = +2$. Neutral nickel is $[\text{Ar}]3d^8 4s^2$, so Ni^{2+} is $[\text{Ar}]3d^8$. Cyanide is a strong-field ligand and causes pairing of the $3d$ electrons. In the valence bond description, the eight electrons occupy four $3d$ orbitals as pairs, leaving one inner $3d$ orbital vacant. This combines with one $4s$ and two $4p$ orbitals to form four dsp^2 hybrid orbitals. The complex is square planar and

Quick Tip to Solve: Find the ionic d-electron count before choosing hybridisation: weak-field water gives high-spin iron, whereas cyanide pairs the nickel electrons.

has no unpaired electrons, so it is diamagnetic.

Step 3: Conclusion (i) $[Fe(H_2O)_6]^{2+}$: $\boxed{sp^3d^2}$, paramagnetic with four unpaired electrons.

(ii) $[Ni(CN)_4]^{2-}$: $\boxed{dsp^2}$, diamagnetic with no unpaired electrons.

Quick Tip to Solve: Find the ionic d-electron count before choosing hybridisation: weak-field water gives high-spin iron, whereas cyanide pairs the nickel electrons.

18(a). Explain the method of preparation of sodium dichromate from chromite ore. Give the equation representing oxidation of ferrous salts by dichromate ion. [3 marks]

Solution:

Concept:

- Chromite, $FeCr_2O_4$, contains chromium(III). Oxidative roasting converts chromium into soluble chromate containing chromium(VI).
- Acidification converts chromate to dichromate; acidic dichromate accepts six electrons to form chromium(III).

Step 1: Roast chromite with sodium carbonate Finely powdered chromite is fused with sodium carbonate in the presence of air. Chromium is oxidised, while iron forms ferric oxide:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\Delta} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

The fused mass is extracted with water. Sodium chromate dissolves; insoluble ferric oxide is removed by filtration.

Step 2: Acidify the chromate solution The yellow sodium chromate solution is acidified with sulphuric acid, producing orange sodium dichromate:

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

Concentration and crystallisation give sodium dichromate, commonly as $Na_2Cr_2O_7 \cdot 2H_2O$. The ionic equilibrium is $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$.

Step 3: Oxidise ferrous ions in acidic medium Each ferrous ion loses one electron: $Fe^{2+} \rightarrow Fe^{3+} + e^-$. Dichromate accepts six electrons, giving the balanced equation:

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

Atoms and charge balance: the total charge on either side is +24.

Step 4: Conclusion Sodium dichromate is obtained by roasting chromite to chromate, extracting with water and acidifying. One acidic dichromate ion oxidises six Fe^{2+} ions to Fe^{3+}.

Quick Tip to Solve: Remember chromite to chromate to dichromate; acidic dichromate accepts six electrons.

OR

18(b). Complete the following reactions:

(a) MnO_2 + KOH + O_2 $\rightarrow$

(b) I^- + MnO_4^- + H^+ $\rightarrow$

(c) $Cr_2O_7^{2-}$ + Sn^{2+} + H^+ $\rightarrow$ [3 marks]

Solution:

Concept:

- Balance redox reactions by conserving atoms and charge. Oxidation is electron loss; reduction is electron gain.
- In acidic medium, permanganate forms Mn^{2+}, and dichromate forms Cr^{3+}.

Step 1: (a) Oxidative fusion of manganese dioxide Heating manganese dioxide with potassium hydroxide in oxygen produces green potassium manganate:

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O.$$

Manganese changes from +4 to +6, losing two electrons per atom. Oxygen is the oxidising agent. The product is manganate, not permanganate, because this alkaline oxidative fusion produces manganese(VI).

Step 2: (b) Oxidation of iodide by acidic permanganate Iodide is oxidised to iodine: $2I^- \rightarrow I_2 + 2e^-$. Permanganate is reduced according to $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. Equalising the electrons gives:

$$10I^- + 2MnO_4^- + 16H^+ \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O.$$

The net charge is +4 on both sides. The acidic medium determines the manganese(II) product.

Step 3: (c) Oxidation of tin(II) by acidic dichromate Tin(II) loses two electrons: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$. One dichromate ion gains six electrons; consequently three tin(II) ions are required:

$$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O.$$

The seven oxygen atoms form seven water molecules and require fourteen hydrogen ions. Total charge is +18 on each side.

Step 4: Conclusion The completed reactions produce (a) K_2MnO_4 and water, (b) iodine, Mn^{2+} and water, and (c) Cr^{3+}, Sn^{4+} and water, with coefficients as balanced above.

Quick Tip to Solve: First fix the manganese product using the medium, then equalise electrons before balancing hydrogen.

19(a). What is the role of

(a) Depressants in froth floatation?

(b) Carbon monoxide in Mond's process?

(c) Concentrated sodium hydroxide in leaching of alumina from bauxite? [3 marks]

Solution:

Concept:

- Selective extraction uses differences in wetting, complex formation or solubility to separate a desired mineral or metal.
- Depressants control flotation; carbon monoxide forms a volatile nickel complex; sodium hydroxide dissolves amphoteric alumina.

Step 1: (a) Depressants in froth flotation A depressant selectively prevents one sulphide ore from entering the froth, allowing another to float. For example, in a mixture of ZnS and PbS, sodium cyanide acts as a depressant for ZnS, while PbS is carried into the froth. Thus depressants enable separation of two sulphide ores rather than merely removing gangue. Cyanide forms a complex with zinc and inhibits the flotation of zinc sulphide.

Step 2: (b) Carbon monoxide in Mond's process Carbon monoxide combines with impure nickel at about 330–$350\,K$, forming volatile nickel tetracarbonyl:

$$Ni + 4CO \rightarrow Ni(CO)_4.$$

The vapour is separated from nonvolatile impurities and heated to about 450–$470\,K$:

$$Ni(CO)_4 \rightarrow Ni + 4CO.$$

Pure nickel is deposited. Carbon monoxide therefore enables purification by reversible formation of a volatile carbonyl.

Step 3: (c) Concentrated sodium hydroxide in bauxite leaching Hot concentrated sodium hydroxide dissolves alumina because alumina is amphoteric. It converts alumina into soluble sodium aluminate:

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

Insoluble impurities such as ferric oxide remain in the residue and are filtered off. Silica can also dissolve as sodium silicate, so it is not correct to claim that every impurity remains insoluble. The selective dissolution concentrates alumina for its subsequent recovery.

Step 4: Conclusion Depressants selectively suppress flotation; CO purifies nickel through volatile $Ni(CO)_4$; concentrated NaOH leaches alumina as soluble sodium aluminate.

