CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-4-2

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 is the coordination number of atoms in a (i) bcc structure, and (ii) fcc structure? [1 mark]

Solution:

Concept:

- The coordination number is the number of nearest-neighbour atoms surrounding a given atom in a crystal.
- Count nearest neighbours at the same minimum distance; this is different from the effective number of atoms belonging to a unit cell.

Step 1: Examine the bcc arrangement In a body-centred cubic (bcc) unit cell, the atom at the body centre has the eight corner atoms as its nearest neighbours. All eight are at the same distance from the central atom.

Step 2: Examine the fcc arrangement In a face-centred cubic (fcc) crystal, each atom has twelve nearest neighbours in the extended lattice: six in its own close-packed layer, three in the layer above and three in the layer below.

Step 3: Conclusion (i) bcc: 8. (ii) fcc: 12.

Quick Tip to Solve: Count the nearest neighbours, not the atoms per unit cell: bcc and fcc have 2 and 4 atoms per cell respectively.

2. Why are powdered substances more effective adsorbents than their crystalline forms? [1 mark]

Solution:

Concept:

- Adsorption is the accumulation of molecules or ions on the surface of an adsorbent.
- For a fixed mass of a solid, a greater exposed surface area provides more sites for adsorption.

Step 1: Compare the exposed surfaces Grinding a crystalline solid into a fine powder breaks it into many small particles. The total surface area exposed to the surroundings increases greatly compared with that of the same mass in larger crystals.

Step 2: Relate surface area to adsorption The powder therefore exposes more adsorption sites to the adsorbate. More molecules can attach to its surface under otherwise identical conditions, so its adsorbing capacity per unit mass is greater.

Step 3: Conclusion Powdered substances are more effective adsorbents because they have a larger exposed surface area per unit mass.

Quick Tip to Solve: For adsorption comparisons, first compare exposed surface area for the same mass of the solid.

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 chloride ions outside the coordination sphere ionise freely and give an immediate precipitate with aqueous silver nitrate.
- Chromium(III) in this hydrated complex has coordination number six; water is a neutral monodentate ligand and chloride has charge -1.

Step 1: Locate the ionisable chloride ions Two moles of $AgCl$ per mole of compound mean that two of the three chloride ions are outside the coordination sphere: $Ag^+ + Cl^- \longrightarrow AgCl(s)$. The remaining chloride is coordinated to chromium.

Step 2: Complete the coordination sphere One coordinated chloride occupies one of the six coordination positions, leaving five for water ligands. Of the six water molecules in the formula, five are coordinated and the sixth is water of crystallisation. The complex ion is $[Cr(H_2O)_5Cl]^{2+}$, balanced by two chloride ions.

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

Quick Tip to Solve: Use the moles of AgCl to count outside-sphere chlorides, then fill the six coordination sites around chromium.

OR

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

Solution:

Concept:

- A double salt is a crystalline combination of simple salts that dissociates into its constituent ions in water.
- A complex compound retains its complex ion, with metal-ligand bonds, in aqueous solution.

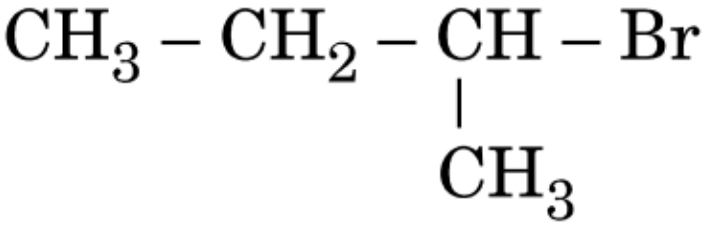
Step 1: Describe a double salt in solution A double salt loses its separate identity in aqueous solution and gives the tests of all its constituent ions. For example, Mohr's salt gives Fe^{2+}, NH_4^+ and SO_4^{2-} ions.

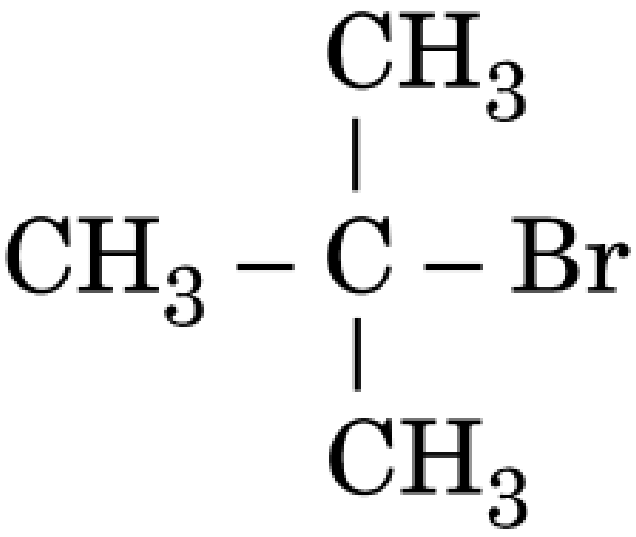
Step 2: Describe a complex in solution A complex retains the identity of its coordination entity. For example, $K_4[Fe(CN)_6]$ gives K^+ and $[Fe(CN)_6]^{4-}$ ions in water; it does not dissociate simply into free Fe^{2+} and CN^- ions.

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

Quick Tip to Solve: Compare the ions actually present in water: retention of the coordination entity distinguishes a complex.

4. Which alkyl halide from the following pair would you expect to react more rapidly by an S_N2 mechanism? [1 mark]





Solution:

Concept:

- An S_N2 reaction occurs by a single-step backside attack of a nucleophile at the carbon bearing the leaving group.
- Steric hindrance slows this attack; for comparable alkyl halides the usual reactivity order is methyl $>$ primary $>$ secondary $\gg$ tertiary.

Step 1: Identify the substitution at the reacting carbon In $CH_3CH_2CH(Br)CH_3$, the carbon bonded to bromine is attached to two other carbons, so 2-bromobutane is secondary. In $(CH_3)_3CBr$, it is attached to three carbons, so 2-bromo-2-methylpropane is tertiary.

Step 2: Compare access for backside attack The secondary halide offers less crowding around the carbon bearing bromine. The three methyl groups in the tertiary halide strongly obstruct the incoming nucleophile. Since both have bromide as the leaving group, steric hindrance determines the comparison.

Step 3: Conclusion $\boxed{CH_3CH_2CH(Br)CH_3}$, 2-bromobutane (the left-hand structure), reacts more rapidly by the S_N2 mechanism.

Quick Tip to Solve: Look only at the carbon directly bonded to Br: two carbon neighbours allow faster SN2 attack than three.

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

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine using bromine and aqueous alkali.
- The product amine has one carbon atom fewer than the starting amide because the carbonyl carbon is removed.

Step 1: Identify the functional-group conversion A primary amide $RCONH_2$ is treated with Br_2 and aqueous $NaOH$ on heating. The group R becomes bonded directly to nitrogen, giving RNH_2; the carbonyl carbon is not retained in the amine.

Step 2: Write the balanced reaction The overall reaction in alkaline medium is

$$RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The removed carbon appears as carbonate, and bromine is converted to bromide.

Step 3: Conclusion Hofmann degradation: $RCONH_2 \xrightarrow{Br_2,\ \text{aq. NaOH},\ \Delta} RNH_2$, with loss of the amide carbonyl carbon.

Quick Tip to Solve: When checking a Hofmann degradation product, remove the carbonyl carbon and attach the remaining R group to NH2.

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:

- Intermolecular hydrogen bonding requires a hydrogen directly bonded to a strongly electronegative atom such as nitrogen.
- Stronger intermolecular attraction requires more energy to separate liquid molecules, increasing the boiling point.

Step 1: Compare the nitrogen-hydrogen bonds Propanamine, $CH_3CH_2CH_2NH_2$, is a primary amine and contains $N-H$ bonds. Its molecules can form intermolecular $N-H\cdots N$ hydrogen bonds with one another. N,N-dimethylmethanamine, $(CH_3)_3N$, is a tertiary amine and has no $N-H$ bond.

Step 2: Relate association to boiling point Although both compounds have the same number of carbon atoms and the same molecular formula, trimethylamine cannot form such hydrogen-bonded associations among its own molecules. More energy is needed to overcome the additional intermolecular hydrogen bonding in propanamine.

Step 3: Conclusion Propanamine has the higher boiling point because its molecules form intermolec-

Quick Tip to Solve: For pure amines, inspect N-H bonds: a nitrogen lone pair alone does not let a tertiary amine self-hydrogen-bond.

ular hydrogen bonds, whereas N,N-dimethylmethanamine lacks an N-H bond.

Quick Tip to Solve: For pure amines, inspect N-H bonds: a nitrogen lone pair alone does not let a tertiary amine self-hydrogen-bond.

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 with hydrated ferrous ions to form a brown nitrosyl complex; sulphate acts as the counter-ion.

Step 1: Identify the anion The appearance of the brown ring confirms the presence of the nitrate ion, NO_3^-. Ferrous ions reduce nitrate to nitric oxide in the acidic medium and are themselves oxidised to ferric ions:

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

Step 2: Give the composition of the ring The nitric oxide produced combines with remaining hydrated ferrous ions at the interface of the layers. The brown compound is pentaaquanitrosyliron(II) sulphate, conventionally written as $[Fe(H_2O)_5(NO)]SO_4$. Its coordination sphere contains five water ligands and one nitrosyl ligand, with sulphate outside the coordination sphere. Formation is represented by

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

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

Quick Tip to Solve: Remember five water ligands and one NO ligand inside the square brackets; sulphate remains outside.

OR

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

Solution:

Concept:

- In the first conversion, chloride in hydrochloric acid is oxidised from oxidation state -1 to 0, while manganese in manganese dioxide is reduced from $+4$ to $+2$. Concentrated hydrochloric acid supplies both chloride ions and the acidic medium; heating assists liberation of chlorine.
- In the second conversion, hydrogen and chlorine combine directly in sunlight to form hydrogen chloride gas. Hydrogen is oxidised from 0 to $+1$, while chlorine is reduced from 0 to -1. The balanced equation contains equal numbers of hydrogen and chlorine atoms on both sides.

