

# CBSE Class 12 Chemistry Question Paper 2011 with Solution PDF-Set 56/1 (Delhi)



## 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) Marks for each question are indicated against it.
- (iii) Question numbers **1 to 8** are very short-answer questions and carry **1** mark each.
- (iv) Question numbers **9 to 18** are short-answer questions and carry **2** marks each.
- (v) Question numbers **19 to 27** are also short-answer questions and carry **3** marks each.
- (vi) Question numbers **28 to 30** are long-answer questions and carry **5** marks each.
- (vii) Use Log Tables, if necessary. Use of calculators is not allowed.

1. 'Crystalline solids are anisotropic in nature.' What does this statement mean?

[1 mark]

**Solution:**

**Concept:**

- Anisotropy means dependence of a physical property on the direction in which it is measured.
- A crystalline solid has an ordered arrangement of constituent particles; the arrangement can differ along different directions.

**Step 1: Relate the property to crystal direction** Consider measuring a physical property along two different directions within the same crystal. Since particle spacing and arrangement along these directions need not be identical, the measured values need not be identical either.

**Step 2: Give the meaning with examples** Properties such as electrical resistance, refractive index or thermal expansion may therefore have different values in different directions. The statement concerns directional measurements on a crystal; it does not mean that the crystal lacks order.

**Step 3: Conclusion** Crystalline solids are anisotropic because their physical properties have different values when measured along different directions in the same crystal.

**Quick Tip to Solve:** Link anisotropy to direction: mention one property and compare its value along two crystal directions.

2. Express the relation between conductivity and molar conductivity of a solution held in a cell.

[1 mark]

**Solution:**

**Concept:**

- Conductivity  $\kappa$  describes the conducting ability per unit geometry of a solution.
- Molar conductivity  $\Lambda_m$  is the conductivity contribution corresponding to one mole of electrolyte:  $\Lambda_m = \kappa/c$  when consistent SI units are used.

**Step 1: Use the volume containing one mole** If the concentration is  $C \text{ mol L}^{-1}$ , one mole is present in  $1/C$  litres, or  $1000/C \text{ cm}^3$ . Molar conductivity equals conductivity multiplied by this volume.

**Step 2: State the relation and units** Thus  $\Lambda_m = 1000\kappa/C$ , with  $\kappa$  in  $\text{S cm}^{-1}$ ,  $C$  in  $\text{mol L}^{-1}$ , and  $\Lambda_m$  in  $\text{S cm}^2 \text{ mol}^{-1}$ . In SI units,  $\Lambda_m = \kappa/c$ , where  $c$  is in  $\text{mol m}^{-3}$ .

**Step 3: Conclusion**

$$\Lambda_m = \frac{1000\kappa}{C}$$

Here  $C$  is the molarity in  $\text{mol L}^{-1}$  and  $\kappa$  is in  $\text{S cm}^{-1}$ .

**Quick Tip to Solve:** Check concentration units before using the factor 1000; it converts litres into cubic centimetres.

### 3. Define 'electrophoresis'.

[1 mark]

#### Solution:

##### Concept:

- Colloidal particles generally carry an electric charge and respond to an applied electric field.
- Oppositely charged electrodes attract the charged colloidal particles.

**Step 1: Apply an electric field** When a potential difference is applied across a colloidal sol, its dispersed particles experience an electrical force because they carry a net charge. They consequently move through the dispersion medium.

**Step 2: Identify the direction of migration** Positively charged particles migrate towards the cathode, while negatively charged particles migrate towards the anode. This is the motion of the dispersed particles under the field; the direction reveals the sign of their charge.

**Step 3: Conclusion** Electrophoresis is the movement of charged colloidal particles towards the oppositely charged electrode under an applied electric field.

**Quick Tip to Solve:** In the definition, include both charged colloidal particles and the applied electric field.

### 4. Draw the structure of $\text{XeF}_2$ molecule.

[1 mark]

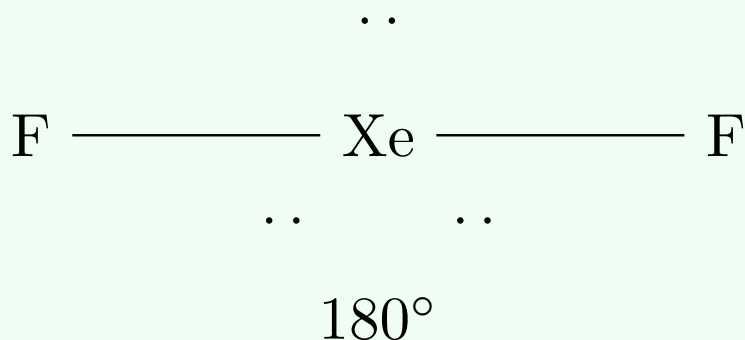
#### Solution:

##### Concept:

- In  $\text{XeF}_2$ , xenon has two bond pairs and three lone pairs: the VSEPR type is  $\text{AX}_2\text{E}_3$ .
- Five electron pairs have a trigonal-bipyramidal arrangement; lone pairs preferentially occupy equatorial positions.

**Step 1: Count the electron pairs around xenon** Xenon has eight valence electrons. Formation of two single Xe-F bonds leaves three lone pairs on the central xenon atom, giving a total of five electron-pair regions.

**Step 2: Place the fluorine atoms** The three lone pairs occupy the equatorial sites to reduce strong lone-pair repulsions. The two fluorine atoms occupy the remaining axial sites, on opposite sides of xenon. Thus the electron-pair arrangement and the molecular shape must be distinguished.



*Linear structure of xenon difluoride; the three lone pairs on Xe occupy equatorial sites.*

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

**Quick Tip to Solve:** For  $\text{XeF}_2$ , remove the three equatorial lone pairs mentally: the two axial bonds form a straight line.

**5. Write the IUPAC name of the following compound:**



[1 mark]

**Solution:**

**Concept:**

- Choose the longest continuous carbon chain as the parent alkane, including the carbon bearing the halogen.
- Number the parent chain to obtain the lowest set of locants; list substituent prefixes alphabetically.

**Step 1: Identify the parent chain** The structure is  $(\text{CH}_3)_3\text{CCH}_2\text{Br}$ . The longest continuous chain has three carbon atoms, so the parent is propane. Choose the chain  $\text{BrCH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_3$ ; two methyl groups remain attached to the middle carbon.

**Step 2: Number and assemble the name** Number from the  $\text{CH}_2\text{Br}$  end. Bromine then has locant 1 and the two methyl groups have locants 2,2. Numbering from the other end would give bromine locant 3. Alphabetically, bromo precedes methyl; the multiplicative prefix di is ignored when ordering prefixes.

**Step 3: Conclusion** The IUPAC name is 1-bromo-2,2-dimethylpropane.

**Quick Tip to Solve:** Do not count all five carbon atoms as a straight chain: the longest continuous chain here contains three.

6. Draw the structure of 3-methylbutanal.

[1 mark]

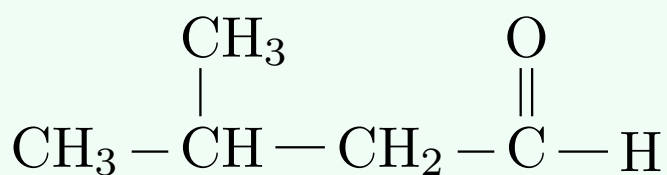
**Solution:**

**Concept:**

- The suffix -al represents an aldehyde group,  $-\text{CHO}$ , whose carbon is numbered 1.
- The parent name butanal requires four carbon atoms in the main chain, including the aldehyde carbon.

**Step 1: Number the parent chain** Start numbering at the aldehyde carbon. The four-carbon chain is  $\text{CHO}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ; the terminal CHO group must remain part of the parent chain.

**Step 2: Attach the methyl group** Replace one hydrogen on carbon 3 by a methyl group,  $-\text{CH}_3$ . Carbon 3 therefore becomes  $\text{CH}(\text{CH}_3)$ . The displayed structure below has the aldehyde carbon at the right, so numbering runs from right to left.



