

CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/1/1 - Compartment



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) All questions are compulsory.
- (ii) Questions number 1 to 8 are very short-answer questions and carry 1 mark each.
- (iii) Questions number 9 to 18 are short-answer questions and carry 2 marks each.
- (iv) Questions number 19 to 27 are also short-answer questions and carry 3 marks each.
- (v) Questions number 28 to 30 are long-answer questions and carry 5 marks each.
- (vi) Use Log Tables, if necessary. Use of calculators is not allowed.

1. How many atoms per unit cell (z) are present in bcc unit cell?

[1 mark]

Solution:

Concept:

- In a body-centred cubic (bcc) unit cell, atoms occupy all eight corners and one body centre.
- An atom at a corner is shared by eight neighbouring unit cells, whereas the body-centred atom belongs wholly to one cell.

Step 1: Count the corner contribution The eight corner atoms together contribute $8 \times \frac{1}{8} = 1$ atom to the unit cell. Counting each corner atom as a whole would overcount atoms shared with neighbouring cells.

Step 2: Include the body-centred atom The atom at the centre is not shared across a cell boundary, so its contribution is $1 \times 1 = 1$. Thus the total is $z = 1 + 1$.

Step 3: Conclusion The number of atoms per bcc unit cell is $z = 2$.

Quick Tip to Solve: For bcc, add eight corner contributions of one-eighth and one complete body-centred atom.

2. What is the difference between lyophobic sol and lyophilic sol?

[1 mark]

Solution:

Concept:

- Lyophilic and lyophobic describe the affinity of the dispersed phase for the dispersion medium.
- In an aqueous sol, this distinction is often expressed as hydrophilic (water-loving) and hydrophobic (water-repelling).

Step 1: Identify a lyophilic sol In a lyophilic sol, the dispersed particles have a strong affinity for the dispersion medium and are well solvated. Such sols are generally stable and can usually be reconstituted by adding the medium after separation.

Step 2: Contrast a lyophobic sol In a lyophobic sol, the dispersed particles have little affinity for the dispersion medium and are poorly solvated. Such sols are comparatively less stable and generally require special methods of preparation.

Step 3: Conclusion A lyophilic sol has strong dispersed-phase-medium affinity, while a lyophobic sol has little or no such affinity.

Quick Tip to Solve: Compare affinity for the dispersion medium first; stability and reversibility follow from that distinction.

3. Draw the structure of XeF₂.

[1 mark]

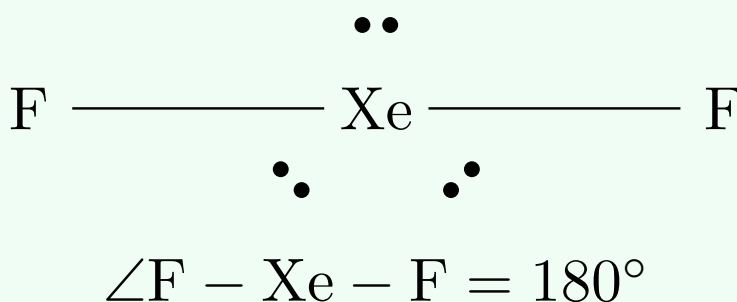
Solution:

Concept:

- According to VSEPR theory, electron pairs around xenon arrange themselves to minimise mutual repulsion.
- In XeF₂, xenon has two bond pairs and three lone pairs: the electron-pair arrangement is trigonal bipyramidal.

Step 1: Place the lone pairs The three lone pairs occupy the three equatorial positions, where they experience fewer 90° interactions. The two Xe–F bonds therefore occupy the two axial positions.

Step 2: Obtain the molecular shape The two fluorine atoms lie on opposite sides of xenon along the same straight line. The molecular shape, which describes the positions of atoms, is linear and the F–Xe–F bond angle is 180°.



Linear structure of xenon difluoride; the three lone pairs on Xe are shown schematically.

Step 3: Conclusion XeF₂ is linear, with $\angle \text{F} - \text{Xe} - \text{F} = 180^\circ$. Xenon carries three equatorial lone pairs.

Quick Tip to Solve: For XeF₂, place all three lone pairs equatorially; the two axial bonds give a straight molecule.

4. What is the function of SiO₂ in the metallurgy of copper?

[1 mark]

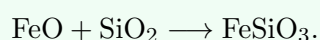
Solution:

Concept:

- A flux combines with an impurity during extraction to form a readily separable slag.
- Silica, SiO₂, is an acidic flux; it reacts with basic iron(II) oxide, FeO.

Step 1: Identify the impurity removed In copper metallurgy, iron impurity is oxidised to FeO. Silica is added so that this basic oxide can be removed from the copper-containing material.

Step 2: Write the slag-forming reaction The iron(II) oxide reacts with silica as follows:



The iron silicate formed is the slag, which separates from the copper matte.

Quick Tip to Solve: Remember the acid-base pairing: acidic SiO₂ removes basic FeO by forming FeSiO₃ slag.

Step 3: Conclusion SiO_2 acts as an acidic flux and removes FeO as iron silicate slag, FeSiO_3 .

Quick Tip to Solve: Remember the acid-base pairing: acidic SiO_2 removes basic FeO by forming FeSiO_3 slag.

5. Why do transition elements show variable oxidation states?

[1 mark]

Solution:

Concept:

- Oxidation states describe the formal electron loss or sharing associated with bond formation.
- For transition elements, the energies of the ns and $(n-1)d$ orbitals are close to one another.

Step 1: Consider the available electrons The outer ns electrons and varying numbers of $(n-1)d$ electrons can participate in bond formation because the energy difference between these subshells is small.

Step 2: Relate participation to oxidation states Different numbers of these electrons can be involved in different compounds, producing variable oxidation states. For example, iron commonly exhibits +2 and +3 states, involving different numbers of electrons beyond the outermost-shell contribution.

Step 3: Conclusion Transition elements show variable oxidation states because both ns and $(n-1)d$ electrons, which have similar energies, can participate in bonding.

Quick Tip to Solve: Link variable oxidation states to the small $ns-(n-1)d$ energy gap and participation of both subshells.

6. Draw the structure of 2-bromopentane.

[1 mark]

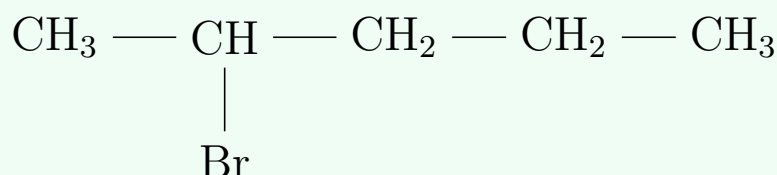
Solution:

Concept:

- The parent name pentane specifies a saturated chain containing five carbon atoms.
- The locant 2 places the bromo substituent on carbon 2, numbering from the nearer end.

Step 1: Choose the parent chain Write five carbon atoms joined by single bonds. The terminal atoms are CH_3 groups; each unsubstituted internal carbon is a CH_2 group.

Step 2: Place the bromine atom Replace one hydrogen on carbon 2 by bromine. That carbon is now $\text{CH}(\text{Br})$, with four bonds: two to carbon, one to hydrogen and one to bromine. The resulting structure is shown below.



Structure of 2-bromopentane

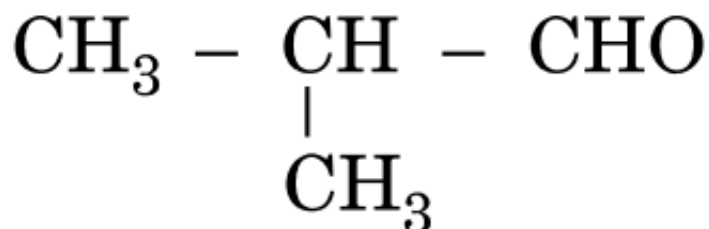
Quick Tip to Solve: Count five carbons first, then put Br on the second carbon from the nearer end.

Step 3: Conclusion The structure is $\text{CH}_3 - \text{CH}(\text{Br}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$.

Quick Tip to Solve: Count five carbons first, then put Br on the second carbon from the nearer end.

7. Write the IUPAC name of the following compound.

[1 mark]



Solution:

Concept:

- The aldehyde group $-\text{CHO}$ is the principal functional group and gives the suffix -al.
- The carbon of the aldehyde group is included in the parent chain and is always numbered 1.

Step 1: Identify and number the parent chain The longest continuous chain containing the $-\text{CHO}$ carbon has three carbon atoms: $\text{CHO} - \text{CH} - \text{CH}_3$. Therefore the parent aldehyde is propanal, not ethanal.

Step 2: Identify the branch The remaining CH_3 group is a methyl substituent attached to carbon 2. Combining its locant and name with propanal gives 2-methylpropanal. The aldehyde position needs no separate locant because it is necessarily terminal.

Step 3: Conclusion The IUPAC name is 2-methylpropanal .

Quick Tip to Solve: Include the CHO carbon in the longest chain and number it 1 before locating the methyl branch.

8. Out of CH_3-NH_2 and $(\text{CH}_3)_3\text{N}$, which one has higher boiling point?

[1 mark]

Solution:

Concept:

- Boiling point depends on the combined intermolecular attractions, including hydrogen bonding and London dispersion forces.
- The primary-amine versus tertiary-amine hydrogen-bonding trend is most useful for compounds of comparable molar mass.

Step 1: Compare the intermolecular forces Methylamine, CH_3NH_2 , has N-H bonds and can form intermolecular hydrogen bonds. Trimethylamine, $(\text{CH}_3)_3\text{N}$, has no N-H bond and cannot form such hydrogen bonds between its own molecules.

Quick Tip to Solve: Check molecular size as well as N-H bonds; these two amines do not have comparable molar masses.

Step 2: Compare these particular compounds Trimethylamine is substantially larger and more polarisable, so its stronger dispersion forces outweigh the hydrogen-bonding advantage of methylamine. Their normal boiling points are approximately 3°C and -6°C , respectively. Thus hydrogen bonding alone does not predict the order for this pair.

Step 3: Conclusion $(\text{CH}_3)_3\text{N}$, trimethylamine, has the higher boiling point.