Step 1: Prepare chlorine from hydrochloric acid

$$\mathrm{MnO_2(s) + 4HCl(conc.) \xrightarrow{\Delta} MnCl_2(aq) + Cl_2(g) + 2H_2O(l).}$$

Step 2: Prepare hydrogen chloride from chlorine

$$\mathrm{H_2(g) + Cl_2(g) \xrightarrow{sunlight} 2HCl(g).}$$

Step 3: Conclusion $\mathrm{MnO_2 + 4HCl(conc.) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O}$; $\mathrm{H_2 + Cl_2 \xrightarrow{sunlight} 2HCl}$.

Quick Tip to Solve: Balance the first reaction with four HCl molecules: two chlorides form MnCl2 and the other two form Cl2.

7. Define electrochemical cell. What happens when applied external potential becomes greater than E^0_{cell} of electrochemical cell? [2 marks]

Solution:

Concept:

- A galvanic electrochemical cell converts the chemical energy of a spontaneous redox reaction into electrical energy.
- An external potential applied in opposition to the cell emf can stop the spontaneous reaction or drive it in reverse.

Step 1: Define an electrochemical cell An electrochemical cell is a device in which the chemical energy released by a spontaneous oxidation-reduction reaction is converted into electrical energy. Oxidation and reduction occur at separate electrodes, and electrons flow through the external circuit from the oxidation electrode to the reduction electrode.

Step 2: Apply an opposing potential greater than the cell potential When the opposing external potential exceeds E^0_{cell}, under the standard conditions implicit in this comparison, the external source drives electrons in the direction opposite to their spontaneous flow. The cell reaction is reversed: the reaction that normally gives electrical energy is forced to run backwards. Electrical energy is then

Quick Tip to Solve: In this comparison the external source opposes the cell: equality stops current, while a larger potential reverses it.

consumed to bring about a non-spontaneous chemical reaction, and the cell behaves as an electrolytic cell. At equality the net current would be zero; reversal requires the applied opposing potential to be greater.

Step 3: Conclusion An electrochemical cell converts chemical energy into electrical energy. A greater opposing external potential reverses the reaction and makes it function as an electrolytic cell.

Quick Tip to Solve: In this comparison the external source opposes the cell: equality stops current, while a larger potential reverses it.

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:

- The solubility of a gas in a liquid generally decreases as temperature rises, so cold water retains more dissolved oxygen.
- Henry's law is $p = K_H x$, where p is the gas partial pressure and x its mole fraction in solution at fixed temperature.

Step 1: (a) Compare oxygen availability in cold and warm water Aquatic organisms obtain oxygen from the oxygen dissolved in water. At a given oxygen partial pressure, oxygen is more soluble in cold water than in warm water. Cold water therefore contains a greater concentration of dissolved oxygen and can supply oxygen for respiration more readily. This makes aquatic species more comfortable in cold water.

Step 2: (b) Explain anoxia at higher altitudes Atmospheric pressure is lower at higher altitudes. Although the proportion of oxygen in air remains approximately the same, its partial pressure falls. From $x = p/K_H$, a lower oxygen partial pressure reduces the amount of oxygen that dissolves in blood. Consequently, less oxygen reaches the tissues and brain. This oxygen deficiency, called anoxia, impairs normal brain function and can produce inability to think clearly.

Step 3: Conclusion Cold water supports more dissolved oxygen. At high altitudes, the lower oxygen partial pressure reduces oxygen uptake into blood, causing anoxia and impaired thinking.

Quick Tip to Solve: For altitude questions use oxygen partial pressure, not a claim that the percentage of oxygen in air falls.

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:

- A solution showing negative deviation from Raoultś law has a lower vapour pressure than the ideal solution at the same composition.
- Stronger unlike-molecule attractions can produce a maximum-boiling azeotrope, whose liquid and vapour compositions are identical at the azeotropic composition.

Step 1: Identify the intermolecular interaction On mixing acetone, $(CH_3)_2CO$, with chloroform, $CHCl_3$, the hydrogen of chloroform forms a hydrogen bond with the oxygen of the acetone carbonyl group. The interaction can be represented as $(CH_3)_2C = O \cdots H - CCl_3$. These acetone-chloroform attractions are stronger than the average attractions between molecules in the pure liquids.

Step 2: Relate attraction strength to vapour pressure and boiling The stronger attractions hold molecules more firmly in the liquid, reducing their escaping tendency. The partial vapour pressures are consequently lower than predicted by Raoultś law, giving negative deviation. Because the total vapour pressure is depressed, a higher temperature is needed for the vapour pressure to equal atmospheric pressure. At the azeotropic composition this results in a maximum in the boiling-point curve; the mixture boils at constant composition.

Step 3: Conclusion Acetone and chloroform form a $\boxed{\text{maximum-boiling azeotrope}}$, owing to strong hydrogen bonding between unlike molecules and negative deviation from Raoultś law.

Quick Tip to Solve: Stronger unlike-molecule attraction lowers vapour pressure and raises boiling point: negative deviation means maximum boiling.

9. Write the equations involved in the following reactions:

(a) Kolbe's reaction

(b) Friedel-Crafts alkylation of anisole [2 marks]

Solution:

Concept:

- In Kolbe's reaction, sodium phenoxide reacts with carbon dioxide under pressure; acidification gives salicylic acid.
- The methoxy group of anisole activates the aromatic ring and directs electrophilic substitution to the ortho and para positions.

Step 1: (a) Kolbe's reaction First convert phenol into sodium phenoxide using sodium hydroxide.

Quick Tip to Solve: In Kolbe's reaction add COOH ortho to OH; in anisole alkylation retain OCH3 and add the alkyl group at ortho and para positions.

Introduce carbon dioxide under pressure at about $400\,\mathrm{K}$, then acidify:

$$\mathrm{C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O}$$
$$\mathrm{C_6H_5ONa + CO_2 \xrightarrow[\text{pressure}]{400\,K} o\text{–}HOC_6H_4COONa}$$
$$\mathrm{o\text{–}HOC_6H_4COONa + HCl \longrightarrow o\text{–}HOC_6H_4COOH + NaCl.}$$

The final product is 2-hydroxybenzoic acid, or salicylic acid; COOH is ortho to OH.

Step 2: (b) Friedel–Crafts alkylation of anisole Methyl chloride in the presence of anhydrous aluminium chloride gives ortho- and para-methylanisole:

$$\mathrm{C_6H_5OCH_3 + CH_3Cl \xrightarrow{anhydrous\ AlCl_3} o\text{–}CH_3C_6H_4OCH_3 + HCl,}$$
$$\mathrm{C_6H_5OCH_3 + CH_3Cl \xrightarrow{anhydrous\ AlCl_3} p\text{–}CH_3C_6H_4OCH_3 + HCl.}$$

The equations show the two products in the mixture. The para product predominates because substitution there encounters less steric hindrance.

Step 3: Conclusion Kolbe's reaction gives salicylic acid after acidification. Friedel–Crafts methylation of anisole gives ortho- and para-methylanisole, with the para isomer predominant.

Quick Tip to Solve: In Kolbe's reaction add COOH ortho to OH; in anisole alkylation retain OCH3 and add the alkyl group at ortho and para positions.

10. 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:

- A reducing agent loses electrons. For the couple M^{3+}/M^{2+}, a lower standard reduction potential means that the reverse oxidation of M^{2+} is easier.
- The half-filled $3d^5$ configuration has extra stability. The stability of an aqueous oxidation state is also reflected in the electrode potentials for its reduction and oxidation.

Step 1: (a) Compare the oxidation of chromium(II) and iron(II) The relevant data are $E^\circ(Cr^{3+}/Cr^{2+}) = -0.41\,V$ and $E^\circ(Fe^{3+}/Fe^{2+}) = +0.77\,V$. Reversing the reductions gives oxidation potentials $+0.41\,V$ and $-0.77\,V$, respectively. Thus Cr^{2+} loses an electron more readily:

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

Quick Tip to Solve: To compare M2+ reducing agents, use the M3+/M2+ row and reverse its sign for oxidation; identify Mn2+ by its stable half-filled d5 shell.

Its oxidation forms the relatively stable $3d^3$ chromium(III) ion. The electron-transfer reaction is

$$Cr^{2+} + Fe^{3+} \longrightarrow Cr^{3+} + Fe^{2+}.$$

Its standard cell potential is $0.77 - (-0.41) = +1.18\,V$.

Step 2: (b) Identify the most stable +2 ion Mn^{2+} has the exceptionally stable half-filled $3d^5$ configuration. Its reduction to metal has the most negative potential in the table, $-1.18\,V$, so this reduction is least favoured. Oxidation to Mn^{3+} also destroys the half-filled shell; the corresponding reduction potential $E^\circ(Mn^{3+}/Mn^{2+}) = +1.57\,V$ favours formation of Mn^{2+}. These facts support the stability of manganese in the +2 state.

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

Quick Tip to Solve: To compare M2+ reducing agents, use the M3+/M2+ row and reverse its sign for oxidation; identify Mn2+ by its stable half-filled d5 shell.

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

(a) Teflon

(b) PHBV [2 marks]

Solution:

Concept:

- Addition polymerisation joins unsaturated monomers by opening their multiple bonds, without eliminating a small molecule.
- Condensation polymerisation uses monomers with suitable functional groups; new linkages form with elimination of small molecules such as water.

Step 1: (a) Classify Teflon Teflon, or polytetrafluoroethene, forms by addition polymerisation of tetrafluoroethene. The carbon–carbon double bond opens and the monomer units join to make the chain:

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

Every atom of each monomer is retained in the polymer. Since no water, hydrogen chloride or other small molecule is removed, this is an addition polymer.