Structure of 3-methylbutanal

**Step 3: Conclusion** The structure of 3-methylbutanal is  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CHO}$ .

**Quick Tip to Solve:** Count the aldehyde carbon as carbon 1 before attaching the methyl group at carbon 3.

7. Arrange the following compounds in an increasing order of their solubility in water:

$\text{C}_6\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{C}_2\text{H}_5\text{NH}_2$

[1 mark]

**Solution:**

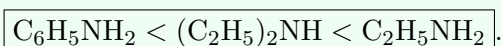
**Concept:**

- Amines dissolve in water by forming hydrogen bonds with water molecules.
- An increase in the nonpolar hydrocarbon portion generally decreases aqueous solubility.

**Step 1: Compare aromatic and aliphatic amines** Aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , has a large hydrophobic phenyl group. Its attraction to water is insufficient to compensate fully for this nonpolar portion, so it is the least soluble of the three compounds.

**Step 2: Compare the ethylamines** Diethylamine,  $(\text{C}_2\text{H}_5)_2\text{NH}$ , contains two ethyl groups whereas ethylamine,  $\text{C}_2\text{H}_5\text{NH}_2$ , contains only one. Both can hydrogen-bond with water, but the smaller hydrocarbon portion of ethylamine makes it more soluble.

**Step 3: Conclusion** The increasing order of solubility in water is



**Quick Tip to Solve:** Compare the size of the water-repelling hydrocarbon portion; do not use the basicity order as the solubility order.

## 8. What are biodegradable polymers?

[1 mark]

### Solution:

#### Concept:

- Biodegradation is the breakdown of a material by biological activity, especially microorganisms.
- Biodegradable polymers contain linkages that can be cleaved under biological conditions, often through enzyme-catalysed reactions.

**Step 1: Identify the defining property** A biodegradable polymer can be decomposed by microorganisms such as bacteria and fungi. Their enzymes attack susceptible bonds in the polymer chains, converting the large molecules into smaller, simpler products.

**Step 2: Give a representative example** Poly( $\beta$ -hydroxybutyrate-co- $\beta$ -hydroxyvalerate), commonly called PHBV, is a biodegradable polymer. Its ester linkages can undergo biological breakdown; nylon-2-nylon-6 is another example.

**Step 3: Conclusion** Biodegradable polymers are polymers that are broken down by microorganisms into simpler products under suitable biological conditions.

**Quick Tip to Solve:** Remember PHBV as an example, and state microbial breakdown as the defining property of a biodegradable polymer.

## 9. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.

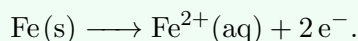
[2 marks]

### Solution:

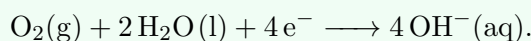
#### Concept:

- Corrosion of iron involves local anodic and cathodic regions on the metal surface; moisture containing dissolved substances acts as the electrolyte.
- Iron is oxidised at the anode while atmospheric oxygen is reduced at the cathode. Further oxidation and hydration produce rust.

**Step 1: Write the electrode reactions** At an anodic region, iron loses electrons:

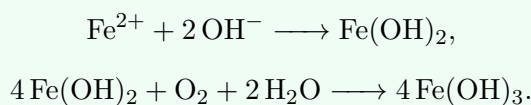


The electrons pass through the metal to a cathodic region. In the moist atmosphere, dissolved oxygen consumes them:



Thus oxidation and reduction occur at different regions of the same iron surface.

**Step 2: Explain the formation of rust** The ions initially form ferrous hydroxide, which is oxidised further by oxygen:

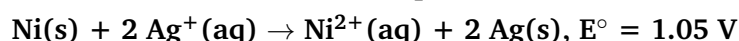


The ferric hydroxide subsequently loses part of its water to form hydrated ferric oxide,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , called rust. The porous rust layer permits oxygen and moisture to reach fresh iron, so corrosion can continue.

**Step 3: Conclusion** Atmospheric corrosion is an electrochemical process: anodic iron dissolution and cathodic oxygen reduction ultimately form rust,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

**Quick Tip to Solve:** Write iron oxidation first, then balance oxygen reduction with four electrons; rust contains iron in the +3 oxidation state.

**10. Determine the values of equilibrium constant ( $K_c$ ) and  $\Delta G^\circ$  for the following reaction:**



(1 F = 96500 C mol<sup>-1</sup>)

[2 marks]

**Solution:**

**Concept:**

- The standard Gibbs energy change is  $\Delta G^\circ = -nFE^\circ$ , where  $n$  is the number of transferred electrons and  $F$  is the Faraday constant.
- At 298 K, the equilibrium constant satisfies  $E^\circ = (0.0591/n) \log_{10} K_c$ .

**Step 1: Determine the electron transfer and Gibbs energy** Nickel is oxidised according to  $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$ , while two silver ions each gain one electron. Hence  $n = 2$ . Using the supplied cell potential,

$$\begin{aligned}\Delta G^\circ &= -2 \times 96500 \times 1.05 \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1}.\end{aligned}$$

The negative sign agrees with a positive standard cell potential.

**Step 2: Calculate the equilibrium constant** Using the conventional temperature 298 K for the standard-potential calculation,

$$\log_{10} K_c = \frac{nE^\circ}{0.0591} = \frac{2 \times 1.05}{0.0591} = 35.53.$$

Taking the antilogarithm gives

$$K_c = 10^{35.53} \simeq 3.4 \times 10^{35}.$$

The very large equilibrium constant shows that the reaction strongly favours products. The pure solids have unit activity and do not appear in the equilibrium expression.

**Step 3: Conclusion** At 298 K,  $K_c \simeq 3.4 \times 10^{35}$  and  $\Delta G^\circ = -202.65 \text{ kJ mol}^{-1}$ .

**Quick Tip to Solve:** Use  $n = 2$  from nickel oxidation; multiply the Gibbs energy by  $n$  but never multiply the given cell potential by a stoichiometric coefficient.

**11. Distinguish between ‘rate expression’ and ‘rate constant’ of a reaction.**

[2 marks]

**Solution:****Concept:**

- The rate law relates reaction rate to reactant concentrations; the powers are determined experimentally.
- For a reaction with rate  $r = k[A]^m[B]^n$ ,  $k$  is the rate constant and  $m + n$  is the overall order.

**Step 1: Rate expression** The rate expression is the complete mathematical dependence of rate on concentrations:

$$r = k[A]^m[B]^n.$$

Here  $[A]$  and  $[B]$  are the molar concentrations of reactants, and  $m, n$  are their respective orders. As concentrations change during the reaction, the numerical rate generally changes. The exponents need not equal the stoichiometric coefficients.

**Step 2: Rate constant** The rate constant is the proportionality constant  $k$  in that expression. For a given reaction at a fixed temperature and fixed catalytic conditions, it is independent of reactant concentrations. Numerically, it equals the rate when each concentration factor has unit value. Its units depend on the total order  $N$ :

$$(\text{mol L}^{-1})^{1-N} \text{s}^{-1}.$$

Unlike concentration, changing temperature generally changes  $k$ .

**Step 3: Conclusion** The rate expression specifies how rate depends on concentrations; the rate constant  $k$  is its concentration-independent proportionality factor under fixed conditions.

**Quick Tip to Solve:** Write one general rate law first, then distinguish the whole expression from its factor  $k$ .

**12(a). State reasons for each of the following:**

(i) The N–O bond in  $\text{NO}_2^-$  is shorter than the N–O bond in  $\text{NO}_3^-$ .

(ii)  $\text{SF}_6$  is kinetically an inert substance.

[2 marks]

**Solution:****Concept:**

- Resonance distributes the double-bond character over equivalent N–O bonds; higher average bond order corresponds to shorter bonds.
- Kinetic inertness means reactions are very slow because the activation barrier is high.

**Step 1: Compare the N–O bond orders** In nitrite,  $\text{NO}_2^-$ , the two equivalent resonance forms distribute one N=O double bond and one N–O single bond over two positions. Thus the average N–O bond order is

$$(2 + 1)/2 = 1.5.$$

In nitrate,  $\text{NO}_3^-$ , one double bond and two single bonds are distributed over three equivalent positions,

giving

$$(2 + 1 + 1)/3 = 4/3.$$

The greater double-bond character in nitrite makes its N–O bonds shorter.