Quick Tip to Solve: Check molecular size as well as N–H bonds; these two amines do not have comparable molar masses.

9. How is the vapour pressure of a solvent affected when a non-volatile solute is dissolved in it?

[2 marks]

Solution:

Concept:

- A non-volatile solute makes a negligible contribution to the vapour pressure of the solution.
- For an ideal solution, Raoult's law gives $p_1 = x_1 p_1^{\circ}$, where x_1 is the solvent mole fraction and p_1° is the pure-solvent vapour pressure at the same temperature.

Step 1: Explain the physical effect Dissolving the solute reduces the mole fraction, and hence the escaping tendency, of solvent molecules in the liquid. At the same temperature, equilibrium between evaporation and condensation is consequently reached at a lower solvent vapour pressure than above the pure solvent.

Step 2: Express the lowering quantitatively Since $x_1 < 1$, Raoult's law implies $p_1 < p_1^{\circ}$. For a binary ideal solution, $x_1 + x_2 = 1$, where x_2 is the solute mole fraction. Thus

$$\Delta p = p_1^{\circ} - p_1 = p_1^{\circ}(1 - x_1) = p_1^{\circ}x_2, \quad \frac{\Delta p}{p_1^{\circ}} = x_2.$$

The solute does not add appreciable vapour of its own.

Step 3: Conclusion The vapour pressure of the solvent decreases on dissolving a non-volatile solute; for an ideal binary solution its relative lowering equals the solute mole fraction.

Quick Tip to Solve: Compare vapour pressures at the same temperature and use the solvent mole fraction in Raoult's law.

10. (a) For a reaction, $A + B \rightarrow \text{Product}$, the rate law is given by, $\text{Rate} = k[A]^1[B]^2$. What is the order of the reaction?

(b) Write the unit of rate constant 'k' for the first order reaction.

[2 marks]

Solution:

Concept:

- The overall order of a reaction is the sum of the concentration exponents in its experimentally determined rate law.
- For a first-order reaction, $r = k[A]$; rate has dimensions of concentration per unit time.

Step 1: (a) Calculate the order The given rate law is

$$r = k[A]^1[B]^2.$$

The reaction is first order with respect to A and second order with respect to B. Adding these exponents gives $n = 1 + 2 = 3$. The coefficients in the written reaction equation do not determine these experimental exponents.

Step 2: (b) Obtain the unit of the first-order rate constant For the separate first-order case, $k = r/[A]$. Using concentration in mol L^{-1} and time in seconds,

$$[k] = \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}.$$

Concentration units cancel, leaving only inverse time. Part (b) refers to a first-order reaction, rather than the third-order law of part (a).

Step 3: Conclusion (a) The overall order is $\boxed{3}$. (b) The unit of a first-order rate constant is $\boxed{\text{s}^{-1}}$.

Quick Tip to Solve: Add powers in the rate law for order; derive the unit of k from rate divided by concentration powers.

11. Define the following terms:

(i) Roasting

(ii) Calcination

[2 marks]

Solution:

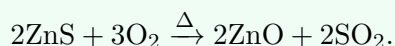
Concept:

- Both roasting and calcination are thermal treatments used to convert a concentrated ore into a form suitable for reduction, commonly its oxide.
- The key distinction is the supply of air: roasting uses excess air, whereas calcination uses absent or limited air.

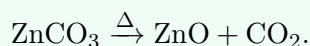
Step 1: Define roasting Roasting is the process of strongly heating an ore, usually a sulphide ore, below its melting point in the presence of excess air. The sulphide is oxidised to the metal oxide and

Quick Tip to Solve: Remember sulphide plus excess air for roasting, and carbonate losing carbon dioxide for calcination.

sulphur escapes as sulphur dioxide. For example,



Step 2: Define calcination Calcination is the process of strongly heating an ore, usually a carbonate or hydrated oxide ore, below its melting point in the absence or a limited supply of air. The ore undergoes thermal decomposition, losing carbon dioxide or water. For example,



Step 3: Conclusion Roasting is heating in excess air; calcination is heating in absent or limited air. Both commonly yield the metal oxide.

Quick Tip to Solve: Remember sulphide plus excess air for roasting, and carbonate losing carbon dioxide for calcination.

12. Draw the structure of each of the following:

(i) H_2SO_4

(ii) Solid PCl_5

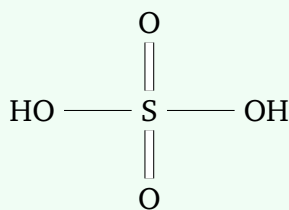
[2 marks]

Solution:

Concept:

- In H_2SO_4 , sulphur is bonded to four oxygen atoms: two oxo groups and two hydroxyl groups.
- Solid PCl_5 is ionic and consists of tetrahedral $[\text{PCl}_4]^+$ cations and octahedral $[\text{PCl}_6]^-$ anions.

Step 1: Structure of sulphuric acid The structure is $\text{HO} - \text{S}(=\text{O})_2 - \text{OH}$. Sulphur has four surrounding oxygen atoms in a roughly tetrahedral arrangement: two oxo groups and two hydroxyl groups. Both acidic hydrogen atoms are bonded to oxygen.



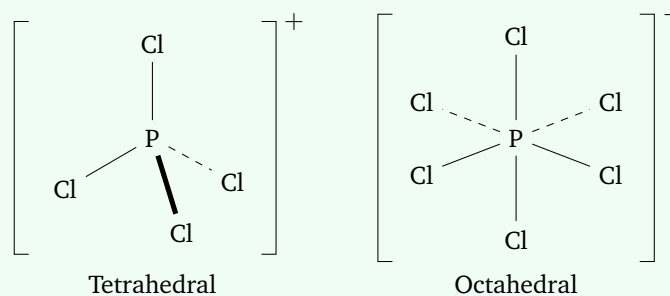
Structure of sulphuric acid

Step 2: Structure of solid phosphorus pentachloride Solid phosphorus pentachloride is an ionic lattice:



The cation has four P-Cl bonds arranged tetrahedrally; the anion has six P-Cl bonds arranged octahedrally. Each cation has charge +1 and each anion charge -1, giving an electrically neutral solid.

Quick Tip to Solve: Always specify the state of PCl_5 : its solid has four- and six-coordinate ions, unlike its gaseous molecules.



Tetrahedral cation and octahedral anion in solid phosphorus pentachloride

Step 3: Conclusion H_2SO_4 has structure $\text{HO} - \text{S}(=\text{O})_2 - \text{OH}$; solid PCl_5 contains tetrahedral $[\text{PCl}_4]^+$ and octahedral $[\text{PCl}_6]^-$ ions.

Quick Tip to Solve: Always specify the state of PCl_5 : its solid has four- and six-coordinate ions, unlike its gaseous molecules.

13(a). Assign a reason for each of the following observations:

- (i) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
- (ii) The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly. [2 marks]

Solution:

Concept:

- Metallic bonding arises from attraction between metal cores and delocalised valence electrons; both the outer ns and available $(n - 1)d$ electrons contribute in transition metals.
- Ionisation enthalpy depends on nuclear attraction, shielding and the relative stability of the initial atom or ion and the species formed.

Step 1: Explain hardness and high melting and boiling points Transition metals generally have several unpaired d electrons as well as outer s electrons available for strong metallic bonding. The resulting large cohesive energy makes the metals hard and requires considerable energy to separate their atoms during melting and boiling. Zn, Cd and Hg have filled d^{10} subshells and comparatively weak metallic bonding, accounting for their exceptional behaviour.

Step 2: Explain irregular ionisation enthalpies Across the first transition series, increasing nuclear charge is accompanied by addition of electrons to the inner $3d$ subshell. Shielding and electron-electron repulsion modify the attraction for the electron removed. In addition, half-filled d^5 and fully filled d^{10} arrangements possess extra stability. Ionisation that produces such a configuration is relatively favoured, while removal that destroys it is relatively difficult. Since the first and second ionisations start from different configurations, these competing effects cause irregular variations.

Step 3: Conclusion Strong metallic bonding explains the hardness and high melting and boiling points; changing $3d$ -electron shielding and special d^5 or d^{10} stability explain the irregular ionisation enthalpies.

Quick Tip to Solve: For ionisation trends compare the configurations before and after removal, especially half-filled and filled d subshells.

13(b). What is lanthanoid contraction? Write a consequence of lanthanoid contraction.

[2 marks]

Solution:

Concept:

- Lanthanoid contraction is a size trend across the lanthanoid series and follows from the poor shielding ability of $4f$ electrons.
- An increase in effective nuclear attraction pulls the electron cloud inward, reducing atomic and ionic radii.

Step 1: Define lanthanoid contraction and its cause The gradual decrease in atomic radii and in the ionic radii of corresponding ions, especially Ln^{3+} , with increasing atomic number from lanthanum to lutetium is called lanthanoid contraction. Across the series, electrons enter the $4f$ subshell. These electrons shield the increasing nuclear charge poorly, so the effective attraction experienced by the outer electrons increases and the radii decrease.

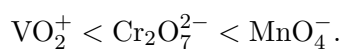
Step 2: State a consequence A consequence is the close similarity in size and properties of the second and third transition-series elements in a group, such as zirconium and hafnium. The normal increase in radius expected on moving from Zr to Hf is largely offset by the intervening lanthanoid contraction. Thus Zr and Hf have almost equal radii, show very similar chemical behaviour and are difficult to separate.

Step 3: Conclusion Lanthanoid contraction is the gradual decrease in lanthanoid atomic and corresponding ionic radii with increasing atomic number. It makes Zr and Hf nearly equal in size and chemically very similar.

Quick Tip to Solve: Link poor shielding by $4f$ electrons to increased nuclear attraction, then cite the near-equal sizes of Zr and Hf.

14. How would you account for the following?

- (i) The highest oxidation state of a transition metal is usually exhibited in its oxide.
 (ii) The oxidising power of the following three oxoions in the series follows the order:



[2 marks]

Solution:

Concept:

- Oxygen is highly electronegative and forms strong metal–oxygen bonds, stabilising high positive oxidation states.
- Oxidising strength is the tendency to gain electrons; larger standard reduction potentials imply stronger oxidising agents.