Step 2: (b) Classify PHBV PHBV is poly(β-hydroxybutyrate-co-β-hydroxyvalerate), a condensation copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid. Each monomer has both hydroxyl and carboxyl groups. Reaction between these groups forms ester linkages, $-COO-$, with elimination of water. Its two types of chain units are

$$-O - CH(CH_3) - CH_2 - CO - \quad \text{and} \quad -O - CH(C_2H_5) - CH_2 - CO - .$$

The ester-forming condensation, rather than opening a carbon–carbon double bond, determines its classification.

Quick Tip to Solve: Look at how the chain forms: opening a C=C bond indicates addition, whereas ester formation from OH and COOH groups indicates condensation.

Step 3: Conclusion Teflon is an addition polymer because tetrafluoroethene molecules join without elimination. PHBV is a condensation polymer because hydroxy acids form ester linkages with elimination of water.

Quick Tip to Solve: Look at how the chain forms: opening a C=C bond indicates addition, whereas ester formation from OH and COOH groups indicates condensation.

12. Write the structures of monomers of the following polymers:

(a) Terylene

(b) Buna-N [2 marks]

Solution:

Concept:

- A polyester such as Terylene is obtained by condensation of a diol with a dicarboxylic acid. Its ester linkages identify the two functional groups supplied by the monomers.
- Buna-N is an addition copolymer of a conjugated diene and an unsaturated nitrile; both monomers provide carbon–carbon double bonds for polymerisation.

Step 1: (a) Monomers of Terylene Terylene is prepared from ethane-1,2-diol (ethylene glycol) and benzene-1,4-dicarboxylic acid (terephthalic acid). Their structural formulae are

$$\underbrace{HO-CH_2-CH_2-OH}_{\text{ethane-1,2-diol}} \quad \text{and} \quad \underbrace{HOOC-C_6H_4-COOH}_{\text{terephthalic acid (1,4-substitution)}}.$$

The two COOH groups of terephthalic acid are on opposite, para positions of the benzene ring. The OH groups of the diol react with COOH groups to give the ester links of the polyester chain, with elimination of water.

Step 2: (b) Monomers of Buna-N Buna-N is made by copolymerisation of buta-1,3-diene and prop-2-enenitrile (acrylonitrile). Their structures are

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

Butadiene has two conjugated double bonds; acrylonitrile has a vinyl group attached to the nitrile group. The nitrile group is retained in the polymer and distinguishes Buna-N from Buna-S.

Step 3: Conclusion Terylene: $HOCH_2CH_2OH$ and para-$HOOC-C_6H_4-COOH$. Buna-N: $CH_2{=}CH-CH{=}CH_2$ and $CH_2{=}CH-C{\equiv}N$.

Quick Tip to Solve: Remember the N in Buna-N as the nitrogen of acrylonitrile; Terylene pairs a two-carbon diol with para-substituted terephthalic acid.

Section C (36 marks)

13(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 the cathode reduction potential minus the anode reduction potential: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the electrons transferred per reaction and $F = 96500\,\text{C mol}^{-1}$.
- The equilibrium constant obeys $\Delta_r G^\circ = -2.303RT \log K_c$. At the usual standard temperature of $298\,\text{K}$, $E^\circ_{\text{cell}} = (0.0591/n) \log K_c$, with potential in volts.

Step 1: Identify the half-reactions and cell potential Zinc is oxidised and cadmium ions are reduced in the stated reaction:

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

Thus $n = 2$, with cadmium as the cathode and zinc as the anode. Both given electrode potentials are reduction potentials, so

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

Step 2: Calculate the standard Gibbs energy change Substitute the cell potential and the electron number:

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

The negative value agrees with the positive cell potential: the written reaction is spontaneous under standard conditions.

Step 3: Calculate the logarithm of the equilibrium constant Using the standard-temperature relation at $298\,\text{K}$,

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

Here log denotes the base-ten logarithm. The large positive value indicates that products are strongly favoured at equilibrium.

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

Quick Tip to Solve: Subtract the zinc reduction potential from the cadmium reduction potential, and use two electrons for both Gibbs energy and log K calculations.

OR

13(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 the deposited mass as $m = MQ/(nF)$, where M is molar mass, Q is charge passed, n is the electrons needed per metal atom and F is the Faraday constant.
- For steady current, $Q = It$, with current I in amperes and time t in seconds. Hence $t = mnF/(MI)$.

Step 1: Determine the electron requirement for chromium deposition The supplied reduction equation is

$$\mathrm{CrO_3(aq) + 6H^+ + 6}e^- \longrightarrow \mathrm{Cr(s) + 3H_2O}.$$

Chromium changes from oxidation state $+6$ in $\mathrm{CrO_3}$ to zero in the metal. Therefore one mole of chromium requires six moles of electrons, so $n = 6$. With $F = 96500\,\mathrm{C\ mol^{-1}}$, the charge required to deposit $52\,\mathrm{g}$ of chromium is $6F = 579000\,\mathrm{C}$.

Step 2: Find the mass deposited by the given charge For $Q = 24000\,\mathrm{C}$ and $M = 52\,\mathrm{g\ mol^{-1}}$,

$$m = \frac{MQ}{nF} = \frac{52(24000)}{6(96500)} = 2.1554\,\mathrm{g}.$$

Thus the charge deposits about $2.16\,\mathrm{g}$ of chromium, taking the supplied reduction as the electrode reaction.

Step 3: Find the time needed to deposit 1.5 g First find the charge needed for this mass:

$$Q = \frac{mnF}{M} = \frac{1.5(6)(96500)}{52} = 16701.9\,\mathrm{C}.$$

At the constant current $I = 12.5\,\mathrm{A} = 12.5\,\mathrm{C\ s^{-1}}$,

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

The second calculation uses the specified mass of $1.5\,\mathrm{g}$, independently of the $24000\,\mathrm{C}$ used in the first calculation.

Step 4: Conclusion The chromium deposited is $\boxed{2.16\,\mathrm{g}}$. Depositing $1.5\,\mathrm{g}$ at $12.5\,\mathrm{A}$ takes $\boxed{1.34 \times 10^3\,\mathrm{s}}$, approximately $\boxed{22.3\,\mathrm{min}}$.

Quick Tip to Solve: Read the six-electron coefficient from the supplied chromium(VI) reduction; using three electrons would double the calculated deposited mass.

14. 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 is solute molarity, R is the gas constant and T is absolute temperature.
- Glucose is a non-electrolyte and does not dissociate into ions. For solutions of the same solute at the same temperature, osmotic pressure is directly proportional to both molarity and mass concentration.

Step 1: Relate the two solutions at equal temperature Let c_1 and c_2 be the glucose concentrations in grams per litre. Since the molar mass M of glucose is the same in both solutions, their molarities are $C_1 = c_1/M$ and $C_2 = c_2/M$. Applying the osmotic-pressure equation to each gives

$$\frac{\pi_2}{\pi_1} = \frac{C_2RT}{C_1RT} = \frac{C_2}{C_1} = \frac{c_2}{c_1}.$$

Both temperatures are $300\,\text{K}$, so temperature and the gas constant cancel. No separate choice of units for R is needed.

Step 2: Substitute the given osmotic pressures The first solution contains $30\,\text{g}$ per litre, so $c_1 = 30\,\text{g L}^{-1}$. With $\pi_1 = 4.98\,\text{bar}$ and $\pi_2 = 1.52\,\text{bar}$,

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

The smaller osmotic pressure corresponds to a smaller solute concentration, as expected from the direct proportionality.

Step 3: Express the concentration in molarity if required Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, has molar mass $180\,\text{g mol}^{-1}$. Therefore

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

This is the same concentration expressed as moles of glucose per litre of solution.

Step 4: Conclusion The required glucose concentration is $\boxed{9.16\,\text{g L}^{-1}}$, equivalent to approximately $\boxed{0.0509\,\text{mol L}^{-1}}$.

Quick Tip to Solve: For the same solute at the same temperature, multiply 30 g per litre by the pressure ratio 1.52/4.98; the gas constant cancels.

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

Solution:

Concept:

- The density of a cubic crystal is $\rho = ZM/(N_A a^3)$, where Z is the number of atoms per unit cell, M the molar mass, a the edge length and N_A Avogadro's constant.
- A bcc cell contains eight corner atoms, each shared by eight cells, and one atom wholly inside it; hence $Z = 8(1/8) + 1 = 2$.

Step 1: Find the mass of one unit cell The atomic mass of chromium is $52\,\text{u}$, so its molar mass is $M = 52\,\text{g mol}^{-1}$. Since a bcc unit cell contains two chromium atoms, its mass is

$$m_{\text{cell}} = \frac{ZM}{N_A} = \frac{2 \times 52}{6.022 \times 10^{23}}\,\text{g} = 1.727 \times 10^{-22}\,\text{g}.$$

The corner contributions must be counted fractionally; counting eight complete corner atoms would overestimate the cell mass.

Step 2: Convert the edge length and calculate density To obtain density in g cm^{-3}, use $1\,\text{pm} = 10^{-10}\,\text{cm}$. Thus

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

Dividing the mass by the cell volume gives

$$\rho = \frac{1.727 \times 10^{-22}}{2.70 \times 10^{-23}} = \frac{2 \times 52}{6.022 \times 10^{23} \times (3.00 \times 10^{-8})^3}\,\text{g cm}^{-3}.$$

Step 3: Conclusion The density of chromium is $\boxed{6.40\,\text{g cm}^{-3}}$, or $6.40 \times 10^3\,\text{kg m}^{-3}$.

Quick Tip to Solve: For bcc use Z = 2, and convert the edge to centimetres before cubing it to obtain density in grams per cubic centimetre.

16. Give reasons for the following:

(a) Brownian movement provides stability to the colloidal solution.

(b) True solution does not show Tyndall effect.

(c) Addition of alum purifies water. [3 marks]

Solution:

Concept:

- Colloidal particles undergo Brownian movement because surrounding dispersion-medium molecules strike them unequally and continuously.
- The Tyndall effect is the scattering of light by dispersed particles; coagulation is the aggregation and separation of colloidal particles after their stabilising charge is neutralised.