**Step 2: Explain the inertness of sulphur hexafluoride** In  $\text{SF}_6$ , the six fluorine atoms form a compact, symmetric octahedral shell around sulphur. They sterically shield the sulphur centre from the approach of attacking reagents. In addition, the S–F bonds are very strong. Consequently, bond breaking and attack require a high activation energy, so reaction proceeds extremely slowly under ordinary conditions.

**Step 3: Conclusion**  $\text{NO}_2^-$  has the higher N–O bond order and hence the shorter bond. Strong S–F bonds and fluorine shielding make  $\text{SF}_6$  kinetically inert.

**Quick Tip to Solve:** Count total bond order and divide by equivalent N–O bonds before comparing their lengths.

OR

**12(b). State reasons for each of the following:**

(i) All the P–Cl bonds in  $\text{PCl}_5$  molecule are not equivalent.

(ii) Sulphur has greater tendency for catenation than oxygen.

[2 marks]

**Solution:**

**Concept:**

- Gaseous  $\text{PCl}_5$  has trigonal-bipyramidal geometry with three equatorial and two axial bonds.
- Catenation is the ability of an element to form chains through bonds between its own atoms.

**Step 1: Non-equivalent P–Cl bonds** The three equatorial P–Cl bonds lie in one plane at  $120^\circ$  to one another. The two axial bonds are perpendicular to that plane. Each axial bond experiences three bond-pair repulsions at  $90^\circ$ , whereas each equatorial bond experiences only two such repulsions from axial bonds. The greater repulsion makes the axial bonds longer and weaker than the equatorial bonds. Thus all five P–Cl bonds are not equivalent.

**Step 2: Greater catenation of sulphur** Oxygen is very small, so the lone pairs on adjacent oxygen atoms in an O–O single bond repel one another strongly. This weakens the O–O bond. Sulphur atoms are larger, so adjacent lone-pair repulsion is less severe and the S–S bond is stronger than the O–O single bond. Sulphur therefore forms more stable chains and rings, for example the  $\text{S}_8$  ring, and has a greater tendency for catenation.

**Step 3: Conclusion** Axial P–Cl bonds are longer and weaker than equatorial bonds. Stronger S–S single bonds give sulphur greater catenation than oxygen.

**Quick Tip to Solve:** For  $\text{PCl}_5$ , compare the number of  $90^\circ$  interactions experienced by each type of bond.

**13. Assign reasons for the following:**

(i) Cu(I) ion is not known in aqueous solution.

(ii) Actinoids exhibit greater range of oxidation states than lanthanoids.

[2 marks]

**Solution:**

**Concept:**

- Aqueous-ion stability depends on hydration as well as electronic configuration.
- Variable oxidation states arise when electrons in several orbitals of similar energy can participate in bonding.

**Step 1: Instability of aqueous copper(I)** Although  $\text{Cu}^+$  has a filled  $3d^{10}$  configuration, it is unstable in ordinary aqueous solution and undergoes disproportionation:



One copper(I) ion is oxidised to copper(II), while the other is reduced to copper metal. The much more favourable hydration enthalpy of  $\text{Cu}^{2+}$ , compared with  $\text{Cu}^+$ , makes this process favourable and stabilises copper(II) in water.

**Step 2: Wider range of actinoid oxidation states** The  $5f$ ,  $6d$  and  $7s$  subshells of actinoids have comparable energies. Consequently, different numbers of electrons from these subshells can participate in bonding, producing a wide range of oxidation states. In lanthanoids the  $4f$  electrons are more deeply buried and less available for bonding, and the +3 state is predominant. Thus actinoids show a greater range of oxidation states.

**Step 3: Conclusion** Copper(I) disproportionates in water because hydration strongly stabilises copper(II). Similar  $5f$ ,  $6d$  and  $7s$  energies account for the wider actinoid oxidation-state range.

**Quick Tip to Solve:** For aqueous copper stability, include hydration energy; a filled  $d^{10}$  shell alone is insufficient.

**14. Explain the following giving one example for each:**

(i) Reimer-Tiemann reaction

(ii) Friedel Craft's acetylation of anisole

[2 marks]

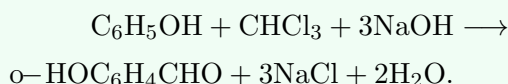
**Solution:**

**Concept:**

- The hydroxyl group activates phenol towards electrophilic substitution, particularly at ortho and para positions.
- The methoxy group of anisole is activating and directs electrophilic substitution to ortho and para positions.

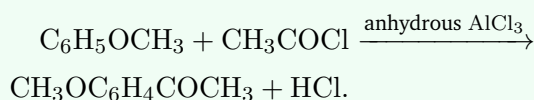
**Step 1: Reimer-Tiemann reaction** Phenol reacts with chloroform and aqueous sodium hydroxide on heating; subsequent acidification gives 2-hydroxybenzaldehyde (salicylaldehyde) as the major product. The reaction introduces a formyl group mainly at the ortho position of phenol. For example,

the net equation is



The mixture is acidified after heating. Dichlorocarbene, :  $\text{CCl}_2$ , generated from chloroform in base, is the reactive intermediate.

**Step 2: Friedel–Crafts acetylation of anisole** Anisole reacts with acetyl chloride in the presence of anhydrous aluminium chloride. The electrophile introduces an acetyl group,  $-\text{COCH}_3$ , onto the benzene ring. For example,



The products are ortho-methoxyacetophenone and para-methoxyacetophenone. The para isomer is the major product because it has less steric crowding. The methoxy group remains attached to the ring.

**Step 3: Conclusion** Reimer–Tiemann formylation gives mainly salicylaldehyde from phenol. Anisole acetylation gives mainly para-methoxyacetophenone, together with the ortho isomer.

**Quick Tip to Solve:** Distinguish the introduced groups: Reimer–Tiemann adds  $-\text{CHO}$ ; acetylation adds  $-\text{COCH}_3$ .

## 15. How would you obtain

(i) Picric acid (2, 4, 6-trinitrophenol) from phenol

(ii) 2-Methylpropene from 2-methylpropanol?

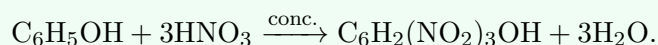
[2 marks]

### Solution:

#### Concept:

- Phenolic  $-\text{OH}$  activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- Acid-catalysed dehydration removes  $\text{H}_2\text{O}$  from an alcohol to form an alkene; concentrated sulphuric acid acts as the dehydrating agent.

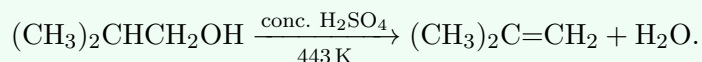
**Step 1: (i) Prepare picric acid from phenol** Treat phenol with concentrated nitric acid. Nitration occurs at both ortho positions and at the para position, giving 2,4,6-trinitrophenol (picric acid):



The three nitro groups occupy positions 2, 4 and 6 relative to the hydroxyl group. Concentrated, rather than dilute, nitric acid is needed for trinitration; dilute nitric acid mainly gives the mononitrophenols.

**Step 2: (ii) Prepare 2-methylpropene** Heat 2-methylpropan-1-ol with concentrated  $\text{H}_2\text{SO}_4$  at about 443 K. Elimination of the hydroxyl group and a hydrogen from the adjacent carbon produces the

required double bond:



If 2-methylpropan-2-ol is used, acid-catalysed dehydration also gives the same alkene, and occurs more readily because it is a tertiary alcohol.

**Step 3: Conclusion** Phenol gives picric acid on nitration with concentrated  $\text{HNO}_3$ ; 2-methylpropanol gives 2-methylpropene on acid-catalysed dehydration.

**Quick Tip to Solve:** For picric acid, put nitro groups at 2, 4 and 6; for the alkene, check that removal of water preserves all four carbon atoms.

