

CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/1/3 - 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. Write a distinguishing feature between a metallic solid and an ionic solid.

[1 mark]

Solution:

Concept:

- Electrical conduction requires mobile charged particles.
- Metallic solids contain delocalised electrons; ionic solids contain oppositely charged ions.

Step 1: Identify the carriers in a metal In a metallic solid, the outer electrons are delocalised throughout the lattice. These electrons can drift under an applied potential difference even while the metal remains solid.

Step 2: Compare the ionic solid In an ionic solid, the ions are fixed at their lattice positions and cannot carry charge through the solid. On melting, the ions become mobile and can conduct electricity.

Step 3: Conclusion A metallic solid conducts electricity in the solid state, whereas an ionic solid does not conduct in the solid state but conducts when molten.

Quick Tip to Solve: For a conduction comparison, identify the mobile carrier: electrons in metals and ions in molten ionic compounds.

2. What is a 'shape selective catalyst'?

[1 mark]

Solution:

Concept:

- Catalysis changes the reaction rate through a catalyst that is regenerated.
- Shape selectivity depends on the molecular dimensions of reactants and products relative to the pores of the catalyst.

Step 1: Relate selectivity to pore size A porous catalyst admits only molecules of suitable size and shape into its channels, where the active sites are situated. Molecules too large to enter cannot react at these internal sites.

Step 2: Identify a standard example Zeolites have well-defined pores and cavities. Their pore geometry restricts which reactant molecules enter and which products can form and diffuse out, making their catalytic action shape selective.

Step 3: Conclusion A shape selective catalyst is a catalyst whose activity depends on its pore structure and on the size and shape of reactant and product molecules; zeolites are examples.

Quick Tip to Solve: Remember shape selectivity as molecular sieving: compare the molecule dimensions with the catalyst pore size.

3. What is the role of NaOH in the metallurgy of aluminium?

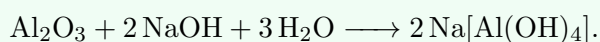
[1 mark]

Solution:

Concept:

- Bauxite is purified by selective leaching before aluminium is extracted.
- Alumina, Al_2O_3 , is amphoteric and dissolves in concentrated NaOH as soluble sodium aluminate.

Step 1: Leach the ore with alkali Concentrated NaOH dissolves the alumina present in bauxite. In aqueous solution this may be written as



Step 2: Separate the insoluble residue The insoluble impurities, notably iron oxides, are removed by filtration. Aluminium hydroxide is subsequently precipitated from the aluminate solution and heated to obtain purified alumina.

Step 3: Conclusion NaOH acts as a leaching agent: it dissolves alumina from bauxite as soluble sodium aluminate, enabling its separation from insoluble impurities.

Quick Tip to Solve: Associate the role of sodium hydroxide with purification of bauxite; alumina dissolves because it is amphoteric.

4. Draw the structure of XeOF_4 .

[1 mark]

Solution:

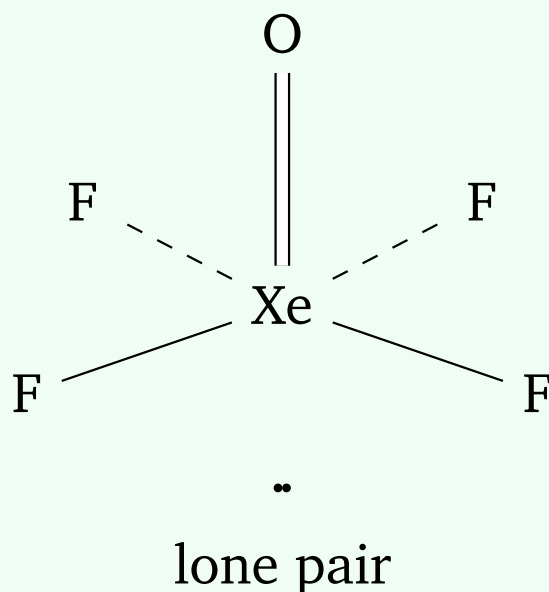
Concept:

- In XeOF_4 , xenon has five bonding domains and one lone pair.
- In VSEPR counting, the $\text{Xe}=\text{O}$ double bond counts as one electron domain. Six domains have an octahedral arrangement.

Step 1: Count the electron domains The four $\text{Xe}-\text{F}$ bonds and one $\text{Xe}=\text{O}$ bond give five bonding domains around xenon. The remaining lone pair occupies the sixth position of the octahedral electron-domain arrangement.

Step 2: Place the atoms in the structure Place the four fluorine atoms at the corners of a square with xenon at its centre. Oxygen occupies the axial position above this plane, joined to xenon by a double bond. The xenon lone pair lies opposite oxygen, below the plane.

Quick Tip to Solve: Count a double bond as one VSEPR domain; remove the lone-pair vertex of an octahedron to obtain the square pyramid.



Square pyramidal structure of xenon oxytetrafluoride

Step 3: Conclusion XeOF_4 has a square pyramidal molecular shape, with oxygen at the apex and four fluorine atoms in the square base.

Quick Tip to Solve: Count a double bond as one VSEPR domain; remove the lone-pair vertex of an octahedron to obtain the square pyramid.

5. Draw the structure of 2-bromopentane.

[1 mark]

Solution:

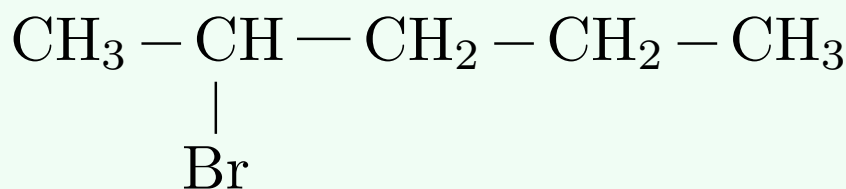
Concept:

- The parent chain in pentane contains five carbon atoms joined by single bonds.
- The prefix 2-bromo places a bromine substituent on carbon 2 of this chain.

Step 1: Number the parent chain Write the straight five-carbon skeleton and number from the end nearer the substituent. The carbon atoms are numbered 1 through 5; bromine is attached to the second carbon.

Step 2: Complete the valencies The second carbon bonds to its two neighbouring carbons and to bromine, so it carries one hydrogen. The end carbons are CH_3 groups and the remaining internal carbons are CH_2 groups.

Quick Tip to Solve: First count five carbons, then place bromine on carbon 2; check that every carbon has four bonds.



Structure of 2-bromopentane

Step 3: Conclusion The structure of 2-bromopentane is $\text{CH}_3 - \text{CH}(\text{Br}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$.

Quick Tip to Solve: First count five carbons, then place bromine on carbon 2; check that every carbon has four bonds.

6. Why do transition elements show variable oxidation states?

[1 mark]

Solution:

Concept:

- Transition elements possess valence electrons in both the outer ns and the penultimate $(n-1)d$ subshells.
- The energies of these subshells are close, so their electrons can participate in bond formation.

Step 1: Compare the subshell energies The small energy difference between the ns and $(n-1)d$ orbitals makes electrons from both subshells available for removal or sharing.

Step 2: Relate electron participation to oxidation state Different numbers of these electrons can take part in forming compounds. For example, iron commonly forms Fe^{2+} and Fe^{3+} , corresponding to different numbers of valence electrons being involved.

Step 3: Conclusion Transition elements show variable oxidation states because the ns and $(n-1)d$ orbitals have similar energies and different numbers of their electrons can participate in bonding.

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

7. Out of $\text{CH}_3 - \text{NH}_2$ 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 dispersion forces.
- The usual primary-versus-tertiary amine comparison by hydrogen bonding applies to amines of comparable molar mass.

Step 1: Compare these particular molecules Methylamine, CH_3NH_2 , can form intermolecular hydrogen bonds. Trimethylamine, $(\text{CH}_3)_3\text{N}$, has no $\text{N} - \text{H}$ bond but has a larger electron cloud and stronger dispersion attractions.

Quick Tip to Solve: Check whether the two amines have comparable molar masses before using hydrogen bonding alone.

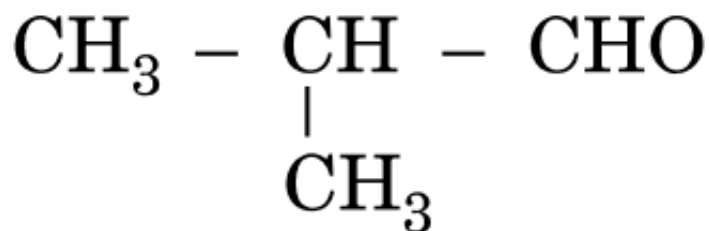
Step 2: Use the actual boiling-point order For this pair, the size effect outweighs the hydrogen-bonding advantage of methylamine. Their normal boiling points are approximately -6.3°C for methylamine and 2.9°C for trimethylamine.