Quick Tip to Solve: Link each reason to the particle property: random motion for stability, very small size for no visible scattering, and charge neutralisation for alum treatment.

Step 1: (a) Brownian movement and stability The continuous, random zigzag movement of colloidal particles arises from bombardment by molecules of the dispersion medium. It keeps the dispersed particles in motion and opposes their settling under gravity. Consequently the particles remain suspended and distributed throughout the medium, helping to provide kinetic stability to the colloidal solution. Brownian movement does not remove gravity; its random agitation counters sedimentation.

Step 2: (b) Absence of the Tyndall effect in a true solution A true solution contains individual solute molecules or ions whose dimensions are much smaller than the wavelength of visible light. They are too small to scatter an appreciable amount of this light, so the path of a beam passing through the solution is not visible. Hence a true solution does not show the Tyndall effect, unlike a colloid with larger dispersed particles.

Step 3: (c) Purification of water by alum Impure water often contains negatively charged colloidal particles of clay and other suspended matter. Alum supplies Al^{3+} ions, which neutralise their charge and cause coagulation. Hydrolysis also produces gelatinous $Al(OH)_3$ flocs that trap suspended impurities. The resulting larger aggregates settle and can be removed by sedimentation and filtration, leaving clarified water.

Step 4: Conclusion Brownian motion opposes settling, true-solution particles scatter too little visible light to reveal the beam, and alum coagulates suspended colloidal impurities so they can be removed.

Quick Tip to Solve: Link each reason to the particle property: random motion for stability, very small size for no visible scattering, and charge neutralisation for alum treatment.

17(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 ore, $FeCr_2O_4$, contains chromium in the +3 oxidation state. Oxidative roasting with sodium carbonate in air converts it into soluble sodium chromate, with chromium in the +6 state.
- Acidification shifts the chromate–dichromate equilibrium towards dichromate. In acidic solution, one dichromate ion accepts six electrons on reduction to two Cr^{3+} ions.

Step 1: Prepare sodium chromate by roasting chromite Finely powdered chromite ore is fused with sodium carbonate in the presence of air. Chromium is oxidised to chromate, whereas iron forms insoluble ferric oxide:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

The fused mass is extracted with water. Sodium chromate dissolves and the insoluble iron oxide is separated by filtration.

Step 2: Convert chromate to sodium dichromate The yellow sodium chromate solution is acidified with sulphuric acid:

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

Quick Tip to Solve: Remember the sequence chromite to chromate to dichromate; balance dichromate reduction with 14 hydrogen ions and six electrons in acid.

This follows $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$. Concentration and crystallisation give sodium dichromate, commonly obtained as the dihydrate.

Step 3: Write the oxidation of ferrous ions Each Fe^{2+} ion loses one electron to form Fe^{3+}. The acidic dichromate half-reaction is

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

Combining it with six iron oxidation half-reactions gives

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

The total charge is $+24$ on each side, confirming the ionic balance.

Step 4: Conclusion Oxidative fusion of chromite yields sodium chromate, which on acidification gives sodium dichromate. In acid medium, one dichromate ion oxidises six ferrous ions to ferric ions.

Quick Tip to Solve: Remember the sequence chromite to chromate to dichromate; balance dichromate reduction with 14 hydrogen ions and six electrons in acid.

OR

17(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:

- In a balanced redox equation, both the number of atoms of each element and the total electric charge are conserved.
- On heating with potassium hydroxide in oxygen, manganese dioxide is oxidised to green potassium manganate, K_2MnO_4. In acidic solution, permanganate and dichromate are reduced to Mn^{2+} and Cr^{3+}, respectively.

Step 1: (a) Oxidation of manganese dioxide Manganese changes from oxidation state $+4$ in MnO_2 to $+6$ in manganate. Potassium hydroxide supplies the alkaline medium and oxygen acts as the oxidising agent. The balanced reaction on fusion is

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

Step 2: (b) Oxidation of iodide by acidified permanganate The reduction half-reaction is $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. Iodide is oxidised according to $2I^- \rightarrow I_2 + 2e^-$. Multiplying these

Quick Tip to Solve: First balance electron transfer: acidified permanganate accepts five electrons per ion, whereas dichromate accepts six per ion.

equations by 2 and 5, respectively, cancels ten electrons:

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

Step 3: (c) Oxidation of tin(II) by acidified dichromate Each tin(II) ion loses two electrons: $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$. Dichromate gains six electrons: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$. Hence three tin(II) ions are required:

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

The total charge is $+18$ on each side, confirming the ionic balance.

Step 4: Conclusion The products are (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 balance electron transfer: acidified permanganate accepts five electrons per ion, whereas dichromate accepts six per ion.

18(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:

- Metallurgical separation uses differences in wettability, complex formation and solubility to separate a useful metal or its compound from other substances.
- Selective action enables separation. A depressant suppresses flotation of one sulphide. CO forms a volatile nickel complex, while NaOH dissolves amphoteric alumina.

Step 1: (a) Depressants in froth floatation Depressants prevent one of the sulphide ores in a mixture from forming froth, allowing the other sulphide to be selectively carried up with the froth. For example, in a mixture of ZnS and PbS, sodium cyanide selectively depresses ZnS by forming a soluble zinc cyanide complex and preventing its flotation. Thus PbS is collected with the froth while ZnS remains behind.

Step 2: (b) Carbon monoxide in Mond's process Carbon monoxide acts as a complexing agent in the purification of nickel. At about 330–350 K, it reacts with impure nickel to form volatile nickel tetracarbonyl:

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

The volatile carbonyl is separated from non-volatile impurities. Heating it to about 450–470 K decomposes it and deposits pure nickel:

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

Quick Tip to Solve: Link each reagent to its selective action: NaCN suppresses ZnS flotation, CO volatilises nickel, and NaOH dissolves alumina.

Step 3: (c) Concentrated sodium hydroxide in leaching bauxite Hot concentrated sodium hydroxide acts as the leaching agent. It dissolves the amphoteric alumina of bauxite as soluble sodium aluminate, while insoluble impurities such as iron(III) oxide are separated by filtration. In aqueous form the reaction is

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

The dissolved aluminium compound can subsequently be precipitated as hydrated alumina and heated to obtain pure alumina.

Step 4: Conclusion Depressants permit selective flotation of sulphide ores; CO purifies nickel through volatile $Ni(CO)_4$; and concentrated NaOH selectively leaches alumina as soluble sodium aluminate.

Quick Tip to Solve: Link each reagent to its selective action: NaCN suppresses ZnS flotation, CO volatilises nickel, and NaOH dissolves alumina.

OR

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

[3 marks]

Solution:

Concept:

- Aluminium extraction involves purification of bauxite to alumina by leaching, followed by electrolytic reduction of alumina in the Hall-Heroult process.
- Alumina is amphoteric and dissolves in hot concentrated alkali. During electrolysis, Al^{3+} gains electrons at the cathode; oxide ions lose electrons at the carbon anode.

Step 1: Leach bauxite to form soluble aluminate Digest the ore with hot concentrated sodium hydroxide under pressure. Alumina dissolves as sodium aluminate, whereas insoluble impurities such as iron(III) oxide are filtered off:

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

The water present in hydrated bauxite joins the aqueous medium.

Step 2: Recover aluminium hydroxide and calcine it Carbon dioxide passed through the aluminate solution precipitates aluminium hydroxide:

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

Filter the precipitate and heat it strongly to obtain pure alumina:

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

Step 3: Reduce alumina electrolytically Dissolve purified alumina in molten cryolite Na_3AlF_6, with fluorspar CaF_2. The mixture has a lower melting point and improved electrical conductivity. The

Quick Tip to Solve: Keep the sequence clear: alkali leaching, hydroxide precipitation, calcination to alumina, and finally electrolytic reduction.

electrode reactions are

$$\text{Cathode:} \quad Al^{3+} + 3e^- \rightarrow Al(l),$$
$$\text{Anode:} \quad 2O^{2-} \rightarrow O_2 + 4e^-.$$

Oxygen formed at the anode reacts with carbon, so the anodes are consumed: $C + O_2 \rightarrow CO_2$; some CO can also form. The overall reaction, representing carbon dioxide formation, is

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2.$$

Step 4: Conclusion Bauxite is converted through soluble sodium aluminate and precipitated $Al(OH)_3$ into pure Al_2O_3. Electrolysis of alumina in molten cryolite then produces aluminium at the cathode.

Quick Tip to Solve: Keep the sequence clear: alkali leaching, hydroxide precipitation, calcination to alumina, and finally electrolytic reduction.

19(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 stabilizes the negatively charged intermediate formed by nucleophilic attack.
- The melting point depends strongly on crystal packing; molecular symmetry can improve packing and strengthen the crystal lattice.
- An alcohol reacts with thionyl chloride to form an alkyl chloride, with gaseous sulphur dioxide and hydrogen chloride as by-products.

Step 1: (a) Activation by an ortho or para nitro group The $-NO_2$ group withdraws electron density through both inductive and resonance effects. When it is ortho or para to the halogen, the negative charge in the intermediate formed on nucleophilic attack can be delocalized onto the nitro group, including its oxygen atoms. This resonance stabilization lowers the energy required for substitution and increases reactivity. At the meta position, the nitro group cannot stabilize this intermediate by the same resonance interaction.

Step 2: (b) Higher melting point of the para isomer The para isomer is more symmetrical than the ortho and meta isomers. Its molecules pack more closely and regularly in the crystal lattice, giving a more stable crystal. More heat is therefore required to disrupt this lattice, so p-dichlorobenzene has the higher melting point. The explanation concerns the solid-state packing of the molecules.

Step 3: (c) Preference for thionyl chloride The reaction is

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 \uparrow + HCl \uparrow.$$

Quick Tip to Solve: For these three reasons, connect reactivity to intermediate stability, melting point to crystal packing, and reagent preference to removable by-products.