**16. What is essentially the difference between  $\alpha$ -form of glucose and  $\beta$ -form of glucose? Explain.**

[2 marks]

**Solution:**

**Concept:**

- Glucose forms a six-membered cyclic hemiacetal when the aldehyde group at C-1 reacts with the hydroxyl group at C-5.
- The new stereogenic carbon C-1 is the anomeric carbon. Stereoisomers differing only at this carbon are called anomers.

**Step 1: Identify the essential difference** The  $\alpha$ - and  $\beta$ -forms of D-glucose differ only in the configuration at C-1, not in the configuration of the other asymmetric carbon atoms. In the usual Haworth projection of D-glucopyranose, the  $\text{CH}_2\text{OH}$  group attached to C-5 is above the ring. In  $\alpha$ -D-glucose, the anomeric  $-\text{OH}$  at C-1 is below the ring, opposite to this  $\text{CH}_2\text{OH}$  group (trans).

**Step 2: Explain the beta form and interconversion** In  $\beta$ -D-glucose, the anomeric  $-\text{OH}$  at C-1 is above the ring, on the same side as the  $\text{CH}_2\text{OH}$  group (cis). Thus the two forms are anomers, rather than mirror images. In aqueous solution the ring can open to the aldehyde form and close again to give either anomer; the resulting change in optical rotation is called mutarotation.

**Step 3: Conclusion** The essential difference is the orientation of the C-1 hydroxyl group: trans to  $\text{CH}_2\text{OH}$  in  $\alpha$ -D-glucose and cis in  $\beta$ -D-glucose.

**Quick Tip to Solve:** Use the C-5  $\text{CH}_2\text{OH}$  group as the reference: alpha is opposite and beta is on the same side; only C-1 changes.

**17. Describe what you understand by primary structure and secondary structure of proteins.** [2 marks]

**Solution:**

**Concept:**

- Proteins are polypeptides: amino-acid residues are joined through covalent peptide linkages,  $-\text{CO}-\text{NH}-$ .

- Protein structure can be described at different levels: the residue sequence and the regular local folding of the polypeptide backbone.

**Step 1: Primary structure** The primary structure is the specific sequence and order of amino-acid residues in a polypeptide chain, conventionally written from its amino (N) terminus to its carboxyl (C) terminus. The residues are held together by peptide bonds. Each protein has a characteristic sequence; changing even one residue can alter the properties and biological activity of the protein. Primary structure therefore specifies which amino acids occur and the order in which they are linked.

**Step 2: Secondary structure** The secondary structure is the regular local arrangement of the polypeptide backbone produced by folding or coiling. Its principal forms are the  $\alpha$ -helix and the  $\beta$ -pleated sheet. These arrangements are stabilised mainly by hydrogen bonds between the carbonyl C=O and N – H groups of peptide bonds. An  $\alpha$ -helix is a coiled chain, whereas a  $\beta$ -pleated sheet contains extended chain segments aligned alongside one another.

**Step 3: Conclusion** Primary structure is the amino-acid sequence; secondary structure is the local hydrogen-bonded folding of the backbone into forms such as the  $\alpha$ -helix and  $\beta$ -pleated sheet.

**Quick Tip to Solve:** Pair sequence with peptide bonds, and local helix or sheet formation with hydrogen bonds between backbone groups.

## 18. Mention two important uses of each of the following:

(i) Bakelite

(ii) Nylon-6

[2 marks]

### Solution:

#### Concept:

- Bakelite is a cross-linked phenol-formaldehyde thermosetting polymer. Its rigidity, heat resistance and electrical insulating character guide its uses.
- Nylon-6 is a polyamide that can be drawn into strong, abrasion-resistant fibres; it is prepared from caprolactam.

**Step 1: (i) Two uses of Bakelite** Bakelite is used to manufacture electrical switches and insulating fittings because it is a good electrical insulator and retains its shape under normal operating conditions. It is also used for handles of cooking utensils because it is heat resistant and transmits heat poorly compared with metals. These are two distinct uses: electrical fittings and utensil handles. Its cross-linked structure makes the material hard and prevents it from softening and being remoulded like an ordinary thermoplastic.

**Step 2: (ii) Two uses of Nylon-6** Nylon-6 is used in tyre cords, where strong reinforcing fibres help the tyre withstand repeated stress. It is also used to make ropes because its fibres have high tensile strength and resist abrasion. In both applications the useful property is the strength and durability of the drawn polyamide fibre. Hydrogen bonding between neighbouring polyamide chains contributes to its mechanical strength.

**Step 3: Conclusion** Bakelite: electrical switches or insulating fittings, and cooking-utensil handles.

Nylon-6: tyre cords and ropes.

**Quick Tip to Solve:** Link Bakelite to heat-resistant electrical or handle applications, and Nylon-6 to strong fibre products such as tyre cords and ropes.

**19. Silver crystallizes in face-centered cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is each face atom is touching the four corner atoms.)** [3 marks]

**Solution:**

**Concept:**

- In a face-centred cubic (FCC) unit cell, the atoms touch along a face diagonal, not along an edge. Let the cube edge be  $a$  and the atomic radius be  $r$ .
- The diagonal of a square face has length  $\sqrt{2}a$ . Along this diagonal, a corner atom, a face-centred atom and the opposite corner atom contribute a total contact distance of  $4r$ .

**Step 1: Relate the face diagonal to the atomic radius** Consider one square face of the cubic cell. By Pythagoras' theorem its diagonal is

$$d = \sqrt{a^2 + a^2} = \sqrt{2}a.$$

From the centre of one corner atom to the centre of the face atom the distance is  $2r$ ; from that face centre to the opposite corner it is another  $2r$ . Therefore the full diagonal satisfies

$$\sqrt{2}a = 2r + 2r = 4r.$$

The half-atoms at the two ends together account for one atomic diameter, while the face-centred atom accounts for the other diameter.

**Step 2: Substitute the given edge length** Rearranging the contact relation and using  $a = 400$  pm,

$$r = \frac{a}{2\sqrt{2}} = \frac{400}{2\sqrt{2}} \text{ pm} = 100\sqrt{2} \text{ pm} = 141.4 \text{ pm}.$$

Since the edge was given in picometres, the radius is obtained directly in picometres. Equivalently, it is  $1.414 \times 10^{-10}$  m. The ratio  $r/a \approx 0.354$  is consistent with FCC contact along the face diagonal.

**Step 3: Conclusion** The radius of a silver atom is  $r \approx 141 \text{ pm}$ .

**Quick Tip to Solve:** For FCC use the face diagonal: write  $4r = \sqrt{2}a$  before substituting the edge length.

20. Nitrogen pentoxide decomposes according to equation:  $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ .

This first order reaction was allowed to proceed at  $40^\circ\text{C}$  and the data below were collected:

$[\text{N}_2\text{O}_5]$  (M) | Time (min)

0.400 | 0.00

0.289 | 20.0

0.209 | 40.0

0.151 | 60.0

0.109 | 80.0

(a) Calculate the rate constant. Include units with your answer.

(b) What will be the concentration of  $\text{N}_2\text{O}_5$  after 100 minutes?

(c) Calculate the initial rate of reaction.

[3 marks]

### Solution:

#### Concept:

- For first-order disappearance of  $\text{N}_2\text{O}_5$ ,  $k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$ , where  $[A]_0$  and  $[A]_t$  are its initial and remaining concentrations.
- The concentration after time  $t$  is  $[A]_t = [A]_0 e^{-kt}$ , and its instantaneous disappearance rate is  $-d[A]/dt = k[A]$ . Time in minutes gives  $k$  in  $\text{min}^{-1}$ .

**Step 1: (a) Calculate the first-order rate constant** Use the initial concentration 0.400 M and the concentration 0.109 M at 80.0 min:

$$k = \frac{2.303}{80.0} \log_{10} \left( \frac{0.400}{0.109} \right) \approx 1.63 \times 10^{-2} \text{ min}^{-1}.$$

As a check, using the first interval gives

$$k = \frac{2.303}{20.0} \log_{10} \left( \frac{0.400}{0.289} \right) \approx 1.63 \times 10^{-2} \text{ min}^{-1}.$$

Their agreement, within the rounding of the tabulated concentrations, is consistent with the stated first-order law.

