CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-4-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) All questions are compulsory.

(ii) 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.

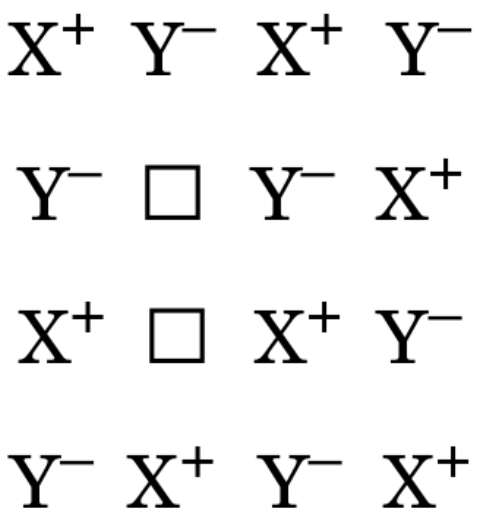
(v) Section D : Questions number **25 to 27** are long answer questions and carry **5 marks** each.

(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. Name the defect in the following crystal: [1 mark]



Solution:

Concept:

- A Schottky defect consists of vacancies at the normal lattice sites of equal numbers of cations and anions.
- Removing equal numbers of oppositely charged ions preserves electrical neutrality and the stoichiometric ratio.

Step 1: Inspect the empty sites The crystal contains alternating X^+ and Y^- ions. One empty square occupies a site where an X^+ ion should occur, and the other occupies a site where a Y^- ion should occur.

Step 2: Identify the vacancy pattern There is one missing cation and one missing anion, with no ion shown at an interstitial site. This paired vacancy pattern is characteristic of a Schottky defect; a Frenkel defect would instead show an ion displaced to an interstitial site.

Step 3: Conclusion The crystal shows a $\boxed{\text{Schottky defect}}$.

Quick Tip to Solve: Check whether both ion types are missing: equal cation and anion vacancies identify Schottky defects.

2(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 precipitate immediately as $AgCl$ with $AgNO_3$.
- Chromium(III) has coordination number six in these hydrated complexes. Water is neutral and a coordinated chloride carries 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: $Ag^+ + Cl^- \longrightarrow AgCl(s)$. The remaining chloride is coordinated to chromium.

Step 2: Complete the coordination sphere The coordinated chloride occupies one of six coordination sites, so five water molecules are ligands. The sixth water molecule is water of crystallisation. With chromium in oxidation state $+3$, the complex ion has charge $+2$, 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: Count precipitated chloride ions outside the brackets first, then fill six chromium coordination sites.

OR

2(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 on dissolution in water.
- A complex salt retains its coordination entity in aqueous solution under ordinary conditions.

Step 1: Describe a double salt For example, Mohr's salt gives Fe^{2+}, NH_4^+ and SO_4^{2-} ions in water. Its constituent ions can show their usual qualitative tests; the combined crystalline identity does not persist in solution.

Step 2: Describe a complex salt For example, $K_4[Fe(CN)_6]$ gives potassium ions and the intact $[Fe(CN)_6]^{4-}$ complex ion in water. The coordinated iron and cyanide do not behave as free Fe^{2+} and CN^- ions in their ordinary tests.

Step 3: Conclusion A double salt loses its identity by complete dissociation, whereas a complex retains its complex ion in solution.

Quick Tip to Solve: Use the ions present in water as the distinction: simple constituent ions versus an intact coordination entity.

3. Define associated colloid with an example. [1 mark]

Solution:

Concept:

- Associated colloids are substances whose particles associate into aggregates called micelles at sufficiently high concentration.
- Micelles form above the critical micelle concentration (CMC) and above the appropriate Krafft temperature.

Step 1: Define their concentration-dependent behaviour At low concentration, these substances behave as normal strong electrolytes and exist as individual ions. When their concentration exceeds the CMC under suitable temperature conditions, many amphiphilic ions aggregate, producing particles of colloidal size.

Step 2: Give an example Soap, such as sodium stearate $C_{17}H_{35}COONa$, is an associated colloid. In water its hydrocarbon tails collect inside a micelle while its ionic carboxylate heads face the surrounding water.

Step 3: Conclusion Associated colloids form micelles above the CMC; soap solution is an example.

Quick Tip to Solve: Include both parts of the definition: ordinary electrolyte at low concentration and micelles above the CMC.

4. Why is *t*-butyl bromide more reactive towards S_N1 reaction as compared to *n*-butyl bromide? [1 mark]

Solution:

Concept:

- An S_N1 reaction proceeds through slow ionisation of the carbon–halogen bond to form a carbocation.
- The more stable the carbocation, the easier this rate-determining ionisation and the greater the S_N1 reactivity.

Step 1: Compare the intermediates t-Butyl bromide, $(CH_3)_3CBr$, forms the tertiary carbocation $(CH_3)_3C^+$. In contrast, n-butyl bromide would have to form the primary carbocation $CH_3CH_2CH_2CH_2^+$.

Step 2: Explain the difference in stability Three methyl groups stabilise the tertiary carbocation by their positive inductive effect and hyperconjugation. The primary carbocation has much less stabilisation. Thus the activation barrier for ionisation of t-butyl bromide is lower, so its S_N1 reaction is faster.

Step 3: Conclusion t-Butyl bromide is more reactive because it forms a much more stable tertiary carbocation than the primary carbocation from n-butyl bromide.

Quick Tip to Solve: For an SN1 comparison, rank the carbocations formed in the slow step before considering the nucleophile.

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 fewer carbon atom than the original amide because the carbonyl carbon is removed.

Step 1: State the reagents and transformation Heat a primary amide, $RCONH_2$, with bromine and aqueous sodium hydroxide. The alkyl or aryl group R becomes attached directly to the nitrogen in RNH_2.

Step 2: Write the balanced reaction

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

The carbonyl carbon appears in sodium carbonate, accounting for the loss of one carbon from the organic product.

Step 3: Conclusion $RCONH_2$ gives RNH_2 with $Br_2/NaOH$; this is Hofmann bromamide degradation.

Quick Tip to Solve: Retain the group R unchanged and remove the carbonyl carbon when writing the amine product.

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 bonded to an electronegative atom such as nitrogen.
- Stronger intermolecular attractions require more energy to separate molecules, increasing the boiling point.

Step 1: Identify the hydrogen-bonding ability Propanamine, $CH_3CH_2CH_2NH_2$, is a primary amine and has $N-H$ bonds. Its molecules form intermolecular $N-H\cdots N$ hydrogen bonds with one another.

Step 2: Compare the tertiary amine N,N-Dimethylmethanamine is trimethylamine, $(CH_3)_3N$, a tertiary amine. It has no $N-H$ bond, so its molecules cannot hydrogen-bond to one another. Although it can accept hydrogen bonds from water, that does not provide self-association in the pure liquid.

Step 3: Conclusion Propanamine has a higher boiling point because it forms intermolecular hydrogen

Quick Tip to Solve: For boiling points of pure amines, check for an N–H bond; a nitrogen lone pair alone does not permit self hydrogen bonding.

bonds, whereas trimethylamine cannot form these bonds between its own molecules.

Quick Tip to Solve: For boiling points of pure amines, check for an N–H bond; a nitrogen lone pair alone does not permit self hydrogen bonding.

Section B (14 marks)

6(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 gas partial pressure and x its mole fraction in solution.
- Gas solubility generally decreases with increasing temperature; at fixed temperature, it increases with gas partial pressure.

Step 1: Explain the effect of water temperature Oxygen is more soluble in cold water than in warm water. Thus, under comparable conditions, cold water contains more dissolved oxygen available for respiration. Aquatic organisms obtain oxygen dissolved in water, so this greater oxygen supply makes them more comfortable in cold water.

Step 2: Explain the effect of altitude At higher altitudes the atmospheric pressure, and hence the partial pressure of oxygen, is lower. According to Henry's law, less oxygen dissolves in blood at this lower partial pressure. The resulting oxygen deficiency, called anoxia, reduces oxygen delivery to the brain and can impair clear thinking.

Step 3: Conclusion (a) Cold water supplies more dissolved oxygen for aquatic respiration. (b) Lower oxygen partial pressure at high altitude causes oxygen deficiency in the blood and brain.

Quick Tip to Solve: Compare temperature for aquatic life and oxygen partial pressure for altitude; both affect dissolved oxygen.

OR

6(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:

- Negative deviation from Raoult's law occurs when unlike molecular attractions exceed the corresponding like molecular attractions.
- A negative-deviation azeotrope is a maximum-boiling mixture: its total vapour pressure has a minimum.

Step 1: Identify the new intermolecular attraction Acetone has an electron-rich carbonyl oxygen,

Quick Tip to Solve: Stronger unlike attractions mean lower vapour pressure and a higher boiling temperature.

while the hydrogen of chloroform is made relatively electron-deficient by its three chlorine atoms. In their mixture, hydrogen bonding develops between the oxygen of acetone and the hydrogen of chloroform:

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

These unlike interactions are stronger than the interactions in the separate liquids.

Step 2: Relate attraction to vapour pressure and boiling Stronger acetone–chloroform attractions make molecular escape into the vapour more difficult. The partial pressures and total vapour pressure are therefore lower than the Raoult-law prediction, giving negative deviation. At the azeotropic composition, a minimum in total vapour pressure corresponds to a maximum in boiling temperature; liquid and vapour compositions are the same.

Step 3: Conclusion Acetone and chloroform form a maximum-boiling azeotrope because strong intermolecular hydrogen bonding produces negative deviation from Raoult's law.

Quick Tip to Solve: Stronger unlike attractions mean lower vapour pressure and a higher boiling temperature.