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

Quick Tip to Solve: Check whether the two amines have comparable molar masses before using hydrogen bonding alone.

8. Write the IUPAC name of the following compound.

[1 mark]



Solution:

Concept:

- The parent chain must contain the aldehyde carbon; its carbon is numbered 1.
- For an aldehyde, replace the final -e of the parent alkane name by -al.

Step 1: Select and number the parent chain The structure is $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CHO}$. The longest chain containing the $-\text{CHO}$ carbon has three carbons, so its parent aldehyde is propanal. Numbering begins at the aldehyde carbon.

Step 2: Locate the substituent The remaining CH_3 group is attached to carbon 2. Combining its locant and name with the parent gives 2-methylpropanal. The aldehyde carbon needs no separate locant because it is necessarily carbon 1.

Step 3: Conclusion The IUPAC name is $\boxed{2\text{-methylpropanal}}$.

Quick Tip to Solve: Always include the CHO carbon in the parent chain and number it carbon 1.

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 contributes negligibly to the vapour above the solution.
- For an ideal solution, Raoult's law is $p_1 = x_1 p_1^{\circ}$, where x_1 is the solvent mole fraction and p_1° is its pure vapour pressure at the same temperature.

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

Step 1: Explain the change at the surface Dissolving a non-volatile solute lowers the fraction of solvent molecules in the liquid. Fewer solvent molecules are available at the surface to escape into the vapour. At the same temperature, the equilibrium vapour pressure of the solvent is therefore lower than that of the pure solvent.

Step 2: Express the lowering quantitatively As $x_1 < 1$, Raoult's law gives $p_1 < p_1^\circ$. If x_2 is the solute mole fraction, then

$$\Delta p = p_1^\circ - p_1 = p_1^\circ(1 - x_1) = p_1^\circ x_2.$$

Thus, for an ideal solution, the relative lowering is $\Delta p/p_1^\circ = x_2$.

Step 3: Conclusion The solvent's vapour pressure decreases on dissolving a non-volatile solute at the same temperature; for an ideal solution, $p_1 = x_1 p_1^\circ$.

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

10. Define the following terms:

(i) Rate constant (k)

(ii) Activation energy (E_a)

[2 marks]

Solution:

Concept:

- A rate law relates reaction rate to reactant concentrations: $r = k[A]^m[B]^n$, where m, n are the reaction orders.
- Activation energy is the energy barrier between the reactants and the activated complex along a reaction pathway.

Step 1: (i) Define the rate constant The rate constant k is the proportionality constant in the experimentally determined rate law. Numerically, it equals the rate when each concentration appearing in the rate law is unity. For a given reaction, its value is fixed at a specified temperature and catalyst condition; its units depend on the overall reaction order.

Step 2: (ii) Define the activation energy The activation energy E_a is the minimum additional energy that reactant molecules must acquire to reach the activated complex and permit effective reaction. It is the energy difference between the activated complex and the reactants. It commonly has units kJ mol^{-1} and appears in the Arrhenius equation $k = Ae^{-E_a/(RT)}$, where A is the frequency factor and R the gas constant.

Step 3: Conclusion (i) k is the rate-law proportionality constant, numerically equal to the rate at unit reactant concentrations. (ii) E_a is the energy required to raise reactants to the activated complex.

Quick Tip to Solve: Define k using the rate law; define E_a as an energy barrier above the reactants, not the reaction enthalpy.

11. Describe the principle involved in each of the following processes:

(i) Zone refining of metals

(ii) Vapour phase refining of metals

[2 marks]

Solution:

Concept:

- Zone refining exploits the greater solubility of impurities in molten metal than in solid metal.
- Vapour phase refining requires a volatile metal compound that can be separated and then decomposed to yield pure metal.

Step 1: (i) State the principle of zone refining A narrow molten zone is formed in an impure metal rod and moved slowly along it. As the liquid cools behind the heater, relatively pure metal crystallises out, while the impurities preferentially remain in the molten zone. Repeated passage of this zone concentrates impurities at one end, which is cut off. The separation therefore depends on the unequal distribution of impurities between solid and liquid metal.

Step 2: (ii) State the principle of vapour phase refining The impure metal is converted selectively into a volatile compound using a suitable reagent. This compound is separated from the non-volatile impurities and decomposed under appropriate conditions to deposit pure metal. For example, nickel forms volatile $\text{Ni}(\text{CO})_4$, which subsequently decomposes to nickel and carbon monoxide. A suitable volatile compound must form readily and also decompose readily to regenerate the metal.

Step 3: Conclusion Zone refining uses preferential solubility of impurities in the melt; vapour phase refining uses formation, separation and decomposition of a volatile metal compound.

Quick Tip to Solve: Remember the separation basis: impurity distribution for zone refining, volatility of a metal compound for vapour refining.

12. Complete the following chemical equations:

(i) $\text{PCl}_5 \rightarrow$ (on heating)

(ii) $\text{NaHCO}_3 + \text{HCl} \rightarrow$

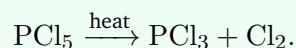
[2 marks]

Solution:

Concept:

- On heating, phosphorus pentachloride dissociates into phosphorus trichloride and chlorine; atom conservation fixes the coefficients.
- An acid reacts with a hydrogen carbonate to give the corresponding salt, water and carbon dioxide.

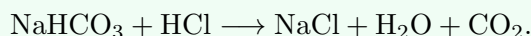
Step 1: Complete the thermal dissociation The products are phosphorus trichloride and chlorine:



There is one phosphorus atom and five chlorine atoms on each side, so all coefficients are unity. This thermal dissociation is reversible; cooling favours recombination of the products to form phosphorus pentachloride.

Quick Tip to Solve: For a hydrogen carbonate plus acid, always include both water and carbon dioxide along with the salt.

Step 2: Complete the acid-hydrogen carbonate reaction Hydrochloric acid converts sodium hydrogen carbonate into sodium chloride, with evolution of carbon dioxide:



The hydrogen carbonate ion first accepts a proton to form carbonic acid, which decomposes into water and carbon dioxide. Sodium and chloride ions form the salt. The equation is balanced with every coefficient equal to one.

Step 3: Conclusion (i) $\text{PCl}_5 \xrightarrow{\text{heat}} \text{PCl}_3 + \text{Cl}_2$. (ii) $\text{NaHCO}_3 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$.

Quick Tip to Solve: For a hydrogen carbonate plus acid, always include both water and carbon dioxide along with the salt.

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:

- Transition metals generally have strong metallic bonding because both outer s electrons and available d electrons contribute to bonding.
- Ionisation enthalpy depends on nuclear attraction, shielding, electron pairing and the stability of the electronic configurations before and after ionisation.

Step 1: Explain hardness and high melting and boiling points Most transition metals have several electrons available for metallic bonding, including electrons from the partially filled d subshell. Their strong interatomic metallic bonds give high enthalpies of atomisation. Considerable energy is therefore needed to separate their atoms, accounting for hardness and generally high melting and boiling points. In Zn, Cd and Hg the d subshell is completely filled; the weaker contribution of these d electrons to metallic bonding accounts for their exceptional behaviour.

Step 2: Explain irregular first and second ionisation enthalpies Across the first transition series, increasing nuclear charge tends to increase ionisation enthalpy, but added 3d electrons also change shielding and electron-electron repulsion. The especially stable half-filled $3d^5$ and filled $3d^{10}$ arrangements introduce further irregularities. Removing an electron may create or destroy one of these stable arrangements, so the first and second ionisation enthalpies do not vary smoothly. For example, the second ionisation of copper removes an electron from the stable $3d^{10}$ configuration of Cu^+ , making it particularly difficult.

Step 3: Conclusion Strong metallic bonding explains the hardness and high phase-change temperatures; changes in shielding and the stability of d-electron configurations explain the irregular ionisation enthalpies.

Quick Tip to Solve: For irregular ionisation trends, compare the d configurations of both the starting ion and the ion formed.

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

[2 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series as atomic number increases.
- The added 4f electrons shield the increasing nuclear charge poorly, increasing the effective attraction on the outer electrons.

Step 1: Define and explain the contraction Lanthanoid contraction is the progressive decrease in the size of lanthanoid atoms and, especially, their Ln^{3+} ions from La to Lu with increasing atomic number. Successive electrons enter the 4f subshell. Since 4f electrons shield one another inefficiently, they do not compensate fully for the increasing nuclear charge. The effective nuclear attraction therefore rises and the electron cloud contracts.

Step 2: State one consequence A consequence is the very similar atomic radii of corresponding second- and third-row transition elements, such as zirconium and hafnium. The expected increase in size on passing from the 4d to the 5d series is largely offset by the intervening lanthanoid contraction. Thus Zr and Hf have almost equal radii and show closely similar chemical properties; their separation is consequently difficult.

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

Quick Tip to Solve: Connect poor 4f shielding to increasing effective nuclear attraction, then cite the Zr-Hf size similarity.