Both by-products escape as gases. Their removal drives the reaction forward and leaves the alkyl chloride comparatively pure, making its isolation and purification convenient.

Step 4: Conclusion The nitro group activates an ortho/para haloarene by stabilizing the substitution intermediate; the para dichloro isomer melts higher because of efficient crystal packing; and $SOCl_2$ is preferred because its gaseous by-products escape.

Quick Tip to Solve: For these three reasons, connect reactivity to intermediate stability, melting point to crystal packing, and reagent preference to removable by-products.

OR

19(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:

- Finkelstein reaction exchanges chloride or bromide for iodide using sodium iodide in dry acetone; precipitation of the sodium halide drives the exchange.
- For comparable alkyl halides, the usual ease of dehydrohalogenation is tertiary greater than secondary greater than primary; elimination forms an alkene by loss of a beta hydrogen and the halogen.
- In naming an unsaturated compound, the parent chain includes the double bond and is numbered to give that double bond the lowest locant before substituents are considered.

Step 1: (a) Prepare 1-iodobutane 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 iodide dissolves in acetone, whereas sodium chloride precipitates. This halogen-exchange reaction is called the Finkelstein reaction.

Step 2: (b) Compare elimination reactivity 2-Bromo-2-methylbutane is a tertiary alkyl bromide, 2-bromopentane is secondary, and 1-bromopentane is primary. Thus, the most reactive is 2-bromo-2-methylbutane. Alkyl substitution favours elimination and stabilizes the more substituted alkene

Quick Tip to Solve: In part (c), assign the double bond its lowest locant first; numbering to lower the bromo locant would give the incorrect parent pent-3-ene.

through electron donation and hyperconjugation; the usual reactivity order is tertiary $>$ secondary $>$ primary.

Step 3: (c) Name the given structure The longest chain containing the double bond has five carbon atoms. Numbering from the left in the printed formula places the double bond at carbon 2, giving the parent name pent-2-ene; the opposite direction gives carbon 3. Both the bromo substituent and the extra methyl substituent are attached to carbon 4. Alphabetically, bromo precedes methyl.

Step 4: Conclusion (a) Use NaI in dry acetone (Finkelstein reaction). (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: In part (c), assign the double bond its lowest locant first; numbering to lower the bromo locant would give the incorrect parent pent-3-ene.

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

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

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

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

Solution:

Concept:

- Find the metal oxidation state from the total complex charge and ligand charges, then remove the outer $4s$ electrons before $3d$ electrons to obtain the metal-ion configuration.
- Weak-field water gives a high-spin complex, whereas strong-field cyanide can cause pairing of the metal-ion d electrons.
- Unpaired electrons produce paramagnetism; a complex with all electrons paired is diamagnetic. Six-coordinate outer-orbital octahedral complexes use sp^3d^2 hybridization, while square-planar complexes use dsp^2.

Step 1: (i) Hexaaquairon(II) ion Water is neutral, so iron has oxidation state $+2$ in $[\mathrm{Fe}(\mathrm{H_2O})_6]^{2+}$. The configurations are

$$\mathrm{Fe} : [\mathrm{Ar}]\, 3d^6 4s^2, \qquad \mathrm{Fe}^{2+} : [\mathrm{Ar}]\, 3d^6.$$

Water is a weak-field ligand and does not cause pairing of the four unpaired $3d$ electrons. The high-spin octahedral configuration is $t_{2g}^4 e_g^2$, containing four unpaired electrons. Because two vacant inner $3d$ orbitals are unavailable, the ion uses one $4s$, three $4p$ and two $4d$ orbitals to form six sp^3d^2 hybrid orbitals. Thus it is an outer-orbital octahedral complex and is paramagnetic.

Step 2: (ii) Tetracyanidonickelate(II) ion Each cyanide ligand has charge -1. If the oxidation state of nickel is x, then $x - 4 = -2$, so $x = +2$. Hence

$$\mathrm{Ni} : [\mathrm{Ar}]\, 3d^8 4s^2, \qquad \mathrm{Ni}^{2+} : [\mathrm{Ar}]\, 3d^8.$$

The strong-field CN^- ligands cause the eight $3d$ electrons to pair in four orbitals, leaving one $3d$ orbital vacant. This orbital combines with one $4s$ and two $4p$ orbitals to form four dsp^2 hybrid orbitals

Quick Tip to Solve: Both metals are in the $+2$ oxidation state: first count their d electrons, then use weak-field water versus strong-field cyanide to decide pairing.

directed towards the corners of a square. All electrons are paired, so the square-planar complex is diamagnetic.

Step 3: Conclusion (i) $[Fe(H_2O)_6]^{2+}$: sp^3d^2 hybridization; paramagnetic with four unpaired electrons. (ii) $[Ni(CN)_4]^{2-}$: dsp^2 hybridization; diamagnetic with no unpaired electrons.

Quick Tip to Solve: Both metals are in the +2 oxidation state: first count their d electrons, then use weak-field water versus strong-field cyanide to decide pairing.

21. (a) Show how you will synthesise the following alcohol, prepared by the reaction of a suitable Grignard reagent on methanal: (b) Write the mechanism of the following reaction:

$$CH_2 = CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$$

[3 marks]

$$\begin{array}{l} CH_3 - CH - CH_2 - OH \\ \quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad CH_3 \end{array}$$

Solution:

Concept:

- Methanal with RMgX, followed by hydrolysis, gives RCH_2OH; its terminal alcohol carbon comes from methanal.
- Acid-catalysed hydration involves protonation of the double bond, water attack on the carbocation and deprotonation.

Step 1: (a) Synthesis using isopropylmagnesium bromide In the target $(CH_3)_2CHCH_2OH$, remove the terminal CH_2OH group to identify $R = (CH_3)_2CH-$. Therefore use isopropylmagnesium bromide with methanal in dry ether, then hydrolyse the alkoxide:

$$\begin{aligned} &HCHO + (CH_3)_2CHMgBr \\ &\xrightarrow{\text{dry ether}} (CH_3)_2CHCH_2OMgBr \\ &\xrightarrow{H_3O^+} (CH_3)_2CHCH_2OH. \end{aligned}$$

Water is excluded during addition because it destroys the Grignard reagent.

Step 2: (b) Protonation of ethene The double bond accepts a proton, giving an ethyl carbocation:

$$CH_2 = CH_2 + H_3O^+ \longrightarrow CH_3CH_2^+ + H_2O.$$

Step 3: Water attack and deprotonation Water attacks the carbocation through an oxygen lone pair,

Quick Tip to Solve: With methanal, remove terminal CH2OH from the target to identify the Grignard reagent's alkyl group.

giving an oxonium ion. Another water molecule then removes a proton:

$$CH_3CH_2^+ + H_2O \longrightarrow CH_3CH_2OH_2^+,$$
$$CH_3CH_2OH_2^+ + H_2O \longrightarrow CH_3CH_2OH + H_3O^+.$$

This forms ethanol and regenerates the acid catalyst.

Step 4: Conclusion (a) The reagent is isopropylmagnesium bromide. (b) Hydration gives ethanol through the three steps above.

Quick Tip to Solve: With methanal, remove terminal CH2OH from the target to identify the Grignard reagent's alkyl group.

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 only: heating with chloroform and alcoholic potassium hydroxide produces an offensive-smelling isocyanide.
- Aniline strongly activates the benzene ring towards bromination, while a Lewis acid such as $AlCl_3$ binds the nitrogen lone pair and deactivates the ring towards Friedel-Crafts substitution.

Step 1: (a)(i) Distinguish methylamine and dimethylamine Heat separate samples with chloroform and alcoholic KOH. Methylamine, a primary amine, gives methyl isocyanide, recognised by its highly unpleasant odour:

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

Dimethylamine, $(CH_3)_2NH$, is a secondary amine and does not give the carbylamine reaction. Thus the positive isocyanide test identifies methylamine.

Step 2: (a)(ii) Distinguish aniline and ethanamine Add bromine water to separate samples. Aniline gives a white precipitate of 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow 2,4,6\text{-}C_6H_2Br_3NH_2 + 3HBr.$$

Ethanamine does not form this white aromatic tribromo precipitate. The diagnostic observation is the precipitate, rather than bromine decolourisation alone. Aniline reacts readily because its amino group donates electron density to the ring and directs substitution to both ortho positions and the para position.

Step 3: (b) Explain the failure of Friedel-Crafts reaction Friedel-Crafts alkylation or acylation normally

Quick Tip to Solve: Use carbylamine to distinguish primary from secondary amines, and the white tribromo precipitate to distinguish aniline from an aliphatic amine.

uses the Lewis acid catalyst $AlCl_3$. The nitrogen lone pair of aniline coordinates strongly to this catalyst:

$$C_6H_5NH_2 + AlCl_3 \longrightarrow C_6H_5NH_2 \rightarrow AlCl_3.$$

The resulting salt-like Lewis acid-base complex withdraws electron density from the aromatic ring. The amino group can no longer activate the ring by lone-pair donation, and the ring becomes strongly deactivated towards the required electrophilic substitution. Hence aniline does not undergo the usual Friedel-Crafts reaction.

Step 4: Conclusion (a)(i) Methylamine gives the carbylamine test; dimethylamine does not. (ii) Aniline gives a white precipitate with bromine water; ethanamine does not give this precipitate. (b) Aniline complexes with $AlCl_3$, strongly deactivating its ring.

Quick Tip to Solve: Use carbylamine to distinguish primary from secondary amines, and the white tribromo precipitate to distinguish aniline from an aliphatic amine.

23. What happens when D-Glucose is treated with the following reagents:

(a) Br_2 water

(b) HCN

(c) $(CH_3CO)_2O$ [3 marks]

Solution:

Concept:

- The open-chain form of D-glucose is $CHO - (CHOH)_4 - CH_2OH$. Its aldehyde group undergoes mild oxidation and nucleophilic addition.
- Glucose contains five hydroxyl groups. Acetic anhydride acetylates these groups, replacing each hydroxyl hydrogen by an acetyl group CH_3CO-.