7. Explain with a graph, the variation of molar conductivity of a strong electrolyte with dilution.

[2 marks]

Solution:

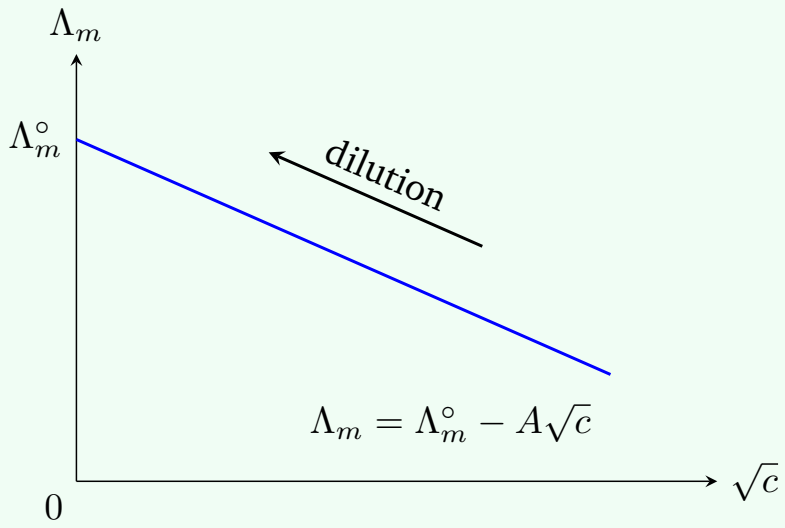
Concept:

- Molar conductivity $\Lambda_m = \kappa/c$ in consistent units is the conducting ability of the solution containing one mole of electrolyte.
- For a dilute strong electrolyte, $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$, where $A > 0$, c is concentration and Λ_m° is the limiting molar conductivity.

Step 1: Explain the change on dilution A strong electrolyte is almost completely dissociated in solution. On dilution, ions move farther apart and interionic attractions become weaker. Ionic mobility therefore increases and molar conductivity increases gradually. This increase mainly reflects increased mobility, rather than a large increase in dissociation. Although specific conductivity falls on dilution, molar conductivity rises.

Step 2: Interpret the graph Plot Λ_m vertically against $\sqrt{c}$ horizontally. In the dilute range the plot is a straight line with negative slope $-A$. Dilution means moving towards smaller $\sqrt{c}$, hence upward along the line. Extrapolation to $c = 0$ gives the intercept Λ_m°, the maximum limiting value at infinite dilution.

Quick Tip to Solve: On a conductivity-versus-root-concentration graph, dilution moves left and molar conductivity moves up.



Molar conductivity of a strong electrolyte in the dilute range

Step 3: Conclusion The molar conductivity of a strong electrolyte increases on dilution and approaches Λ_m°; its dilute-solution plot against $\sqrt{c}$ is a descending straight line.

Quick Tip to Solve: On a conductivity-versus-root-concentration graph, dilution moves left and molar conductivity moves up.

8(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 identifies nitrate ions through formation of a nitrosyl complex of iron.
- Acidified ferrous ions reduce nitrate to nitric oxide; nitric oxide then coordinates to an iron centre.

Step 1: Identify the anion and reduction reaction The anion confirmed is nitrate, NO_3^-. In the acidic medium, ferrous ions reduce nitrate to nitric oxide while being oxidised to ferric ions:

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

Careful addition of concentrated sulphuric acid produces separate layers, so the characteristic colour appears near their interface.

Step 2: Give the composition of the ring The nitric oxide formed combines with hydrated ferrous ions to produce the brown nitrosyl complex:

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

Quick Tip to Solve: Remember the brown-ring complex as five waters plus one NO ligand around iron, with sulphate outside the brackets.

The brown-ring compound is $[Fe(H_2O)_5(NO)]SO_4$, commonly called nitrosyl ferrous sulphate. It contains five coordinated water molecules and one coordinated nitric oxide ligand, with sulphate as counter-ion.

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

Quick Tip to Solve: Remember the brown-ring complex as five waters plus one NO ligand around iron, with sulphate outside the brackets.

OR

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

Solution:

Concept:

- $$MnO_2(s) + 4HCl(aq) \xrightarrow{\text{heat; concentrated HCl}} MnCl_2(aq) + Cl_2(g) + 2H_2O(l).$$

- $$H_2(g) + Cl_2(g) \xrightarrow{\text{diffused sunlight}} 2HCl(g).$$

Step 1: HCl to chlorine

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

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

Step 2: Chlorine to HCl

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

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g).$$

Step 3: Conclusion

$$MnO_2 + 4HCl \xrightarrow{\text{heat}} MnCl_2 + Cl_2 + 2H_2O,$$
$$H_2 + Cl_2 \xrightarrow{\text{diffused sunlight}} 2HCl.$$

Quick Tip to Solve: Balance the HCl oxidation reaction with four HCl; combine hydrogen and chlorine in a one-to-one mole ratio.

9. 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: $M^{2+} \rightarrow M^{3+} + e^-$. Its oxidation potential is the negative of $E^\circ_{M^{3+}/M^{2+}}$.
- Half-filled $3d^5$ configurations have additional stability; stability of an oxidation state must consider both oxidation and reduction.

Step 1: Compare reducing strengths For chromium, $E^\circ_{Cr^{3+}/Cr^{2+}} = -0.41\,V$, whereas for iron it is $+0.77\,V$. Thus the corresponding oxidation potentials are $+0.41\,V$ and $-0.77\,V$. Chromium(II) therefore loses an electron more readily and is the stronger reducing agent. Its oxidation also gives the stable $3d^3$ chromium(III) ion.

Step 2: Identify the stable divalent ion Mn^{2+} has the half-filled configuration $[Ar]3d^5$. The positive potential $E^\circ_{Mn^{3+}/Mn^{2+}} = +1.57\,V$ shows that oxidation of this ion is difficult. Its very negative $E^\circ_{Mn^{2+}/Mn} = -1.18\,V$ also shows that reduction to the metal is difficult. These features together favour manganese remaining in the +2 state; the highest value in the second row alone does not establish stability against both changes.

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

Quick Tip to Solve: For reducing strength, reverse the trivalent/divalent half-reaction and change the sign of its potential.

10. Define with equation:

(a) Reimer-Tiemann Reaction

(b) Williamson's Synthesis [2 marks]

Solution:

Concept:

- Reimer–Tiemann formylation introduces a $-CHO$ group mainly ortho to the hydroxyl group of phenol.
- Williamson synthesis forms an ether by nucleophilic substitution of an alkyl halide with an alkoxide ion.

Step 1: Define Reimer–Tiemann reaction Phenol reacts with chloroform and aqueous sodium hydrox-

Quick Tip to Solve: Remember the reagent pairs: phenol plus chloroform/base for formylation, and alkoxide plus alkyl halide for ether formation.

ide on heating; acidification gives mainly 2-hydroxybenzaldehyde (salicylaldehyde). Dichlorocarbene generated from chloroform is the reactive intermediate. The net equation, after acid work-up, is

$$C_6H_5OH + CHCl_3 + 3NaOH \longrightarrow o\text{–}\ HOC_6H_4CHO + 3NaCl + 2H_2O.$$

A smaller amount of the para isomer may also form.

Step 2: Define Williamson synthesis An alkyl halide reacts with a sodium alkoxide to form an ether and sodium halide:

$$RONa + R'X \longrightarrow ROR' + NaX.$$

For example,

$$C_2H_5ONa + CH_3I \longrightarrow C_2H_5OCH_3 + NaI.$$

The alkoxide attacks the carbon bonded to the halogen by the S_N2 mechanism. A methyl or primary alkyl halide is preferred to minimise competing elimination.

Step 3: Conclusion Reimer–Tiemann reaction converts phenol mainly to salicylaldehyde; Williamson synthesis produces ethers from alkoxides and alkyl halides.

Quick Tip to Solve: Remember the reagent pairs: phenol plus chloroform/base for formylation, and alkoxide plus alkyl halide for ether formation.

11. Give the structures of monomers of the following polymers:

(a) Nylon-6,6

(b) Buna-S [2 marks]

Solution:

Concept:

- A monomer is a small molecule whose units are incorporated into a polymer chain.
- Nylon-6,6 is formed from a diamine and a dicarboxylic acid; Buna-S is a copolymer of a diene and styrene.

Step 1: Write the Nylon-6,6 monomer structures The monomers are hexane-1,6-diamine (hexamethylenediamine) and hexanedioic acid (adipic acid):

$$H_2N - (CH_2)_6 - NH_2 \qquad HOOC - (CH_2)_4 - COOH.$$

Each molecule has two reactive end groups. Amino groups react with carboxyl groups to make amide linkages with elimination of water. The two sixes denote the six carbon atoms in the diamine and the six carbon atoms in the acid, including its two carboxyl carbons.

Step 2: Write the Buna-S monomer structures The monomers are buta-1,3-diene and styrene (phenylethene):

$$CH_2 = CH - CH = CH_2 \qquad C_6H_5 - CH = CH_2.$$

Here C_6H_5 denotes the phenyl ring bonded directly to the vinyl carbon. Both monomers contain

Quick Tip to Solve: Count the carboxyl carbons in adipic acid: four methylene carbons plus two carboxyl carbons give six.

carbon-carbon double bonds that participate in addition copolymerisation. The S in Buna-S identifies styrene, rather than acrylonitrile, as the comonomer.

Step 3: Conclusion Nylon-6,6: $H_2N-(CH_2)_6-NH_2$ and $HOOC-(CH_2)_4-COOH$. Buna-S: $CH_2=CH-CH=CH_2$ and $C_6H_5-CH=CH_2$.