Step 1: (i) Stabilisation by oxygen The small, highly electronegative oxygen atom forms strong bonds

Quick Tip to Solve: For an oxoion series, compare reduction potentials in the same medium: the larger positive value identifies the stronger oxidant.

with transition metals, including multiple bonds through metal–oxygen orbital overlap. The large bond energy compensates for the energy needed to remove several metal electrons. Thus oxygen stabilises the metal in a high oxidation state, as in CrO_3 and Mn_2O_7 , containing Cr(VI) and Mn(VII), respectively.

Step 2: (ii) Compare reduction tendencies In acidic aqueous solution, the standard reduction potentials for $\text{VO}_2^+/\text{VO}^{2+}$, $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ and $\text{MnO}_4^-/\text{Mn}^{2+}$ are approximately +1.00, +1.33 and +1.51 V, respectively. Their increasing positive values show increasing readiness to accept electrons and undergo reduction. Hence their oxidising powers increase in the printed order.

Step 3: Conclusion Strong metal–oxygen bonding stabilises the highest oxidation states; oxidising power follows $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$.

Quick Tip to Solve: For an oxoion series, compare reduction potentials in the same medium: the larger positive value identifies the stronger oxidant.

15. Write the equations involved in the following reactions:

(i) Williamson ether synthesis

(ii) Kolbe's reaction

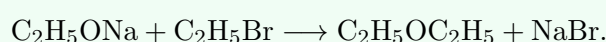
[2 marks]

Solution:

Concept:

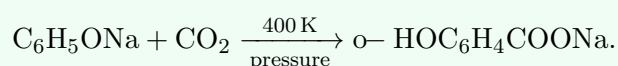
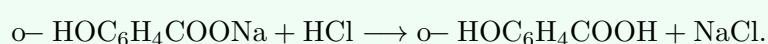
- Williamson synthesis forms an ether by nucleophilic substitution of a primary alkyl halide with an alkoxide ion.
- In the Kolbe reaction of phenol, sodium phenoxide undergoes carboxylation with carbon dioxide and then acidification.

Step 1: (i) Williamson ether synthesis An alkoxide attacks the carbon carrying the halogen; the halide ion leaves in an $\text{S}_{\text{N}}2$ reaction. For example, sodium ethoxide and ethyl bromide give diethyl ether:



A primary alkyl halide is preferred because a more hindered halide can undergo elimination.

Step 2: (ii) Kolbe reaction Sodium phenoxide is heated with carbon dioxide under pressure at about 400 K. Carboxylation occurs mainly at the ortho position; acidification gives salicylic acid:



Here the product is 2-hydroxybenzoic acid, with hydroxyl and carboxyl groups on adjacent ring carbons.

Step 3: Conclusion Williamson synthesis gives an ether; Kolbe carboxylation of sodium phenoxide followed by acidification gives salicylic acid.

Quick Tip to Solve: In the phenols chapter, Kolbe means carbon dioxide carboxylation of sodium phenoxide; always include the acidification step.

16. How are the following conversions carried out?

(i) Propene to Propan-2-ol

(ii) Ethyl chloride to Ethanal

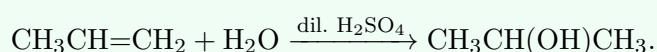
[2 marks]

Solution:

Concept:

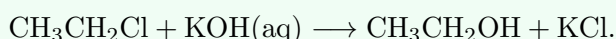
- Acid-catalysed hydration adds water to an unsymmetrical alkene according to Markovnikov orientation.
- Aqueous hydroxide replaces chloride by hydroxyl; controlled oxidation of a primary alcohol yields an aldehyde.

Step 1: (i) Propene to propan-2-ol Treat propene with water in the presence of dilute sulphuric acid. Hydrogen adds to the terminal carbon, while hydroxyl adds to the more substituted middle carbon, yielding the secondary alcohol:

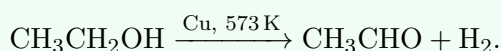


This is Markovnikov hydration; it produces propan-2-ol rather than propan-1-ol.

Step 2: (ii) Ethyl chloride to ethanal First heat ethyl chloride with aqueous potassium hydroxide to form ethanol by nucleophilic substitution:



Pass ethanol vapour over heated copper at 573 K; dehydrogenation produces ethanal:



The carbon chain remains unchanged, and removal of two hydrogen atoms creates the aldehyde group.

Step 3: Conclusion Propene gives propan-2-ol by acid-catalysed hydration; ethyl chloride gives ethanol with aqueous KOH, followed by Cu-catalysed dehydrogenation to ethanal.

Quick Tip to Solve: Use aqueous KOH for substitution to ethanol; alcoholic KOH would favour elimination and divert this conversion.

17. Answer the following questions:

(i) Why are vitamin A and vitamin C essential for us?

(ii) What is the difference between a nucleoside and a nucleotide?

[2 marks]

Solution:

Concept:

- Vitamins are essential micronutrients; a deficiency causes characteristic physiological disorders.
- A nucleoside contains a nitrogenous base and a pentose sugar; a nucleotide additionally contains

Quick Tip to Solve: Remember the extra component: adding phosphate to a nucleoside makes a nucleotide; use adenosine and AMP as the comparison.

phosphate.

Step 1: (i) Importance of vitamins A and C Vitamin A is essential for normal vision, especially in dim light, and for maintaining healthy epithelial tissues. Its deficiency causes night blindness and can damage the eyes. Vitamin C is required for collagen formation and hence healthy connective tissues, gums and wound healing. Its deficiency causes scurvy, characterised by bleeding gums and poor wound healing. Both must be supplied adequately in the diet to support these essential functions.

Step 2: (ii) Nucleoside and nucleotide A nucleoside consists of a nitrogenous base linked to a pentose sugar by an N-glycosidic bond; it contains no phosphate group. A nucleotide is a nucleoside bearing one or more phosphate groups, usually esterified to the sugar. Thus adenosine is a nucleoside, whereas adenosine monophosphate (AMP) is a nucleotide. Nucleotides are the structural units that join through phosphodiester bonds to form nucleic-acid chains.

Step 3: Conclusion Vitamin A supports vision and vitamin C supports collagen formation. A nucleoside is base plus sugar; a nucleotide is base plus sugar plus phosphate.

Quick Tip to Solve: Remember the extra component: adding phosphate to a nucleoside makes a nucleotide; use adenosine and AMP as the comparison.

18. Enumerate the reactions of glucose which cannot be explained by its open chain structure.

[2 marks]

Solution:

Concept:

- The open-chain formula of glucose contains a free aldehyde group and five hydroxyl groups.
- A free aldehyde normally gives characteristic carbonyl reactions, whereas cyclic hemiacetal formation masks that group.

Step 1: List the anomalous carbonyl reactions Despite the aldehyde group in its proposed open-chain formula, glucose does not give Schiff's test and does not form an addition compound with sodium hydrogensulphite, NaHSO_3 . These are expected reactions of a freely available aldehydic carbonyl group. Their absence therefore cannot be satisfactorily explained by a structure in which every glucose molecule has a free $-\text{CHO}$ group.

Step 2: Use the pentaacetate observation Glucose pentaacetate does not react with hydroxylamine, NH_2OH , to form an oxime. If glucose retained a free aldehyde group after acetylation of its five hydroxyl groups, oxime formation would be expected. This observation indicates that the carbonyl group is not free. These results are explained by the predominantly cyclic hemiacetal structure of glucose; acetylation locks its anomeric oxygen functionality in a form without a free aldehyde.

Step 3: Conclusion The unexplained observations are absence of Schiff's test, absence of a NaHSO_3 addition product, and failure of glucose pentaacetate to form an oxime with hydroxylamine.

Quick Tip to Solve: Distinguish glucose from its pentaacetate: glucose can form an oxime, but glucose pentaacetate cannot because its aldehyde group is unavailable.

19. The density of copper is 8.95 g cm^{-3} . It has a face centred cubic structure. What is the radius of copper atom?

(Atomic mass Cu = 63.5 g mol^{-1} , $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

[3 marks]

Solution:

Concept:

- The density of a cubic unit cell is $\rho = \frac{ZM}{N_A a^3}$, where Z is the number of atoms per cell, M the molar mass and a the edge length.
- In a face-centred cubic (fcc) cell, $Z = 4$. Atoms touch along a face diagonal, giving $4r = \sqrt{2}a$, where r is the atomic radius.

Step 1: Count atoms in the fcc unit cell The eight corner atoms each contribute $1/8$ and the six face-centred atoms each contribute $1/2$ to one unit cell. Thus

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

The mass of one unit cell is therefore $4M/N_A$. Since the density is given in g cm^{-3} , using M in g mol^{-1} gives the cell volume in cm^3 .

Step 2: Calculate the edge length Using the given values without converting the density to SI units,

$$\begin{aligned} a^3 &= \frac{ZM}{\rho N_A} \\ &= \frac{4(63.5)}{8.95(6.02 \times 10^{23})} \\ &= 4.7144 \times 10^{-23} \text{ cm}^3. \end{aligned}$$

Taking the cube root gives $a = 3.6125 \times 10^{-8} \text{ cm}$.

Step 3: Convert the edge length to atomic radius A face diagonal passes through the centres of a corner atom, a face-centred atom and the opposite corner atom. Their contact distances total four radii. Hence

$$r = \frac{a}{2\sqrt{2}} = \frac{3.6125 \times 10^{-8}}{2\sqrt{2}} \text{ cm} = 1.2772 \times 10^{-8} \text{ cm}.$$

Since $1 \text{ cm} = 10^{10} \text{ pm}$, this corresponds to 127.72 pm .

Step 4: Conclusion The radius of a copper atom is $1.28 \times 10^{-8} \text{ cm} \approx 128 \text{ pm}$.

Quick Tip to Solve: For fcc, first use four atoms per cell in the density formula, then divide the edge by $2\sqrt{2}$.

20. Some ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is added to your car's cooling system along with 5 kg of water. If the freezing point of the water-glycol solution is -15.0°C , what is the boiling point of the solution?