Quick Tip to Solve: Associate each reagent with its separation mechanism: wetting, volatile carbonyl, or soluble aluminate.

OR

19(b). Write chemical reactions taking place in the extraction of Aluminium from Bauxite ore.

[3 marks]

Solution:

Concept:

- Bauxite contains hydrated alumina. Bayer leaching converts alumina into soluble sodium aluminate, from which pure hydrated alumina is precipitated.
- Aluminium is obtained by electrolytic reduction of alumina dissolved in molten cryolite. Carbon anodes are consumed by oxygen released during electrolysis.

Step 1: Leach bauxite and precipitate hydrated alumina Heat powdered bauxite with concentrated sodium hydroxide under pressure. Alumina dissolves as sodium aluminate and insoluble impurities are filtered off:

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

Pass carbon dioxide through the filtered solution and seed it with hydrated alumina to precipitate aluminium hydroxide:

$$2Na[Al(OH)_4] + CO_2 \longrightarrow 2Al(OH)_3 + Na_2CO_3 + H_2O.$$

Step 2: Calcine the precipitate Filter the aluminium hydroxide precipitate and heat it strongly to obtain pure alumina for electrolysis:

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

This removes the water associated with the hydrated oxide.

Step 3: Reduce alumina electrolytically Dissolve alumina in molten cryolite and electrolyse using a carbon-lined cathode and carbon anodes. The electrode reactions and anode consumption are

$$\begin{aligned} \text{Cathode: } Al^{3+} + 3e^- &\longrightarrow Al, \\ \text{Anode: } 2O^{2-} &\longrightarrow O_2 + 4e^-, \\ C + O_2 &\longrightarrow CO_2. \end{aligned}$$

Molten aluminium collects at the bottom. Carbon anodes need periodic replacement because they react with the oxygen formed.

Step 4: Conclusion The extraction involves Bayer leaching, precipitation, calcination and Hall–Heroult electrolysis. The overall electrolysis reaction is $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$.

Quick Tip to Solve: Remember the reaction sequence: sodium aluminate, aluminium hydroxide, pure alumina, then aluminium metal.

20. (a) What are antidepressant drugs? Give an example.

(b) Name the sweetening agent used in preparation of sweets for a diabetic patient.

(c) Why are detergents non-biodegradable? [3 marks]

Solution:

Concept:

- Antidepressants are drugs used to treat depression by affecting neurotransmission in the brain.
- Artificial sweeteners provide sweetness without requiring ordinary sugar. Detergent biodegradability depends on the structure of the hydrocarbon chain.

Step 1: (a) Antidepressant drugs Antidepressant drugs help relieve depression and improve mood. For example, iproniazid inhibits enzymes that degrade noradrenaline. Noradrenaline is a neurotransmitter involved in mood; when its level is low, the signal-sending activity associated with mood decreases. By slowing its degradation, the drug makes this neurotransmitter available for longer and helps counter depression. Thus, **iproniazid** is an example of an antidepressant drug.

Step 2: (b) Sweetener for a diabetic patient **Saccharin** can be used as the sweetening agent in sweets prepared for a diabetic patient. It provides sweetness without adding ordinary sugar and passes through the body without being metabolised as sugar. Only a small amount is required because it is much sweeter than sucrose.

Step 3: (c) Non-biodegradable detergents Detergents with highly branched hydrocarbon chains are not readily decomposed by microorganisms. The branching makes microbial attack and enzymatic breakdown difficult, so these detergents persist in water and cause pollution. The statement refers to branched-chain detergents: detergents having straight hydrocarbon chains are more readily biodegradable.

Step 4: Conclusion (a) Antidepressants treat depression; example: iproniazid. (b) Saccharin. (c) Highly branched hydrocarbon chains resist microbial decomposition.

Quick Tip to Solve: For detergent biodegradability, identify chain branching: branched chains resist decomposition more than straight chains.

21. (a) What is the difference between native protein and denatured protein?

(b) Which one of the following is a disaccharide:

Glucose, Lactose, Amylose, Fructose

(c) Write the name of the vitamin responsible for the coagulation of blood. [3 marks]

Solution:

Concept:

- A native protein has its characteristic folded structure and biological activity. Denaturation disrupts higher-order structure without normally cleaving peptide bonds.
- A disaccharide yields two monosaccharide units on hydrolysis. Vitamins are required in small amounts for specific physiological functions.

Quick Tip to Solve: Count sugar units to classify carbohydrates, and remember vitamin K for clotting rather than vitamin C for connective tissue.

Step 1: (a) Native and denatured protein A **native protein** possesses its natural secondary and tertiary structures and performs its characteristic biological function. A **denatured protein** has lost this natural folding and therefore usually loses its biological activity. Heat or a change in pH can disrupt hydrogen bonds and other interactions maintaining the fold. The primary structure, namely the amino-acid sequence joined by peptide bonds, remains intact during ordinary denaturation. Coagulation of egg white on heating is a familiar example.

Step 2: (b) Identify the disaccharide **Lactose** is the disaccharide in the given list. On hydrolysis it yields one glucose unit and one galactose unit:

$$\text{Lactose} + \text{H}_2\text{O} \longrightarrow \text{Glucose} + \text{Galactose}.$$

Glucose and fructose are monosaccharides, so each is already a single sugar unit. Amylose is a polysaccharide consisting of many glucose units; it is therefore not a disaccharide.

Step 3: (c) Vitamin for blood coagulation **Vitamin K** is responsible for normal blood coagulation. It supports the formation of functional clotting proteins, including prothrombin, so its deficiency can impair clotting and cause prolonged bleeding.

Step 4: Conclusion (a) Native protein has its natural folding and activity; denatured protein loses these while its primary structure remains intact. (b) Lactose. (c) Vitamin K.

Quick Tip to Solve: Count sugar units to classify carbohydrates, and remember vitamin K for clotting rather than vitamin C for connective tissue.

22. (a) Give one chemical test to distinguish between the compounds of the following pairs:

(i) CH_3NH_2 and $(CH_3)_2NH$

(ii) Aniline and Ethanamine

(b) Why aniline does not undergo Friedel-Crafts reaction? [3 marks]

Solution:

Concept:

- The carbylamine test is given by primary amines, which contain the $-NH_2$ group, but not by secondary or tertiary amines.
- Primary aromatic amines form relatively stable diazonium salts at $273-278\,K$; primary aliphatic diazonium salts decompose immediately with nitrogen evolution.
- A Lewis base donates its lone pair to a Lewis acid. Aniline coordinates to $AlCl_3$, the catalyst used in Friedel–Crafts reactions.