Quick Tip to Solve: Count the carboxyl carbons in adipic acid: four methylene carbons plus two carboxyl carbons give six.

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

(a) Teflon

(b) PHBV [2 marks]

Solution:

Concept:

- Addition polymerisation joins unsaturated monomers without eliminating small molecules.
- Condensation polymerisation forms linkages between functional groups, usually with elimination of a small molecule such as water.

Step 1: Classify Teflon Teflon is an addition polymer of tetrafluoroethene. Its double bond opens as monomers join to form the chain:

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

No water, hydrogen chloride or other small molecule is lost. All the atoms of each tetrafluoroethene molecule remain in the polymer repeat unit, which distinguishes this reaction from condensation polymerisation.

Step 2: Classify PHBV PHBV, poly(β-hydroxybutyrate-co-β-hydroxyvalerate), is a condensation copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid:

$$CH_3CH(OH)CH_2COOH, \qquad CH_3CH_2CH(OH)CH_2COOH.$$

Each hydroxy acid has both hydroxyl and carboxyl groups. These groups react to form ester linkages, $-COO-$, with elimination of water. Thus the classification follows the linkage-forming process rather than simply the fact that two types of monomers are used.

Step 3: Conclusion Teflon is an addition polymer; PHBV is a condensation polymer, with ester formation and elimination of water.

Quick Tip to Solve: Look for double-bond opening without by-products versus functional-group coupling with water loss.

Section C (36 marks)

13. 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:

- Density is mass per unit volume. For a cubic unit cell, $\rho = \dfrac{ZM}{N_A a^3}$, where Z is the number of atoms per cell, M is molar mass and a is edge length.
- A body-centred cubic (bcc) unit cell has eight corner atoms, each shared by eight cells, and one atom entirely inside the cell. Hence $Z = 8(1/8) + 1 = 2$.

Step 1: Determine the mass of one unit cell The atomic mass of chromium is $52\,\text{u}$, so its molar mass is $52\,\text{g mol}^{-1}$. Since one mole contains $N_A = 6.022 \times 10^{23}$ atoms, the mass of one atom is M/N_A. A bcc cell contains two atoms in total, giving

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

Counting only the central atom would miss the net contribution of the eight corner atoms.

Step 2: Convert the edge length and calculate density Use centimetres so that the final density is in g cm^{-3}. Since $1\,\text{pm} = 10^{-10}\,\text{cm}$,

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

Dividing the mass by this cell volume,

$$\rho = \frac{1.727 \times 10^{-22}}{2.70 \times 10^{-23}} = 6.396\,\text{g cm}^{-3}.$$

The edge length is cubed after conversion; this is essential because the denominator represents volume.

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

Quick Tip to Solve: For a bcc density calculation, put Z = 2 and convert the edge to centimetres before cubing it.

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 follows $\pi = CRT$, where C is molar concentration, R is the gas constant and T is absolute temperature.
- Glucose is a non-electrolyte and does not dissociate. At the same temperature, its osmotic pressure is directly proportional to its molar concentration and, because the solute is unchanged, to its mass concentration.

Step 1: Relate the two solutions at the same temperature Write the osmotic-pressure expressions for both glucose solutions:

$$\pi_1 = C_1RT, \qquad \pi_2 = C_2RT.$$

Both solutions are at $300\,\text{K}$, so division eliminates R and T:

$$\frac{C_2}{C_1} = \frac{\pi_2}{\pi_1} = \frac{1.52}{4.98}.$$

The original solution contains $30\,\text{g}$ per litre. If the required mass concentration is $x\,\text{g L}^{-1}$, its molar concentration is x/M, while the first has molar concentration $30/M$, using the same glucose molar mass M.

Step 2: Calculate the required concentration The common molar mass cancels in the ratio, giving

$$\frac{x/M}{30/M} = \frac{x}{30} = \frac{1.52}{4.98}, \qquad x = \frac{30 \times 1.52}{4.98} = 9.1566\,\text{g L}^{-1}.$$

To express the result as molarity, use the molar mass of glucose, $180\,\text{g mol}^{-1}$:

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

The lower osmotic pressure requires a lower concentration, consistent with this result. The given initial pressure is used directly, avoiding unnecessary rounding of the gas constant.

Step 3: Conclusion The required glucose concentration is $\boxed{9.16\,\text{g L}^{-1}}$, or 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 ratio of osmotic pressures.

15(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:

- Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using both tabulated values as reduction potentials.
- The standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant.
- Since $\Delta_r G^\circ = -RT \ln K_c$, at 298 K the relation is $\log_{10} K_c = nE^\circ_{\text{cell}}/0.0591$, with potential in volts.

Step 1: Identify the electrodes and electron transfer In the given reaction, zinc is oxidised and cadmium ions are reduced:

$$\begin{aligned} \text{Anode:} \quad & \text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-, \\ \text{Cathode:} \quad & \text{Cd}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cd(s)}. \end{aligned}$$

Therefore $n = 2$. Using the given reduction potentials without reversing their signs in the subtraction formula,

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

Step 2: Calculate the standard Gibbs energy Take $F = 96500\,\text{C mol}^{-1}$. Then

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

The negative sign is required: the positive standard cell potential means the reaction as written is thermodynamically favourable under standard conditions.

Step 3: Calculate the logarithm of the equilibrium constant With no temperature specified, use the conventional 298 K form of the standard electrochemical relation. Equating $-nFE^\circ_{\text{cell}}$ and $-2.303RT \log_{10} K_c$ gives

$$\log_{10} K_c = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{2 \times 0.360}{0.0591} = 12.18.$$

Thus the equilibrium constant is much greater than unity, in agreement with the negative standard Gibbs energy. The logarithm here is base ten, whereas $\ln K_c$ in the thermodynamic relation is the natural logarithm.

Step 4: Conclusion $\boxed{\Delta_r G^\circ = -69.48\,\text{kJ mol}^{-1}}$ and $\boxed{\log_{10} K_c \approx 12.18}$ at 298 K.

Quick Tip to Solve: Subtract the zinc reduction potential from the cadmium reduction potential, then use two electrons in both formulae.

OR

15(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 relates deposited mass to charge: $m = MQ/(nF)$, where M is molar mass, Q is charge, n is electrons required per metal atom and F is the Faraday constant.
- Charge passed by a constant current is $Q = It$, with current I in amperes and time t in seconds. The given reduction consumes six electrons per chromium atom.

Step 1: Determine the electrochemical equivalent In CrO_3, chromium has oxidation state $+6$; the deposited metal has oxidation state zero. Thus the printed half-reaction requires $n = 6$. One mole of chromium, weighing $52\,g$, needs $6F = 6 \times 96500 = 579000\,C$. The electrochemical equivalent is therefore $52/579000\,g\,C^{-1}$, rather than $52/96500$, since six moles of electrons deposit only one mole of chromium.

Step 2: Calculate the mass deposited by the given charge Substitute $Q = 24000\,C$ into Faraday's law:

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

The charge is supplied directly in coulombs, so no current or time conversion is needed for this calculation.

Step 3: Calculate the time needed for the specified mass Rearranging $m = MIt/(nF)$ gives

$$t = \frac{mnF}{MI} = \frac{1.5 \times 6 \times 96500}{52 \times 12.5} = 1336.15\,s.$$

Dividing by 60 converts this to $22.27\,min$. These calculations use the supplied reaction and assume the passed charge is used for chromium deposition.

Step 4: Conclusion The mass electroplated is approximately $2.16\,g$, and depositing $1.5\,g$ at $12.5\,A$ takes $1.34 \times 10^3\,s$, or $22.3\,min$.

Quick Tip to Solve: Read the electron coefficient first: here use six Faradays per mole of Cr, then use Q = It only for the time calculation.

16. Give reasons for the following:

(a) Leather gets hardened after tanning.

(b) $FeCl_3$ is preferred over KCl in case of a cut leading to bleeding.

(c) Freundlich isotherm becomes independent of pressure at high pressure for a gas absorbed on a solid. [3 marks]

Solution:

Concept:

- Coagulation precipitates colloidal particles by neutralising their charge. Oppositely charged colloids can also coagulate each other on mixing.
- By the Hardy–Schulze rule, the coagulating power of a counter-ion increases strongly with its valency. For a negatively charged sol, the active ions are cations.
- The Freundlich adsorption relation is $x/m = kp^{1/n}$, where x/m is the mass of gas adsorbed per unit mass of adsorbent and p is gas pressure. At saturation the amount adsorbed is essentially constant.

Step 1: Explain hardening during tanning Animal hide contains positively charged colloidal particles, whereas tannin has negatively charged colloidal particles. Their mutual interaction causes mutual coagulation. This coagulation of the colloidal material in the hide makes leather hard during tanning. The key feature is the opposite charge of the two colloidal systems, rather than a simple drying effect.

Step 2: Compare ferric chloride and potassium chloride Blood is a negatively charged colloidal system, so positive ions act as its coagulating ions. $FeCl_3$ supplies Fe^{3+}, whereas KCl supplies K^+. The trivalent ferric ion has greater coagulating power than the monovalent potassium ion by the Hardy–Schulze rule. Therefore ferric chloride promotes coagulation of blood more effectively, helping arrest bleeding. Chloride is common to both salts and is not the counter-ion responsible for this comparison.

Step 3: Explain pressure independence at high pressure As pressure increases, more gas molecules occupy the available adsorption sites on the solid. At sufficiently high pressure the surface approaches saturation, so a further increase in pressure produces practically no increase in x/m. In the limiting representation of the Freundlich relation, $1/n$ tends to zero and $p^{1/n}$ becomes unity, giving $x/m = k$. Thus the empirical power law is used over its applicable pressure range; the high-pressure limit is understood as the saturated plateau.