($K_b = 0.52 \text{ K kg mol}^{-1}$ and $K_f = 1.86 \text{ K kg mol}^{-1}$ for water)

[3 marks]

Solution:

Concept:

- For a non-volatile solute, freezing-point depression and boiling-point elevation are $\Delta T_f = K_f m$ and $\Delta T_b = K_b m$, where m is the solution molality.
- Ethylene glycol is a non-electrolyte, so it does not dissociate into ions and its van't Hoff factor is $i = 1$. The same solution has the same molality in both colligative-property equations.

Step 1: Find the freezing-point depression Pure water freezes at 0.0°C . The depression is the positive difference between the pure solvent and solution freezing points:

$$\Delta T_f = T_f^\circ - T_f = 0.0 - (-15.0) = 15.0 \text{ K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius. The negative solution freezing point therefore corresponds to a positive depression.

Step 2: Determine molality and boiling-point elevation From the freezing-point data,

$$m = \frac{\Delta T_f}{K_f} = \frac{15.0}{1.86} = 8.0645 \text{ mol kg}^{-1}.$$

This molality refers to kilograms of water, not kilograms of the whole solution. The given 5 kg of water would determine the total glycol amount, but is unnecessary for finding the boiling-point elevation once molality is known. Thus

$$\Delta T_b = K_b m = 0.52(8.0645) = 4.1935 \text{ K}.$$

Step 3: Calculate the boiling point At normal atmospheric pressure the boiling point of pure water is 100°C . A non-volatile solute lowers the vapour pressure, so a higher temperature is required for boiling. Add the positive elevation:

$$T_b = T_b^\circ + \Delta T_b = 100 + 4.1935 = 104.1935^\circ\text{C}.$$

Step 4: Conclusion The boiling point of the water-ethylene glycol solution is 104.2°C at normal atmospheric pressure.

Quick Tip to Solve: Eliminate molality directly: $\Delta T_b = (K_b/K_f)\Delta T_f$; the solvent mass cancels.

21. Hydrogen peroxide, H_2O_2 (aq) decomposes to H_2O (l) and O_2 (g) in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3} \text{ min}^{-1}$.

(i) How long will it take for 15% of a sample of H_2O_2 to decompose?

(ii) How long will it take for 85% of the sample to decompose?

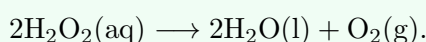
[3 marks]

Solution:

Concept:

- For a first-order reaction, $t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations.
- If the decomposed fraction is f , the remaining fraction is $1 - f$, so $t = \frac{1}{k} \ln \frac{1}{1 - f}$. With k in min^{-1} , time is obtained in minutes.

Step 1: Set up the first-order expression The decomposition is



The given first-order rate constant applies to hydrogen peroxide disappearance. Integrating $-d[\text{H}_2\text{O}_2]/dt = k[\text{H}_2\text{O}_2]$ gives

$$t = \frac{1}{1.06 \times 10^{-3}} \ln \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t}.$$

The initial concentration cancels when the concentration ratio is expressed using percentages; no sample concentration is needed.

Step 2: Part (i): 15 percent decomposed If 15% decomposes, 85% remains. Use an initial amount of 100 units:

$$\begin{aligned} t_{15\%} &= \frac{1}{1.06 \times 10^{-3}} \ln \frac{100}{85} \\ &= \frac{0.162519}{1.06 \times 10^{-3}} \\ &= 153.32 \text{ min.} \end{aligned}$$

The denominator must contain the remaining 85 units, rather than the decomposed 15 units.

Step 3: Part (ii): 85 percent decomposed Now only 15% of the initial hydrogen peroxide remains. The total time measured from the start is

$$\begin{aligned} t_{85\%} &= \frac{1}{1.06 \times 10^{-3}} \ln \frac{100}{15} \\ &= \frac{1.897120}{1.06 \times 10^{-3}} \\ &= 1789.74 \text{ min.} \end{aligned}$$

This is the total time from the start. The reaction slows as reactant concentration falls.

Step 4: Conclusion (i) For 15% decomposition: $t \approx 153 \text{ min}$. (ii) For 85% decomposition: $t \approx 1.79 \times 10^3 \text{ min}$.

Quick Tip to Solve: Always subtract the decomposed percentage from 100 before inserting the remaining concentration into the logarithm.

22. Define the following terms:

- (i) Adsorption
- (ii) Peptization
- (iii) Sol

[3 marks]

Solution:

Concept:

- Adsorption is a surface phenomenon: the concentration of a substance increases at a surface relative to the bulk.
- A colloid has a dispersed phase and a dispersion medium. Its classification depends on the physical states of these two components.

Step 1: (i) Adsorption Adsorption is the accumulation of molecular species at the surface of a solid or a liquid rather than throughout its bulk. The substance accumulated is the adsorbate and the substance providing the surface is the adsorbent. For example, activated charcoal adsorbs gases on its surface. This differs from absorption, in which a substance enters the bulk.

Step 2: (ii) Peptization Peptization is the conversion of a freshly formed precipitate into a colloidal sol by shaking it with the dispersion medium in the presence of a small amount of a suitable electrolyte, called the peptizing agent. Ions from the electrolyte adsorb on the precipitate particles, give them like charges, and help disperse them by mutual repulsion. For example, freshly precipitated ferric hydroxide forms a sol with a small amount of ferric chloride.

Step 3: (iii) Sol A sol is a colloidal system in which a solid is the dispersed phase and a liquid is the dispersion medium. Thus, solid colloidal particles remain distributed throughout a continuous liquid medium. Examples include gold sol and ferric hydroxide sol in water.

Step 4: Conclusion Adsorption means surface accumulation; peptization means conversion of a precipitate into a colloidal sol; a sol is a solid-in-liquid colloid.

Quick Tip to Solve: For a sol, state both phases explicitly: solid dispersed phase and liquid dispersion medium.

23(a). Write down the IUPAC name for each of the following complexes:

- (i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- (ii) $\text{K}_3[\text{Fe}(\text{CN})_6]$
- (iii) $[\text{NiCl}_4]^{2-}$

[3 marks]

Solution:

Concept:

- Name ligands alphabetically, then the metal with its oxidation state in Roman numerals; an anionic coordination entity takes the metal ending -ate.
- Ammine is neutral, whereas chlorido and cyanido each carry charge -1 . Counterions establish the charge on the coordination entity.

Step 1: (i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ The two chloride counterions show that the complex cation has charge $+2$. If the oxidation state of cobalt is x , then $x + 5(0) - 1 = +2$, giving $x = +3$. Five

Quick Tip to Solve: Find the complex charge from counterions before calculating the metal oxidation state.

ammonia ligands are named pentaammine and the coordinated chloride is chlorido. Ammine precedes chlorido alphabetically; the cation is named before the chloride counterion. The name is **pentaamminechloridocobalt(III) chloride**.

Step 2: (ii) $K_3[Fe(CN)_6]$ Three potassium ions balance the complex charge -3 . Therefore $x + 6(-1) = -3$, giving iron oxidation state $+3$. Six cyanido ligands give hexacyanido. Since the coordination entity is an anion, iron is named ferrate. Name the potassium cation first: **potassium hexacyanidoferrate(III)**.

Step 3: (iii) $[NiCl_4]^{2-}$ For nickel, $x + 4(-1) = -2$, hence $x = +2$. The four coordinated chloride ligands give tetrachlorido. Because this is an anionic complex, nickel takes the ending -ate, giving nickelate. Its name is **tetrachloridonickelate(II) ion**. The charge $2-$ is the overall ion charge, whereas (II) specifies the metal oxidation state.

Step 4: Conclusion (i) Pentaamminechloridocobalt(III) chloride; (ii) potassium hexacyanidoferrate(III); (iii) tetrachloridonickelate(II) ion.

Quick Tip to Solve: Find the complex charge from counterions before calculating the metal oxidation state.

OR

23(b). Draw the structures of optical isomers of each of the following complex ions:

$[Cr(C_2O_4)_3]^{3-}$, $[PtCl_2(en)_2]^{2+}$, $[Cr(NH_3)_2Cl_2(en)]^+$

[3 marks]

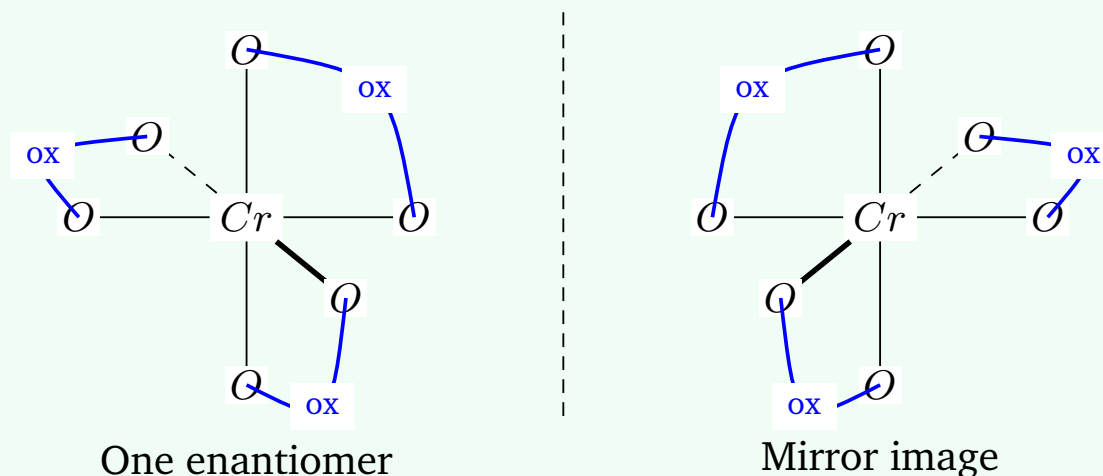
Solution:

Concept:

- Optical isomers are non-superimposable mirror images. Chelating ligands can impose handedness on an octahedral coordination arrangement.
- In the drawings, opposite sites are top/bottom, left/right and the two diagonal sites. A thick bond projects towards the viewer; a dashed bond projects away. Blue links join donor atoms belonging to one bidentate ligand.