Step 1: (a)(i) Distinguish methylamine and dimethylamine Heat separate samples with chloroform and alcoholic potassium hydroxide. Methylamine, a primary amine, produces methyl isocyanide with a characteristic offensive smell:

$$CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O.$$

Dimethylamine, $(CH_3)_2NH$, is secondary and does not give this reaction. Thus a positive carbylamine

Quick Tip to Solve: Use carbylamine for primary versus secondary amines, but use cold diazotisation and coupling for aromatic versus aliphatic primary amines.

test identifies methylamine and a negative test identifies dimethylamine.

Step 2: (a)(ii) Distinguish aniline and ethanamine Treat each amine with nitrous acid, generated from sodium nitrite and dilute hydrochloric acid, at $273-278\,\text{K}$. Aniline forms benzenediazonium chloride:

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

Couple this cold solution with phenol in alkaline medium: an orange azo dye forms. Ethanamine instead gives brisk nitrogen evolution and ethanol because its aliphatic diazonium intermediate is unstable:

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2\uparrow + H_2O.$$

It does not give the azo-dye test. Both compounds are primary amines, so the carbylamine test cannot distinguish this pair.

Step 3: (b) Explain the failure of Friedel–Crafts reaction The nitrogen lone pair in aniline coordinates with the Lewis-acid catalyst $AlCl_3$, forming a salt-like complex. Nitrogen thereby acquires positive character and the amino group can no longer donate its lone pair effectively to the ring. The resulting group strongly deactivates the benzene ring towards electrophilic substitution. Catalyst complex formation and this deactivation prevent the normal Friedel–Crafts alkylation or acylation of aniline.

Step 4: Conclusion Methylamine alone gives the carbylamine test; aniline gives a cold diazotisation–azo coupling test while ethanamine evolves nitrogen. Aniline does not undergo Friedel–Crafts reaction because its complex with $AlCl_3$ deactivates the aromatic ring.

Quick Tip to Solve: Use carbylamine for primary versus secondary amines, but use cold diazotisation and coupling for aromatic versus aliphatic primary amines.

23. (a) Butan-1-ol has a higher boiling point than diethyl ether. Why?

(b) Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow[413\,\text{K}]{H^+} CH_3CH_2 - O - CH_2CH_3$$

[3 marks]

Solution:

Concept:

- Intermolecular hydrogen bonds increase the energy needed to separate molecules into the vapour phase. Alcohols have an $O-H$ group, whereas ethers do not.
- At $413\,\text{K}$, acid-catalysed intermolecular dehydration of ethanol forms diethyl ether. Protonation converts the hydroxyl group into water, a good leaving group.

Step 1: (a) Compare the intermolecular attractions Butan-1-ol and diethyl ether are isomers with the same molecular formula, $C_4H_{10}O$, and the same molar mass. Butan-1-ol molecules form intermolecular hydrogen bonds through their $O-H$ groups. Diethyl ether molecules lack a hydrogen bonded directly to oxygen and therefore cannot form hydrogen bonds with one another. They do have dipole attractions and dispersion forces, but these are weaker overall than the attractions in

Quick Tip to Solve: For ethanol at 413 K, use a second alcohol molecule as the nucleophile and show regeneration of the proton in the final step.

the hydrogen-bonded alcohol. More energy is therefore needed to vaporise butan-1-ol, so its boiling point is higher. Ether can accept hydrogen bonds from water; that does not imply hydrogen bonding between pure ether molecules.

Step 2: (b) Step 1: Protonate ethanol The oxygen lone pair accepts a proton from the acid catalyst, giving protonated ethanol:

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

The original hydroxyl group is a poor leaving group. After protonation it can depart as a neutral water molecule, making substitution possible.

Step 3: Step 2: Attack by a second ethanol molecule The oxygen of another ethanol molecule attacks the primary carbon bonded to $\mathrm{OH_2^+}$. Water leaves as the new carbon–oxygen bond forms in an $\mathrm{S_N2}$ substitution, producing protonated ether:

$$\mathrm{CH_3CH_2OH + CH_3CH_2OH_2^+ \longrightarrow (C_2H_5)_2OH^+ + H_2O}.$$

The second alcohol is the nucleophile. A free primary ethyl carbocation is not required for this mechanism.

Step 4: Step 3: Regenerate the acid catalyst Loss of a proton from the oxonium ion gives neutral diethyl ether:

$$\mathrm{(C_2H_5)_2OH^+ \longrightarrow C_2H_5OC_2H_5 + H^+}.$$

Thus the acid is regenerated. Adding the three steps gives the overall intermolecular dehydration:

$$\mathrm{2C_2H_5OH \xrightarrow[413\,K]{H^+} C_2H_5OC_2H_5 + H_2O}.$$

The specified temperature favours ether formation from primary ethanol; a higher temperature favours elimination to ethene.

Step 5: Conclusion Butan-1-ol boils higher because of intermolecular hydrogen bonding. Ethanol forms diethyl ether at $413\,\mathrm{K}$ through protonation, attack by a second ethanol molecule with water departure, and deprotonation.

Quick Tip to Solve: For ethanol at 413 K, use a second alcohol molecule as the nucleophile and show regeneration of the proton in the final step.

24(a). Give reasons for the following:

(a) The presence of $-NO_2$ group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution reactions.

(b) p-dichlorobenzene has higher melting point than that of ortho or meta isomer.

(c) Thionyl chloride method is preferred for preparing alkyl chloride from alcohols. [3 marks]

Solution:

Concept:

- In nucleophilic aromatic substitution, an electron-withdrawing group at an ortho or para position stabilises the negatively charged intermediate by resonance.
- Melting point depends on crystal packing and lattice stability. A more symmetrical molecule often packs more efficiently in the solid state.
- Thionyl chloride converts an alcohol into an alkyl chloride, with sulphur dioxide and hydrogen chloride as gaseous by-products.

Step 1: (a) Activation by an ortho or para nitro group The $-NO_2$ group withdraws electrons by both its inductive and resonance effects. A nucleophile attacks the carbon bearing the halogen, forming an anionic addition intermediate before the halide ion departs. In this intermediate, the negative charge is delocalised to positions ortho and para to the attacked carbon. If a nitro group occupies one of these positions, it accepts electron density by resonance and allows the negative charge to be delocalised further onto its oxygen atoms. This stabilises the intermediate and facilitates substitution. A meta nitro group cannot provide the same direct resonance stabilisation of this intermediate. Hence ortho- and para-nitro-substituted haloarenes undergo nucleophilic substitution more readily than the corresponding unsubstituted haloarene.