14. Describe the general trends in the following properties of the first series (3d) of the transition elements:

(i) Number of oxidation states exhibited

(ii) Formation of oxometal ions

[2 marks]

Solution:

Concept:

- Both 4s and 3d electrons can participate in bonding because their energies are relatively close, allowing variable oxidation states.
- Oxygen stabilises high metal oxidation states through strong metal-oxygen bonding, including multiple bonding.

Step 1: Trend in the number of oxidation states The number of oxidation states generally increases from the beginning of the 3d series towards the middle and then decreases towards the end. Manganese exhibits the largest range of common oxidation states, from +2 to +7. On the early side, increasing numbers of 3d and 4s electrons can take part in bonding. Beyond the middle, increasing

Quick Tip to Solve: Use Mn as the turning point; calculate the metal oxidation state in each oxometal ion using oxygen as -2.

nuclear attraction and electron pairing make the higher oxidation states less accessible. Thus the end members show fewer states; zinc is essentially restricted to +2.

Step 2: Trend in formation of oxometal ions Metals in high oxidation states tend to form oxometal ions because oxygen can stabilise the high positive oxidation state by strong metal-oxygen bonds. Familiar 3d examples are vanadium(V) in VO_2^+ , chromium(VI) in CrO_4^{2-} , and manganese(VII) in MnO_4^- . This tendency is characteristic of the early and middle members, which attain high oxidation states, and becomes less prominent towards the end as the highest accessible oxidation states decrease.

Step 3: Conclusion The number of oxidation states rises towards Mn and then falls. High oxidation states form oxometal ions, for example VO_2^+ , CrO_4^{2-} and MnO_4^- .

Quick Tip to Solve: Use Mn as the turning point; calculate the metal oxidation state in each oxometal ion using oxygen as -2.

15. How are the following conversions carried out?

(i) Propene to Propan-2-ol

(ii) Ethyl chloride to Ethanal

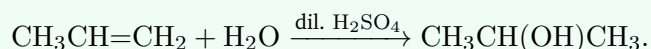
[2 marks]

Solution:

Concept:

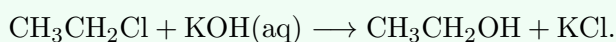
- Acid-catalysed hydration of an unsymmetrical alkene follows Markovnikov addition: the hydroxyl group attaches to the more substituted carbon.
- An alkyl chloride gives an alcohol with aqueous alkali; a primary alcohol gives an aldehyde by controlled oxidation or catalytic dehydrogenation.

Step 1: Convert propene to propan-2-ol Hydrate propene using water in the presence of dilute sulphuric acid:

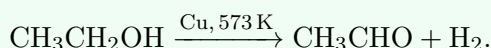


By Markovnikov addition, hydrogen attaches to the terminal carbon and the hydroxyl group to the middle carbon. The product is therefore propan-2-ol. The acid acts as a catalyst and is regenerated during the reaction.

Step 2: Convert ethyl chloride to ethanal First heat ethyl chloride with aqueous potassium hydroxide to substitute chlorine by hydroxyl:



Next pass ethanol vapour over heated copper at 573 K:



This dehydrogenation converts the primary alcohol to ethanal while preserving the two-carbon chain. Aqueous alkali is used in the first stage to favour substitution; alcoholic alkali would favour elimination to ethene.

Quick Tip to Solve: Choose aqueous KOH for chloroethane substitution, then heated Cu at 573 K to stop at the aldehyde.

Step 3: Conclusion Propene gives propan-2-ol by acid-catalysed hydration. Ethyl chloride gives ethanol with aqueous KOH, followed by dehydrogenation over Cu at 573 K to give ethanal.

Quick Tip to Solve: Choose aqueous KOH for chloroethane substitution, then heated Cu at 573 K to stop at the aldehyde.

16. Write the equations involved in the following reactions:

(i) Williamson ether synthesis

(ii) Kolbe's reaction

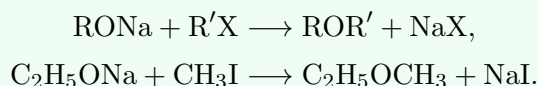
[2 marks]

Solution:

Concept:

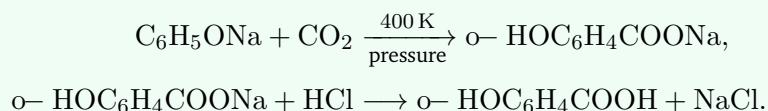
- Williamson synthesis forms an ether by the reaction of a sodium alkoxide, RONa , with an alkyl halide, $\text{R}'\text{X}$.
- Kolbe's reaction in this chapter is carboxylation of sodium phenoxide followed by acidification, giving salicylic acid.

Step 1: Williamson ether synthesis The alkoxide ion displaces the halide ion from a primary alkyl halide. The general equation and a specific example are



Here the example produces methoxyethane. A primary halide favours substitution.

Step 2: Kolbe's reaction Sodium phenoxide reacts with carbon dioxide under pressure at about 400 K. Acidification of sodium salicylate then gives the ortho-hydroxy acid:



The product is salicylic acid (2-hydroxybenzoic acid).

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

Quick Tip to Solve: For Kolbe's reaction in the phenols chapter, show both carbon dioxide addition and acidification.

17. 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, $-\text{CHO}$, and five hydroxyl groups.
- A free aldehyde should undergo characteristic carbonyl addition reactions; glucose shows exceptions that support its cyclic hemiacetal structure.

Step 1: List the missing aldehyde reactions Despite its aldehyde group in the open-chain formula, glucose does not give Schiff's test and does not form an addition product with sodium hydrogensulphite, NaHSO_3 . These are expected reactions of an ordinary free aldehyde group, so their absence is not explained by a permanently open-chain structure.

Step 2: Examine glucose pentaacetate Glucose pentaacetate does not react with hydroxylamine, NH_2OH , to form an oxime. If a free $-\text{CHO}$ group were present in this derivative, oxime formation would be expected. This shows that the carbonyl group is unavailable in glucose pentaacetate. The existence of distinct α - and β -forms of glucose is further evidence for a cyclic structure, although it is not itself a reaction.

Step 3: Conclusion The unexplained reactions are the negative Schiff test, absence of a sodium hydrogensulphite addition product, and failure of glucose pentaacetate to form an oxime with hydroxylamine.

Quick Tip to Solve: Remember that glucose itself forms an oxime; the hydroxylamine exception concerns glucose pentaacetate.

18. 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 required in small quantities for normal physiological functions; deficiencies produce characteristic disorders.
- A nucleoside contains a nitrogenous base and a pentose sugar; adding phosphate gives a nucleotide.

Step 1: (i) Explain the importance of vitamins A and C Vitamin A is essential for normal vision, particularly vision in dim light, and for maintenance of healthy epithelial tissues. Its deficiency can cause night blindness. Vitamin C is essential for collagen formation and maintenance of connective tissues, healthy gums and wound healing. Its deficiency causes scurvy, with bleeding gums and impaired wound healing.

Step 2: (ii) Distinguish a nucleoside from a nucleotide A nucleoside consists of a nitrogenous base linked to a pentose sugar by a glycosidic bond. A nucleotide consists of a nucleoside with a phosphate

Quick Tip to Solve: Use adenosine versus AMP to remember that phosphate is the additional component in a nucleotide.

group attached to the sugar through an ester linkage. Thus,

Nucleoside = base + pentose sugar,

Nucleotide = base + pentose sugar + phosphate.

For example, adenosine is a nucleoside and adenosine monophosphate (AMP) is a nucleotide.

Step 3: Conclusion Vitamin A supports vision; vitamin C supports collagen formation and healthy tissues. A nucleotide differs from a nucleoside by the presence of phosphate.

Quick Tip to Solve: Use adenosine versus AMP to remember that phosphate is the additional component in a nucleotide.

19. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3} . Use this information to calculate Avogadro's number. (Atomic mass of Fe = 55.84 g mol^{-1}) [3 marks]

Solution:

Concept:

- A body-centred cubic (bcc) unit cell contains $Z = 8(1/8) + 1 = 2$ atoms: one from the corners and one at the body centre.
- The density relation is $\rho = ZM/(N_A a^3)$, where M is molar mass, a is cell edge and N_A is Avogadro's constant.

Step 1: Convert the cell edge and calculate the cell volume The given edge is $a = 286.65 \text{ pm}$. Since $1 \text{ pm} = 10^{-10} \text{ cm}$,

$$a = 286.65 \times 10^{-10} \text{ cm} = 2.8665 \times 10^{-8} \text{ cm}.$$

For a cubic unit cell,

$$V = a^3 = (2.8665 \times 10^{-8})^3 = 2.35535 \times 10^{-23} \text{ cm}^3.$$

Converting the edge before cubing ensures that the volume unit agrees with the density unit.