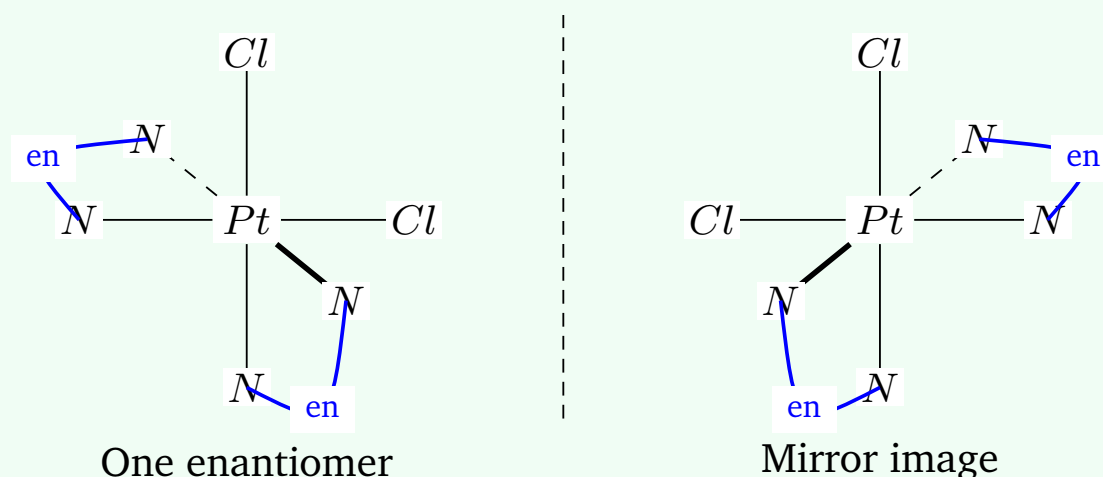
Step 1: (i) $[Cr(C_2O_4)_3]^{3-}$ Each oxalate ion, abbreviated ox, binds through two oxygen donor atoms to adjacent sites. Three such chelates occupy all six octahedral sites. Their two possible helically arranged forms are the Δ and Λ enantiomers. The first drawing fixes all three donor pairings; reflecting the entire arrangement gives the second. No rotation superimposes these two arrangements while preserving the chelate connections.

Quick Tip to Solve: Keep the donor pairs connected when checking mirror images: rotating isolated donor labels loses chelate handedness.



Optical pair of $[Cr(ox)_3]^{3-}$; each blue O–O link denotes one oxalate chelate.

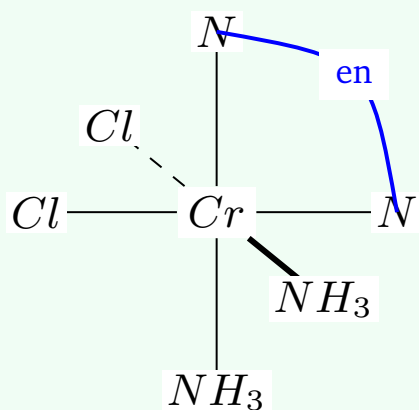
Step 2: (ii) $[PtCl_2(en)_2]^{2+}$ Ethylenediamine, en, binds through two nitrogen atoms. Select the cis geometrical arrangement, in which the two chlorido ligands occupy adjacent octahedral sites. Joining each pair of nitrogen donors belonging to an en ligand gives the two non-superimposable mirror structures shown. These are the optical isomers of the cis complex. The trans geometrical arrangement has symmetry and does not furnish this optical pair.



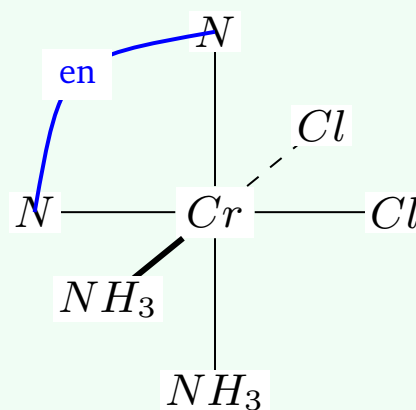
Optical pair of $cis-[PtCl_2(en)_2]^{2+}$; linked N atoms belong to the same en ligand.

Step 3: (iii) $[Cr(NH_3)_2Cl_2(en)]^+$ Place the two nitrogen donors of en at adjacent positions. In the optically active arrangement, the two ammonia ligands are mutually cis, and the two chlorido ligands are also mutually cis. Reflecting this complete arrangement, including the en connection, produces the second structure. The ammonia and chlorido labels must be preserved when testing superposition. The pair shown has no internal mirror plane and consists of non-superimposable mirror images.

Quick Tip to Solve: Keep the donor pairs connected when checking mirror images: rotating isolated donor labels loses chelate handedness.



One enantiomer



Mirror image

Optical pair with both ammonia ligands cis and both chlorido ligands cis in $[Cr(NH_3)_2Cl_2(en)]^+$.

Step 4: Conclusion The drawings give one optical pair for each ion: the tris(oxalato) pair, the cis bis(en) pair and the all-cis mixed-ligand pair, respectively.

Quick Tip to Solve: Keep the donor pairs connected when checking mirror images: rotating isolated donor labels loses chelate handedness.

24. (a) Which compound in each of the following pairs will react faster in S_N2 reaction with $-OH$ group?

(i) CH_3Br or CH_3I

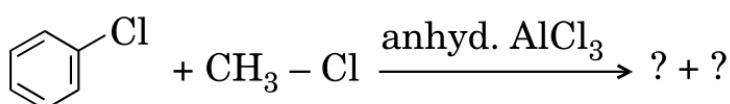
(ii) $(CH_3)_3CCl$ or CH_3Cl

(b) Write the product of the following reactions:

(i) $CH_3-Cl + KCN \rightarrow ?$

(ii) Chlorobenzene + $CH_3-Cl \xrightarrow{\text{anhyd. } AlCl_3} ? + ?$

[3 marks]



Solution:

Concept:

- An S_N2 reaction is a single-step substitution in which the nucleophile attacks the carbon from the side opposite the leaving group. Lower steric hindrance favours this attack.
- For the same alkyl group, a better leaving group increases the substitution rate. Cyanide ion from ionic KCN attacks mainly through carbon, giving a nitrile.
- In electrophilic aromatic substitution, chlorine deactivates the ring but directs an incoming electrophile to the ortho and para positions by resonance.

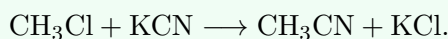
Step 1: Compare the methyl halides in (a)(i) Both substrates are methyl halides, so their steric

Quick Tip to Solve: Compare leaving groups only when the alkyl groups are alike; otherwise check crowding at the carbon undergoing backside attack first.

environments are the same. The C–I bond is weaker than the C–Br bond, and iodide is a better leaving group than bromide. Consequently, CH_3I reacts faster with OH^- than CH_3Br .

Step 2: Compare steric hindrance in (a)(ii) Methyl chloride, CH_3Cl , offers the least hindrance to backside attack. In tert-butyl chloride, $(\text{CH}_3)_3\text{CCl}$, three methyl groups crowd the carbon bonded to chlorine and prevent efficient backside approach. Therefore methyl chloride reacts faster by the $\text{S}_{\text{N}}2$ mechanism.

Step 3: Identify the cyanide substitution product in (b)(i) KCN supplies CN^- , which replaces chlorine through its carbon end. The product is ethanenitrile (acetonitrile), with one more carbon atom than methyl chloride:



It is a nitrile, not methyl isocyanide; the latter is associated with AgCN .

Step 4: Identify the aromatic substitution products in (b)(ii) Methyl chloride with anhydrous AlCl_3 introduces a methyl group into the chlorobenzene ring. Chlorine directs substitution to the ortho and para positions. Thus the two organic products are 1-chloro-2-methylbenzene (o-chlorotoluene) and 1-chloro-4-methylbenzene (p-chlorotoluene). The para product is favoured by lower steric crowding; HCl is eliminated during substitution.

Step 5: Conclusion (a) Faster substrates: (i) CH_3I ; (ii) CH_3Cl . (b) Products: (i) CH_3CN ; (ii) o-chlorotoluene and p-chlorotoluene.

Quick Tip to Solve: Compare leaving groups only when the alkyl groups are alike; otherwise check crowding at the carbon undergoing backside attack first.

25. Account for the following:

- (i) Aniline does not give Friedel-Crafts reaction.
- (ii) Ethylamine is soluble in water whereas aniline is not.
- (iii) $\text{p}K_{\text{b}}$ of methylamine is less than that of aniline.

[3 marks]

Solution:

Concept:

- The nitrogen lone pair controls the Lewis basicity and proton-accepting ability of an amine. Its availability changes with inductive effects and resonance.
- Water solubility depends on favourable hydrogen bonding relative to the hydrophobic size of the organic group. Basicity is measured by K_{b} , with $\text{p}K_{\text{b}} = -\log_{10} K_{\text{b}}$.

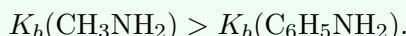
Step 1: Explain the absence of Friedel-Crafts reaction Aniline has a lone pair on nitrogen that coordinates strongly to the Lewis acid catalyst, anhydrous AlCl_3 . Formation of this Lewis acid–base complex ties up the lone pair and gives nitrogen a positive character. The ring is consequently strongly deactivated towards the electrophilic substitution required in a Friedel–Crafts alkylation or acylation. Thus aniline does not undergo the normal Friedel–Crafts reaction.

Step 2: Explain the difference in water solubility Ethylamine can form hydrogen bonds with water through its nitrogen lone pair and its N–H bonds. Its ethyl group is small enough that these favourable

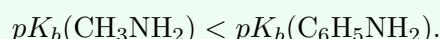
Quick Tip to Solve: For amines, ask whether the nitrogen lone pair is localised, delocalised or coordinated before comparing basicity or reactivity.

interactions allow it to dissolve readily. Aniline can also hydrogen-bond, but its much larger nonpolar phenyl ring makes the hydrophobic contribution dominant. Its interaction with water therefore cannot compensate sufficiently for the large aromatic group, and aniline is only sparingly soluble in water.