Step 1: (a) Reaction with bromine water Bromine water is a mild oxidising agent. It oxidises the aldehyde group at carbon 1 to a carboxylic acid without oxidising the terminal primary alcohol group. D-gluconic acid is obtained:

$$CHO - (CHOH)_4 - CH_2OH + Br_2 + H_2O \longrightarrow COOH - (CHOH)_4 - CH_2OH + 2HBr.$$

The reddish-brown bromine water is decolourised. This reaction supplies evidence for an aldehydic group in the open-chain form of glucose.

Step 2: (b) Reaction with hydrogen cyanide HCN adds across the aldehyde carbonyl group to form glucose cyanohydrin:

$$CHO - (CHOH)_4 - CH_2OH + HCN \longrightarrow NC - CH(OH) - (CHOH)_4 - CH_2OH.$$

Cyanide attacks the carbonyl carbon and the carbonyl oxygen is subsequently protonated. The original aldehyde carbon becomes a carbon bearing both OH and CN groups; the original hydroxyl groups are retained. This is a carbonyl addition reaction.

Quick Tip to Solve: Match each reagent to its functional group: bromine water oxidises CHO, HCN adds to C=O, and acetic anhydride acetylates all five OH groups.

Step 3: (c) Reaction with acetic anhydride Acetic anhydride acetylates all five hydroxyl groups of glucose, giving glucose pentaacetate. Each acetylation also produces one molecule of acetic acid. The overall stoichiometry is

$$C_6H_{12}O_6 + 5(CH_3CO)_2O \longrightarrow C_{16}H_{22}O_{11} + 5CH_3COOH.$$

Here $C_{16}H_{22}O_{11}$ is the molecular formula of glucose pentaacetate. Formation of a pentaacetate shows the presence of five hydroxyl groups in glucose; it is acetylation of OH groups, not oxidation by the reagent.

Step 4: Conclusion D-glucose gives (a) D-gluconic acid with bromine water, (b) glucose cyanohydrin with HCN and (c) glucose pentaacetate with acetic anhydride.

Quick Tip to Solve: Match each reagent to its functional group: bromine water oxidises CHO, HCN adds to C=O, and acetic anhydride acetylates all five OH groups.

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

(a) Antacids

(b) Artificial sweeteners

(c) Anionic detergents [3 marks]

Solution:

Concept:

- Antacids counter excess acid in the stomach; mild basic substances neutralise the acid without making the stomach strongly alkaline.
- Artificial sweeteners provide sweetness as substitutes for sugar, usually in much smaller quantities because of their high sweetening power.
- Anionic detergents are cleansing agents whose surface-active portion is a negatively charged ion, typically a long-chain alkyl sulphate or alkylbenzene sulphonate.

Step 1: (a) Antacids Antacids are substances used to neutralise excess hydrochloric acid in the stomach and relieve acidity. A suitable example is magnesium hydroxide, $Mg(OH)_2$, used as milk of magnesia. Its neutralisation reaction is

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O.$$

It is a mild base, so it removes excess acid rather than acting as a strong caustic alkali.

Step 2: (b) Artificial sweeteners Artificial sweeteners are synthetic substances used to impart a sweet taste to food and beverages in place of sugar. For example, saccharin is an artificial sweetener. It is much sweeter than sucrose and passes through the body largely unchanged; hence it provides sweetness without the calorific contribution of an equivalent sweetening amount of sugar.

Step 3: (c) Anionic detergents Anionic detergents are detergents in which the large organic anion is responsible for the cleansing action. An example is sodium lauryl sulphate (sodium dodecyl sulphate), $CH_3(CH_2)_{11}OSO_3^-Na^+$. Its hydrocarbon chain associates with grease while its negatively charged

Quick Tip to Solve: Identify an anionic detergent by the negative charge on its long-chain cleansing ion; the sodium counter-ion does not determine the detergent class.

sulphate head interacts with water, helping to disperse oily dirt. The sodium ion is the counter-ion; it is not the cleansing part.

Step 4: Conclusion Examples are: (a) magnesium hydroxide for an antacid, (b) saccharin for an artificial sweetener, and (c) sodium lauryl sulphate for an anionic detergent.

Quick Tip to Solve: Identify an anionic detergent by the negative charge on its long-chain cleansing ion; the sodium counter-ion does not determine the detergent class.

Section D (15 marks)

25(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 of p-nitrotoluene occurs at a position ortho to the methyl group and meta to the nitro group, since both groups direct substitution to these positions.
- An aromatic amino group can be removed by diazotisation followed by reduction with hypophosphorous acid. Oxidation of a benzylic methyl group gives a carboxyl group.
- Hunsdiecker degradation converts a silver carboxylate into an alkyl bromide with one fewer carbon atom. Ozonolysis cleaves an alkene double bond into carbonyl groups.
- Ethanal gives both Fehling's test and the iodoform test; a methyl ketone gives the iodoform test but not Fehling's test.

Step 1: (a)(i) Introduce bromine and remove the nitro substituent Brominate p-nitrotoluene using $\mathrm{Br_2/FeBr_3}$. The equivalent positions 2 and 6 are favoured by both substituents, giving 2-bromo-4-nitrotoluene. Reduce its nitro group using $\mathrm{Sn/HCl}$, followed by alkaline work-up, to obtain 2-bromo-4-aminotoluene.

$$\text{p-nitrotoluene} \xrightarrow{\mathrm{Br_2/FeBr_3}} \text{2-bromo-4-nitrotoluene}$$
$$\xrightarrow{\mathrm{Sn/HCl;\ then\ OH^-}} \text{2-bromo-4-aminotoluene.}$$

Diazotise the amino group with $\mathrm{NaNO_2/HCl}$ at 273–278 K; then treat the diazonium salt with $\mathrm{H_3PO_2}$ to replace that group by hydrogen. Finally oxidise the methyl side chain with hot alkaline $\mathrm{KMnO_4}$,

Quick Tip to Solve: For ozonolysis identification, use the tests first, then conserve carbon atoms: ethanal uses two carbons, leaving three for the methyl ketone.

followed by acidification:

$$\begin{aligned}\text{2-bromo-4-aminotoluene} &\xrightarrow[273\text{–}278\ \text{K}]{\text{NaNO}_2/\text{HCl}} \text{diazonium salt}\\ &\xrightarrow{\text{H}_3\text{PO}_2} \text{2-bromotoluene}\\ &\xrightarrow{\text{KMnO}_4/\text{OH}^-,\ \text{heat; then H}^+} \text{2-bromobenzoic acid.}\end{aligned}$$

Bromine remains ortho to the side chain throughout, so oxidation places it at position 2 relative to the carboxyl group.

Step 2: (a)(ii) Shorten the carbon chain and oxidise to acetic acid Prepare silver propanoate from propanoic acid using Ag_2O, and carry out Hunsdiecker degradation with bromine in CCl_4 on heating:

$$CH_3CH_2COOAg + Br_2 \longrightarrow CH_3CH_2Br + CO_2 + AgBr.$$

Hydrolyse bromoethane with aqueous KOH to form ethanol, then oxidise ethanol with acidified potassium dichromate under reflux:

$$\begin{aligned}CH_3CH_2Br &\xrightarrow{\text{aq. KOH}} CH_3CH_2OH\\ &\xrightarrow[\text{reflux}]{K_2Cr_2O_7/H^+} CH_3COOH.\end{aligned}$$

The degradation removes the original carboxyl carbon as carbon dioxide, reducing the chain from three carbons to two.

Step 3: (b) Identify the two ozonolysis products A positive Fehling test identifies B as an aliphatic aldehyde. Among such aldehydes, ethanal, CH_3CHO, gives the iodoform test because it contains the CH_3CO- arrangement. Thus B is ethanal. C fails Fehling's test but gives iodoform, so it is a methyl ketone. Since A has five carbon atoms and ethanal contains two, C must contain three: it is propanone, CH_3COCH_3.

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O.$$

Propanone similarly yields yellow CHI_3, together with sodium acetate, under the iodoform-test conditions.

Step 4: Reconstruct the alkene A Rejoin the carbonyl carbons of ethanal and propanone with a double bond, removing their oxygen atoms. The ethanal carbon retains H and CH_3, while the propanone carbon retains two methyl groups:

$$(CH_3)_2C{=}CHCH_3 \xrightarrow[Zn/H_2O]{O_3} CH_3COCH_3 + CH_3CHO.$$

This alkene is 2-methylbut-2-ene and has the required molecular formula C_5H_{10}.

Step 5: Conclusion The conversions proceed through 2-bromotoluene to 2-bromobenzoic acid, and through bromoethane and ethanol to acetic acid. In (b), A is 2-methylbut-2-ene, B is ethanal and C is propanone.

Quick Tip to Solve: For ozonolysis identification, use the tests first, then conserve carbon atoms: ethanal uses two carbons, leaving three for the methyl ketone.

OR

25(b). (a) Carry out the following conversions:

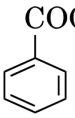
(i) Benzoic acid to aniline

(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)  $\xrightarrow{NaOH}$

Solution:

Concept:

- Hofmann bromamide degradation converts an amide into a primary amine with one fewer carbon atom. Thus benzamide gives aniline while losing its carbonyl carbon.
- Cyanide substitution adds one carbon to an alkyl halide. Hydrolysis of the nitrile and reduction of the acid then give a primary alcohol.
- Wolff–Kishner reduction replaces a carbonyl group by a methylene group. An aldehyde without an alpha-hydrogen undergoes Cannizzaro disproportionation with concentrated alkali.

Step 1: (a)(i) Convert benzoic acid into aniline First form ammonium benzoate with ammonia and heat it to obtain benzamide. Then treat the amide with bromine and aqueous alkali:

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COONH_4$$

$$C_6H_5COONH_4 \xrightarrow{\text{heat}} C_6H_5CONH_2 + H_2O$$

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

The benzene ring is retained and the carboxyl carbon is removed during Hofmann degradation.