Step 2: Relate the mass of a cell to its density The molar mass is $M = 55.84 \text{ g mol}^{-1}$, so the mass of one iron atom is M/N_A . There are two atoms in a bcc unit cell; hence the cell mass is $2M/N_A$. Therefore,

$$\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{2M}{N_A a^3}, \quad N_A = \frac{2M}{\rho a^3}.$$

The atoms at the corners are shared among eight cells, whereas the body-centre atom belongs wholly to this cell.

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

Step 3: Substitute the numerical values Using $\rho = 7.874 \text{ g cm}^{-3}$,

$$\begin{aligned} N_A &= \frac{2(55.84)}{7.874(2.8665 \times 10^{-8})^3} \\ &= \frac{111.68}{1.85460 \times 10^{-22}} \\ &\approx 6.0218 \times 10^{23} \text{ mol}^{-1}. \end{aligned}$$

The unit is mol^{-1} , since $(\text{g mol}^{-1})/[(\text{g cm}^{-3})(\text{cm}^3)] = \text{mol}^{-1}$.

Step 4: Conclusion The calculated Avogadro constant is $N_A \approx 6.022 \times 10^{23} \text{ mol}^{-1}$, corresponding to this many atoms per mole.

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

20. 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, $t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are initial and remaining reactant concentrations.
- The fraction remaining is one minus the fraction decomposed. Since k is in min^{-1} , the calculated time is in minutes.

Step 1: Identify the amount remaining Take an initial sample containing 100 arbitrary units of hydrogen peroxide. Its first-order decomposition obeys $[\text{H}_2\text{O}_2]_t/[\text{H}_2\text{O}_2]_0 = e^{-kt}$. Thus the initial sample size cancels from the time calculation. For 15% decomposition, 85 units remain; for 85% decomposition, 15 units remain. The percentage decomposed must therefore not be used as the remaining concentration.

Step 2: (i) Calculate the time for 15% decomposition Using $k = 1.06 \times 10^{-3} \text{ min}^{-1}$ and a remaining fraction of 0.85,

$$t_{15} = \frac{2.303}{1.06 \times 10^{-3}} \log_{10} \frac{100}{85} = \frac{0.16252}{1.06 \times 10^{-3}} \approx 153.3 \text{ min}.$$

Step 3: (ii) Calculate the time for 85% decomposition Here the remaining fraction is 0.15, so

$$t_{85} = \frac{2.303}{1.06 \times 10^{-3}} \log_{10} \frac{100}{15} = \frac{1.89712}{1.06 \times 10^{-3}} \approx 1789.7 \text{ min}.$$

The second interval is much longer because the instantaneous rate $k[\text{H}_2\text{O}_2]$ decreases as hydrogen peroxide is consumed. Both times are measured from the start of decomposition.

Quick Tip to Solve: Convert percentage decomposed into percentage remaining before inserting it into the first-order logarithm.

Step 4: Conclusion (i) $t \approx 153$ min. (ii) $t \approx 1.79 \times 10^3$ min (about 29.8 h).

Quick Tip to Solve: Convert percentage decomposed into percentage remaining before inserting it into the first-order logarithm.

21. 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 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-electrolyte, freezing-point depression is $\Delta T_f = K_f m$ and boiling-point elevation is $\Delta T_b = K_b m$, where m is the molality.
- Ethylene glycol is a nonvolatile molecular solute, so its van't Hoff factor is $i = 1$ in the usual colligative-property treatment.

Step 1: Find the freezing-point depression At normal atmospheric pressure, pure water freezes at 0.0°C . The positive depression of freezing point is therefore

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

A temperature difference has the same numerical value in kelvin and degrees Celsius. The negative freezing temperature does not make the depression negative.

Step 2: Determine the solution molality Using $K_f = 1.86 \text{ K kg mol}^{-1}$,

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

The given 5 kg of water would correspond to $8.0645 \times 5 = 40.32$ mol of glycol. Its amount need not be calculated separately because the freezing point already fixes the molality.

Step 3: Calculate the elevation and boiling point The same solution has the same molality in the two colligative-property equations. Thus

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

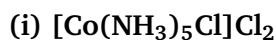
Equivalently, $\Delta T_b = (K_b/K_f)\Delta T_f$. Adding the elevation to the normal boiling point of pure water gives

$$T_b = 100.0 + 4.1935 = 104.1935^\circ\text{C}.$$

Step 4: Conclusion The boiling point of the solution is approximately 104.2°C at normal atmospheric pressure.

Quick Tip to Solve: Eliminate molality directly: multiply the freezing-point depression by K_b/K_f , then add 100°C .

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



[3 marks]

Solution:

Concept:

- Name ligands before the central metal, alphabetically, using prefixes such as penta-, hexa- and tetra- to indicate their numbers.
- Write the oxidation state of the metal in Roman numerals. For an anionic coordination entity, the metal name ends in -ate.
- NH_3 is neutral ammine; Cl^- and CN^- are the anionic ligands chlorido and cyanido, each carrying charge -1 .

Step 1: (i) Name the cobalt complex salt In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, the two chloride counter-ions give the complex cation a charge of $+2$. If the cobalt oxidation state is x , then $x + 5(0) - 1 = +2$, giving $x = +3$. The ligand names are placed in alphabetical order: ammine precedes chlorido, with penta- indicating five ammine ligands. Because the coordination entity is cationic, the metal retains the name cobalt. The counter-ion is named separately after the cation.

Step 2: (ii) Name the potassium complex salt In $\text{K}_3[\text{Fe}(\text{CN})_6]$, three potassium ions require the complex ion to carry charge -3 . Hence $x + 6(-1) = -3$, so iron is in oxidation state $+3$. Six cyanido ligands give the prefix hexacyanido. The anionic iron complex uses the metal name ferrate, and the potassium cation is named first.

Step 3: (iii) Name the nickel complex ion For $[\text{NiCl}_4]^{2-}$, charge balance gives $x + 4(-1) = -2$, so $x = +2$. Four chlorido ligands give tetrachlorido. Since the entire coordination entity is negatively charged, nickel becomes nickelate. No counter-ion is supplied in the formula, so the name refers to the complex ion itself.

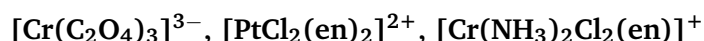
Step 4: Conclusion (i) Pentaamminechloridocobalt(III) chloride.

(ii) Potassium hexacyanidoferrate(III).

(iii) Tetrachloridonickelate(II) ion.

Quick Tip to Solve: First find the charge inside the square brackets; use it to calculate the metal oxidation state and decide whether the metal ends in -ate.

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



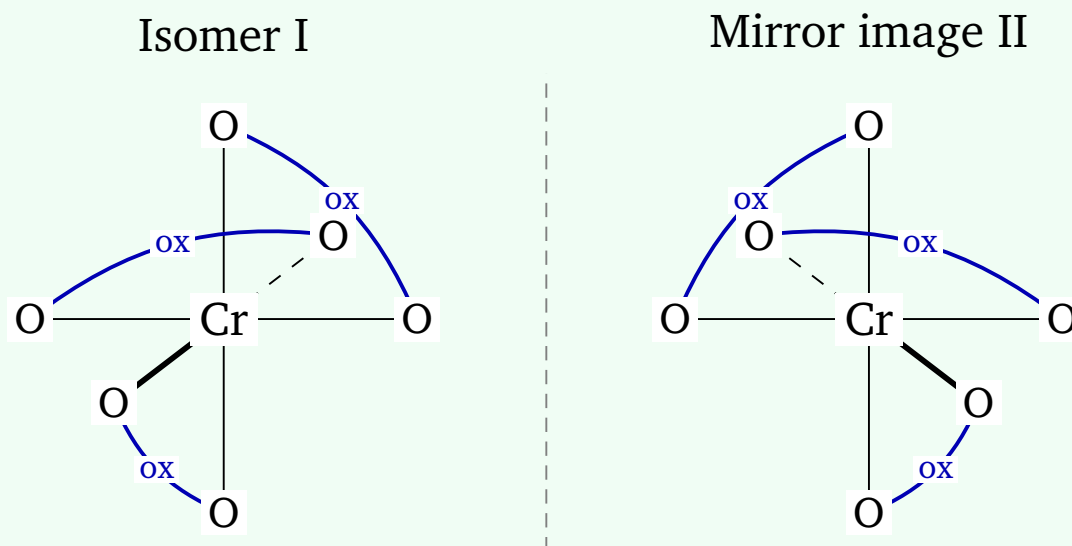
[3 marks]

Solution:

Concept:

- Optical isomers are non-superimposable mirror images of an octahedral complex.
- Each oxalate ion (ox) binds through two O atoms, and each ethane-1,2-diamine ligand (en) binds through two N atoms.
- In the projections below, the thick bond points towards the observer and the dashed bond points away; the other four bonds lie in the plane. Blue links join the two donors of one chelating ligand.