**Step 2: (b) Find the concentration at 100 minutes** Applying the integrated law with  $t = 100$  min,

$$[\text{N}_2\text{O}_5]_{100} = 0.400 e^{-(0.0163)(100)} \approx 0.0784 \text{ mol L}^{-1}.$$

This is smaller than the concentration at 80 minutes, as expected for continued decomposition.

**Step 3: (c) Calculate the initial rate** The initial rate of disappearance of nitrogen pentoxide is

$$v_0 = k[A]_0 = (1.63 \times 10^{-2})(0.400) = 6.52 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}.$$

If reaction rate is defined with the stoichiometric normalization for the equation as written, then

$$r_0 = -\frac{1}{2} \left( \frac{d[\text{N}_2\text{O}_5]}{dt} \right)_0 = 3.26 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}.$$

Thus the disappearance rate and the normalized reaction rate differ by the reactant coefficient 2; the first-order decay constant above describes disappearance of  $\text{N}_2\text{O}_5$ .

**Step 4: Conclusion**  $k \approx 1.63 \times 10^{-2} \text{ min}^{-1}$ ; after 100 minutes,  $[\text{N}_2\text{O}_5] \approx 0.0784 \text{ M}$ . The initial disappearance rate is  $6.52 \times 10^{-3} \text{ M min}^{-1}$ , or  $3.26 \times 10^{-3} \text{ M min}^{-1}$  when normalized to the equation as written.

**Quick Tip to Solve:** Keep time in minutes throughout, and distinguish disappearance rate from reaction rate divided by the stoichiometric coefficient.

**21(a).** Explain how the phenomenon of adsorption finds application in each of the following processes:

(i) Production of vacuum

(ii) Heterogeneous catalysis

(iii) Froth Floatation process

[3 marks]

**Solution:**

**Concept:**

- Adsorption is the accumulation of molecules or ions at the surface of a solid or liquid. The substance accumulated is the adsorbate; the surface providing it sites is the adsorbent.
- A finely divided or porous solid has a large surface area and can adsorb appreciable quantities of a gas. Selective adsorption can also alter the wetting of mineral particles or bring reactants together on a catalyst.

**Step 1: (i) Production of vacuum** After most of the air has been pumped out of a vessel, small amounts of gas remain. Activated charcoal placed in the vessel adsorbs these residual gases on its large porous surface. Cooling the charcoal increases the adsorption of gases. The number of freely moving gas molecules in the vessel decreases, lowering its pressure and producing a high vacuum.

**Step 2: (ii) Heterogeneous catalysis** In heterogeneous catalysis, reactants and catalyst are in different phases, commonly gaseous reactants and a solid catalyst. Reactant molecules are adsorbed at active sites on the catalyst surface. Adsorption brings the molecules close together and can weaken their bonds, providing a reaction pathway of lower activation energy. The products then desorb, leaving the sites available for further reaction. For example, finely divided nickel adsorbs hydrogen and unsaturated organic compounds during catalytic hydrogenation.

**Step 3: (iii) Froth floatation process** Froth floatation concentrates sulphide ores by the different surface affinities of ore and gangue particles. Collector molecules are preferentially adsorbed on sulphide particles and make them water-repellent, so they are preferentially wetted by oil. Gangue is preferentially wetted by water. When air is blown through the suspension, the sulphide particles attach to air bubbles and rise with the froth, which is skimmed off; the water-wetted gangue remains behind. Thus selective surface adsorption helps separate the useful ore from gangue.

**Step 4: Conclusion** Adsorption removes residual gases to produce vacuum, activates and concentrates reactants on a heterogeneous catalyst, and selectively changes ore-particle wetting for froth floatation.

**Quick Tip to Solve:** Link each application to its surface effect: gas removal, reactant activation, or selective wetting of sulphide ore.

**21(b). Define each of the following terms:**

(i) Micelles

(ii) Peptization

(iii) Desorption

[3 marks]

**Solution:**

**Concept:**

- Colloidal particles have dimensions between those of individual molecules and coarse suspensions; aggregation or dispersion can produce such particles.
- Adsorption is accumulation of a substance on a surface. Desorption is the reverse process, while peptization uses adsorbed ions to disperse a precipitate.

**Step 1: Define micelles** Micelles are aggregates of a large number of molecules or ions of an associated colloid, such as soap, formed above a characteristic concentration called the critical micelle concentration (CMC). In water, their nonpolar hydrocarbon tails point towards the interior and their polar or ionic heads face the surrounding water. Thus a substance that behaves as an ordinary electrolyte at low concentration forms colloidal-size aggregates at higher concentration. Micelle formation also requires a temperature above the Kraft temperature.

**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 quantity of a suitable electrolyte, called a peptizing agent. Preferential adsorption of one type of ion gives particles a common charge; mutual repulsion then disperses them. For example, a little ferric chloride peptizes freshly precipitated ferric hydroxide by supplying adsorbed  $\text{Fe}^{3+}$  ions.

**Step 3: Define desorption** Desorption is the removal or release of an adsorbed substance from the surface of an adsorbent. The released adsorbate returns to the surrounding gas or liquid phase. For example, a gas previously adsorbed on charcoal can be removed by heating or by reducing the pressure. Desorption therefore reverses surface accumulation; it does not mean dissolution of the adsorbent itself.

**Step 4: Conclusion** Micelles are molecular aggregates; peptization converts a fresh precipitate into a sol; desorption releases an adsorbate from a surface.

**Quick Tip to Solve:** Link each definition to its direction: molecules aggregate, precipitate disperses, adsorbate leaves.

**22. Describe the principle behind each of the following processes:**

(i) Vapour phase refining of a metal

(ii) Electrolytic refining of a metal

(iii) Recovery of silver after silver ore was leached with NaCN

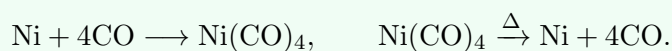
[3 marks]

**Solution:**

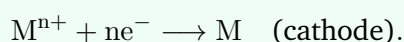
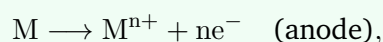
**Concept:**

- Refining separates a metal from impurities by exploiting differences in volatility, electrode behaviour or chemical reactivity.
- A more reactive metal can reduce the complex ion of a less reactive metal and thereby displace it from solution.

**Step 1: Principle of vapour phase refining** The impure metal is converted into a volatile compound by reaction with a suitable reagent. This compound is separated from nonvolatile impurities, then decomposed to give the pure metal. The metal must form a readily volatile compound, and that compound must decompose readily under suitable conditions. For example, nickel forms volatile  $\text{Ni(CO)}_4$  with carbon monoxide and is recovered by heating the purified carbonyl vapour:

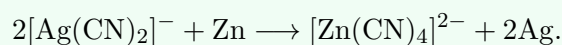


**Step 2: Principle of electrolytic refining** The impure metal is made the anode, a thin sheet of pure metal the cathode, and a solution of a suitable soluble salt of the same metal the electrolyte. On passing electric current, metal dissolves from the anode and is deposited in pure form at the cathode:



Less reactive insoluble impurities collect below the anode as anode mud; more reactive impurities may enter solution but are not deposited under the chosen conditions.

**Step 3: Principle of recovering silver** After leaching, silver is present in solution as the soluble dicyanoargentate(I) complex,  $[\text{Ag(CN)}_2]^-$ . Zinc, being more reactive than silver, displaces it from this solution. Zinc is oxidized and silver(I) is reduced to metallic silver:

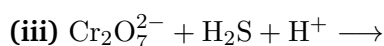
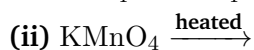
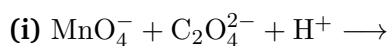


The precipitated silver is separated from the liquid. Thus recovery depends on reduction or displacement, rather than evaporation of the cyanide solution.