Step 2: (b) Higher melting point of the para isomer In p-dichlorobenzene the two chlorine substituents are opposite each other, making the molecule more symmetrical than the ortho and meta isomers. This symmetry permits more regular, efficient packing in the crystal lattice. The resulting solid lattice is more stable and requires more thermal energy to disrupt during melting. Therefore p-dichlorobenzene has the higher melting point. The explanation concerns packing in the solid, so comparing molecular mass would not distinguish these isomers: all three have the same molecular formula.

Step 3: (c) Preference for thionyl chloride Alcohols react with thionyl chloride according to

$$\mathrm{ROH} + \mathrm{SOCl_2} \longrightarrow \mathrm{RCl} + \mathrm{SO_2} \uparrow + \mathrm{HCl} \uparrow.$$

Here R represents an alkyl group. Both by-products, sulphur dioxide and hydrogen chloride, are gases and escape from the reaction mixture. Their removal helps drive the reaction towards alkyl chloride and leaves the liquid organic product comparatively easy to separate in a pure form. This convenient removal of by-products is the chief reason the thionyl chloride method is preferred over methods that leave nonvolatile inorganic residues mixed with the product.

Step 4: Conclusion An ortho or para nitro group stabilises the anionic substitution intermediate; the para dichloro isomer packs more efficiently in its crystal; and thionyl chloride gives gaseous by-products that escape, facilitating purification of the alkyl chloride.

Quick Tip to Solve: Match these three reasons to intermediate stability, crystal symmetry, and gaseous by-products respectively.

OR

24(b). (a) Write equation for preparation of 1-iodobutane from 1-chlorobutane.

(b) Out of 2-bromopentane, 2-bromo-2-methylbutane and 1-bromopentane, which compound is most reactive towards elimination reaction and why?

(c) Give IUPAC name of: [3 marks]

$$CH_3 - CH = CH - \underset{\displaystyle Br}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3$$

Solution:

Concept:

- The Finkelstein reaction replaces chlorine or bromine in an alkyl halide by iodine using sodium iodide in dry acetone. Precipitation of sodium chloride drives the exchange forward.
- On heating with alcoholic alkali, alkyl halides undergo beta-elimination: a hydrogen from a carbon adjacent to the halogen-bearing carbon and the halogen are removed to form an alkene. The usual reactivity order is tertiary greater than secondary greater than primary.
- For an unsaturated haloalkane, choose the longest chain containing the double bond and number it to give the double bond the lowest locant; then locate the substituents.

Step 1: (a) Prepare 1-iodobutane by halogen exchange Treat 1-chlorobutane with sodium iodide in dry acetone:

$$CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow{\text{dry acetone}} CH_3CH_2CH_2CH_2I + NaCl \downarrow .$$

Sodium chloride is insoluble in acetone and separates out. Its removal favours formation of 1-iodobutane; the four-carbon skeleton remains unchanged.

Step 2: (b) Compare elimination reactivity In 2-bromo-2-methylbutane, the carbon carrying bromine is bonded to three other carbon atoms, so this is a tertiary alkyl bromide. In 2-bromopentane that carbon is secondary, while in 1-bromopentane it is primary. Hence the order towards elimination under comparable conditions is

$$\text{2-bromo-2-methylbutane} > \text{2-bromopentane} > \text{1-bromopentane}.$$

The tertiary bromide most readily gives the more substituted, more stable alkene. Alkyl groups stabilise the developing double bond by their electron-releasing effect and hyperconjugation, favouring elimination. The principal alkene from the tertiary bromide is 2-methylbut-2-ene.

Step 3: (c) Name the displayed compound The displayed structure is $CH_3CH{=}CHC(Br)(CH_3)CH_3$. The longest chain containing the double bond has five carbons. Numbering from the left gives the

Quick Tip to Solve: For the name, give the double bond the lower number before considering the locants of bromo or methyl.

double bond locant 2, whereas numbering from the right gives 3, so the parent is pent-2-ene. Both bromo and methyl substituents are then at carbon 4. List bromo before methyl alphabetically. The drawing does not specify an alkene stereochemical configuration, so no stereochemical prefix is required.

Step 4: Conclusion (a) Use NaI in dry acetone to obtain 1-iodobutane. (b) 2-Bromo-2-methylbutane is most reactive towards elimination because it is tertiary. (c) The IUPAC name is 4-bromo-4-methylpent-2-ene.

Quick Tip to Solve: For the name, give the double bond the lower number before considering the locants of bromo or methyl.

Section D (15 marks)

25(a). (a) Draw the structure of the following:

(i) $HClO_3$

(ii) $H_2S_2O_8$

(b) Give reasons for the following:

(i) Above 1000 K sulphur shows paramagnetism.

(ii) Although electron gain enthalpy of fluorine is less negative than that of chlorine, yet fluorine is a better oxidising agent than chlorine.

(iii) In solid state PCl_5 exists as an ionic compound. [5 marks]

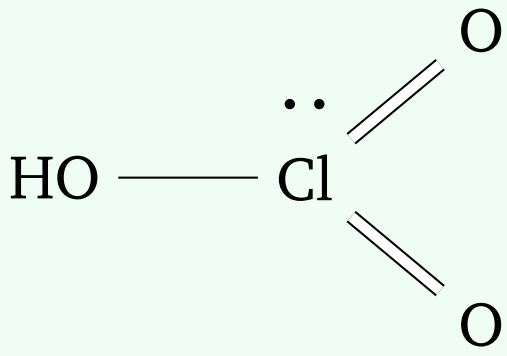
Solution:

Concept:

- In an oxoacid, acidic hydrogen is attached to oxygen. Chloric acid has one hydroxyl group and two terminal oxo groups; peroxodisulphuric acid contains an oxygen-oxygen linkage joining two sulphur centres.
- A species with unpaired electrons is paramagnetic. Molecular sulphur S_2, like O_2, has two unpaired electrons in antibonding molecular orbitals.
- Oxidising strength of a halogen in aqueous solution depends on the overall energetics of reduction, including bond dissociation, electron gain and hydration of the resulting halide ion.
- Solid phosphorus pentachloride contains tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ ions, which are held together by electrostatic attraction.

Step 1: (a)(i) Structure of chloric acid In $HClO_3$, chlorine is central, with one single bond to the oxygen of an $-OH$ group and two double bonds to terminal oxygen atoms. Thus the connectivity is $HO-Cl(=O)_2$. Chlorine also has one lone pair, shown as two dots in the structure. Hydrogen is attached to oxygen rather than directly to chlorine. The oxidation state of chlorine is $+5$, consistent with one hydrogen and three oxygen atoms.

Quick Tip to Solve: Count the oxygen atoms in each oxoacid drawing, and keep the O-O single bond visible in peroxodisulphuric acid.