Step 4: Conclusion Tanning hardens leather by mutual coagulation; Fe^{3+} coagulates blood more effectively than K^+; at high pressure, saturation makes adsorption effectively independent of pressure.

Quick Tip to Solve: For each colloid, identify its charge and the opposite ion; for high-pressure adsorption, check whether the surface sites are saturated.

17(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:

- Froth flotation separates sulphide ores through selective wetting: ore particles wetted by oil attach to bubbles and rise into the froth.
- Metallurgical purification can exploit selective formation of a soluble compound or a volatile compound, followed by recovery of the metal or oxide.

Step 1: State the role of depressants in froth flotation A depressant selectively prevents one sulphide ore from entering the froth, allowing another sulphide ore to be separated from the mixture. For example, when ZnS and PbS are present together, NaCN acts as a depressant for ZnS. It prevents zinc sulphide from being collected in the froth while lead sulphide is carried into the froth. Thus a depressant improves selective separation of ores rather than merely producing more froth.

Step 2: State the role of carbon monoxide in Mond's process Carbon monoxide converts nickel into volatile nickel tetracarbonyl at about 330–$350\,\mathrm{K}$:

$$\mathrm{Ni} + 4\mathrm{CO} \longrightarrow \mathrm{Ni(CO)_4}.$$

The volatile carbonyl is separated from non-volatile impurities and heated to about 450–$470\,\mathrm{K}$, when it decomposes:

$$\mathrm{Ni(CO)_4} \longrightarrow \mathrm{Ni} + 4\mathrm{CO}.$$

Pure nickel is deposited. Carbon monoxide therefore serves as the ligand forming the volatile carbonyl used for purification.

Step 3: State the role of concentrated sodium hydroxide Concentrated NaOH selectively dissolves the amphoteric alumina present in bauxite by converting it into soluble sodium aluminate. Using the hydrated aluminate representation,

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

Iron oxide impurities remain largely undissolved and can be filtered off, so alumina is separated from them. Silica can also dissolve as sodium silicate; the selective leaching step is followed by precipitation and purification of hydrated alumina.

Step 4: Conclusion Depressants enable selective flotation; CO purifies nickel through volatile $\mathrm{Ni(CO)_4}$; concentrated NaOH leaches alumina as soluble sodium aluminate.

Quick Tip to Solve: Link each reagent to its separation mechanism: selective flotation, volatile carbonyl formation, or soluble aluminate formation.

OR

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

[3 marks]

Solution:

Concept:

- Bauxite contains hydrated alumina, $Al_2O_3 \cdot 2H_2O$. Alumina is amphoteric and dissolves in concentrated sodium hydroxide as soluble sodium aluminate.
- Purified alumina is reduced electrolytically in molten cryolite. Aluminium ions gain electrons at the cathode; oxide ions lose electrons at the carbon anode.

Step 1: Leach bauxite with concentrated sodium hydroxide Heat powdered bauxite with concentrated $NaOH$ under pressure. Alumina dissolves while insoluble impurities are filtered out. The leaching reaction is

$$Al_2O_3 \cdot 2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O.$$

In aqueous solution, sodium aluminate can also be represented as $Na[Al(OH)_4]$.

Step 2: Precipitate aluminium hydroxide and obtain alumina Pass carbon dioxide through the filtered aluminate solution to precipitate aluminium hydroxide:

$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow 2Al(OH)_3 + Na_2CO_3.$$

Filter and heat the precipitate strongly to obtain pure alumina:

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

Step 3: Reduce alumina by electrolysis Dissolve purified alumina in molten cryolite, with calcium fluoride added to the bath. Cryolite lowers the melting temperature and improves electrical conductivity. At the cathode,

$$Al^{3+} + 3e^- \longrightarrow Al(l).$$

At the anode,

$$2O^{2-} \longrightarrow O_2 + 4e^-.$$

The oxygen formed reacts with the carbon anode: $C + O_2 \longrightarrow CO_2$. Thus the carbon anodes are consumed and replaced periodically; the overall reaction is

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

Step 4: Conclusion Aluminium is extracted by leaching bauxite to obtain pure alumina, followed by electrolytic reduction of alumina in molten cryolite. The overall electrolytic reaction is $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$.

Quick Tip to Solve: Write the stages in order: aluminate, hydroxide, alumina, then cathode and carbon-anode reactions.

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 is $FeCr_2O_4$. Oxidative roasting converts chromium(III) into soluble chromate, containing chromium(VI).
- Acidification converts chromate into dichromate: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$.
- In acid, each dichromate ion accepts six electrons. Each ferrous ion loses one electron to become a ferric ion.

Step 1: Roast chromite in air with sodium carbonate Finely powdered chromite ore is fused with sodium carbonate in an adequate supply of air. Chromium is oxidised to soluble sodium chromate:

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

Extract the roasted mass with water. Sodium chromate dissolves, whereas insoluble iron(III) oxide and other insoluble material are removed by filtration.

Step 2: Convert chromate solution to sodium dichromate Acidify the filtered yellow sodium chromate solution with sulphuric acid. Chromate ions combine to give orange dichromate ions:

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

Concentrate and crystallise the solution to obtain $Na_2Cr_2O_7 \cdot 2H_2O$.

Step 3: Write oxidation of a ferrous salt in acidic medium The reduction half-reaction is

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

The oxidation half-reaction is $Fe^{2+} \longrightarrow Fe^{3+} + e^-$. Multiply it by six and add, cancelling electrons:

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

Thus chromium is reduced from $+6$ to $+3$, while iron is oxidised from $+2$ to $+3$.

Step 4: Conclusion Sodium dichromate is prepared by oxidative roasting of chromite, water extraction and acidification of sodium chromate. One dichromate ion oxidises six Fe^{2+} ions to Fe^{3+} in acidic medium.

Quick Tip to Solve: Remember the dichromate half-reaction first: two chromium atoms need six electrons, so six ferrous ions are required.

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 both atoms and total charge. In acidic solution, use H_2O for oxygen, H^+ for hydrogen and electrons for charge.
- In alkaline fusion, manganese(IV) is oxidised to manganese(VI) manganate; acidic permanganate and dichromate are reduced to Mn^{2+} and Cr^{3+}, respectively.

Step 1: (a) Oxidise manganese dioxide in alkaline medium Heating MnO_2 with potassium hydroxide in oxygen produces green potassium manganate. Manganese changes from $+4$ to $+6$; two manganese atoms lose four electrons, matching reduction of one oxygen molecule. The balanced equation is

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O.$$

All atoms are balanced.

Step 2: (b) Oxidise iodide with acidic permanganate The half-reactions are

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O,$$
$$2I^- \longrightarrow I_2 + 2e^-.$$

Multiply the first by two and the second by five to cancel ten electrons:

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

The total charge on either side is $+4$. Iodide is oxidised to iodine; permanganate is reduced to manganese(II).

Step 3: (c) Oxidise tin(II) with acidic dichromate Dichromate accepts six electrons:

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

Each Sn^{2+} ion loses two electrons: $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$. Therefore three tin(II) ions are required:

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

The total charge on either side is $+18$, and chromium, tin, oxygen and hydrogen are balanced.

Step 4: Conclusion The completed equations above conserve both atoms and charge, with electron transfers of four, ten and six respectively.

Quick Tip to Solve: Use electron counts to get the ratios: permanganate needs five electrons and dichromate needs six; iodide gives one and tin(II) gives two.

19. 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 oxidation state of the central ion gives its electronic configuration. Remove electrons from the $4s$ orbital before the $3d$ orbitals for these transition-metal cations.
- Weak-field ligands preserve unpaired electrons, whereas strong-field ligands can pair them. A complex with unpaired electrons is paramagnetic; one with all electrons paired is diamagnetic.

Step 1: Analyse the iron complex In $[Fe(H_2O)_6]^{2+}$, water is neutral, so iron is Fe^{2+}. From $Fe : [Ar]3d^6 4s^2$, its ion has configuration $[Ar]3d^6$. Water is a weak-field ligand and does not pair the $3d$ electrons. The five $3d$ orbitals have one pair and four singly occupied orbitals. Six ligand pairs are accommodated in hybrid orbitals formed from one $4s$, three $4p$, and two $4d$ orbitals. This is an outer-orbital octahedral complex with four unpaired electrons.

Step 2: Analyse the nickel complex In $[Ni(CN)_4]^{2-}$, let the nickel oxidation state be x. Since each cyanide ion has charge -1, $x - 4 = -2$, giving $x = +2$. Thus Ni^{2+} has configuration $[Ar]3d^8$. Cyanide is a strong-field ligand and pairs the eight $3d$ electrons in four orbitals, leaving one $3d$ orbital vacant. This orbital, one $4s$ orbital and two $4p$ orbitals form four equivalent hybrid orbitals accepting the ligand lone pairs. The resulting complex is square planar, with no unpaired electrons.

Step 3: Conclusion $[Fe(H_2O)_6]^{2+}$: sp^3d^2 hybridization, paramagnetic (four unpaired electrons). $[Ni(CN)_4]^{2-}$: dsp^2 hybridization, diamagnetic.

Quick Tip to Solve: First find the metal-ion configuration; then use water as weak field and cyanide as strong field before counting unpaired electrons.

20(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:

- An electron-withdrawing substituent can activate a haloarene by stabilising the negatively charged intermediate formed during nucleophilic attack.
- Melting point depends strongly on crystal packing. A preparation is convenient when its by-products separate readily from the desired organic product.