Step 3: Compare the basicities and their pK_b values The methyl group in methylamine exerts a positive inductive effect, increasing electron density on nitrogen and making its lone pair readily available to accept a proton. In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance and is less available for protonation. Methylamine is therefore the stronger base:



Since $pK_b = -\log_{10} K_b$, the order reverses on taking negative logarithms:



Step 4: Conclusion Aniline binds the Friedel–Crafts catalyst and deactivates its ring; ethylamine is readily hydrated whereas the phenyl group limits aniline solubility; methylamine has a more available nitrogen lone pair and hence a lower pK_b .

Quick Tip to Solve: For amines, ask whether the nitrogen lone pair is localised, delocalised or coordinated before comparing basicity or reactivity.

26. Write the names of the monomers of the following polymers:

(i) Polythene

(ii) Polyvinyl chloride

(iii) Bakelite

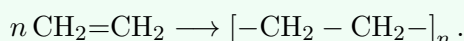
[3 marks]

Solution:

Concept:

- A monomer is a small molecule that participates in polymerisation to build a macromolecule. Addition polymers retain the atoms of their unsaturated monomers as the double bonds open.
- Condensation polymers are formed from suitable multifunctional monomers, usually with elimination of a small molecule such as water. Bakelite is a cross-linked phenol–formaldehyde resin.

Step 1: Identify the monomer of polythene Polythene is obtained by addition polymerisation of ethene, also called ethylene. Each ethene molecule supplies a two-carbon unit as its double bond opens and new carbon–carbon single bonds join neighbouring units:

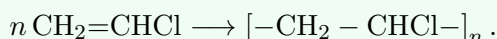


Thus its monomer is ethene, $\text{CH}_2=\text{CH}_2$; no small molecule is eliminated in this addition process.

Step 2: Identify the monomer of polyvinyl chloride Polyvinyl chloride, abbreviated PVC, is the

Quick Tip to Solve: For an addition polymer, restore a double bond in a two-carbon repeat unit; for Bakelite, remember the pair phenol plus formaldehyde.

addition polymer of vinyl chloride, whose systematic name is chloroethene:



The chlorine substituent remains attached to the polymer chain. Therefore the monomer is vinyl chloride, $\text{CH}_2=\text{CHCl}$, rather than ethene itself.

Step 3: Identify both monomers of Bakelite Bakelite is formed by condensation of phenol, $\text{C}_6\text{H}_5\text{OH}$, with formaldehyde (methanal), HCHO . Reaction at the ortho and para positions of phenol forms methylene bridges between aromatic units. Further condensation and cross-linking produce the rigid three-dimensional thermosetting resin. Both phenol and methanal must be named, because Bakelite is formed from two different starting monomers.

Step 4: Conclusion (i) Polythene: ethene (ethylene). (ii) Polyvinyl chloride: chloroethene (vinyl chloride). (iii) Bakelite: phenol and methanal (formaldehyde).

Quick Tip to Solve: For an addition polymer, restore a double bond in a two-carbon repeat unit; for Bakelite, remember the pair phenol plus formaldehyde.

27. Explain the following terms with a suitable example for each:

(i) Disinfectants

(ii) Antacids

(iii) Food preservatives

[3 marks]

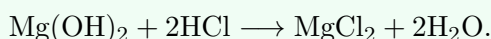
Solution:

Concept:

- Disinfectants control disease-causing microorganisms on non-living objects, whereas antacids act chemically on excess stomach acid.
- Food preservatives protect food from spoilage, commonly by inhibiting the growth of microorganisms.

Step 1: (i) Disinfectants Disinfectants are chemical substances used to kill or inhibit microorganisms on inanimate objects such as floors, drains and instruments. They are generally unsuitable for application to living tissues at their disinfecting concentrations. For example, a 1 percent solution of phenol is used as a disinfectant. Its use on surfaces reduces the microbial load and therefore the spread of infection.

Step 2: (ii) Antacids Antacids are substances that neutralise excess hydrochloric acid in the stomach and provide relief from acidity. A suitable example is magnesium hydroxide, $\text{Mg}(\text{OH})_2$, present in milk of magnesia. Its action can be represented by



Thus, the excess acid is consumed in a neutralisation reaction.

Step 3: (iii) Food preservatives Food preservatives are substances added to food to retard spoilage and increase its useful storage life. They commonly prevent or slow the growth of bacteria, yeasts and

Quick Tip to Solve: Link each term to its site and purpose: surfaces, stomach acid, and stored food respectively.

moulds. Sodium benzoate is a suitable example; it is used to preserve acidic foods and beverages such as fruit juices. It is added in the permitted small quantity rather than being used as a nutrient.

Step 4: Conclusion Suitable examples are phenol solution for disinfectants, magnesium hydroxide for antacids, and sodium benzoate for food preservatives.

Quick Tip to Solve: Link each term to its site and purpose: surfaces, stomach acid, and stored food respectively.

28(a). Define the terms conductivity and molar conductivity for the solution of an electrolyte. Comment on their variation with temperature.

(b) The measured resistance of a conductivity cell was 100 ohm. Calculate (i) the specific conductance and (ii) the molar conductance of the solution.

(Molar mass of KCl = 74.5 g mol^{-1} and cell constant = 1.25 cm^{-1})

[5 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$. Conductivity is $\kappa = G(l/A)$, where l/A is the cell constant.
- Molar conductivity is $\Lambda_m = \kappa/c$ when concentration c is in mol m^{-3} and SI units are used. For C in mol L^{-1} and κ in S cm^{-1} , $\Lambda_m = 1000\kappa/C$.

Step 1: (a) Define conductivity and molar conductivity Conductivity, or specific conductance, is the conductance of an electrolyte solution column having unit length and unit cross-sectional area. It is the reciprocal of resistivity. Its SI unit is S m^{-1} ; S cm^{-1} is also commonly used.

Molar conductivity is the conductance of the volume of solution containing one mole of the electrolyte, placed between electrodes of unit separation and sufficient cross-sectional area to contain that volume. Its SI unit is $\text{S m}^2 \text{ mol}^{-1}$, or commonly $\text{S cm}^2 \text{ mol}^{-1}$.

Step 2: (a) Explain the temperature dependence Both conductivity and molar conductivity of an electrolyte solution generally increase when temperature increases. Heating decreases the viscosity of the solvent, so the ions move more readily and their mobility increases. In a weak electrolyte, increased ionisation can also contribute to the rise in conductance.

Step 3: (b)(i) Calculate the specific conductance The resistance is $R = 100 \Omega$ and the cell constant is $l/A = 1.25 \text{ cm}^{-1}$. Therefore,

$$\begin{aligned} G &= \frac{1}{100} = 0.0100 \text{ S}, \\ \kappa &= G \frac{l}{A} = 0.0100 \times 1.25 \\ &= 0.0125 \text{ S cm}^{-1}. \end{aligned}$$

In SI units this is 1.25 S m^{-1} .

Step 4: (b)(ii) Express the molar conductance using concentration Let the molar concentration be $C \text{ mol L}^{-1}$. Then

$$\Lambda_m = \frac{1000 \times 0.0125}{C} = \frac{12.5}{C} \text{ S cm}^2 \text{ mol}^{-1}.$$

Quick Tip to Solve: Multiply reciprocal resistance by the cell constant first; molar conductivity additionally requires the solution concentration.

The printed question supplies no concentration, mass of KCl, or solution volume. Consequently a unique numerical molar conductance cannot be calculated from the given data. The molar mass 74.5 g mol^{-1} alone does not determine concentration: a mass per unit volume would also be required.

Step 5: Conclusion Both conductivity and molar conductivity generally increase with temperature. The specific conductance is 0.0125 S cm^{-1} . The molar conductance is $12.5/C \text{ S cm}^2 \text{ mol}^{-1}$, with C in mol L^{-1} ; a numerical value requires the missing concentration.

Quick Tip to Solve: Multiply reciprocal resistance by the cell constant first; molar conductivity additionally requires the solution concentration.

OR

28(b). (a) Predict the products of electrolysis in each of the following:

(i) An aqueous solution of AgNO_3 with platinum electrodes.

(ii) An aqueous solution of H_2SO_4 with platinum electrodes.

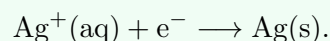
(b) Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C . The Gibbs energy change for the decomposition reaction $\frac{2}{3}\text{Al}_2\text{O}_3 \rightarrow \frac{4}{3}\text{Al} + \text{O}_2$ is 960 kJ . ($F = 96500 \text{ C mol}^{-1}$) [5 marks]

Solution:

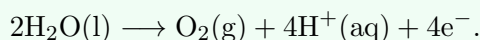
Concept:

- Electrolysis involves reduction at the cathode and oxidation at the anode. Platinum is an inert electrode, so the electrolyte or water supplies the electrode products.
- The reversible electrical work required for a non-spontaneous decomposition is $\Delta G = nFE_{\min}$, where n is the number of moles of electrons transferred per reaction as written and F is the Faraday constant.

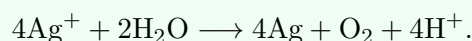
Step 1: (a)(i) Electrolysis of aqueous silver nitrate At the cathode, silver ions are preferentially reduced rather than water:



Thus silver deposits on the platinum cathode. At the inert platinum anode, nitrate ions are not discharged; water is oxidised:



Oxygen gas is evolved at the anode. Combining the half-reactions gives

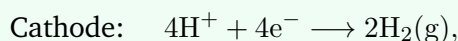
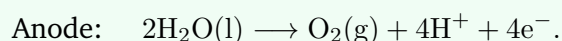


Nitrate remains in solution, which becomes more acidic as electrolysis proceeds.

Step 2: (a)(ii) Electrolysis of aqueous sulphuric acid Hydrogen ions are reduced at the cathode, while

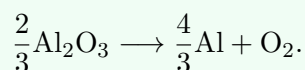
Quick Tip to Solve: Count electrons from the reaction exactly as written: $4/3$ mol of aluminium requires four mol of electrons.

water is oxidised at the anode:



The net reaction is $2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$. Hence the gaseous products are hydrogen at the cathode and oxygen at the anode, in the volume ratio 2 : 1 at the same temperature and pressure. Sulphate ions remain in solution.