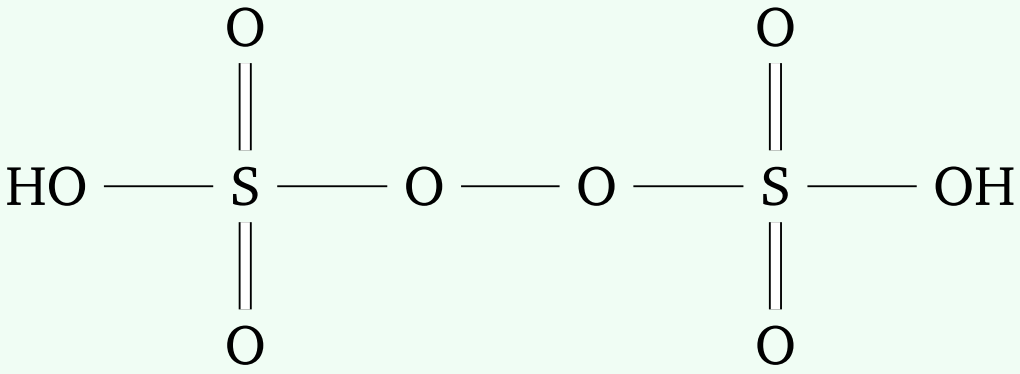


Structure of chloric acid; dots indicate the chlorine lone pair.

Step 2: (a)(ii) Structure of peroxodisulphuric acid In $H_2S_2O_8$, each sulphur atom has two terminal $S=O$ bonds, one $S-OH$ bond, and one single bond to a bridging peroxide oxygen. The two bridging oxygen atoms are joined by a single $O-O$ bond. Its connectivity is

$$HO-S(=O)_2-O-O-S(=O)_2-OH.$$

This accounts for all eight oxygen atoms: four terminal oxo oxygens, two hydroxyl oxygens and two peroxide oxygens. The peroxide oxygens have oxidation state -1; each sulphur has oxidation state $+6$.



Structure of peroxodisulphuric acid, showing the peroxide linkage.

Step 3: (b)(i) Paramagnetism of sulphur above 1000 K At temperatures above $1000\,K$, sulphur vapour contains S_2 molecules. Their molecular-orbital electronic arrangement is analogous to that of O_2: the two degenerate antibonding π^* orbitals each contain one unpaired electron. These unpaired electrons cause attraction towards an external magnetic field, so sulphur shows paramagnetism under these conditions.

Step 4: (b)(ii) Compare fluorine and chlorine as oxidising agents The relevant overall reduction is

$$X_2(g)+2e^-\longrightarrow 2X^-(aq).$$

It involves breaking the $X-X$ bond, adding electrons to gaseous atoms, and hydrating the resulting ions. Although electron gain by a fluorine atom releases less energy than electron gain by a chlorine

Quick Tip to Solve: Count the oxygen atoms in each oxoacid drawing, and keep the O-O single bond visible in peroxodisulphuric acid.

atom, the $F-F$ bond has a low dissociation enthalpy because lone-pair repulsions are strong in the small molecule. Also, the very small F^- ion has a much more negative hydration enthalpy than Cl^-. These factors outweigh the less negative electron gain enthalpy. Overall reduction to hydrated fluoride is therefore more favourable, making fluorine the stronger oxidising agent.

Step 5: (b)(iii) Ionic nature of solid phosphorus pentachloride In the solid state, two PCl_5 units redistribute chloride to form oppositely charged ions:

$$2PCl_5 \longrightarrow [PCl_4]^+[PCl_6]^-.$$

The $[PCl_4]^+$ cation is tetrahedral and the $[PCl_6]^-$ anion is octahedral. Electrostatic attractions between these ions stabilise the crystal lattice; hence the solid exists as an ionic compound. The equation preserves the total of two phosphorus and ten chlorine atoms.

Step 6: Conclusion The structures are $HO-Cl(=O)_2$ and $HO-S(=O)_2-O-O-S(=O)_2-OH$. High-temperature S_2 is paramagnetic due to two unpaired electrons; fluorine's low bond dissociation enthalpy and strongly exothermic fluoride hydration make it a stronger oxidant; solid PCl_5 consists of $[PCl_4]^+$ and $[PCl_6]^-$ ions.

Quick Tip to Solve: Count the oxygen atoms in each oxoacid drawing, and keep the O-O single bond visible in peroxodisulphuric acid.

OR

25(b). (a) Complete the following reactions:

(i) PbS(s) + O_3 $\rightarrow$

(ii) XeF_6 + NaF $\rightarrow$

(b) Arrange the following in increasing order of property indicated, giving reason:

(i) Hydrides of group 15 - boiling points

(ii) Hydrides of group 17 - acidic strength

(iii) Hydrides of group 16 - reducing character [5 marks]

Solution:

Concept:

- Ozone is a strong oxidising agent: sulphide sulphur is oxidised from -2 to $+6$ in sulphate.
- XeF_6 accepts a fluoride ion from NaF, forming the complex anion $[XeF_7]^-$.
- Boiling points depend on intermolecular attractions; acidic strength and reducing character of hydrides depend strongly on the strength of the element–hydrogen bond.

Step 1: (a)(i) Oxidation of lead sulphide Ozone converts black lead sulphide into lead sulphate. The balanced reaction is

$$PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g).$$

Lead remains in the $+2$ oxidation state, while sulphur loses eight electrons in changing from sulphide to sulphate. Four ozone molecules supply the four oxygen atoms incorporated into sulphate; the

Quick Tip to Solve: Place ammonia between arsine and stibine in the boiling-point order; for acidity and reducing power, follow the weakening element–hydrogen bond down the group.

remaining oxygen forms four oxygen molecules. Thus both atoms and the oxidation change are accounted for.

Step 2: (a)(ii) Formation of a xenon fluoride complex Sodium fluoride supplies F^-, and xenon hexafluoride accepts this ion as a Lewis acid:

$$XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-.$$

The product may also be written as $NaXeF_7$. This is fluoride-ion addition rather than a change in xenon's oxidation state; xenon remains in the $+6$ state.

Step 3: (b)(i) Increasing boiling points of group 15 hydrides The required order is

$$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3.$$

From phosphine down the group, increasing molecular size and polarisability strengthen London dispersion forces, so boiling points generally rise. Ammonia has an unusually high boiling point compared with phosphine and arsine because its molecules form intermolecular hydrogen bonds. However, the stronger dispersion forces in the much heavier antimony and bismuth hydrides give them boiling points above that of ammonia. The hydrogen-bond exception must therefore be placed within the full order, rather than putting ammonia first or last automatically.