Step 1: Explain the nitro-group effect (a) The $-NO_2$ group withdraws electron density through its

Quick Tip to Solve: For these three reasons, connect the property respectively to intermediate stability, crystal symmetry and removal of gaseous by-products.

inductive and resonance effects. When it is ortho or para to the halogen, the negative charge in the intermediate produced by nucleophilic attack can be delocalised towards the nitro group and onto its oxygen atoms. This resonance stabilisation favours formation of the intermediate and facilitates subsequent loss of the halide ion. Hence nucleophilic substitution becomes easier. At the meta position, this direct resonance stabilisation of the intermediate is unavailable.

Step 2: Explain the melting-point difference (b) The para isomer has a more symmetrical arrangement of the two chlorine substituents than the ortho or meta isomer. Consequently, p-dichlorobenzene packs more efficiently into the crystal lattice. Its stronger overall lattice stabilisation requires more thermal energy to disrupt the ordered solid, so its melting point is higher. This comparison concerns packing of the solid, rather than merely the molecular mass, which is identical for all three isomers.

Step 3: Explain the thionyl-chloride preference (c) Alcohols react with thionyl chloride according to

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

Both by-products, sulphur dioxide and hydrogen chloride, are gases and escape from the reaction mixture. Their removal helps drive the conversion forward and leaves the alkyl chloride relatively free of these by-products. Thus separation and purification of the desired chloride are convenient.

Step 4: Conclusion (a) Ortho/para nitro groups stabilise the anionic substitution intermediate by resonance. (b) The symmetrical para isomer packs better in crystals. (c) Thionyl chloride produces gaseous by-products that escape, facilitating isolation of alkyl chloride.

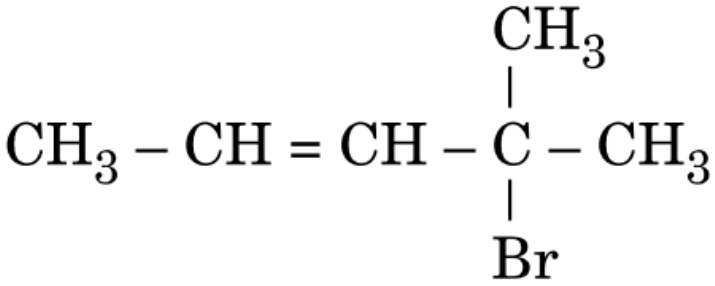
Quick Tip to Solve: For these three reasons, connect the property respectively to intermediate stability, crystal symmetry and removal of gaseous by-products.

OR

20(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]



Solution:

Concept:

- Finkelstein halogen exchange uses sodium iodide in dry acetone; precipitation of sodium chloride favours conversion of an alkyl chloride to an alkyl iodide.
- Under comparable elimination conditions, tertiary alkyl halides eliminate more readily than secondary and primary halides. In naming an alkene, give the double bond the lowest possible locant.

Step 1: Prepare 1-iodobutane (a) Treat 1-chlorobutane with sodium iodide in dry acetone. The iodide ion replaces chloride in the primary haloalkane by nucleophilic substitution:

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

Sodium chloride is insoluble in acetone and precipitates, driving the halogen-exchange reaction towards 1-iodobutane. This preparation is called the Finkelstein reaction.

Step 2: Compare elimination reactivity (b) The carbon bearing bromine in 2-bromo-2-methylbutane is tertiary, whereas it is secondary in 2-bromopentane and primary in 1-bromopentane. The usual elimination-reactivity order is tertiary $>$ secondary $>$ primary. The tertiary compound favours elimination because loss of a beta hydrogen and bromide can form a more substituted, more stable alkene; alkyl groups stabilise such alkenes through hyperconjugation and their electron-releasing effect. Therefore 2-bromo-2-methylbutane is the most reactive of the three towards elimination.

Step 3: Name the displayed structure (c) The longest chain containing the double bond has five carbons: $CH_3 - CH = CH - C(Br)(CH_3) - CH_3$. Numbering from the left places the double bond between carbons 2 and 3; numbering from the right would give it locant 3. Thus the parent is pent-2-ene. Both the bromo substituent and the additional methyl group are on carbon 4. List substituent names alphabetically, with bromo before methyl. No stereochemical descriptor is required by the displayed condensed structure.

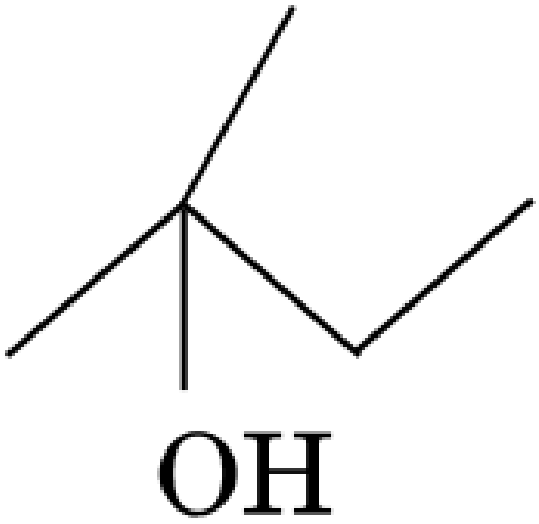
Step 4: Conclusion (a) Use NaI in dry acetone as shown above. (b) 2-Bromo-2-methylbutane is most reactive. (c) The IUPAC name is **4-bromo-4-methylpent-2-ene**.

Quick Tip to Solve: For the structure, choose numbering by the double bond first: locant 2 takes priority over smaller substituent locants.

21. (a) How will you synthesise the following alcohol from appropriate alkene:
(b) Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow[443\,K]{H^+} CH_2{=}CH_2 + H_2O$$

[3 marks]



Solution:

Concept:

- Acid-catalysed hydration adds water across an alkene double bond according to Markovnikov's rule: hydrogen adds to the carbon already bearing more hydrogen atoms.
- Acid-catalysed dehydration of an alcohol involves protonation of oxygen, removal of water and loss of a beta hydrogen; the acid catalyst is regenerated.

Step 1: (a) Choose and hydrate the appropriate alkene The given skeletal structure is 2-methylbutan-2-ol, $(CH_3)_2C(OH)CH_2CH_3$. Use 2-methylbut-1-ene and water in the presence of dilute sulphuric acid:

$$CH_2{=}C(CH_3)CH_2CH_3 + H_2O \xrightarrow{H^+} (CH_3)_2C(OH)CH_2CH_3.$$

Protonation at the terminal carbon produces the more stable tertiary carbocation at carbon 2. Water attacks this carbon and subsequent loss of a proton gives the required tertiary alcohol. Thus the hydroxyl group occupies carbon 2.

Step 2: (b) Protonate ethanol At $443\,K$, ethanol undergoes dehydration in the presence of acid. The oxygen lone pair accepts a proton:

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2^+.$$

Protonation converts the poor leaving group $-OH$ into water, a good leaving group.

Step 3: (b) Eliminate water and regenerate the catalyst In the conventional board-level mechanism,

Quick Tip to Solve: Identify the carbon bearing OH first; choose an alkene whose Markovnikov hydration places OH on that same carbon.

protonated ethanol loses water in the slow step:

$$CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2^+ + H_2O.$$

Loss of a proton from the adjacent carbon gives the double bond:

$$CH_3CH_2^+ \longrightarrow CH_2{=}CH_2 + H^+.$$

The net reaction therefore removes one water molecule from ethanol. The regenerated proton shows that acid is a catalyst, and the high temperature favours the alkene product.

Step 4: Conclusion (a) Acid-catalysed hydration of 2-methylbut-1-ene gives 2-methylbutan-2-ol. (b) Ethanol gives ethene through protonation, loss of water and loss of a beta proton, regenerating H^+.

Quick Tip to Solve: Identify the carbon bearing OH first; choose an alkene whose Markovnikov hydration places OH on that same carbon.

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, but not by secondary or tertiary amines.
- Aniline readily undergoes bromination because its amino group activates the aromatic ring. A Lewis acid such as $AlCl_3$ binds the amino nitrogen lone pair.

Step 1: (a)(i) Distinguish methylamine and dimethylamine Heat each compound with chloroform and alcoholic potassium hydroxide. Methylamine, a primary amine, produces foul-smelling methyl isocyanide:

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

Dimethylamine, $(CH_3)_2NH$, is a secondary amine and does not give this carbylamine reaction. Thus a positive isocyanide test identifies methylamine; the negative sample is dimethylamine. This test depends on the primary amino group, not merely on the compound being basic.

Step 2: (a)(ii) Distinguish aniline and ethanamine Add bromine water at room temperature. Aniline decolourises it and gives a white precipitate of 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr.$$

The amino group strongly activates the benzene ring and directs substitution to both ortho positions and the para position. Ethanamine has no aromatic ring and does not form this white tribromoaniline precipitate. The precipitate is the decisive observation for distinguishing the samples.

Step 3: (b) Explain the failure of Friedel–Crafts reaction The nitrogen lone pair of aniline reacts with

Quick Tip to Solve: Use carbylamine to identify a primary amine and the white bromine-water precipitate to identify aniline.

the Lewis acid catalyst $AlCl_3$, forming a salt or coordination complex. The resulting positive character on nitrogen withdraws electron density and strongly deactivates the ring towards electrophilic substitution. Consequently aniline does not undergo the usual Friedel–Crafts alkylation or acylation in the presence of $AlCl_3$.

Step 4: Conclusion (a)(i) Methylamine gives the carbylamine test; dimethylamine does not. (a)(ii) Aniline gives a white precipitate with bromine water; ethanamine does not. (b) Aniline binds $AlCl_3$, forming a ring-deactivating salt/complex.

Quick Tip to Solve: Use carbylamine to identify a primary amine and the white bromine-water precipitate to identify aniline.