Step 3: (b) Count electrons for the stated decomposition The reaction is



Each aluminium ion requires three electrons: $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$. Therefore the formation of $4/3$ mol of aluminium requires $n = (4/3) \times 3 = 4$ mol of electrons. The given Gibbs energy refers to this reaction, so it must be paired with $n = 4$, not with the electron count for one mole of alumina.

Step 4: Calculate the minimum external potential Convert the Gibbs energy into joules and use the reversible-work relation at the stated temperature:

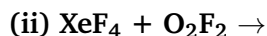
$$E_{\min} = \frac{\Delta G}{nF} = \frac{960 \times 10^3}{4 \times 96500} \text{ V} = 2.487 \text{ V}.$$

The decomposition has positive Gibbs energy, so the corresponding spontaneous-cell potential is negative; an external potential of this positive magnitude must be applied in the decomposition direction. Practical operation requires a higher voltage because of resistance and electrode overpotentials. No additional temperature correction is needed because the Gibbs energy is supplied at the specified temperature.

Step 5: Conclusion (a)(i) Cathode: Ag; anode: O_2 . (a)(ii) Cathode: H_2 ; anode: O_2 . (b) The minimum applied potential difference is 2.49 V.

Quick Tip to Solve: Count electrons from the reaction exactly as written: $4/3$ mol of aluminium requires four mol of electrons.

29(a). Complete the following chemical equations:



(b) How would you account for the following situations?

(i) The acidic strength of these compounds increases in the following order: $\text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$

(ii) The oxidising power of oxoacids of chlorine follows the order: $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$

(iii) In vapour state sulphur exhibits paramagnetic behaviour.

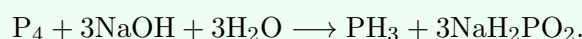
[5 marks]

Solution:

Concept:

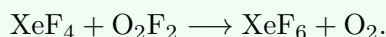
- Disproportionation is simultaneous oxidation and reduction of the same element; reaction coefficients must conserve both atoms and charge.
- Across a period, increasing electronegativity increases the polarity of covalent hydrides and generally favours proton release. Oxidising power concerns reduction, whereas paramagnetism requires unpaired electrons.

Step 1: (a)(i) Reaction of phosphorus with alkali White phosphorus reacts with aqueous sodium hydroxide to give phosphine and sodium hypophosphite:



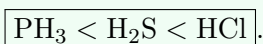
Phosphorus starts in oxidation state zero. It is reduced to -3 in PH_3 and oxidised to $+1$ in H_2PO_2^- . One phosphorus atom gains three electrons while three phosphorus atoms each lose one electron, accounting for the product ratio. The balanced equation conserves four phosphorus atoms, three sodium atoms, nine hydrogen atoms and six oxygen atoms.

Step 2: (a)(ii) Reaction of xenon tetrafluoride Dioxygen difluoride fluorinates xenon tetrafluoride to xenon hexafluoride:



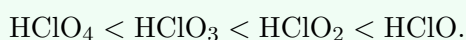
There are six fluorine atoms on each side and both oxygen atoms leave as molecular oxygen. Xenon changes from oxidation state $+4$ to $+6$; oxygen in O_2F_2 changes from $+1$ to zero, so this is a redox reaction.

Step 3: (b)(i) Increasing acidic strength of the hydrides Phosphorus, sulphur and chlorine lie in the same period, and their electronegativities increase in the order $\text{P} < \text{S} < \text{Cl}$. The bond to hydrogen becomes increasingly polar, with greater positive character on hydrogen, and the electronegative atom better accommodates the electron pair retained when a proton is released. Consequently the tendency to donate a proton increases as



This comparison across a period is governed principally by electronegativity and bond polarity; it should not be confused with the bond-strength argument used for hydrides down a group.

Step 4: (b)(ii) Oxidising power of chlorine oxoacids The stated order is



Quick Tip to Solve: For sulphur vapour, identify the high-temperature S_2 species and explicitly state its two unpaired electrons.

In the textbook comparison, the higher oxoacids have more oxygen atoms and greater stabilisation of their chlorine–oxygen framework; their conjugate anions distribute negative charge over more oxygen atoms. They therefore show a decreasing tendency to undergo reduction in the stated series. Hypochlorous acid is less stabilised and is readily reduced to chloride, making it the strongest oxidising agent of these four in this comparison. A higher formal oxidation state of chlorine alone does not establish greater oxidising power: the stability of the starting species also matters.

Step 5: (b)(iii) Paramagnetism of sulphur vapour At high temperature, sulphur vapour contains S_2 molecules. The molecular-orbital arrangement of S_2 resembles that of O_2 , with two electrons occupying separate degenerate antibonding π^* orbitals. Hund's rule leaves these two electrons unpaired. Their magnetic moments cause attraction to an applied magnetic field, so the vapour exhibits paramagnetism. This behaviour is associated with the diatomic vapour species rather than the closed-shell ring structure of ordinary solid sulphur.

Step 6: Conclusion The products are $PH_3 + 3NaH_2PO_2$ and $XeF_6 + O_2$ in the balanced equations above. Increasing hydride polarity explains the acid order; greater stabilisation of the higher chlorine oxoacids explains the stated oxidising order; two unpaired electrons in S_2 explain paramagnetism.

Quick Tip to Solve: For sulphur vapour, identify the high-temperature S_2 species and explicitly state its two unpaired electrons.

OR

29(b). (a) Using VSEPR theory predict the probable structures of the following:

(i) N_2O_3

(ii) BrF_3

(b) Arrange the following groups of substances in the order of the property indicated against each group:

(i) NH_3 , PH_3 , AsH_3 , SbH_3 – increasing order of boiling points.

(ii) O, S, Se, Te – increasing order of electron gain enthalpy with negative sign.

(iii) F_2 , Cl_2 , Br_2 , I_2 – increasing order of bond dissociation enthalpy.

[5 marks]

Solution:

Concept:

- VSEPR theory counts each single or multiple bond as one electron domain. Lone pairs repel more strongly than bonding pairs and determine the observed molecular shape.
- Boiling points depend on intermolecular forces. Electron gain enthalpy depends on atomic size and electron repulsion; bond dissociation enthalpy depends on bond strength.

Step 1: (a)(i) Structure of dinitrogen trioxide The molecular connectivity is $O = N - NO_2$, with resonance between the two terminal N–O bonds of the NO_2 group. A Lewis form is $O = N - N^+(=O) - O^-$. At the nitrogen in the $O = N-$ end, the N–O bond, N–N bond and one lone pair give three electron domains. Its electron-domain arrangement is trigonal planar, while the local molecular shape is bent. The other nitrogen has three bonding domains and no lone pair, giving

Quick Tip to Solve: Apply the exceptions before the group trend: hydrogen bonding raises ammonia's boiling point, compact oxygen resists electron addition, and lone-pair repulsion weakens F–F.

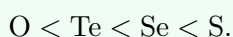
a trigonal-planar local arrangement. Thus the probable molecular structure is planar, with a bent nitrosyl end attached to a trigonal-planar NO_2 end; it is not a linear molecule.

Step 2: (a)(ii) Structure of bromine trifluoride Bromine has seven valence electrons. Three Br-F bonds leave two lone pairs, so there are five domains around Br: AX_3E_2 . The electron-domain arrangement is trigonal bipyramidal. Both lone pairs occupy equatorial sites, where they experience fewer 90° interactions. The remaining equatorial fluorine and two axial fluorines produce a T-shaped molecule. Lone-pair repulsion slightly reduces the axial-equatorial angle from 90° .

Step 3: (b)(i) Increasing boiling points Among PH_3 , AsH_3 and SbH_3 , increasing molecular size and polarizability strengthen dispersion forces. Ammonia exhibits intermolecular hydrogen bonding, raising its boiling point above those of phosphine and arsine. Stibine still has a higher boiling point than ammonia because its much stronger dispersion forces dominate. Hence



Step 4: (b)(ii) Increasing electron gain enthalpy with negative sign Interpreting the property as the magnitude of the negative electron gain enthalpy, oxygen is anomalously low: an added electron enters its compact $2p$ shell and experiences substantial repulsion. Sulphur accepts an electron more favourably. Below sulphur, increasing size reduces attraction for the added electron. Thus the increasing magnitudes are



Equivalently, the signed enthalpies obey $\Delta_{\text{eg}}H(\text{S}) < \Delta_{\text{eg}}H(\text{Se}) < \Delta_{\text{eg}}H(\text{Te}) < \Delta_{\text{eg}}H(\text{O})$, since the most negative value is numerically smallest.

Step 5: (b)(iii) Increasing bond dissociation enthalpies The unusually short F-F bond suffers strong repulsions between lone pairs on adjacent small fluorine atoms, making it weaker than Cl-Cl and Br-Br. From chlorine to iodine, increasing bond length weakens the bond. The I-I bond is weaker still than F-F. Therefore



Step 6: Conclusion N_2O_3 is planar with bent and trigonal-planar nitrogen environments; BrF_3 is T-shaped. The required increasing orders are $\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3$, $\text{O} < \text{Te} < \text{Se} < \text{S}$ for negative electron gain enthalpy magnitude, and $\text{I}_2 < \text{F}_2 < \text{Br}_2 < \text{Cl}_2$.

Quick Tip to Solve: Apply the exceptions before the group trend: hydrogen bonding raises ammonia's boiling point, compact oxygen resists electron addition, and lone-pair repulsion weakens F-F.

30(a). Describe:

(i) Aldol condensation

(ii) Cannizzaro reaction

(b) Describe a chemical test to distinguish between:

(i) Ethanal and Propanal

(ii) Benzaldehyde and Acetophenone

(iii) Propan-2-one and Propan-3-one

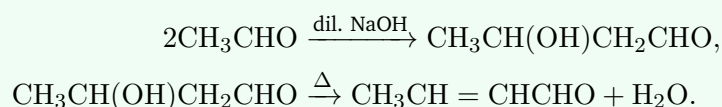
[5 marks]

Solution:

Concept:

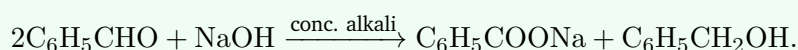
- Carbonyl compounds containing an α -hydrogen undergo aldol condensation with dilute base. Aldehydes without an α -hydrogen undergo Cannizzaro disproportionation with concentrated alkali.
- The iodoform test detects $\text{CH}_3\text{CO}-$ compounds and ethanal by formation of yellow CHI_3 . Tollens' reagent oxidises aldehydes but ordinary ketones do not give a silver mirror.