Step 1: Tris(oxalato)chromate(III) The six oxygen donors occupy the six octahedral positions around chromium. Join the O atoms in three adjacent pairs as shown; each blue ox link represents one bidentate $\text{C}_2\text{O}_4^{2-}$ ligand. Reflection reverses the handed arrangement of the three chelate rings. The two structures are the Δ and Λ forms and cannot be superimposed by rotating the whole complex.

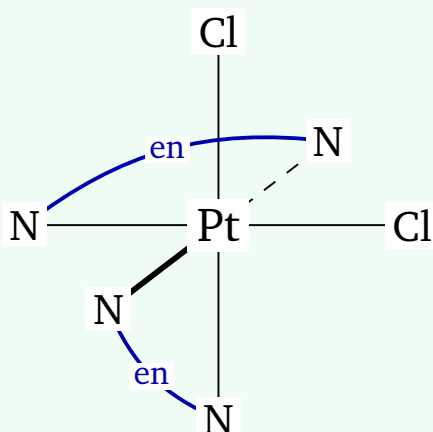


Optical pair of $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

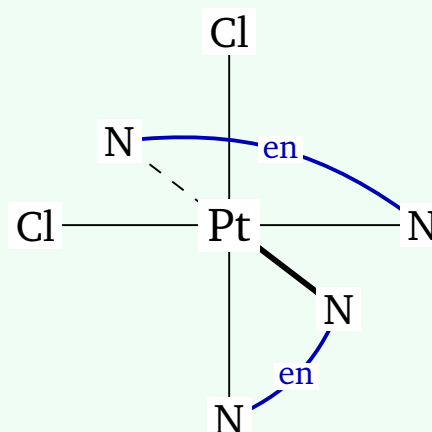
Step 2: Dichloridobis(ethane-1,2-diamine)platinum(IV) Choose the cis arrangement: the two chloride ligands occupy adjacent octahedral positions, and the other four sites are occupied by two en chelate rings. The two indicated pairs of nitrogen donors belong to separate en ligands. The displayed structure and its reflected image have opposite handedness, so $\text{cis-}[\text{PtCl}_2(\text{en})_2]^{2+}$ gives a pair of optical isomers. The trans arrangement has symmetry and does not form this optical pair.

Quick Tip to Solve: For the mixed-ligand complex, keep both identical monodentate pairs cis before taking its mirror image.

Isomer I



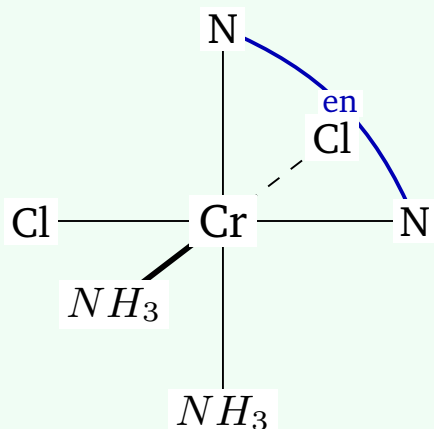
Mirror image II



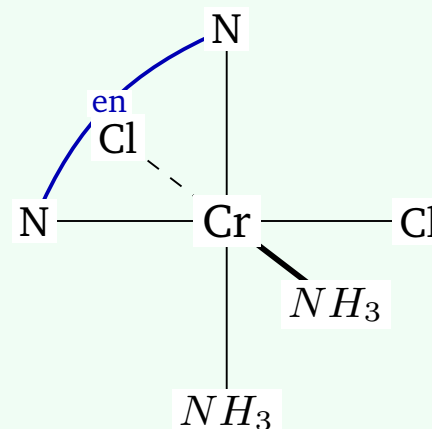
Optical pair of cis-[PtCl₂(en)₂]²⁺

Step 3: Diamminedichlorido(ethane-1,2-diamine)chromium(III) Place the en nitrogen donors at adjacent sites and choose the all-cis arrangement: the two ammonia ligands are mutually cis and the two chloride ligands are also mutually cis. The drawing explicitly locates all six donors. Its mirror image reverses their spatial ordering around chromium and cannot be brought into coincidence by rotation. These two all-cis structures therefore constitute the required optical pair.

Isomer I



Mirror image II



Optical pair of all-cis-[Cr(NH₃)₂Cl₂(en)]⁺

Step 4: Conclusion The three pairs drawn are non-superimposable mirror images: the tris(oxalato) pair, the cis-platinum pair and the all-cis mixed-ligand chromium pair.

Quick Tip to Solve: For the mixed-ligand complex, keep both identical monodentate pairs cis before taking its mirror image.

23. Define the following terms:

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

[3 marks]

Solution:

Concept:

- Adsorption is a surface phenomenon; the adsorbate accumulates on the adsorbent.
- Peptization forms a colloidal dispersion from a freshly prepared precipitate.
- A sol has a solid dispersed phase and a liquid dispersion medium.

Step 1: Define adsorption Adsorption is the accumulation of molecules of a gas or a dissolved substance at the surface of a solid or liquid, so that their concentration at the surface exceeds that in the bulk. The substance accumulated is the adsorbate and the material providing the surface is the adsorbent. For example, charcoal adsorbs gases on its surface. Adsorption must be distinguished from absorption, in which the substance enters the bulk of the material.

Step 2: Define peptization Peptization is the conversion of a freshly prepared 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. Preferential adsorption of an ion gives the particles a common charge and helps disperse them. For example, freshly precipitated ferric hydroxide forms a sol on adding a small amount of ferric chloride solution.

Step 3: Define sol A sol is a colloidal system in which solid particles form the dispersed phase and a liquid forms the dispersion medium. The solid is present as colloidal particles rather than as individual dissolved molecules. Examples include a gold sol in water and a ferric hydroxide sol.

Step 4: Conclusion Adsorption is surface accumulation; peptization converts a fresh 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 is dispersed in a liquid.

24. Account for the following:

- (i) Aniline does not give Friedel-Crafts reaction.
- (ii) Ethylamine is soluble in water whereas aniline is not.
- (iii) pK_b of methylamine is less than that of aniline.

[3 marks]

Solution:

Concept:

- The nitrogen lone pair determines the Lewis basicity and proton-accepting ability of an amine.
- Hydrogen bonding favours dissolution in water, whereas a large hydrocarbon group opposes it.
- For a base, $pK_b = -\log_{10} K_b$; a stronger base has a larger K_b and a smaller pK_b .

Step 1: Explain the failure of Friedel-Crafts reaction Aniline has a lone pair on nitrogen that coordinates strongly with the Lewis-acid catalyst, anhydrous $AlCl_3$, forming an aniline-aluminium

Quick Tip to Solve: Compare lone-pair availability first, then reverse the basic-strength order when writing pK_b .

chloride complex. Coordination gives nitrogen a positive character and makes the attached group strongly electron withdrawing. Consequently the benzene ring is deactivated towards the electrophilic substitution required for Friedel–Crafts alkylation or acylation. Hence aniline does not give the usual Friedel–Crafts reaction under these conditions.

Step 2: Compare solubility in water Ethylamine forms hydrogen bonds with water through its amino group. Its ethyl group is small, so favourable amine–water interactions are sufficient to give high solubility. Aniline can also form hydrogen bonds through its amino group, but its large hydrophobic phenyl group considerably reduces its affinity for water. Thus aniline is only sparingly soluble in water, which accounts for the stated contrast; the difference does not mean that aniline cannot hydrogen bond.

Step 3: Compare basic strength and pK_b In methylamine, the methyl group shows the electron-releasing $+I$ effect, increasing electron density at nitrogen and favouring acceptance of a proton. In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance and is less available for protonation. Therefore methylamine is a stronger base than aniline:

$$K_b(\text{CH}_3\text{NH}_2) > K_b(\text{C}_6\text{H}_5\text{NH}_2).$$

Taking the negative logarithm reverses the inequality, giving

$$pK_b(\text{CH}_3\text{NH}_2) < pK_b(\text{C}_6\text{H}_5\text{NH}_2).$$

Step 4: Conclusion Aniline complexes with AlCl_3 and its ring becomes deactivated; its phenyl group limits water solubility; resonance makes it less basic than methylamine and hence gives it a higher pK_b .

Quick Tip to Solve: Compare lone-pair availability first, then reverse the basic-strength order when writing pK_b .

25. (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

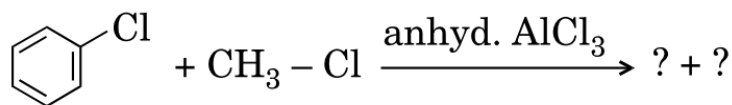
(ii) $(CH_3)_3CCl$ or CH_3Cl

(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:

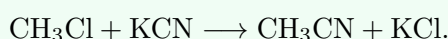
Concept:

- An S_N2 reaction is a single-step nucleophilic substitution involving backside attack. Its rate depends on accessibility of the carbon atom and the ability of the leaving group to depart.
- With other factors unchanged, iodide is a better leaving group than bromide. Steric hindrance increases from methyl to tertiary substrates, strongly suppressing S_N2 attack.
- Ionic KCN supplies cyanide ions, which predominantly attack through carbon to form nitriles. In electrophilic aromatic substitution, chlorine is deactivating but ortho- and para-directing.