---

23. (a) Give any one property of glucose that cannot be explained by the open chain structure.
(b) Compare amylase with amylopectin in terms of constituting structure.
(c) Why do amino acids show amphoteric behaviour? [3 marks]

Solution:

Concept:

- The open-chain structure of glucose contains an aldehyde group, but glucose exists predominantly as cyclic hemiacetals.
- Amylose and amylopectin are both polymers of α-D-glucose, differing in the arrangement of their glycosidic linkages.
- Amino acids contain an acidic carboxyl group and a basic amino group; therefore they react with both bases and acids.

Step 1: (a) State an observation unexplained by open-chain glucose Despite having an aldehyde group in its proposed open-chain structure, glucose does not give Schiff's test. An ordinary free aldehyde would restore the pink/magenta colour of Schiff's reagent, so its absence cannot be explained by a structure that presents glucose simply as an open-chain aldehyde. Formation of a cyclic hemiacetal involves the aldehyde group and accounts for the lack of the expected free-aldehyde behaviour. Only one such property is required here.

Step 2: (b) Compare the constituting structures The Hindi text and starch context identify the intended comparison as amylose versus amylopectin. The English spelling amylase literally denotes a protein enzyme made of amino-acid residues, whereas amylopectin is a glucose polysaccharide. For the intended starch comparison, amylose is an unbranched polymer of α-D-glucose in which the units are joined by $\alpha(1 \rightarrow 4)$ glycosidic linkages. Its chain adopts a helical arrangement. Amylopectin is a branched polymer of the same glucose units: $\alpha(1 \rightarrow 4)$ linkages form the chains, whereas $\alpha(1 \rightarrow 6)$ linkages occur at the branch points. Thus the structural distinction is branching and the additional 1-to-6 bonds, not a difference in the glucose monomer.

Step 3: (c) Explain amphoteric behaviour The $-COOH$ group can donate a proton and the $-NH_2$ group can accept one. In aqueous solution amino acids commonly exist as zwitterions,

Quick Tip to Solve: Remember: amylose is unbranched; amylopectin adds 1-to-6 branch bonds to the same 1-to-4 glucose chains.

$H_3N^+ - CHR - COO^-$. They accept a proton in acid and donate a proton in base:

$$H_3N^+ - CHR - COO^- + H^+ \longrightarrow H_3N^+ - CHR - COOH,$$
$$H_3N^+ - CHR - COO^- + OH^- \longrightarrow H_2N - CHR - COO^- + H_2O.$$

Their ability to behave both as acids and as bases is called amphoteric behaviour.

Step 4: Conclusion (a) Glucose does not give Schiff's test. (b) Amylose has unbranched $\alpha(1 \to 4)$ chains; amylopectin has these chains with $\alpha(1 \to 6)$ branches. (c) Amino acids are amphoteric because they contain both acidic and basic groups.

Quick Tip to Solve: Remember: amylose is unbranched; amylopectin adds 1-to-6 branch bonds to the same 1-to-4 glucose chains.

24. Define the following with suitable example of each:

(a) Antiseptics

(b) Non-narcotic analgesics

(c) Cationic detergents [3 marks]

Solution:

Concept:

- Drugs used against microorganisms are classified by where they can safely be applied: antiseptics are suitable for living tissues at their prescribed concentration.
- Analgesics relieve pain; non-narcotic analgesics do so without the narcotic effects associated with opioid analgesics.
- A detergent has a hydrophobic hydrocarbon chain and a hydrophilic head. Its classification as cationic depends on the positive charge of its active head group.

Step 1: (a) Define antiseptics and give an example Antiseptics are chemical substances that kill microorganisms or prevent their growth and can be applied to living tissues such as wounds, cuts and diseased skin. They are used at a concentration that does not injure the tissue. A suitable example is tincture of iodine, a solution containing about 2–3 percent iodine in an alcohol–water mixture, used on wounds. This living-tissue use distinguishes an antiseptic from a disinfectant used on inanimate objects.

Step 2: (b) Define non-narcotic analgesics and give an example Non-narcotic analgesics are drugs that relieve pain without producing narcotic effects such as stupor or addiction. They are useful for mild to moderate pain, including headache and muscular pain. Aspirin is a suitable example: it relieves pain and also reduces fever. Its analgesic action involves inhibition of the synthesis of prostaglandins, substances associated with pain and inflammation.

Step 3: (c) Define cationic detergents and give an example Cationic detergents are generally quaternary ammonium salts of amines with acetate, chloride or bromide counterions. Their surface-active species carries a positive charge, and a long hydrocarbon chain supplies the hydrophobic part. A suitable example is cetyltrimethylammonium bromide, $[CH_3(CH_2)_{15}N(CH_3)_3]^+Br^-$. The positively

Quick Tip to Solve: Pair each definition with its identifying feature: living tissue, pain relief without narcotic effects, and a positively charged detergent head.

charged ammonium head is the hydrophilic group; bromide is its counterion.

Step 4: Conclusion Suitable examples are tincture of iodine for antiseptics, aspirin for non-narcotic analgesics and cetyltrimethylammonium bromide for cationic detergents.

Quick Tip to Solve: Pair each definition with its identifying feature: living tissue, pain relief without narcotic effects, and a positively charged detergent head.

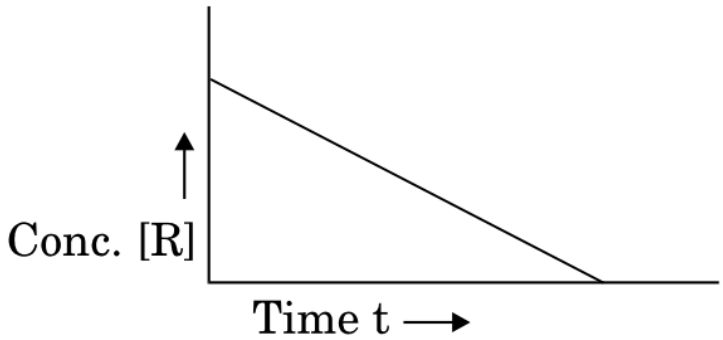
Section D (15 marks)

25(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: $-d[R]/dt = k$, where $[R]$ denotes reactant concentration and k is the rate constant.
- The integrated zero-order law is $[R] = [R]_0 - kt$. Thus a plot of concentration against time is linear, with intercept $[R]_0$ and slope $-k$.
- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the pre-exponential factor, E_a is activation energy, R is the gas constant and T is absolute temperature.

Step 1: (a)(i) Identify the order from the graph The printed graph shows that $[R]$ decreases linearly with time: equal time intervals correspond to equal decreases in concentration. Compare this with the integrated rate law

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

This is the straight-line form $y = c + mx$, with $y = [R]$ and $x = t$. Therefore, the reaction is of zero order. A first-order reaction instead gives a straight line for $\ln[R]$ against time, while a second-order reaction gives a straight line for $1/[R]$ against time. Here the ordinate is concentration itself.

Quick Tip to Solve: Check the vertical-axis label before identifying order, and use the lower-temperature reciprocal minus the higher-temperature reciprocal in Arrhenius calculations.

Step 2: (a)(ii) Interpret the slope For the decreasing straight line,

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

Thus the slope indicates the negative of the zero-order rate constant; its magnitude equals k, which also equals the constant reaction rate while reactant remains. The negative sign records consumption of R, not a negative rate constant. If concentration is in mol L^{-1} and time in seconds, the units of k are $\text{mol L}^{-1}\,\text{s}^{-1}$. The concentration reaches zero at $t = [R]_0/k$; the linear law is used only until exhaustion of the reactant.

Step 3: (b) Apply the two-temperature Arrhenius equation At the same reactant concentration, the fourfold increase in reaction rate gives $k_2/k_1 = 4$. In particular, for a zero-order reaction rate equals k directly. Take $T_1 = 293\,\text{K}$, $T_2 = 313\,\text{K}$, and treat E_a and the pre-exponential factor as constant over this interval. Dividing the Arrhenius expressions and taking natural logarithms gives

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

The reciprocal-temperature difference is positive because $T_2 > T_1$, consistent with an increase in rate for positive activation energy.

Step 4: (b) Substitute and calculate the activation energy Rearranging before substituting prevents sign errors:

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

The gas constant is in joules, so the first energy result is in joules per mole; dividing by 1000 gives kilojoules per mole. Substituting this result back makes the logarithm of the rate-constant ratio approximately 1.3863, corresponding to a ratio of four.

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

Quick Tip to Solve: Check the vertical-axis label before identifying order, and use the lower-temperature reciprocal minus the higher-temperature reciprocal in Arrhenius calculations.

OR

25(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:

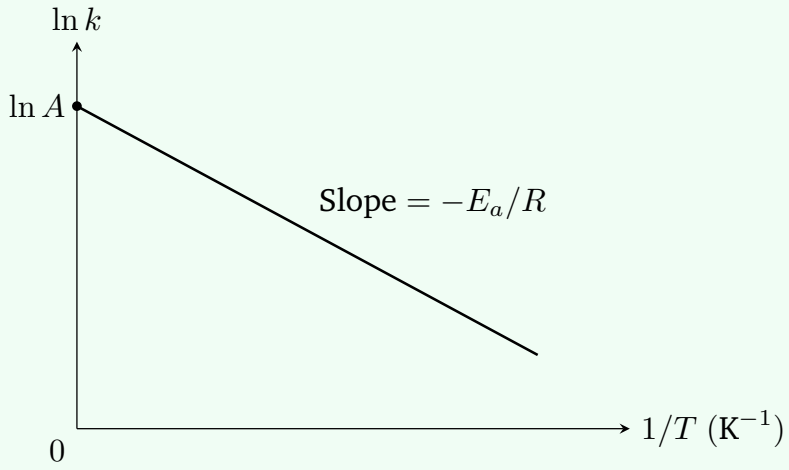
- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the pre-exponential factor, E_a the activation energy, R the gas constant and T the absolute temperature. For constant A and E_a, its logarithmic form is linear in $1/T$.
- For a first order reaction, $k = \dfrac{2.303}{t}\log_{10}\dfrac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are initial and remaining reactant concentrations. Its half-life is $t_{1/2} = 0.693/k$, independent of initial concentration.