Step 2: (a)(ii) Extend the carbon chain and form ethanol Use alcoholic potassium cyanide to replace bromide by cyanide. Hydrolyse ethanenitrile with dilute acid and heat; reduce the resulting ethanoic acid with lithium aluminium hydride in dry ether, followed by hydrolysis:

$$CH_3Br + KCN \xrightarrow{\text{alcohol}} CH_3CN + KBr$$

$$CH_3CN + 2\,H_2O + HCl \xrightarrow{\text{heat}} CH_3COOH + NH_4Cl$$

$$CH_3COOH + 4\,[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$$

Quick Tip to Solve: Count carbons before choosing a conversion: cyanide adds one carbon and Hofmann degradation removes the amide carbon. With concentrated alkali, check for an alpha-hydrogen before choosing aldol or Cannizzaro.

The nitrile carbon becomes the alcohol's terminal carbon. Direct hydrolysis of bromomethane would give methanol and would not extend the chain.

Step 3: (b)(i) Reduce propanal Hydrazine followed by potassium hydroxide in glycol on heating is the Wolff–Kishner reduction. The aldehyde carbon becomes a terminal methyl group, with the carbon skeleton unchanged:

$$CH_3CH_2CHO + H_2NNH_2 \xrightarrow[\text{heat}]{\text{KOH, glycol}} CH_3CH_2CH_3 + N_2 + H_2O$$

The major organic product is propane, $CH_3-CH_2-CH_3$.

Step 4: (b)(ii) Apply the Cannizzaro reaction In $(CH_3)_3CCHO$, the carbon next to the aldehyde group is bonded to three methyl groups and has no hydrogen. Hence aldol condensation cannot occur. Concentrated sodium hydroxide causes one molecule to be oxidised to a carboxylate salt while another is reduced to an alcohol:

$$2\,(CH_3)_3CCHO + NaOH \longrightarrow (CH_3)_3CCOONa + (CH_3)_3CCH_2OH$$

The products are sodium 2,2-dimethylpropanoate and 2,2-dimethylpropan-1-ol. The salt remains a carboxylate because no acid work-up is specified.

Step 5: (b)(iii) Neutralise benzoic acid Sodium hydroxide removes the acidic proton from the carboxyl group:

$$C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O$$

The major organic product is sodium benzoate. The given reagent is sodium hydroxide alone; soda lime and heating, needed for decarboxylation, are not specified.

Step 6: Conclusion (a) Benzoic acid gives aniline through benzamide and Hofmann degradation; bromomethane gives ethanol through ethanenitrile and ethanoic acid. (b) The products are (i) propane; (ii) $(CH_3)_3CCOONa$ and $(CH_3)_3CCH_2OH$; (iii) C_6H_5COONa.

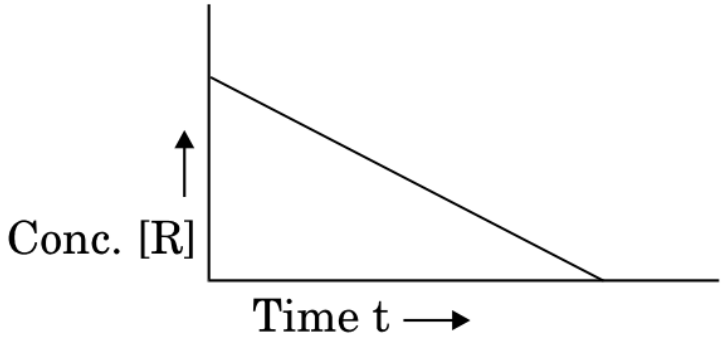
Quick Tip to Solve: Count carbons before choosing a conversion: cyanide adds one carbon and Hofmann degradation removes the amide carbon. With concentrated alkali, check for an alpha-hydrogen before choosing aldol or Cannizzaro.

26(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 does not depend on reactant concentration: $-d[R]/dt = k$. Integration gives $[R]_t = [R]_0 - kt$, where k is the rate constant.
- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$. Here A is the pre-exponential factor, E_a is activation energy, R is the gas constant and T is absolute temperature.
- At the same reactant concentrations, the ratio of reaction rates equals the ratio of rate constants. The two-temperature Arrhenius relation determines E_a from this ratio.

Step 1: (a)(i) Identify the integrated rate law The graph of reactant concentration $[R]$ against time is a straight line descending from a positive intercept. Thus concentration decreases by equal amounts in equal time intervals, until the reactant is exhausted. Comparing the straight-line equation $y = c + mx$ with

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

shows that the reaction is zero order. A first-order reaction instead gives a straight line when $\ln[R]$, rather than $[R]$, is plotted against time.

Step 2: (a)(ii) Interpret the slope The ordinate is concentration and the abscissa is time, so the slope is

$$m = \frac{\Delta[R]}{\Delta t} = -k.$$

It indicates the negative of the rate constant. Equivalently, the magnitude of the downward slope equals the rate of disappearance of reactant. Its units are concentration per unit time, for example mol L^{-1} s^{-1} when time is measured in seconds. The vertical intercept represents the initial concentration $[R]_0$.

Step 3: (b) Relate the fourfold rate change to temperature Given $T_1 = 293\,\text{K}$, $T_2 = 313\,\text{K}$, and

Quick Tip to Solve: A straight falling plot of concentration itself identifies zero order. For the temperature calculation, use $\ln 4$ with R, or use $\log_{10} 4$ with $2.303R$; do not mix the two forms.

$k_2/k_1 = 4$, use the two-temperature equation with the same activation energy:

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

This follows by subtracting $\ln k_1 = \ln A - E_a/(RT_1)$ from $\ln k_2 = \ln A - E_a/(RT_2)$. The higher temperature gives a larger rate constant, consistent with a positive activation energy.

Step 4: Substitute and calculate the activation energy Rearrange before substitution, using kelvin throughout:

$$\begin{aligned} E_a &= \frac{R\ln 4}{1/293 - 1/313} \\ &= \frac{8.314 \times 1.386294 \times 293 \times 313}{313 - 293} \\ &\approx 5.285 \times 10^4\ \text{J mol}^{-1} \\ &\approx 52.85\ \text{kJ mol}^{-1}. \end{aligned}$$

The reciprocal-temperature difference is positive, so the calculated activation energy is positive. Keeping R in joules gives E_a in joules per mole; divide by 1000 to obtain kilojoules per mole.

Step 5: Conclusion (a)(i) The reaction is zero order. (ii) The slope is $-k$, and its magnitude gives the rate constant. (b) The activation energy is $\boxed{E_a \approx 52.85\ \text{kJ mol}^{-1}}$.

Quick Tip to Solve: A straight falling plot of concentration itself identifies zero order. For the temperature calculation, use $\ln 4$ with R, or use $\log_{10} 4$ with $2.303R$; do not mix the two forms.

OR

26(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 k is the rate constant, A is the frequency factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature.
- For a first-order reaction, $k = \frac{2.303}{t}\log_{10}\frac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are the initial concentration and the concentration remaining after time t. Its half-life is $t_{1/2} = \frac{0.693}{k}$.

Step 1: (a) Obtain the straight-line form of the Arrhenius equation Taking natural logarithms gives

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

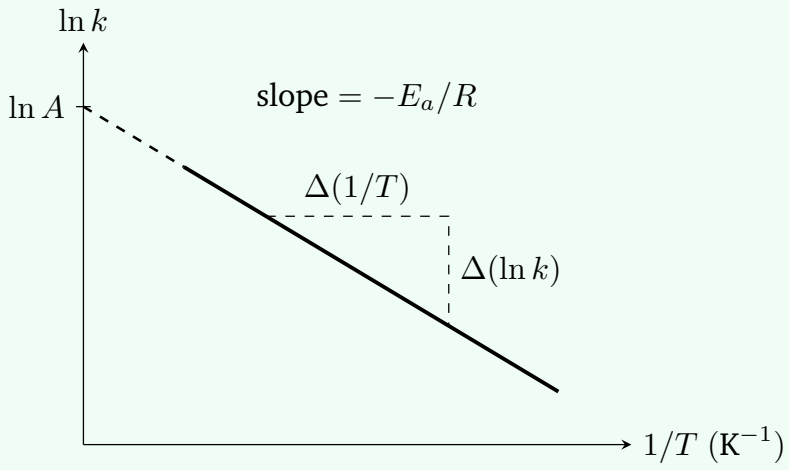
This has the form $y = c + mx$ with $y = \ln k$ and $x = 1/T$. Therefore, for constant activation energy,

Quick Tip to Solve: For first-order percentage problems, use the fraction remaining: here 20 percent decomposed means 80 percent remains, so $t_{1/2} = 30\log 2/\log(100/80)$.

the plot is a straight line of negative slope. Its extrapolated intercept on the vertical axis represents $\ln A$, the natural logarithm of the frequency factor. The slope m satisfies

$$m = -\frac{E_a}{R}, \qquad E_a = -mR.$$

Thus a positive activation energy gives a descending line as reciprocal temperature increases. The intercept is $\ln A$, rather than A itself; the frequency factor is recovered by exponentiating the intercept.



Arrhenius plot: the extrapolated vertical intercept is $\ln A$, and the slope is $-E_a/R$.

Step 2: (b) Find the first-order rate constant from the decomposition Choose an initial amount of 100 units. Since 20 percent has decomposed in 30 minutes, 80 units remain; the logarithmic ratio must use this remaining amount. Hence

$$\begin{aligned} k &= \frac{2.303}{30}\log_{10}\frac{100}{80} \\ &= \frac{2.303}{30}\log_{10}\frac{5}{4}. \end{aligned}$$

Using the supplied $\log_{10} 2 = 0.3010$, we have

$$\log_{10}\frac{5}{4} = \log_{10} 5 - \log_{10} 4 = (1 - 0.3010) - 2(0.3010) = 0.0970.$$

Therefore $k = \dfrac{2.303(0.0970)}{30} = 7.446 \times 10^{-3}\,\text{min}^{-1}$. The arbitrary choice of 100 units cancels in the concentration ratio and does not affect the result.