Step 4: (b)(ii) Increasing acidic strength of group 17 hydrides The order is

$$HF < HCl < HBr < HI.$$

Atomic size increases down the group, so the $H - X$ bond becomes longer and weaker. Release of a proton consequently becomes easier. The very strong $H - F$ bond makes HF the weakest acid in this series, despite fluorine's high electronegativity; HI has the weakest bond and is the strongest acid.

Step 5: (b)(iii) Increasing reducing character of group 16 hydrides The order is

$$H_2O < H_2S < H_2Se < H_2Te.$$

Down group 16, increasing size weakens the element–hydrogen bond and decreases the thermal stability of the hydride. The hydrides are therefore more readily oxidised and act as progressively stronger reducing agents. Water has strong $O - H$ bonds and the least reducing character; hydrogen telluride has the greatest reducing character among these hydrides.

Step 6: Conclusion The products are $PbSO_4 + 4O_2$ from $PbS + 4O_3$, and $Na[XeF_7]$. The increasing orders are:

$$\text{Boiling points: } PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3,$$
$$\text{Acidic strength: } HF < HCl < HBr < HI,$$
$$\text{Reducing character: } H_2O < H_2S < H_2Se < H_2Te.$$

Quick Tip to Solve: Place ammonia between arsine and stibine in the boiling-point order; for acidity and reducing power, follow the weakening element–hydrogen bond down the group.

26(a). Carry out the following conversions:

(i) p-nitrotoluene to 2-bromobenzoic acid

(ii) Propanoic acid to acetic acid

(b) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds, B and C. Compound B gives positive Fehling test and also reacts with iodine and NaOH solution. Compound C does not give Fehling solution test but forms iodoform. Identify the compounds A, B and C. [5 marks]

Solution:

Concept:

- Electrophilic bromination is directed ortho by $-CH_3$ and meta by $-NO_2$. A nitro group can be removed after reduction and diazotisation.
- Hunsdiecker bromination of a silver carboxylate produces an alkyl bromide with one fewer carbon atom.
- Reductive ozonolysis cleaves an alkene into carbonyl compounds. Aliphatic aldehydes give Fehling's test, while a CH_3CO- group gives the iodoform test.

Step 1: (a)(i) Introduce bromine at the required position Number the methyl-bearing carbon of p-nitrotoluene as carbon 1. Bromination with $Br_2/FeBr_3$ gives 2-bromo-4-nitrotoluene. Positions 2 and 6 are equivalent: each is ortho to methyl and meta to nitro, so both substituents direct bromination to the same position.

$$\text{p-Nitrotoluene} \xrightarrow{Br_2/FeBr_3} \text{2-bromo-4-nitrotoluene.}$$

Reduce only the nitro group with Sn/HCl, followed by alkaline work-up, to obtain 2-bromo-4-aminotoluene. Diazotise with $NaNO_2/HCl$ at 273–278 K, then treat the diazonium salt with hypophosphorous acid, H_3PO_2, to replace the diazonium group by hydrogen. This gives o-bromotoluene.

$$\begin{aligned}\text{2-bromo-4-nitrotoluene} &\xrightarrow{Sn/HCl} \text{2-bromo-4-aminotoluene,}\\ \text{2-bromo-4-aminotoluene} &\xrightarrow[273\text{–}278\,K]{NaNO_2/HCl} \text{diazonium salt}\\ &\xrightarrow{H_3PO_2} \text{o-bromotoluene.}\end{aligned}$$

Finally, oxidise the methyl side chain with hot alkaline $KMnO_4$ and acidify. The methyl carbon becomes the carboxyl carbon, while the ring bromine remains ortho to it, giving 2-bromobenzoic acid.

Step 2: (a)(ii) Shorten propanoic acid by one carbon Prepare silver propanoate using silver oxide. Its Hunsdiecker reaction with bromine in CCl_4 on heating removes the carboxyl carbon as carbon dioxide:

$$CH_3CH_2COOAg + Br_2 \xrightarrow[\Delta]{CCl_4} CH_3CH_2Br + CO_2 + AgBr.$$

Hydrolyse bromoethane with aqueous KOH to obtain ethanol, then oxidise the primary alcohol with acidified potassium dichromate under reflux:

$$\begin{aligned}CH_3CH_2Br &\xrightarrow{KOH(aq)} CH_3CH_2OH,\\ CH_3CH_2OH + 2[O] &\xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH + H_2O.\end{aligned}$$

Quick Tip to Solve: The aldehyde that gives iodoform is ethanal; subtract its two carbons from the alkene's five to identify the other product as propanone.

The initial carbon loss changes the three-carbon acid into a two-carbon chain; the subsequent oxidation gives acetic acid without further carbon loss.

Step 3: (b) Identify the two ozonolysis products B gives Fehling's test, so it is an aliphatic aldehyde. It also reacts with iodine and NaOH in the iodoform test. The aldehyde with the required methyl carbonyl group is ethanal, CH_3CHO. Thus B contains two carbons. C fails Fehling's test but gives iodoform, so it is a methyl ketone. Since A contains five carbons and ozonolysis conserves them between B and C, C contains three carbons and is propanone, CH_3COCH_3. A ketone does not reduce Fehling's solution, and propanone has the CH_3CO- group needed for the iodoform test.

Step 4: Reconstruct and check the alkene Join the carbonyl carbons of ethanal and propanone by a double bond, removing their oxygen atoms. This gives 2-methylbut-2-ene:

$$A = CH_3CH = C(CH_3)_2.$$

Its formula is C_5H_{10}. Reductive ozonolysis verifies both products:

$$CH_3CH = C(CH_3)_2 \xrightarrow[Zn/H_2O]{O_3} CH_3CHO + CH_3COCH_3.$$

The double-bond carbon carrying hydrogen forms the aldehyde B; the carbon carrying two methyl groups forms the ketone C. Both products yield yellow CHI_3 in the iodoform test, but only B gives the red Cu_2O precipitate with Fehling's solution.

Step 5: Conclusion Bromination, nitro reduction, diazotisation, H_3PO_2 treatment and side-chain oxidation convert p-nitrotoluene to 2-bromobenzoic acid. Hunsdiecker shortening followed by hydrolysis and oxidation converts propanoic acid to acetic acid. A is 2-methylbut-2-ene, B is ethanal and C is propanone.

Quick Tip to Solve: The aldehyde that gives iodoform is ethanal; subtract its two carbons from the alkene's five to identify the other product as propanone.