Step 1: (a)(i) Compare the leaving groups Both substrates are methyl halides, so their steric environments are the same. The $C-I$ bond is weaker than the $C-Br$ bond, and I^- leaves more readily than Br^- . Hence CH_3I reacts faster with OH^- by the S_N2 mechanism.

Step 2: (a)(ii) Compare steric hindrance In CH_3Cl , the reacting carbon is readily accessible to backside attack. In $(CH_3)_3CCl$, three methyl groups obstruct the incoming nucleophile. Therefore methyl chloride reacts faster by S_N2 ; tertiary alkyl halides are highly unfavourable for this mechanism.

Step 3: (b)(i) Reaction with potassium cyanide Cyanide replaces chlorine through its carbon end, increasing the carbon chain by one carbon atom:



The organic product is ethanenitrile (acetonitrile), rather than methyl isocyanide.

Step 4: (b)(ii) Methylation of chlorobenzene With methyl chloride and anhydrous $AlCl_3$, methyl substitution occurs at the ortho and para positions relative to chlorine. The two organic products are *o*-chlorotoluene (1-chloro-2-methylbenzene) and *p*-chlorotoluene (1-chloro-4-methylbenzene). The para product is favoured sterically because its methyl group is farther from chlorine. HCl is the accompanying by-product.

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: For an S_N2 comparison, first compare crowding at carbon; when crowding is equal, compare leaving-group ability.

26. What are biodegradable and non-biodegradable detergents? Give one example of each. [3 marks]

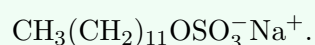
Solution:

Concept:

- Detergents are cleansing agents with a hydrophobic hydrocarbon portion and a hydrophilic ionic or polar head. Biodegradability describes their breakdown by microorganisms after use.
- The structure of the hydrocarbon chain controls how readily microbes attack it: straight chains are generally more biodegradable than highly branched chains.

Step 1: Biodegradable detergents: meaning Biodegradable detergents are detergents that microorganisms, such as bacteria, can decompose into simpler substances. Their hydrocarbon chains are generally unbranched, allowing microbial enzymes to attack and progressively break down the chain. Consequently, they are more readily removed by biological wastewater treatment and do not persist as long in water.

Step 2: Example of a biodegradable detergent Sodium n-dodecyl sulphate, also called sodium lauryl sulphate, is an example. Its formula is



Its straight, twelve-carbon chain can undergo microbial degradation; the sulphate-containing head provides the hydrophilic part needed for cleansing.

Step 3: Non-biodegradable detergents: meaning and example Non-biodegradable detergents resist decomposition by microorganisms under ordinary biological treatment conditions. They commonly contain highly branched hydrocarbon chains, whose branching hinders microbial attack. They therefore persist in wastewater and may cause prolonged foaming and water pollution. An example is sodium branched-chain dodecylbenzenesulphonate, the branched alkylbenzene sulphonate detergent. The word branched is essential here, since linear alkylbenzene sulphonates are biodegradable.

Step 4: Conclusion Biodegradable: readily decomposed by microorganisms; example, sodium n-dodecyl sulphate. Non-biodegradable: resistant to microbial decomposition; example, sodium branched-chain dodecylbenzenesulphonate.

Quick Tip to Solve: Attach the chain structure to the example: straight-chain detergents biodegrade more readily, whereas highly branched chains resist microbial attack.

27. Write the names of monomers used for getting the following polymers:

(i) Teflon

(ii) Bakelite

(iii) Neoprene

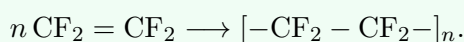
[3 marks]

Solution:

Concept:

- A monomer is a small molecule that joins repeatedly to form a polymer. Addition polymerisation uses unsaturated monomers; condensation polymerisation joins suitable functional groups with loss of small molecules.
- Teflon and neoprene arise from unsaturated addition monomers, whereas Bakelite is a cross-linked phenol-formaldehyde condensation polymer.

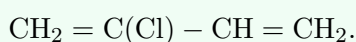
Step 1: (i) Monomer of Teflon The monomer is tetrafluoroethene, also called tetrafluoroethylene, $\text{CF}_2 = \text{CF}_2$. Opening its carbon-carbon double bond links many monomer molecules into polytetrafluoroethene (PTFE), known as Teflon:



The fluorine substituents remain attached to the carbon backbone; ethene itself would give polyethylene, not Teflon.

Step 2: (ii) Monomers of Bakelite Bakelite requires two monomers: phenol, $\text{C}_6\text{H}_5\text{OH}$, and methanal (formaldehyde), HCHO . These undergo condensation. Formaldehyde introduces links between phenol units, and further reaction produces the rigid, cross-linked phenol-formaldehyde network called Bakelite. Both monomers must be named because neither phenol nor formaldehyde alone specifies this polymer.

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



Addition polymerisation of this conjugated diene produces polychloroprene, commonly called neoprene. The chlorine substituent at carbon 2 distinguishes chloroprene from buta-1,3-diene, the monomer associated with polybutadiene.

Step 4: Conclusion (i) Teflon: tetrafluoroethene. (ii) Bakelite: phenol and methanal (formaldehyde). (iii) Neoprene: chloroprene (2-chlorobuta-1,3-diene).

Quick Tip to Solve: Remember the identifying groups: Teflon has fluorine, Bakelite needs phenol plus formaldehyde, and neoprene comes from the chlorine-containing diene.

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:

- Conductivity κ is the conductance of a solution contained between electrodes of unit area separated by unit distance. It equals the reciprocal of resistivity; its SI unit is S m⁻¹.
- Molar conductivity Λ_m is the conductance of the volume of solution containing one mole of electrolyte, placed between electrodes a unit distance apart. For concentration c in mol L⁻¹, $\Lambda_m = 1000\kappa/c$ when κ is in S cm⁻¹.
- The cell constant is l/A , where l is electrode separation and A is electrode area. Conductivity is $\kappa = (l/A)/R$, where R is the measured resistance.

Step 1: (a) Explain the effect of temperature Both conductivity and molar conductivity of an electrolyte solution generally increase with increase in temperature. The viscosity of the solvent decreases, so ions experience less resistance to movement and their mobilities increase. In weak electrolytes, increased ionisation also contributes to the increase. Thus the electrical conductance of an electrolyte solution rises as temperature rises.

Step 2: (b)(i) Calculate the specific conductance Specific conductance is another name for conductivity. The conductance of the cell is

$$G = \frac{1}{R} = \frac{1}{100} = 0.0100 \text{ S.}$$

Multiplying by the given cell constant gives

$$\kappa = G \frac{l}{A} = 0.0100 \times 1.25 = 0.0125 \text{ S cm}^{-1}.$$

In SI units this is 1.25 S m⁻¹.

Step 3: (b)(ii) Express the molar conductance If the concentration of this solution is c mol L⁻¹, then

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

The printed question supplies neither the molar concentration nor the mass of KCl and volume of solution. The molar mass 74.5 g mol⁻¹ alone cannot determine concentration: it converts a known mass to moles, but no mass is given. Therefore a numerical molar conductance cannot be determined from the supplied data.

Step 4: Conclusion Both conductivity and molar conductivity increase with temperature. The specific conductance is 0.0125 S cm⁻¹. The molar conductance is 12.5/ c S cm² mol⁻¹, with c in mol L⁻¹; a numerical value requires the missing concentration.

Quick Tip to Solve: First multiply reciprocal resistance by the cell constant; use the factor 1000 in molar conductivity only when concentration is in mol per litre and conductivity is in S per centimetre.

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.

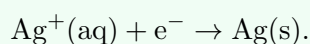
(b) Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C . The Gibbs energy change for the decomposition reaction $\frac{2}{3}\text{Al}_2\text{O}_3 \rightarrow \frac{4}{3}\text{Al} + \text{O}_2$ is 960 kJ. ($F = 96500 \text{ C mol}^{-1}$) [5 marks]

Solution:

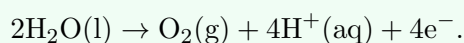
Concept:

- Electrolysis uses electrical energy to drive a non-spontaneous reaction. Reduction occurs at the cathode and oxidation at the anode. Platinum is inert, so it does not supply metal ions or dissolve as an active anode.
- In aqueous solutions, water or its ions can compete with dissolved ions for discharge. Nitrate and sulphate ions remain in solution under the conditions considered here.
- The minimum reversible electrical work equals the positive Gibbs energy of decomposition: $\Delta G = nFE_{\min}$, where n is the number of moles of electrons transferred for the reaction as written and F is the Faraday constant.