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

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

Compare this with $y = c + mx$, choosing $y = \ln k$ and $x = 1/T$. The vertical intercept represents $\ln A$, the natural logarithm of the pre-exponential factor. The slope is $m = -E_a/R$, so $E_a = -mR$. Thus, for positive activation energy, the straight line slopes downward as $1/T$ increases. The intercept is obtained by extrapolating the line to $1/T = 0$; it is not a measured point at a finite temperature.

Step 2: (a) Draw and label the Arrhenius plot Plot $\ln k$ on the vertical axis and reciprocal absolute temperature, $1/T$, on the horizontal axis. The line has a negative slope. The marked vertical intercept and slope show directly how the two Arrhenius parameters can be obtained from a graph. No numerical scale is needed because the question supplies no rate constants or temperatures for this plot.



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

Step 3: (b) Calculate the first order rate constant A decomposition of 20% means that 80% of the reactant remains after 30 min. Choose an initial amount of 100 units; the remaining amount is then

Quick Tip to Solve: For percentage decomposition, first subtract it from 100 to obtain the percentage remaining; then use the initial-to-remaining ratio in the logarithm.

80 units, and the ratio is independent of the chosen initial amount.

$$\begin{aligned} k &= \frac{2.303}{30}\log_{10}\frac{100}{80} \\ &= \frac{2.303}{30}\log_{10}(1.25) \\ &\simeq \frac{2.303 \times 0.0969}{30} \\ &\simeq 7.44 \times 10^{-3}\,\text{min}^{-1}. \end{aligned}$$

The concentration ratio uses reactant remaining, rather than the amount decomposed. Taking $100/20$ would describe 80% decomposition and would give a different rate constant.

Step 4: (b) Evaluate the half-life At half-life the remaining fraction is $1/2$. Therefore the first order integrated equation gives

$$\begin{aligned} t_{1/2} &= \frac{2.303\log_{10}2}{k} \\ &= \frac{2.303 \times 0.3010}{7.44 \times 10^{-3}} \\ &\simeq 93.2\,\text{min}. \end{aligned}$$

Equivalently, the rate constant cancels in the ratio $t_{1/2} = 30\log_{10}2/\log_{10}(1.25)$. This also checks the numerical result. The half-life exceeds 30 minutes, as expected because the reactant has lost only one fifth of its initial amount in that time.

Step 5: Conclusion (a) The $\ln k$ versus $1/T$ plot is a straight line with intercept $\ln A$ and slope $-E_a/R$; hence $E_a = -R \times$ slope. (b) The half-life is $\boxed{t_{1/2} \simeq 93.2\,\text{min}}$.

Quick Tip to Solve: For percentage decomposition, first subtract it from 100 to obtain the percentage remaining; then use the initial-to-remaining ratio in the logarithm.

26(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:

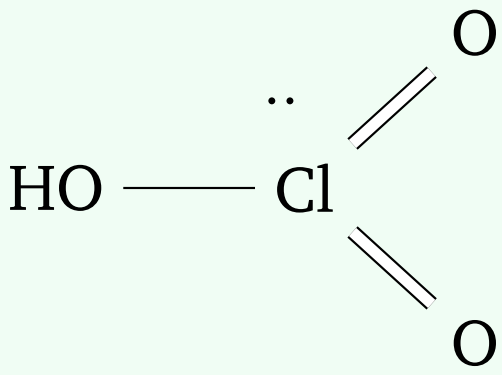
- In oxoacids, acidic hydrogen is attached to oxygen. Chloric acid contains one hydroxyl group, whereas peroxodisulphuric acid contains a peroxide linkage, $-O-O-$.
- Paramagnetism arises from unpaired electrons. The oxidising strength of a halogen in water

Quick Tip to Solve: Count all oxygen atoms in each oxoacid drawing: chloric acid has three, and peroxodisulphuric acid has eight including the two in the peroxide bridge.

depends on the total energy change for converting the molecule into hydrated halide ions.

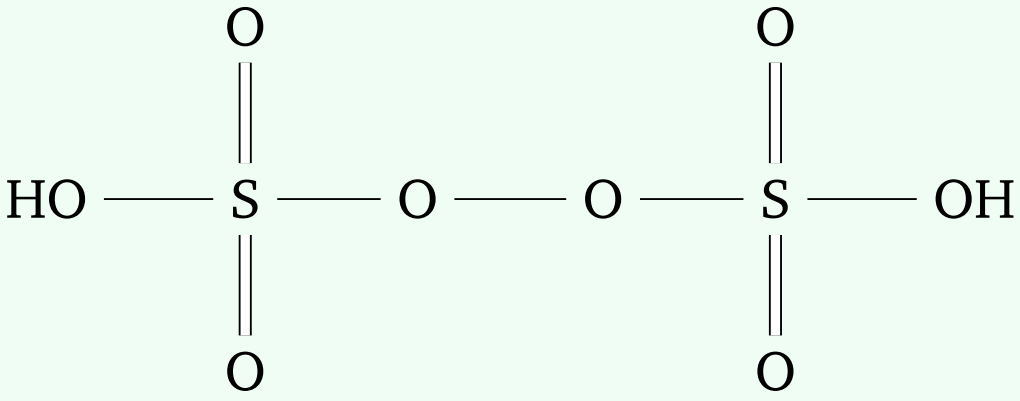
- Solid phosphorus pentachloride contains discrete cations and anions; their opposite charges are stabilised by the crystal lattice.

Step 1: (a)(i) Structure of chloric acid Chloric acid, $HClO_3$, has chlorine as the central atom. It is bonded to one hydroxyl oxygen by a single bond and to two other oxygen atoms by double bonds. Its structural formula is $HO-Cl(=O)_2$. Chlorine also has one lone pair, so the arrangement about chlorine is pyramidal. The hydrogen is on oxygen, rather than directly bonded to chlorine.



Chloric acid: chlorine has one lone pair.

Step 2: (a)(ii) Structure of peroxodisulphuric acid In $H_2S_2O_8$, the two sulphur centres are joined through an $S-O-O-S$ chain. Each sulphur is also bonded to two oxygen atoms by double bonds and to one hydroxyl group by a single bond. Thus the structure is $HO-S(=O)_2-O-O-S(=O)_2-OH$. The central oxygen–oxygen single bond is the characteristic peroxide linkage. Each sulphur has an approximately tetrahedral arrangement of its four attached oxygen atoms.



Peroxodisulphuric acid with its central peroxide bond.

Step 3: (b)(i) Paramagnetism of sulphur above 1000 K At high temperature, sulphur vapour contains S_2 molecules. Like O_2, each S_2 molecule has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons cause its attraction towards a magnetic field and hence its paramagnetic behaviour.

Quick Tip to Solve: Count all oxygen atoms in each oxoacid drawing: chloric acid has three, and peroxodisulphuric acid has eight including the two in the peroxide bridge.

Step 4: (b)(ii) Greater oxidising strength of fluorine Oxidation by a halogen involves its reduction to hydrated halide ions:

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

The overall process includes breaking the $X - X$ bond, electron gain by the gaseous atoms, and hydration of the resulting ions. Although fluorine's electron gain enthalpy is less negative than chlorine's, the $F - F$ bond has a low bond dissociation enthalpy and the small F^- ion has a very large negative hydration enthalpy. Together these contributions make reduction of fluorine more favourable. Consequently, fluorine has greater oxidising power than chlorine; electron gain enthalpy alone cannot decide their order.

Step 5: (b)(iii) Ionic nature of solid phosphorus pentachloride In the solid state, PCl_5 forms tetrahedral $[PCl_4]^+$ cations and octahedral $[PCl_6]^-$ anions:

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

The ions are held together by electrostatic attraction in the crystal lattice. The resulting lattice stabilisation favours this ionic arrangement in the solid, giving solid PCl_5 the formulation $[PCl_4]^+[PCl_6]^-$.

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 has unpaired electrons; fluorine's low bond dissociation enthalpy and strongly favourable hydration make it the stronger oxidant; solid PCl_5 consists of $[PCl_4]^+$ and $[PCl_6]^-$ ions.

Quick Tip to Solve: Count all oxygen atoms in each oxoacid drawing: chloric acid has three, and peroxodisulphuric acid has eight including the two in the peroxide bridge.

OR

26(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 and converts sulphide sulphur to sulphate sulphur.
- Xenon hexafluoride accepts a fluoride ion to form the complex anion $[XeF_7]^-$.
- Hydride properties depend on intermolecular forces and on the strength of the element–hydrogen bond. Hydrogen bonding raises the boiling point of ammonia.

Step 1: (a)(i) Oxidation of lead sulphide Sulphur in PbS has oxidation state -2, whereas in sulphate it is $+6$. Lead remains in the $+2$ state. Ozone oxidises black lead sulphide to white lead sulphate. The

Quick Tip to Solve: Place ammonia separately using hydrogen bonding; for acidic and reducing strength, track the weakening element–hydrogen bond down the group.

balanced reaction is

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

Both sides contain one lead atom, one sulphur atom and twelve oxygen atoms. The oxygen released as O_2 accompanies the oxidation of sulphide.