**Step 4: Conclusion** Vapour phase refining uses formation and decomposition of a volatile compound; electrolytic refining transfers metal from anode to cathode; zinc displaces silver from its cyanide complex.

**Quick Tip to Solve:** For cyanide-leached silver, write the complex first and balance two silver ions against one zinc atom.

### 23. Complete the following chemical equations:



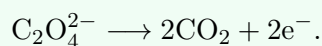
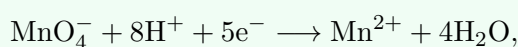
[3 marks]

#### Solution:

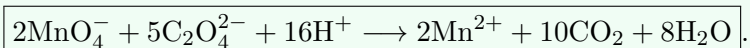
##### Concept:

- In acidic medium, permanganate is reduced from Mn(VII) to Mn(II), and dichromate is reduced from Cr(VI) to Cr(III).
- Balance redox equations by equalizing electrons, then check atoms and total ionic charge on both sides.

**Step 1: Oxidation of oxalate by acidified permanganate** Oxalate is oxidized to carbon dioxide. The reduction and oxidation half-equations are

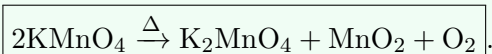


Multiply these equations by 2 and 5 respectively to cancel ten electrons. The completed equation is



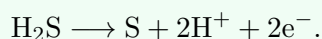
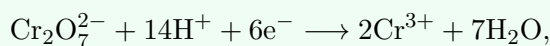
The total charge is +4 on either side, and carbon, manganese, oxygen and hydrogen are balanced.

**Step 2: Thermal decomposition of potassium permanganate** On heating, potassium permanganate decomposes into potassium manganate, manganese dioxide and oxygen:

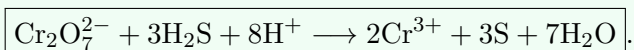


The two manganese atoms initially at oxidation state +7 finish at +6 and +4. Oxygen is partly oxidized from -2 to zero. The equation contains two potassium atoms, two manganese atoms and eight oxygen atoms on each side.

**Step 3: Oxidation of hydrogen sulphide by acidified dichromate** Dichromate oxidizes hydrogen sulphide to sulphur. The half-equations are



Multiply the second equation by 3, add, and cancel six electrons and six hydrogen ions:



Sulphur changes from -2 to zero; the net charge is +6 on each side.

**Step 4: Conclusion** The completed products are (i) manganese(II), carbon dioxide and water; (ii)

potassium manganate, manganese dioxide and oxygen; (iii) chromium(III), sulphur and water, with coefficients as balanced above.

**Quick Tip to Solve:** In acidic redox balancing, check ionic charge after checking atoms; it catches a wrong hydrogen coefficient.

**24. Write the name, stereochemistry and magnetic behaviour of the following: (At. nos. Mn = 25, Co = 27, Ni = 28)**

(i)  $K_4[Mn(CN)_6]$

(ii)  $[Co(NH_3)_5Cl]Cl_2$

(iii)  $K_2[Ni(CN)_4]$

[3 marks]

**Solution:**

**Concept:**

- Determine the metal oxidation state from the complex charge; then obtain its  $d$ -electron configuration from the atomic number.
- Strong-field ligands can pair the metal's  $d$  electrons. Unpaired electrons cause paramagnetism; a complex with all electrons paired is diamagnetic.
- Six-coordinate complexes here are octahedral; the strong-field four-coordinate nickel(II) complex is square planar.

**Step 1: Analyse potassium hexacyanomanganate(II)** In  $K_4[Mn(CN)_6]$ , the complex ion is  $[Mn(CN)_6]^{4-}$ . If the oxidation state of manganese is  $x$ , then  $x - 6 = -4$ , so  $x = +2$ . Manganese(II) is  $3d^5$ . The strong-field  $CN^-$  ligands produce the low-spin configuration  $t_{2g}^5e_g^0$ , with one unpaired electron. Hence its name is potassium hexacyanomanganate(II), its geometry is octahedral and it is paramagnetic. Its inner-orbital hybridisation is  $d^2sp^3$ .

**Step 2: Analyse pentaamminechloridocobalt(III) chloride** In  $[Co(NH_3)_5Cl]Cl_2$ , the two outside chloride ions show that the complex cation has charge +2. Since ammonia is neutral and coordinated chloride has charge  $-1$ ,  $x - 1 = +2$ , giving cobalt(III), with configuration  $3d^6$ . The cobalt(III) complex is low spin, with  $t_{2g}^6e_g^0$ , so all electrons are paired. Its name is pentaamminechloridocobalt(III) chloride, its geometry is octahedral, its hybridisation is  $d^2sp^3$ , and it is diamagnetic.

**Step 3: Analyse potassium tetracyanonickelate(II)** In  $K_2[Ni(CN)_4]$ ,  $x - 4 = -2$  gives nickel(II), which is  $3d^8$ . The strong-field cyanide ligands pair the electrons, leaving a vacant  $3d$  orbital for  $dsp^2$  hybridisation. The resulting complex is square planar and has no unpaired electron. Its name is potassium tetracyanonickelate(II), and it is diamagnetic.

**Step 4: Conclusion** (i) Potassium hexacyanomanganate(II): octahedral, paramagnetic (one unpaired electron). (ii) Pentaamminechloridocobalt(III) chloride: octahedral, diamagnetic. (iii) Potassium tetracyanonickelate(II): square planar, diamagnetic.

**Quick Tip to Solve:** First use the outside potassium or chloride ions to find the complex charge. Count unpaired electrons only after accounting for ligand-field pairing.

**25. Answer the following:**

(i) Haloalkanes easily dissolve in organic solvents, why?

(ii) What is known as a racemic mixture? Give an example.

(iii) Of the two bromoderivatives,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$  and  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ , which one is more reactive in  $\text{S}_{\text{N}}1$  substitution reaction and why?

[3 marks]

**Solution:**

**Concept:**

- Dissolution is favourable when the interactions formed between solute and solvent compensate for the interactions broken in the pure substances.
- Enantiomers rotate plane-polarised light equally in opposite directions; an equimolar mixture shows external compensation.
- The slow step of an  $\text{S}_{\text{N}}1$  reaction is ionisation to a carbocation. Greater carbocation stability gives faster substitution under comparable conditions.

**Step 1: Explain solubility in organic solvents** Haloalkanes and typical organic solvents have comparable intermolecular attractions, including dispersion forces and, where applicable, dipolar interactions. On mixing, new haloalkane-solvent attractions are formed. These are of similar strength to the attractions between haloalkane molecules and between solvent molecules that must be broken. Thus dissolution is energetically favourable, and haloalkanes dissolve readily in organic solvents.

**Step 2: Define a racemic mixture and give an example** A racemic mixture contains equal amounts of the two enantiomers of an optically active compound. For example, an equimolar mixture of (+)-butan-2-ol and (–)-butan-2-ol is racemic, often written as (±)-butan-2-ol. Each enantiomer produces an equal but opposite rotation of plane-polarised light, so the net rotation of the mixture is zero. The mixture is optically inactive due to external compensation; its individual enantiomers remain optically active.

**Step 3: Compare the carbocations formed in substitution** The two bromides form  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)^+$  and  $(\text{C}_6\text{H}_5)_2\text{CH}^+$ , respectively, on heterolytic cleavage of the carbon-bromine bond. The second carbocation can delocalise its positive charge into two phenyl rings, whereas the first has only one phenyl ring available for resonance. This additional resonance stabilisation makes formation of the diphenylmethyl carbocation easier. Therefore  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$  undergoes  $\text{S}_{\text{N}}1$  substitution more rapidly than  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ .

**Step 4: Conclusion** (i) Comparable solute-solvent attractions favour dissolution. (ii) A racemic mixture is an equimolar, optically inactive mixture of enantiomers, for example (±)-butan-2-ol. (iii)  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$  is more reactive because its carbocation is resonance-stabilised by two phenyl rings.

**Quick Tip to Solve:** For an  $\text{S}_{\text{N}}1$  comparison, remove bromide first and compare the resulting carbocations; count the phenyl rings directly attached to the positively charged carbon.