OR

26(b). **(a) Carry out the following conversions:**

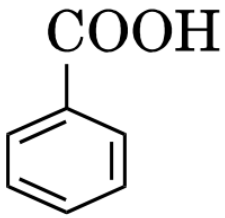
(i) Benzoic acid to aniline

(ii) Bromomethane to ethanol

(b) Write the structure of major product(s) in the following: [5 marks]

(i) $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - H \xrightarrow[\text{(b) KOH, Glycol/heat}]{\text{(a) } H_2N - NH_2}$

(ii) $CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CHO \xrightarrow{\text{conc. NaOH}}$

(iii)  $\xrightarrow{\text{NaOH}}$

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine with one fewer carbon atom; the carbonyl carbon is lost.
- Cyanide substitution extends a carbon chain by one carbon. Reduction of a nitrile gives an amine, which reacts with nitrous acid to give the corresponding aliphatic alcohol.
- Wolff–Kishner reduction replaces a carbonyl group by a methylene group. Aldehydes without an alpha hydrogen undergo the Cannizzaro reaction in concentrated alkali.

Step 1: (a)(i) Convert benzoic acid into benzamide, then aniline First convert the acid to the acid chloride using thionyl chloride, then treat with ammonia to form benzamide. Finally use bromine and aqueous sodium hydroxide for Hofmann degradation:

$$C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl$$

$$C_6H_5COCl + 2NH_3 \longrightarrow C_6H_5CONH_2 + NH_4Cl$$

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

The benzene ring remains intact; only the amide carbonyl carbon is removed to give aniline.

Step 2: (a)(ii) Extend bromomethane by one carbon Treat bromomethane with alcoholic potassium cyanide to obtain ethanenitrile. Reduce the nitrile with lithium aluminium hydride in dry ether, then

Quick Tip to Solve: Count carbon atoms during each conversion, and check for alpha hydrogens before choosing aldol or Cannizzaro chemistry.

hydrolyse the reaction mixture to obtain ethanamine. Nitrous acid generated from sodium nitrite and hydrochloric acid converts this primary aliphatic amine into ethanol:

$$\mathrm{CH_3Br} \xrightarrow{\text{alcoholic KCN}} \mathrm{CH_3CN}$$

$$\mathrm{CH_3CN} \xrightarrow[\text{then water}]{\mathrm{LiAlH_4/ether}} \mathrm{CH_3CH_2NH_2}$$

$$\mathrm{CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O.}$$

Potassium cyanide is used because its carbon end attacks and adds the required carbon atom.

Step 3: (b)(i) Reduce propanal by the Wolff–Kishner method Hydrazine first forms a hydrazone. Heating with KOH in glycol eliminates nitrogen and converts the aldehyde carbonyl group into a terminal methyl group:

$$\mathrm{CH_3CH_2CHO} \xrightarrow[\text{KOH, glycol, heat}]{\mathrm{H_2NNH_2}} \mathrm{CH_3CH_2CH_3.}$$

Thus the product retains all three carbon atoms and is propane.

Step 4: (b)(ii) Identify both Cannizzaro products The carbon adjacent to the aldehyde group in $(\mathrm{CH_3})_3\mathrm{CCHO}$ has no hydrogen. Hence it cannot undergo ordinary aldol condensation. In concentrated NaOH, two molecules disproportionate: one aldehyde group is reduced to $\mathrm{CH_2OH}$, while the other is oxidised to the carboxylate salt.

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

These are 2,2-dimethylpropan-1-ol and sodium 2,2-dimethylpropanoate. The salt, rather than the free acid, is the product under the given alkaline conditions.

Step 5: (b)(iii) Neutralise benzoic acid The printed reagent is NaOH alone. It removes the acidic proton of the carboxyl group:

$$\mathrm{C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O.}$$

The major organic product is sodium benzoate. Decarboxylation to benzene would require soda lime and heating, which are not specified here.

Step 6: Conclusion (a) The conversions are completed as above. (b) Products: (i) propane; (ii) 2,2-dimethylpropan-1-ol and sodium 2,2-dimethylpropanoate; (iii) sodium benzoate.

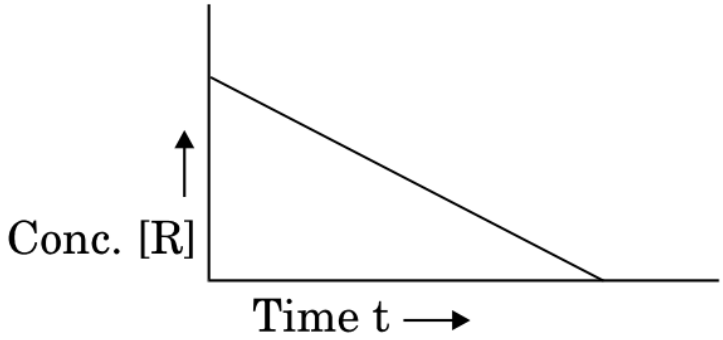
Quick Tip to Solve: Count carbon atoms during each conversion, and check for alpha hydrogens before choosing aldol or Cannizzaro chemistry.

27(a). **Consider the reaction R $\rightarrow$ P for which the change in concentration of R with time is shown by the following graph:**

(i) Predict the order of reaction.

(ii) What does the slope of the curve indicate?

(b) The rate of reaction quadruples when temperature changes from 293 K to 313 K. Calculate E_a assuming that it does not change with time. [R = 8.314 J K^{-1} mol^{-1}] [5 marks]



Solution:

Concept:

- For a zero-order reaction, the rate is independent of reactant concentration: $-d[R]/dt = k$. Its integrated rate equation is $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration and k is the rate constant.
- Arrhenius equation relates rate constant to absolute temperature: $k = Ae^{-E_a/(RT)}$, where A is the pre-exponential factor, E_a the activation energy and R the gas constant.
- For unchanged concentration conditions and reaction order, the ratio of rates at two temperatures equals the ratio of their rate constants. Assume the Arrhenius parameters remain constant over the stated temperature interval.

Step 1: (a)(i) Read the concentration-time graph The graph is a straight line with concentration $[R]$ on the vertical axis and time t on the horizontal axis. Concentration decreases uniformly as time increases. Compare it with

$$[R] = [R]_0 - kt.$$

This is of the form $y = c + mx$, with intercept $[R]_0$ and slope $-k$. It is therefore the characteristic plot for a zero-order reaction. A first-order reaction instead gives a straight line when $\ln[R]$, rather than $[R]$, is plotted against time. The linear expression applies while the reactant remains present, up to its depletion.