Step 1: (a)(i) Aldol condensation Aldehydes or ketones having at least one α -hydrogen react in the presence of dilute alkali to form a β -hydroxy aldehyde or ketone. On heating, this aldol loses water to form an α, β -unsaturated carbonyl compound. For example, ethanal gives 3-hydroxybutanal, which on heating forms but-2-enal:



The first step makes a new carbon-carbon bond; dehydration completes the condensation.

Step 2: (a)(ii) Cannizzaro reaction An aldehyde that has no α -hydrogen undergoes self-oxidation and reduction with concentrated alkali. One molecule is oxidised to a carboxylate salt and another is reduced to a primary alcohol. Benzaldehyde provides an example:



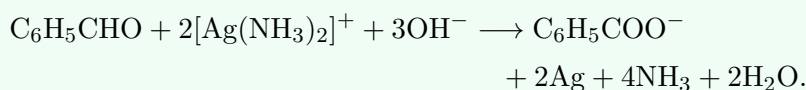
The products are sodium benzoate and benzyl alcohol. The carboxylate salt gives benzoic acid only after acidification.

Step 3: (b)(i) Ethanal and propanal: iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal produces a yellow precipitate of iodoform, whereas propanal does not. The positive reaction is



Both compounds are aldehydes, so Tollens' reagent would give a positive result with both and would not distinguish this pair.

Step 4: (b)(ii) Benzaldehyde and acetophenone: Tollens' test Warm each sample gently with freshly prepared ammoniacal silver nitrate in a water bath. Benzaldehyde reduces Tollens' reagent to metallic silver, producing a silver mirror. Acetophenone, an ordinary ketone, gives no silver mirror. The aldehyde reaction in alkaline solution is



Alternatively, acetophenone gives yellow iodoform with iodine/alkali because it contains $\text{CH}_3\text{CO}-$, while benzaldehyde does not.

Quick Tip to Solve: Use iodoform for ethanal or a methyl ketone and Tollens' reagent for an aldehyde; first check that every printed compound name defines a possible structure.

Step 5: (b)(iii) Examine the printed name before selecting a test The printed pair is propan-2-one and propan-3-one. Propan-2-one is CH_3COCH_3 , but propan-3-one is not a valid ketone name: in a three-carbon ketone the carbonyl carbon must be the middle carbon, bonded to two carbon groups. A terminal carbonyl group bearing hydrogen is an aldehyde, whose correct name here would be propanal. Thus no chemically valid distinction can be assigned to the pair exactly as printed. For completeness, if a terminal three-carbon aldehyde (propanal) is being described, iodine/aqueous NaOH distinguishes it from propan-2-one: propan-2-one gives yellow iodoform, whereas propanal gives no precipitate. This conditional test does not identify a compound called propan-3-one.

Step 6: Conclusion Aldol condensation gives a β -hydroxy carbonyl compound followed by dehydration; Cannizzaro reaction gives an alcohol and a carboxylate. Ethanal gives the iodoform test while propanal does not; benzaldehyde gives Tollens' silver mirror while acetophenone does not. The last printed pair contains the invalid name propan-3-one and therefore cannot literally be distinguished as two named ketones.

Quick Tip to Solve: Use iodoform for ethanal or a methyl ketone and Tollens' reagent for an aldehyde; first check that every printed compound name defines a possible structure.

OR

30(b). (a) Draw the structures of the following compounds:

(i) 4-Chloropentan-2-one

(ii) But-2-en-1-al

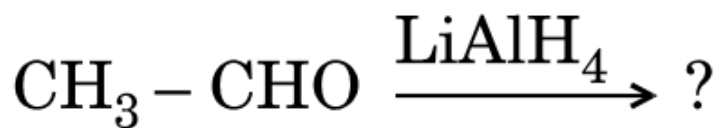
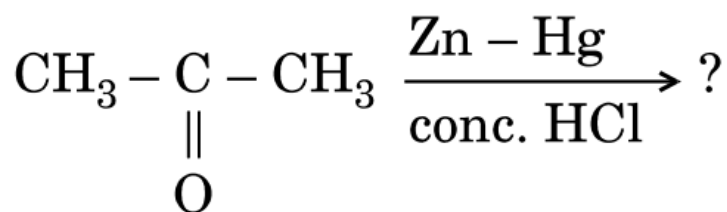
(b) Write the product(s) in the following:

(i) $\text{CH}_3-\text{COOH} \xrightarrow{(\text{Br}_2/\text{P})} ?$

(ii) $\text{CH}_3-\text{CHO} \xrightarrow{(\text{LiAlH}_4)} ?$

(iii) $\text{CH}_3-\text{CO}-\text{CH}_3 \xrightarrow{(\text{Zn}-\text{Hg} / \text{conc. HCl})} ?$

[5 marks]



Solution:

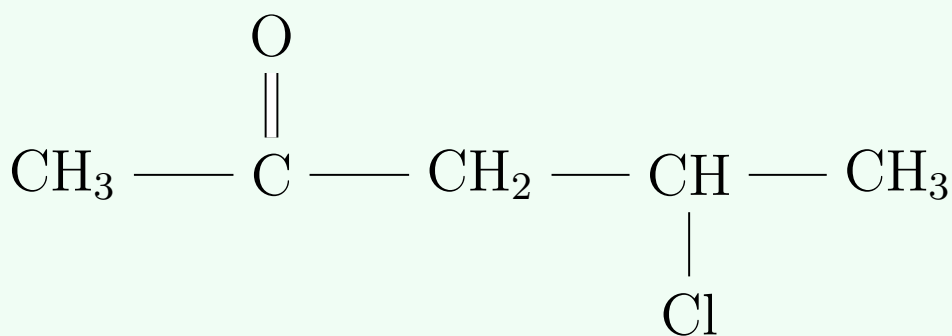
Concept:

- In naming carbonyl compounds, number the parent chain to give the principal functional group its required lowest locant. The aldehyde carbon is always carbon 1.
- The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by bromine using Br_2/P ; the carboxyl group remains intact.
- LiAlH_4 reduces an aldehyde to a primary alcohol. Clemmensen reduction, using $\text{Zn} - \text{Hg}$ and concentrated HCl , converts a carbonyl group into a methylene group.

Step 1: (a)(i) Draw 4-chloropentan-2-one Take a five-carbon chain, place the ketone carbonyl at carbon 2 and attach chlorine to carbon 4. The resulting connectivity is

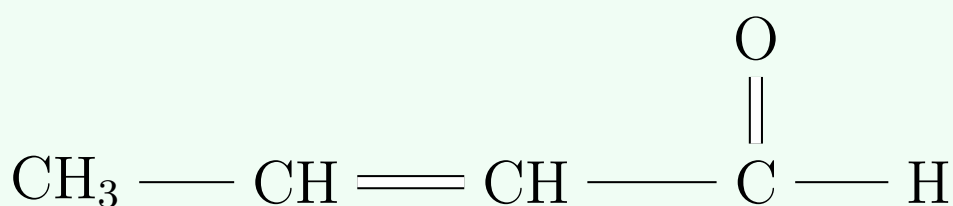


Numbering from the opposite end would give the ketone a higher locant, so it is not the required numbering. The displayed structure below shows both substituent positions explicitly.



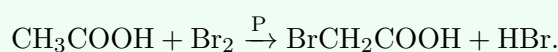
Structure of 4-chloropentan-2-one

Step 2: (a)(ii) Draw but-2-en-1-al Begin numbering at the aldehyde carbon, which is carbon 1. Place the double bond between carbons 2 and 3 in a four-carbon chain. Thus the structure is $\text{OHC} - \text{CH} = \text{CH} - \text{CH}_3$, equivalently $\text{CH}_3 - \text{CH} = \text{CH} - \text{CHO}$. The name does not specify alkene stereochemistry; the required answer is this connectivity.



Structure of but-2-en-1-al

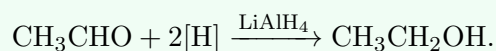
Step 3: (b)(i) Bromination of ethanoic acid Ethanoic acid has alpha hydrogens on the methyl carbon adjacent to the carboxyl group. Under Hell–Volhard–Zelinsky conditions, one of these hydrogens is replaced by bromine:



Quick Tip to Solve: Number an aldehyde from CHO; distinguish LiAlH_4 reduction to an alcohol from Clemmensen reduction to an alkane.

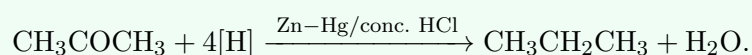
The organic product is 2-bromoethanoic acid (bromoacetic acid). This is alpha substitution, so the $-\text{COOH}$ group is retained.

Step 4: (b)(ii) Reduction of ethanal Lithium aluminium hydride supplies hydride to the aldehyde carbonyl. Subsequent protonation during work-up gives the corresponding primary alcohol:



The product is ethanol. The carbon skeleton is unchanged, while the aldehyde $-\text{CHO}$ group becomes $-\text{CH}_2\text{OH}$.

Step 5: (b)(iii) Clemmensen reduction of propanone Zinc amalgam in concentrated hydrochloric acid reduces the ketone carbonyl completely to a methylene group:



The organic product is propane. These conditions remove the carbonyl oxygen; they do not stop at the secondary-alcohol stage.

Step 6: Conclusion (a) The structures are $\text{CH}_3\text{COCH}_2\text{CH}(\text{Cl})\text{CH}_3$ and $\text{CH}_3\text{CH}=\text{CHCHO}$, respectively. (b) The organic products are (i) BrCH_2COOH , (ii) $\text{CH}_3\text{CH}_2\text{OH}$, and (iii) $\text{CH}_3\text{CH}_2\text{CH}_3$.

Quick Tip to Solve: Number an aldehyde from CHO; distinguish LiAlH_4 reduction to an alcohol from Clemmensen reduction to an alkane.