26. (a) Explain why an alkylamine is more basic than ammonia.

(b) How would you convert

(i) Aniline to nitrobenzene

(ii) Aniline to iodobenzene?

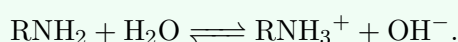
[3 marks]

**Solution:**

**Concept:**

- Amines act as bases by donating the nitrogen lone pair to a proton. Electron-releasing alkyl groups increase electron density on nitrogen through the +I effect.
- Aniline forms benzenediazonium chloride on treatment with nitrous acid generated in situ from sodium nitrite and hydrochloric acid at 273–278 K.
- A diazonium group can be replaced by other groups with evolution of nitrogen; this provides a route from aniline to substituted benzenes.

**Step 1: Explain the greater basicity of an alkylamine** In an alkylamine, the alkyl group releases electron density towards nitrogen by its positive inductive effect. Consequently the nitrogen lone pair is more readily available for donation to a proton than in ammonia. Proton acceptance gives the corresponding alkylammonium ion:



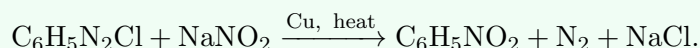
The electron-releasing alkyl group also helps stabilise the positive charge of the conjugate acid. Thus an alkylamine is more basic than ammonia.

**Step 2: Prepare the common diazonium intermediate** Diazotise aniline using  $\text{NaNO}_2$  and dilute  $\text{HCl}$ , keeping the temperature at 273–278 K:



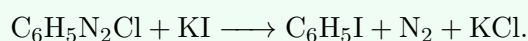
The low temperature preserves benzenediazonium chloride for the subsequent replacement reaction. The same intermediate is used independently for each of the two conversions.

**Step 3: Convert the diazonium salt to nitrobenzene** Treat the diazonium salt with sodium nitrite in the presence of copper and warm. Replacement of the diazonium group by a nitro group gives nitrobenzene:



This is substitution of the diazonium group, rather than nitration of aniline.

**Step 4: Convert the diazonium salt to iodobenzene** Add potassium iodide to a separately prepared portion of benzenediazonium chloride:



Nitrogen is liberated and iodobenzene forms. Copper is not required for this iodide replacement.

**Step 5: Conclusion** (a) The +I effect of an alkyl group makes the nitrogen lone pair more available for protonation. (b) Diazotise aniline first, then use  $\text{NaNO}_2/\text{Cu}$  with warming for nitrobenzene, or  $\text{KI}$  for iodobenzene.

**Quick Tip to Solve:** Use the same cold diazotisation step for both conversions, then choose the replacement reagent: nitrite with copper for nitro, and potassium iodide for iodo.

27. Describe the following giving one example for each:

(i) Detergents

(ii) Food preservatives

(iii) Antacids

[3 marks]

**Solution:**

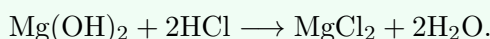
**Concept:**

- Detergents are cleansing agents whose molecules contain a water-attracting polar head and an oil-attracting hydrocarbon tail.
- Food preservatives inhibit spoilage, while antacids relieve acidity by reducing the effect of excess acid in the stomach.

**Step 1: (i) Detergents** Detergents are synthetic cleansing agents which help remove grease and dirt from surfaces. Their hydrophobic hydrocarbon tails associate with oily dirt, while their hydrophilic heads interact with water, allowing the dirt to be washed away. A common example is sodium lauryl sulphate (sodium dodecyl sulphate),  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ . This is an anionic detergent because its cleansing action is associated with the anionic part of the molecule.

**Step 2: (ii) Food preservatives** Food preservatives are substances added to food to prevent or retard spoilage caused by microorganisms and thus increase its useful storage life. For example, sodium benzoate,  $\text{C}_6\text{H}_5\text{COONa}$ , is used to preserve acidic foods and beverages such as fruit juices. By inhibiting microbial growth it helps protect the food during storage.

**Step 3: (iii) Antacids** Antacids are medicines used to relieve acidity by neutralising excess hydrochloric acid in the stomach. For example, magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , is used as milk of magnesia. Being a mild base, it neutralises stomach acid according to



**Step 4: Conclusion** Examples are sodium lauryl sulphate for detergents, sodium benzoate for food preservatives and magnesium hydroxide for antacids.

**Quick Tip to Solve:** Associate each class with its function first: cleansing, prevention of spoilage, and neutralisation of stomach acid.

**28(a).** Differentiate between molarity and molality for a solution. How does a change in temperature influence their values?

**(b)** Calculate the freezing point of an aqueous solution containing 10.50 g of  $\text{MgBr}_2$  in 200 g of water. (Molar mass of  $\text{MgBr}_2 = 184 \text{ g}$ ) ( $K_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ ) [5 marks]

**Solution:**

**Concept:**

- Molarity is  $M = n/V$ , where  $n$  is moles of solute and  $V$  is the volume of solution in litres. Molality is  $m = n/w$ , where  $w$  is the mass of solvent in kilograms.
- Freezing-point depression is  $\Delta T_f = iK_fm$ , where  $i$  is the van't Hoff factor and  $K_f$  is the molal freezing-point depression constant of the solvent.

**Step 1: (a) Distinguish molarity from molality** Molarity is the number of moles of solute dissolved per litre of the final solution, whereas molality is the number of moles of solute dissolved per kilogram of solvent. Thus, their denominators refer to different quantities: solution volume for molarity and solvent mass for molality. Their respective units are  $\text{mol L}^{-1}$  and  $\text{mol kg}^{-1}$ .

**Step 2: Explain the temperature dependence** For a fixed composition, a temperature change does not alter the number of moles of solute or the mass of solvent. However, the volume of the solution changes with temperature. Therefore molarity depends on temperature: on ordinary thermal expansion, heating increases the volume and decreases molarity. Molality remains independent of temperature because both the solute amount and solvent mass remain unchanged.

**Step 3: (b) Calculate the molality of the magnesium bromide solution** The mass of solvent, rather than the total solution mass, must be used. Here,

$$\begin{aligned}n(\text{MgBr}_2) &= \frac{10.50}{184} = 0.057065 \text{ mol}, \\w(\text{water}) &= \frac{200}{1000} = 0.200 \text{ kg}, \\m &= \frac{0.057065}{0.200} = 0.285326 \text{ mol kg}^{-1}.\end{aligned}$$

**Step 4: Account for dissociation and determine the freezing point** Taking magnesium bromide to dissociate completely in this aqueous solution,



Each formula unit gives three ions, so the van't Hoff factor is  $i = 3$ . The depression is therefore

$$\begin{aligned}\Delta T_f &= iK_fm \\&= 3 \times 1.86 \times 0.285326 \\&= 1.5921 \text{ K}.\end{aligned}$$

Pure water freezes at  $0^\circ\text{C}$ . A freezing-point depression lowers this temperature, giving

$$T_f = 0 - 1.5921 = -1.5921^\circ\text{C}.$$

A temperature difference of one kelvin equals a difference of one degree Celsius; hence the calculated depression can be subtracted directly on the Celsius scale.

**Step 5: Conclusion** Molarity depends on temperature through solution volume; molality is temperature independent. The freezing point of the given solution is approximately  $-1.59^{\circ}\text{C}$ , assuming complete dissociation of  $\text{MgBr}_2$ .

**Quick Tip to Solve:** Use the 0.200 kg mass of water in molality and multiply by three for the three ions produced by magnesium bromide.

OR

**28(b).** (a) Define the terms osmosis and osmotic pressure. Is the osmotic pressure of a solution a colligative property? Explain.

(b) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250.0 g of water. ( $K_b$  for water =  $0.512\text{ K kg mol}^{-1}$ , Molar mass of NaCl = 58.44 g) [5 marks]

**Solution:**

**Concept:**

- Osmosis is the spontaneous passage of solvent through a semipermeable membrane from pure solvent or a dilute solution into a more concentrated solution.
- Osmotic pressure,  $\pi$ , is the minimum excess pressure applied on the solution side to stop osmosis. For a dilute solution,  $\pi = i(n/V)RT$ .
- Boiling-point elevation obeys  $\Delta T_b = iK_b m$ , where  $m$  is the molality in moles of solute formula units per kilogram of solvent and  $i$  is the van't Hoff factor.