Step 2: (a)(ii) Interpret the slope Choose any two points on the sloping straight line:

$$m = \frac{[R]_2 - [R]_1}{t_2 - t_1} = -k.$$

Hence the negative slope represents the zero-order rate constant; its magnitude equals k. Equivalently, the slope is the negative of the constant rate of disappearance of reactant R. It is negative because the numerator is negative for increasing time. If concentration is expressed in $\mathrm{mol\,L^{-1}}$ and time in seconds, the slope has units $\mathrm{mol\,L^{-1}\,s^{-1}}$.

Quick Tip to Solve: Identify which concentration function is plotted before deciding the order; use the rate ratio four directly in the Arrhenius equation.

Step 3: (b) Apply the two-temperature Arrhenius equation Put $T_1 = 293\,\text{K}$, $T_2 = 313\,\text{K}$, and $k_2/k_1 = 4$, since the rate quadruples. Subtracting the logarithmic Arrhenius equations eliminates A:

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Solving for the activation energy gives

$$\begin{aligned} E_a &= \frac{R\ln 4}{1/293 - 1/313} \\ &= \frac{8.314 \times 1.386294 \times 293 \times 313}{313 - 293} \\ &\approx 52848\,\text{J mol}^{-1} \\ &= 52.85\,\text{kJ mol}^{-1}. \end{aligned}$$

The temperatures must be in kelvin. The reciprocal-temperature difference is positive because $T_2 > T_1$; the logarithm of four is also positive, so the calculated activation energy is positive. Using the common-log version with the factor 2.303 gives the same value within rounding.

Step 4: Conclusion (a)(i) The reaction is zero order. (a)(ii) The slope is $-k$, so its magnitude gives the rate constant. (b) $\boxed{E_a \approx 52.85\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Identify which concentration function is plotted before deciding the order; use the rate ratio four directly in the Arrhenius equation.

OR

27(b). (a) Draw the plot of *ln* k vs 1/T for a chemical reaction. What does the intercept represent? What is the relation between slope and E_a?

(b) A first order reaction takes 30 minutes for 20% decomposition. Calculate $t_{1/2}$. [log 2 = 0.3010]

[5 marks]

Solution:

Concept:

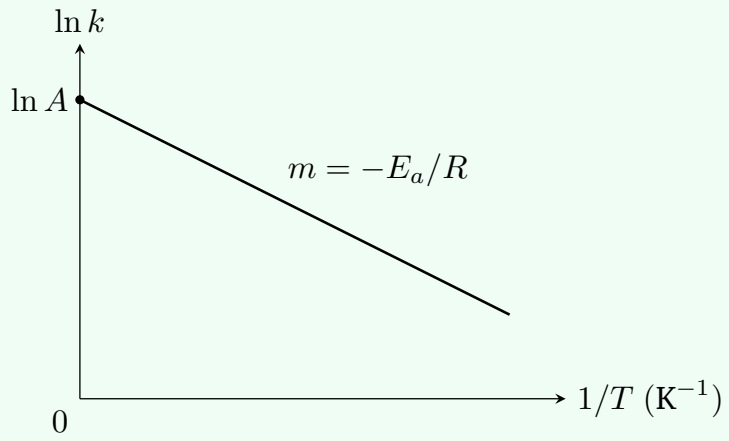
- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature.
- Taking natural logarithms gives $\ln k = \ln A - (E_a/R)(1/T)$. Comparing with $y = mx + c$ identifies the slope and vertical intercept.
- For a first order reaction, $k = (2.303/t)\log([R]_0/[R]_t)$ and $t_{1/2} = 2.303\log 2/k = 0.693/k$. Concentrations must describe the reactant remaining, not the amount decomposed.

Step 1: (a) Obtain the straight-line plot Write the logarithmic form of the Arrhenius equation as

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

Quick Tip to Solve: Convert percent decomposed into percent remaining first; then use $t_{1/2}/t = \log 2/\log(100/\%\text{ remaining})$ to cancel the factor 2.303.

Thus take $\ln k$ along the vertical axis and $1/T$ along the horizontal axis. For positive activation energy the straight line slopes downwards as $1/T$ increases: lower temperature corresponds to a smaller rate constant. Its extrapolation to $1/T = 0$ cuts the vertical axis at $\ln A$, the natural logarithm of the pre-exponential factor. This intercept does not represent A itself.



Arrhenius plot: vertical intercept $\ln A$ *and slope* $-E_a/R$.

Step 2: (a) Relate the slope to activation energy For any two points on the line,

$$m = \frac{\Delta(\ln k)}{\Delta(1/T)} = -\frac{E_a}{R}, \qquad E_a = -mR.$$

The negative sign is essential: a positive activation energy produces a negative slope. Since $1/T$ has units K^{-1}, the slope has units K; multiplying its negative by R gives activation energy in J mol^{-1}.

Step 3: (b) Calculate the first order rate constant Let the initial amount of reactant be 100 units. After 30 min, 20 units have decomposed and 80 units remain. Hence

$$\begin{aligned} k &= \frac{2.303}{30} \log\left(\frac{100}{80}\right) \\ &= \frac{2.303}{30} \log(1.25) \\ &= \frac{2.303 \times 0.0970}{30} \\ &\simeq 7.45 \times 10^{-3}\ \mathrm{min}^{-1}. \end{aligned}$$

Here $\log(1.25) = \log(10/8) = 1 - 3\log 2 = 1 - 3(0.3010) = 0.0970$, using the supplied rounded value of $\log 2$. The rate constant is expressed per minute because the time is given in minutes.

Step 4: (b) Find the half-life At the half-life the remaining amount is one-half of its initial value.

Quick Tip to Solve: Convert percent decomposed into percent remaining first; then use $t_{1/2}/t = \log 2/\log(100/\%\ \text{remaining})$ to cancel the factor 2.303.

Using the given common logarithm of 2, eliminate k between the two first order expressions:

$$\begin{aligned} t_{1/2} &= \frac{2.303 \log 2}{k} \\ &= \frac{30 \log 2}{\log(100/80)} \\ &= \frac{30 \times 0.3010}{0.0970} \\ &\simeq 93.1 \text{ min}. \end{aligned}$$

This is greater than 30 min, as expected because the observed interval decomposes only 20%, whereas the half-life corresponds to 50% decomposition. For first order kinetics this half-life is independent of the chosen initial amount.

Step 5: Conclusion (a) The $\ln k$ versus $1/T$ plot is a straight line with vertical intercept $\ln A$ and slope $-E_a/R$, so $E_a = -R \times$ slope. (b) The half-life is $\boxed{t_{1/2} \simeq 93.1 \text{ min}}$.

Quick Tip to Solve: Convert percent decomposed into percent remaining first; then use $t_{1/2}/t = \log 2 / \log(100/\%\text{ remaining})$ to cancel the factor 2.303.