Step 3: (b) Calculate the half-life At the half-life, half the initial reactant remains. Substituting $[R]_0/[R]_t = 2$ into the same integrated rate law gives

$$\begin{aligned} t_{1/2} &= \frac{2.303\log_{10} 2}{k} \\ &= \frac{2.303(0.3010)}{2.303(0.0970)/30} \\ &= 30\frac{0.3010}{0.0970} = 93.09\,\text{min}. \end{aligned}$$

Quick Tip to Solve: For first-order percentage problems, use the fraction remaining: here 20 percent decomposed means 80 percent remains, so $t_{1/2} = 30\log 2/\log(100/80)$.

The factors 2.303 cancel, so this calculation consistently uses the logarithm given in the question. A half-life longer than 30 minutes is expected because only 20 percent has decomposed during those 30 minutes.

Step 4: Conclusion (a) The $\ln k$ versus $1/T$ plot is a descending straight line with vertical intercept $\ln A$ and slope $-E_a/R$, so $E_a = -R \times$ slope. (b) The half-life is $\boxed{t_{1/2} \approx 93.1\ \text{min}}$.

Quick Tip to Solve: For first-order percentage problems, use the fraction remaining: here 20 percent decomposed means 80 percent remains, so $t_{1/2} = 30 \log 2 / \log(100/80)$.

27(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.

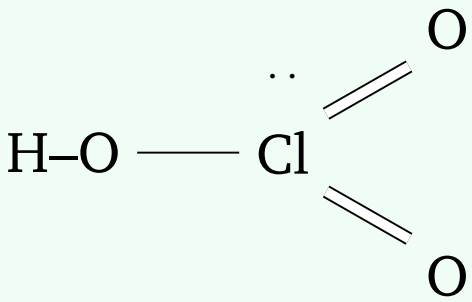
(iii) In solid state PCl_5 exists as an ionic compound. [5 marks]

Solution:

Concept:

- Oxyacid structures distinguish terminal double-bonded oxygen, hydroxyl groups and peroxide links. An $O-O$ single bond is the characteristic peroxide linkage.
- Paramagnetism results from unpaired electrons. Oxidising strength in aqueous solution depends on the overall energetics of reduction, including bond dissociation, electron gain and hydration.
- In a crystal, electrostatic attraction can stabilise complex cations and anions formed by transfer of a chloride ion between two molecules.

Step 1: (a)(i) Structure of chloric acid In $HClO_3$, chlorine is bonded to two terminal oxygen atoms by double bonds and to one hydroxyl oxygen by a single bond. Thus its connectivity is $HO-Cl(=O)_2$. The hydrogen is attached to oxygen, not directly to chlorine. Chlorine retains one lone pair; the arrangement of its three oxygen neighbours is pyramidal.



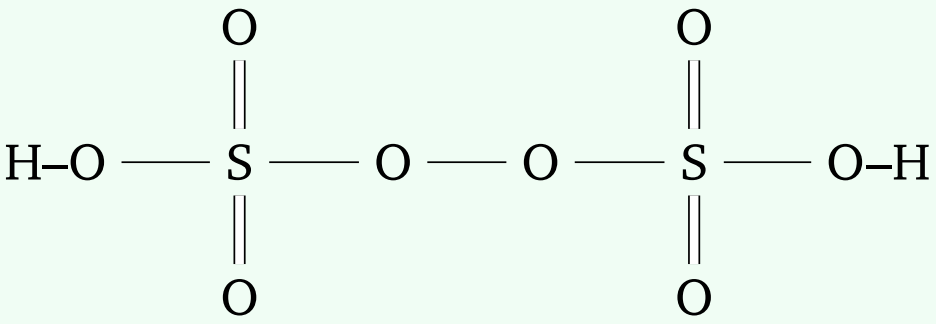
Chloric acid: two terminal oxo groups and one hydroxyl group.

Quick Tip to Solve: In peroxodisulphuric acid, count two hydroxyl oxygens, four terminal oxygens and two peroxide oxygens to check the formula before finalising the structure.

Step 2: (a)(ii) Structure of peroxodisulphuric acid In $H_2S_2O_8$, the two sulphur atoms are connected through the peroxide bridge $-O-O-$. Each sulphur also has two terminal $S=O$ bonds and one $S-OH$ group:

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

Each sulphur has an approximately tetrahedral arrangement of its four oxygen neighbours. The peroxide oxygen atoms have oxidation number -1, while sulphur is in the $+6$ oxidation state.



Peroxodisulphuric acid, showing the central peroxide linkage.

Step 3: (b)(i) Paramagnetism of sulphur above 1000 K At high temperature, the larger sulphur molecules dissociate, and above $1000\,K$ sulphur vapour contains mainly S_2 molecules. Like O_2, S_2 has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons cause attraction towards an applied magnetic field, so the vapour shows paramagnetism.

Step 4: (b)(ii) Stronger oxidising action of fluorine The relevant aqueous reduction is

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

Its energetics include dissociation of X_2, electron gain by the gaseous atoms and hydration of the resulting ions. Although electron gain by an isolated fluorine atom is less exothermic than for chlorine, the $F-F$ bond has a low dissociation enthalpy and the small F^- ion has a much more negative hydration enthalpy than Cl^-. Together these factors outweigh the electron-gain disadvantage. The overall reduction of fluorine is therefore more favourable, making F_2 the stronger oxidising agent.

Step 5: (b)(iii) Ionic nature of solid phosphorus pentachloride In the solid state, a chloride ion is transferred from one PCl_5 unit to another:

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

The cation $[PCl_4]^+$ is tetrahedral and the anion $[PCl_6]^-$ is octahedral. Strong electrostatic attraction between these oppositely charged ions provides lattice stabilisation. Thus solid PCl_5 exists as an ionic crystal containing these two complex ions.

Step 6: Conclusion The structures are $HO-Cl(=O)_2$ and $HO-S(=O)_2-O-O-S(=O)_2-OH$. Sulphur vapour is paramagnetic because S_2 has two unpaired electrons; fluorine is the stronger oxidant owing to favourable overall reduction energetics; and solid PCl_5 contains tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ ions.

Quick Tip to Solve: In peroxodisulphuric acid, count two hydroxyl oxygens, four terminal oxygens and two peroxide oxygens to check the formula before finalising the structure.

OR

27(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, O_3, is a strong oxidising agent; it oxidises sulphide to sulphate.
- XeF_6 accepts a fluoride ion from an ionic fluoride, forming a fluoroanion.
- Boiling points depend on intermolecular attractions. Hydrogen bonding makes NH_3 exceptional among group 15 hydrides.
- Down groups 16 and 17, increasing atomic size weakens the element–hydrogen bond. This increases reducing character in group 16 and acidic strength in group 17.

Step 1: Complete the oxidation of lead sulphide (a)(i) Ozone oxidises black lead sulphide to lead sulphate. Sulphur changes from oxidation state -2 in PbS to $+6$ in $PbSO_4$, while lead remains in oxidation state $+2$. The balanced equation is

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

There are twelve oxygen atoms on either side: four enter the sulphate and eight occur as molecular oxygen.

Step 2: Complete fluoride addition to xenon hexafluoride (a)(ii) Sodium fluoride supplies F^-. Xenon hexafluoride acts as a Lewis acid by accepting this fluoride ion, giving the heptafluoroxenate(VI) ion:

$$XeF_6 + F^- \longrightarrow [XeF_7]^-.$$

Hence, the complete reaction with sodium fluoride is

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

The sodium ion balances the negative charge on $[XeF_7]^-$; xenon's oxidation state remains $+6$.

Step 3: Arrange group 15 hydrides by boiling point (b)(i) The increasing order of boiling points is

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

In the hydrides other than ammonia, increasing molecular size and polarisability strengthen London dispersion forces down the group. Thus, more energy is required to separate the molecules. Ammonia has intermolecular hydrogen bonding because nitrogen is small and highly electronegative. Its boiling point is therefore higher than those of phosphine and arsine. The stronger dispersion forces in the

Quick Tip to Solve: For boiling points, check hydrogen bonding before applying the size trend. For acidity and reducing character here, follow the weakening element–hydrogen bond down the group.

much larger stibine and bismuthine molecules give them boiling points above that of ammonia.

Step 4: Arrange group 17 hydrides by acidic strength (b)(ii) In aqueous solution the increasing order is

$$\mathrm{HF} < \mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}.$$

Down the group, the halogen atom becomes larger, the hydrogen–halogen bond becomes longer, and its bond dissociation enthalpy decreases. The release of a proton becomes progressively easier. The exceptionally strong $\mathrm{H{-}F}$ bond makes hydrofluoric acid the weakest acid in this series, despite fluorine's high electronegativity.

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

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

As the central atom becomes larger down the group, the element–hydrogen bond becomes weaker and the hydride becomes less thermally stable. The hydride is consequently oxidised more readily and acts as a stronger reducing agent. Water has strong $\mathrm{O{-}H}$ bonds and is the weakest reducing agent in this series; hydrogen telluride is the strongest.

Step 6: Conclusion The completed reactions are $\mathrm{PbS + 4\,O_3 \longrightarrow PbSO_4 + 4\,O_2}$ and $\mathrm{XeF_6 + NaF \longrightarrow Na[XeF_7]}$. The increasing orders are: boiling point, $\mathrm{PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3}$; acidic strength, $\mathrm{HF < HCl < HBr < HI}$; and reducing character, $\mathrm{H_2O < H_2S < H_2Se < H_2Te}$.

Quick Tip to Solve: For boiling points, check hydrogen bonding before applying the size trend. For acidity and reducing character here, follow the weakening element–hydrogen bond down the group.