Step 2: (a)(ii) Formation of a xenon fluoride complex Sodium fluoride supplies F^-, which is accepted by XeF_6. Thus xenon hexafluoride acts as a Lewis acid and fluoride as a Lewis base:

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

The product is sodium heptafluoroxenate(VI), also written $NaXeF_7$. Xenon's oxidation state remains $+6$; this is fluoride-ion addition, rather than an oxidation–reduction reaction.

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

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

Among the heavier hydrides, increasing molecular size and polarisability strengthen London dispersion forces and raise the boiling point. Ammonia is an exception to the simple mass trend because its molecules form intermolecular hydrogen bonds. Consequently, NH_3 boils above PH_3 and AsH_3, but below the still heavier SbH_3 and BiH_3.

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

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

Down the group, halogen size increases and the $H - X$ bond becomes longer and weaker. Release of H^+ therefore becomes easier. The particularly strong $H - F$ bond makes HF the weakest acid in this series, despite fluorine's high electronegativity.

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

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

The element–hydrogen bond weakens down the group as the central atom becomes larger. The hydrides therefore become less thermally stable and more readily undergo oxidation. This makes their ability to reduce another substance increase from water to hydrogen telluride.

Step 6: Conclusion The products are $PbSO_4 + 4O_2$ from $PbS + 4O_3$, and $Na[XeF_7]$ from $XeF_6 + NaF$. The increasing orders are $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$, $HF < HCl < HBr < HI$, and $H_2O < H_2S < H_2Se < H_2Te$.

Quick Tip to Solve: Place ammonia separately using hydrogen bonding; for acidic and reducing strength, track the weakening element–hydrogen bond down the group.

27(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 follows the directing effects of substituents: methyl directs ortho/para, whereas nitro directs meta.
- An aromatic amino group can be removed by diazotisation followed by reduction with hypophosphorous acid. Hot alkaline permanganate oxidises a benzylic methyl group to a carboxyl group.
- Hofmann bromamide degradation converts a primary amide to a primary amine with one fewer carbon atom.
- Reductive ozonolysis converts each carbon of a carbon–carbon double bond to a carbonyl group. Ethanal gives both Fehling and iodoform tests; acetone gives only the latter.

Step 1: (a)(i) Introduce bromine at the required position Number the methyl-bearing carbon of p-nitrotoluene as carbon 1. The nitro group is at carbon 4. Brominate using $Br_2/FeBr_3$:

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

Positions 2 and 6 are equivalent: each is ortho to methyl and meta to nitro. Both substituents therefore favour the same position. Introducing bromine before oxidising methyl preserves this favourable directing pattern.

Step 2: Remove the nitro-derived substituent and oxidise methyl Reduce the nitro group with Sn/HCl, followed by alkaline work-up, to obtain 2-bromo-4-aminotoluene. Diazotise its amino group with $NaNO_2/HCl$ at 273–278 K, then treat the diazonium salt with H_3PO_2 to replace the diazonium group by hydrogen:

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

Finally, heat with alkaline $KMnO_4$ and acidify. The methyl side chain becomes $COOH$, while bromine remains at the adjacent ring carbon, yielding 2-bromobenzoic acid.

Step 3: (a)(ii) Shorten the carbon chain of propanoic acid Convert propanoic acid to propanamide by reaction with ammonia followed by heating the ammonium salt. Then use Hofmann bromamide degradation:

$$\begin{aligned}CH_3CH_2COOH &\xrightarrow[\Delta]{NH_3} CH_3CH_2CONH_2\\ CH_3CH_2CONH_2 &\xrightarrow{Br_2/NaOH} CH_3CH_2NH_2.\end{aligned}$$

Quick Tip to Solve: When both Fehling and iodoform tests are positive, identify ethanal first; count the remaining carbons before reconstructing the alkene.

The carbonyl carbon is lost in the degradation, leaving ethylamine with two carbon atoms. Treat ethylamine with nitrous acid generated from $NaNO_2/HCl$ to form ethanol, with nitrogen evolution:

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O.$$

Oxidise ethanol with acidified $K_2Cr_2O_7$ under reflux to obtain CH_3COOH, acetic acid.

Step 4: (b) Identify the two ozonolysis products B gives a positive Fehling test, so it is an aliphatic aldehyde. It also gives the iodine/NaOH reaction, which identifies ethanal as the aldehyde that gives the iodoform test. Hence $B = CH_3CHO$. C gives no Fehling test but gives iodoform, so it is a methyl ketone. B uses two of A's five carbon atoms, leaving three for C; therefore $C = CH_3COCH_3$, propanone (acetone). In the iodoform reaction, ethanal and acetone produce yellow CHI_3; acetone's ketone group accounts for its negative Fehling test.

Step 5: Reconstruct and verify alkene A Join the carbonyl carbons of ethanal and acetone with a double bond, replacing both carbonyl oxygens. This gives

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

namely 2-methylbut-2-ene. Its reductive ozonolysis is

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

The alkene contains five carbons and ten hydrogens, agreeing with C_5H_{10}. Its double-bond carbon bearing hydrogen forms the aldehyde, while the carbon bearing two methyl groups forms acetone.

Step 6: Conclusion Use bromination, nitro reduction, diazotisation/deamination, and side-chain oxidation for the first conversion. Use amide formation, Hofmann degradation, nitrous-acid treatment, and oxidation for the second. The identified compounds are A = 2-methylbut-2-ene, B = ethanal and C = propanone.

Quick Tip to Solve: When both Fehling and iodoform tests are positive, identify ethanal first; count the remaining carbons before reconstructing the alkene.

OR

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

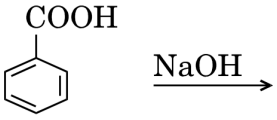
(i) Benzoic acid to aniline

(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) 

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine with one fewer carbon atom: $RCONH_2 \rightarrow RNH_2$.
- A Grignard reagent reacts with methanal to give a primary alcohol containing one additional carbon atom after acidic hydrolysis. The reaction must be performed in dry ether before hydrolysis.
- Wolff–Kishner reduction replaces the carbonyl oxygen of an aldehyde or ketone with two hydrogen atoms. An aldehyde without an alpha-hydrogen undergoes Cannizzaro disproportionation in concentrated alkali.
- A carboxylic acid reacts with sodium hydroxide by acid–base neutralisation to form its sodium carboxylate and water.

Step 1: (a)(i) Convert benzoic acid into benzamide, then aniline First treat benzoic acid with ammonia to form ammonium benzoate; heating this salt removes water and gives benzamide. Then perform Hofmann degradation with bromine and aqueous sodium hydroxide:

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COONH_4,$$
$$C_6H_5COONH_4 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O,$$
$$C_6H_5CONH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The carbonyl carbon is removed in the final reaction, while the phenyl group remains attached to nitrogen.

Step 2: (a)(ii) Increase the carbon chain of bromomethane by one carbon Prepare methylmagnesium bromide from bromomethane and magnesium in dry ether. React it with methanal and then hydrolyse

Quick Tip to Solve: Count carbon atoms in conversions: Hofmann degradation removes the amide carbon, while methanal adds one carbon to a Grignard reagent. For an aldehyde in concentrated alkali, inspect its alpha-carbon for hydrogen before choosing aldol or Cannizzaro.

the magnesium alkoxide with dilute acid:

$$\begin{aligned} CH_3Br + Mg &\xrightarrow{\text{dry ether}} CH_3MgBr, \\ CH_3MgBr + HCHO &\longrightarrow CH_3CH_2OMgBr, \\ CH_3CH_2OMgBr + H_2O &\xrightarrow{H^+} CH_3CH_2OH + Mg(OH)Br. \end{aligned}$$

Methanal supplies the extra carbon required to obtain the two-carbon alcohol from a one-carbon halide.

Step 3: (b)(i) Reduce propanal by the Wolff–Kishner reaction The printed reagents are hydrazine followed by potassium hydroxide in glycol on heating. Propanal first forms its hydrazone; the strongly basic heating conditions then remove nitrogen and replace the carbonyl group by a methylene group:

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

The carbon chain is retained. The terminal aldehyde carbon becomes a methyl carbon rather than an alcohol carbon.

Step 4: (b)(ii) Apply Cannizzaro disproportionation The aldehyde is $(CH_3)_3CCHO$, or 2,2-dimethylpropanal. Its alpha-carbon is bonded to three methyl groups and the aldehyde group, so it carries no hydrogen. Consequently it cannot undergo the usual aldol reaction. In concentrated sodium hydroxide, one molecule is reduced to the primary alcohol and another is oxidised to the sodium carboxylate:

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

The products are 2,2-dimethylpropan-1-ol and sodium 2,2-dimethylpropanoate. The salt is written because the medium is alkaline and no acidic work-up is specified.

Step 5: (b)(iii) Neutralise benzoic acid The printed reagent is sodium hydroxide. The acidic proton of the carboxyl group is replaced by sodium, while the benzene ring and carboxyl carbon remain intact:

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

This is ordinary neutralisation. Decarboxylation would require soda lime and heating, which are not specified here.

Step 6: Conclusion (a) Use benzamide followed by $Br_2/NaOH$ to obtain aniline; use Mg/dry ether, methanal and acidic hydrolysis to obtain ethanol. (b) The major organic products are (i) $CH_3CH_2CH_3$, (ii) $(CH_3)_3CCH_2OH$ and $(CH_3)_3CCOONa$, and (iii) C_6H_5COONa.

Quick Tip to Solve: Count carbon atoms in conversions: Hofmann degradation removes the amide carbon, while methanal adds one carbon to a Grignard reagent. For an aldehyde in concentrated alkali, inspect its alpha-carbon for hydrogen before choosing aldol or Cannizzaro.