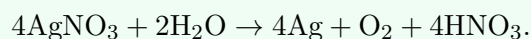
Step 1: (a)(i) Electrolysis of aqueous silver nitrate At the cathode, silver ions are preferentially reduced and metallic silver is deposited:



At the inert platinum anode, water is oxidised and oxygen gas evolves:

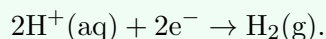


Nitrate ions are not discharged. Combining the half-reactions gives

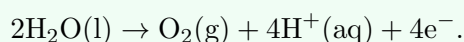


Thus silver is the cathode product and oxygen is the anode product; the solution becomes acidic.

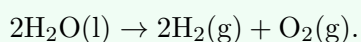
Step 2: (a)(ii) Electrolysis of aqueous sulphuric acid Hydrogen ions are reduced at the cathode:



Water is oxidised at the platinum anode:



Doubling the cathode equation and adding yields the net reaction



Hence hydrogen evolves at the cathode and oxygen at the anode, with volumes in the ratio 2 : 1 under

Quick Tip to Solve: Count electrons using the fractional reaction exactly as printed: four-thirds mole of aluminium needs four moles of electrons, so divide 960000 J by 4F.

the same conditions.

Step 3: (b) Count electrons and calculate the minimum potential The reaction is $\frac{2}{3}\text{Al}_2\text{O}_3 \rightarrow \frac{4}{3}\text{Al} + \text{O}_2$. Each aluminium atom changes from oxidation state +3 to zero and therefore gains three electrons. Thus the reaction as written transfers

$$n = \frac{4}{3} \times 3 = 4$$

moles of electrons. Equivalently, forming one mole of O_2 from oxide ions releases four moles of electrons. Convert the given Gibbs energy to joules and use its value at the stated temperature:

$$E_{\min} = \frac{\Delta G}{nF} = \frac{960 \times 10^3}{4 \times 96500} = 2.487 \text{ V} \simeq 2.49 \text{ V}.$$

This is the magnitude of the applied potential required in the reversible limit. Practical electrolysis requires a greater potential because of resistance and electrode overpotentials.

Step 4: Conclusion Aqueous AgNO_3 gives Ag at the cathode and O_2 at the platinum anode. Aqueous H_2SO_4 gives H_2 at the cathode and O_2 at the anode. The minimum potential difference for the stated alumina decomposition is 2.49 V.

Quick Tip to Solve: Count electrons using the fractional reaction exactly as printed: four-thirds mole of aluminium needs four moles of electrons, so divide 960000 J by 4F.

29(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

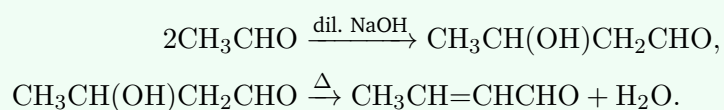
[5 marks]

Solution:

Concept:

- Carbonyl compounds containing an α -hydrogen undergo aldol condensation. Aldehydes lacking an α -hydrogen undergo disproportionation with concentrated alkali (Cannizzaro reaction).
- The iodoform test detects the $\text{CH}_3\text{CO}-$ group (and ethanal): iodine and aqueous sodium hydroxide give yellow CHI_3 . Tollens' reagent oxidises aldehydes, producing a silver mirror; ordinary ketones do not react.

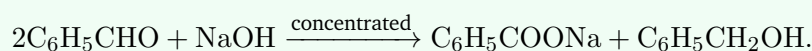
Step 1: (a)(i) Aldol condensation In the presence of dilute alkali, two molecules of an aldehyde or ketone having at least one α -hydrogen combine to form a β -hydroxy aldehyde (aldol) or β -hydroxy ketone (ketol). On heating, loss of water gives an α, β -unsaturated carbonyl compound. For example,



Quick Tip to Solve: First check for an α -hydrogen to choose aldol or Cannizzaro; for the tests, identify the aldehyde group and the methyl-carbonyl group separately.

The initial product is 3-hydroxybutanal; dehydration forms but-2-enal.

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



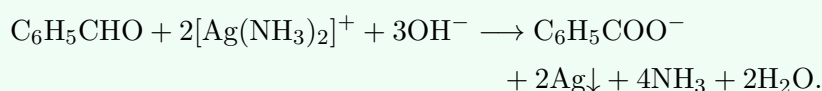
The products are sodium benzoate and benzyl alcohol; the acid itself is obtained only after acidification.

Step 3: (b)(i) Ethanal and propanal Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform; propanal gives no yellow precipitate. Ethanal has the required $\text{CH}_3\text{CO}-$ unit, whereas propanal does not:



Tollens' reagent would not distinguish this pair because both compounds are aldehydes.

Step 4: (b)(ii) Benzaldehyde and acetophenone Warm each sample gently with freshly prepared Tollens' reagent. Benzaldehyde produces a silver mirror, whereas acetophenone gives no silver mirror. Benzaldehyde is oxidised to benzoate:



Alternatively, acetophenone gives the yellow iodoform precipitate because it is a methyl ketone; benzaldehyde does not.

Step 5: (b)(iii) Examine the printed compound names Propan-2-one is CH_3COCH_3 and gives a positive iodoform test. However, the printed name "propan-3-one" does not denote a valid ketone: in a three-carbon chain the ketonic carbonyl carbon must be the middle carbon, numbered 2. A terminal carbonyl would give the aldehyde propanal, not a propanone. Therefore no valid chemical test can distinguish propan-2-one from a distinct compound called propan-3-one. If the terminal carbonyl structure $\text{CH}_3\text{CH}_2\text{CHO}$ is considered, its correct name is propanal; Tollens' reagent gives a silver mirror with that aldehyde and no mirror with propan-2-one.

Step 6: Conclusion Aldol condensation forms a β -hydroxy carbonyl compound followed by dehydration; Cannizzaro reaction forms an alcohol and a carboxylate. Ethanal is distinguished from propanal by a positive iodoform test, and benzaldehyde from acetophenone by a positive Tollens' test. The name propan-3-one in (b)(iii) is chemically invalid, so that pair cannot be distinguished as named.

Quick Tip to Solve: First check for an α -hydrogen to choose aldol or Cannizzaro; for the tests, identify the aldehyde group and the methyl-carbonyl group separately.

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

(i) 4-Chloropentan-2-one

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

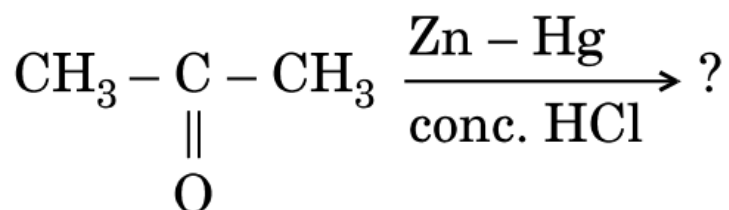
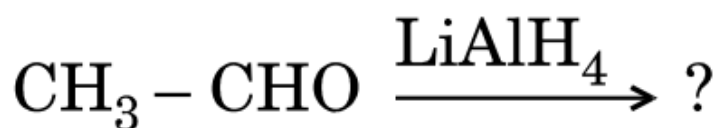
(b) Write the product(s) in the following:

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

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

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

[5 marks]



Solution:

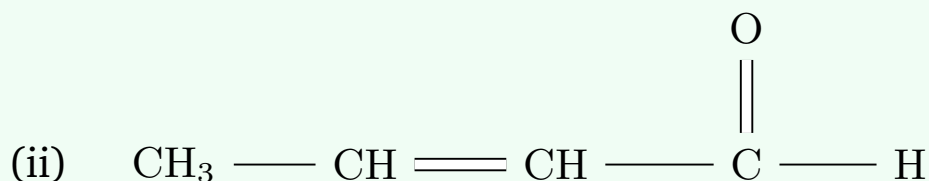
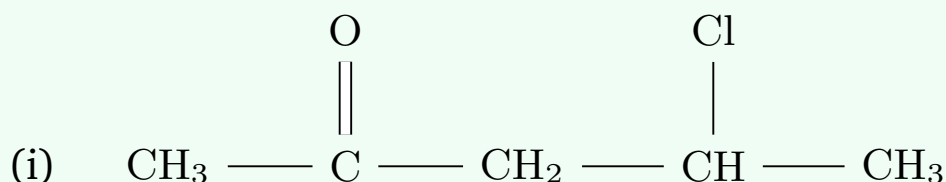
Concept:

- In a ketone, the carbonyl carbon is included in the parent chain and receives the lowest possible locant. In an aldehyde, the carbon of the terminal --CHO group is carbon 1.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by bromine using Br_2 and phosphorus.
- LiAlH_4 reduces aldehydes to primary alcohols after hydrolysis, whereas Zn(Hg)/conc. HCl converts a carbonyl group into a methylene group (Clemmensen reduction).

Step 1: (a)(i) Build the substituted ketone Take a five-carbon chain, place the ketone group at carbon 2, and attach chlorine to carbon 4. The resulting structure is $\text{CH}_3\text{--C(=O)--CH}_2\text{--CH(Cl)--CH}_3$. Counting from the left gives the carbonyl locant 2 and the chlorine locant 4. Reversing the numbering would put the ketone at carbon 4, so that direction is unsuitable.

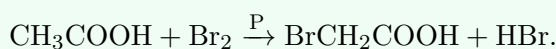
Step 2: (a)(ii) Build the unsaturated aldehyde The aldehyde carbon is carbon 1 of the four-carbon chain. Put the double bond between carbons 2 and 3 to obtain OHC--CH=CH--CH_3 , equivalently $\text{CH}_3\text{--CH=CH--CHO}$. The terminal --CHO group retains its hydrogen; the double bond is between the two adjacent carbon atoms, not between carbon and oxygen alone.

Quick Tip to Solve: Identify the reagent first: Br_2/P changes the alpha carbon, LiAlH_4 gives an alcohol, and Zn(Hg)/HCl removes carbonyl oxygen.



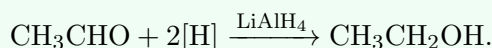
Structures for part (a): carbonyl and substituent positions shown explicitly.

Step 3: (b)(i) Brominate ethanoic acid at the alpha carbon Ethanoic acid contains alpha hydrogens on its methyl group. Bromine in the presence of phosphorus gives the HVZ reaction, replacing one of these hydrogens by bromine:



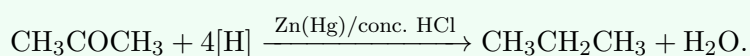
The organic product is 2-bromoethanoic acid (bromoacetic acid). The carboxyl group remains intact; this reagent does not reduce it or replace its hydroxyl group in the final acid product.

Step 4: (b)(ii) Reduce ethanal to the primary alcohol Lithium aluminium hydride supplies hydride to the aldehyde carbonyl; subsequent hydrolysis gives the alcohol:



The organic product is ethanol. Its carbon skeleton still has two carbon atoms, and the former aldehyde carbon becomes the $-\text{CH}_2\text{OH}$ carbon. Complete removal of oxygen is not the reaction of this reagent.

Step 5: (b)(iii) Apply Clemmensen reduction to propanone Zinc amalgam with concentrated hydrochloric acid reduces the ketonic $>\text{C}=\text{O}$ group to $-\text{CH}_2-$:

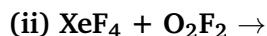


Thus propanone gives propane. Both methyl groups remain attached to the central carbon, so the product retains all three carbons. The product is an alkane, rather than propan-2-ol.

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

Quick Tip to Solve: Identify the reagent first: Br_2/P changes the alpha carbon, LiAlH_4 gives an alcohol, and Zn(Hg)/HCl removes carbonyl oxygen.

30(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.

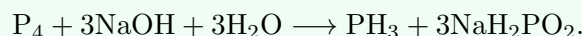
[5 marks]

Solution:

Concept:

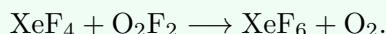
- Disproportionation is simultaneous oxidation and reduction of the same element. Oxidising agents accept electrons and are themselves reduced.
- For hydrides of elements in the same period, increasing electronegativity favours release of hydrogen as H^+ . A species with unpaired electrons is paramagnetic.

Step 1: Part (a)(i): Phosphorus with alkali White phosphorus reacts with aqueous sodium hydroxide to give phosphine and sodium hypophosphite. The balanced equation is



Phosphorus changes from oxidation state zero to -3 in phosphine and $+1$ in hypophosphite. Thus one phosphorus atom is reduced while the other three are oxidised; the electron changes balance.

Step 2: Part (a)(ii): Fluorination of xenon tetrafluoride Dioxygen difluoride converts xenon tetrafluoride into xenon hexafluoride, with liberation of oxygen:



Both sides contain one xenon atom, six fluorine atoms and two oxygen atoms. Xenon is oxidised from $+4$ to $+6$.

Step 3: Part (b)(i): Acidic strength Across the third period, electronegativity increases from phosphorus through sulphur to chlorine. Consequently the hydrogen–element bond becomes increasingly polar towards the element and release of H^+ becomes more favourable. The conjugate base is also better able to accommodate negative charge. Hence the acidic strength increases in the printed order $\text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$.

Step 4: Part (b)(ii): Oxidising power of chlorine oxoacids The higher oxoacids and their conjugate anions are increasingly stabilised by delocalisation of electrons over more oxygen atoms. Their resistance to reduction therefore increases in this series. Hypochlorous acid is readily reduced to chloride, whereas perchloric acid is comparatively resistant to reduction under ordinary conditions. Thus the stated oxidising-power order is $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$; oxidation number alone does not determine oxidising strength.

Step 5: Part (b)(iii): Paramagnetism of sulphur vapour At high temperature sulphur vapour contains S_2 molecules. Like O_2 , an S_2 molecule has two unpaired electrons in its degenerate antibonding π^* molecular orbitals. These electrons produce a magnetic moment, so the vapour is attracted by a

Quick Tip to Solve: Balance phosphorus by making one PH_3 and three hypophosphites; for sulphur vapour, identify S_2 before counting unpaired electrons.

magnetic field and exhibits paramagnetic behaviour.

Step 6: Conclusion The products are $\text{PH}_3 + 3\text{NaH}_2\text{PO}_2$ and $\text{XeF}_6 + \text{O}_2$, with the coefficients shown above. Increasing electronegativity explains hydride acidity, stabilisation explains the oxoacid oxidising-power order, and unpaired electrons in S_2 explain sulphur-vapour paramagnetism.

Quick Tip to Solve: Balance phosphorus by making one PH_3 and three hypophosphites; for sulphur vapour, identify S_2 before counting unpaired electrons.

OR

30(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 minimises repulsions between electron domains; a multiple bond counts as one domain. Lone pairs repel more strongly than bond pairs.
- Boiling points depend on intermolecular forces. Electron gain enthalpy is the enthalpy change for adding an electron to an isolated gaseous atom; its negative magnitude measures energy released.

Step 1: Part (a)(i): Structure of dinitrogen trioxide The molecular skeleton is $\text{ON}-\text{NO}_2$, with a nitrogen–nitrogen bond. A Lewis contributor is $\text{O}=\text{N}-\text{N}^+(\text{=O})-\text{O}^-$, with resonance interchanging the two oxygens on the nitro nitrogen. The nitroso nitrogen has two bond domains and one lone pair: its electron-domain arrangement is approximately trigonal planar and its local molecular shape is bent. The nitro nitrogen has three bond domains and no lone pair, so its environment is trigonal planar. The probable overall structure of N_2O_3 is planar.

Step 2: Part (a)(ii): Structure of bromine trifluoride Bromine has seven valence electrons. Forming three $\text{Br}-\text{F}$ bonds leaves two lone pairs, giving five domains, or AX_3E_2 . The electron-domain arrangement is trigonal bipyramidal. Both lone pairs occupy equatorial positions because these positions have fewer 90° interactions. The fluorine atoms occupy two axial positions and one equatorial position, giving a T-shaped molecule, with angles close to 90° and 180° .

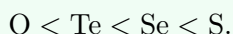
Step 3: Part (b)(i): Increasing boiling points For PH_3 , AsH_3 and SbH_3 , increasing molecular size and polarisability strengthen London dispersion forces. Ammonia has intermolecular hydrogen bonding, so its boiling point is higher than those of phosphine and arsine. Stibine is sufficiently large that its

Quick Tip to Solve: Check three exceptions before ordering: NH_3 hydrogen bonding, compact oxygen orbitals and $\text{F}-\text{F}$ lone-pair repulsion.

boiling point exceeds that of ammonia. Therefore



Step 4: Part (b)(ii): Increasing negative electron gain enthalpy magnitude On the scale of energy released on accepting an electron, the increasing order is



Oxygen has a compact $2p$ subshell, where the incoming electron experiences strong electron–electron repulsion, so electron addition releases less energy than for sulphur. From sulphur to tellurium, increasing size reduces attraction for the added electron. Equivalently, for signed enthalpy values (most negative first), $\Delta_{eg}H(\text{S}) < \Delta_{eg}H(\text{Se}) < \Delta_{eg}H(\text{Te}) < \Delta_{eg}H(\text{O})$.

Step 5: Part (b)(iii): Increasing bond dissociation enthalpy The increasing order is



From chlorine to iodine, increasing bond length reduces orbital overlap and weakens the bond. Fluorine is anomalous: its very short F–F bond brings the three lone pairs on each atom close together, causing strong lone-pair repulsion. Its bond is consequently weaker than both Cl–Cl and Br–Br, though stronger than I–I.

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

Quick Tip to Solve: Check three exceptions before ordering: NH_3 hydrogen bonding, compact oxygen orbitals and F–F lone-pair repulsion.