**Step 1: (a) Explain osmosis and osmotic pressure** A semipermeable membrane permits solvent molecules to pass but prevents solute particles from passing. When it separates pure water (or a more dilute solution) from a concentrated solution, water passes into the concentrated solution. This net passage is osmosis. Applying pressure to the concentrated solution opposes this flow; the minimum excess pressure that just stops it is its osmotic pressure.

**Step 2: Establish its colligative character** At a fixed temperature, the dilute-solution relation is

$$\pi = \frac{n_{\text{particles}}}{V} RT.$$

Thus osmotic pressure depends on the number of dissolved solute particles per unit volume, rather than their chemical identity. It is therefore a colligative property. For electrolytes, dissociation changes the particle count and is included through  $i$ ; this does not change the colligative nature of the property.

**Step 3: (b) Calculate molality and account for NaCl dissociation** Using the given molar mass,

$$n(\text{NaCl}) = \frac{15.00}{58.44} = 0.25667\text{ mol}, \quad m = \frac{0.25667}{0.2500} = 1.0267\text{ mol kg}^{-1}.$$

Taking complete dissociation in water,  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ , each formula unit gives two ions, so  $i = 2$ . This is the ideal dissociation treatment used for this calculation.

**Step 4: Find the elevation and add it to water's boiling point**

$$\begin{aligned}\Delta T_b &= iK_b m \\ &= 2(0.512)(1.0267) = 1.0513 \text{ K}, \\ T_b &= 100.00 + 1.0513 = 101.0513^\circ\text{C}.\end{aligned}$$

The temperature increment has the same numerical value in kelvin and degrees Celsius. The normal boiling point of water is used, so the result refers to normal atmospheric pressure.

**Step 5: Conclusion** Osmotic pressure is a colligative property because it depends on solute particle concentration at fixed temperature. With complete NaCl dissociation, the solution boils at approximately  $101.05^\circ\text{C}$  ( $374.20 \text{ K}$ ).

**Quick Tip to Solve:** For NaCl, first double the formula-unit molality to count both ions; then add the elevation to the boiling point of pure water.

**29(a). Give chemical tests to distinguish between**

(i) Propanal and propanone

(ii) Benzaldehyde and acetophenone

(b) How would you obtain

(i) But-2-enal from ethanal

(ii) Butanoic acid from butanol

(iii) Benzoic acid from ethylbenzene?

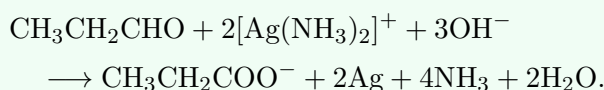
[5 marks]

**Solution:**

**Concept:**

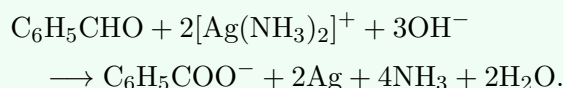
- Tollens' reagent oxidises aldehydes to carboxylate ions while its silver(I) complex is reduced to metallic silver. Ordinary ketones do not give this test.
- An aldehyde with an  $\alpha$ -hydrogen undergoes aldol addition in dilute alkali; heating the aldol eliminates water to form an  $\alpha, \beta$ -unsaturated aldehyde.
- A primary alcohol is oxidised to a carboxylic acid by excess acidified dichromate under reflux. Strong oxidation of an alkylbenzene bearing a benzylic hydrogen gives benzoic acid after acidification.

**Step 1: (a)(i) Distinguish propanal from propanone** Warm separate samples gently with freshly prepared Tollens' reagent. Propanal gives a silver mirror on the test-tube wall, whereas propanone gives no silver mirror. The aldehyde group is readily oxidised, but the ketone group is not oxidised under these mild conditions:



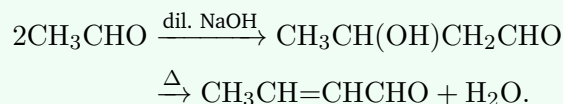
**Step 2: (a)(ii) Distinguish benzaldehyde from acetophenone** Apply the same Tollens' test. Benzaldehyde produces a silver mirror; acetophenone does not. Thus this test also distinguishes an aromatic

aldehyde from the corresponding ketone:



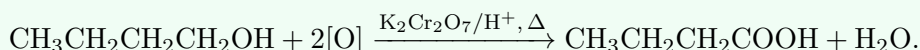
Fehling's solution is unsuitable for this pair because benzaldehyde ordinarily does not reduce it.

**Step 3: (b)(i) Prepare but-2-enal from ethanal** Treat ethanal with dilute aqueous NaOH to form the aldol, 3-hydroxybutanal. Heat it to eliminate water:



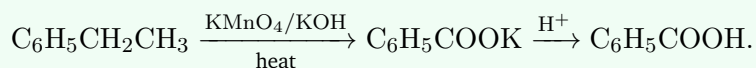
The new carbon-carbon bond joins two ethanal molecules, giving the required four-carbon chain; dehydration then gives the double bond between carbon atoms 2 and 3, counting from the aldehyde carbon.

**Step 4: (b)(ii) Prepare butanoic acid from butanol** Reflux butan-1-ol with excess acidified potassium dichromate. Oxidation proceeds through butanal to the carboxylic acid:



Excess oxidant and reflux ensure oxidation continues to the acid rather than stopping at the aldehyde.

**Step 5: (b)(iii) Prepare benzoic acid from ethylbenzene** Heat ethylbenzene with alkaline potassium permanganate, then acidify the potassium benzoate obtained. The ethyl side chain contains benzylic hydrogens and is oxidised to a carboxyl group:



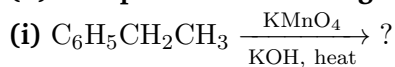
The carbon attached directly to the benzene ring becomes the carboxyl carbon; the remaining side-chain carbon is oxidised away. The aromatic ring remains intact under these conditions.

**Step 6: Conclusion** Tollens' reagent distinguishes both pairs: propanal and benzaldehyde give silver mirrors, while propanone and acetophenone do not. The preparations use aldol condensation of ethanal, oxidation of butan-1-ol, and side-chain oxidation of ethylbenzene followed by acidification, respectively.

**Quick Tip to Solve:** Use Tollens' reagent for both aldehyde-ketone pairs; in each conversion first identify whether carbon-chain growth or oxidation is needed.

**29(b).** (a) Describe the following giving linked chemical equations: (i) Cannizzaro reaction (ii) Decarboxylation.

(b) Complete the following chemical equations:



[5 marks]

### Solution:

#### Concept:

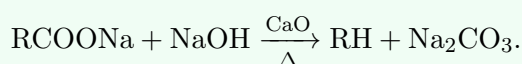
- Aldehydes lacking an alpha hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one molecule is oxidised and another is reduced.
- Soda-lime decarboxylation removes the carboxyl carbon from a sodium carboxylate; strong side-chain oxidation, acid-chloride formation and amide hydrolysis are distinct transformations.

**Step 1: (a)(i) Cannizzaro reaction** An aldehyde without an alpha hydrogen gives an alcohol and a carboxylate salt on treatment with concentrated alkali. Benzaldehyde is a suitable example:

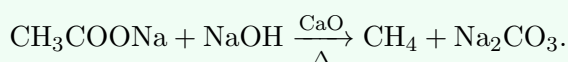


The reagent is concentrated aqueous KOH. One aldehyde group is reduced to an alcohol while the other is oxidised to a carboxylate; this is disproportionation. Acidification of the salt gives benzoic acid.

**Step 2: (a)(ii) Decarboxylation** Heating a sodium carboxylate with soda lime, a mixture of NaOH and CaO, gives an alkane with one carbon atom fewer than the original acid:



For example, sodium ethanoate gives methane:



The carboxyl carbon enters sodium carbonate; the remaining alkyl group acquires hydrogen.

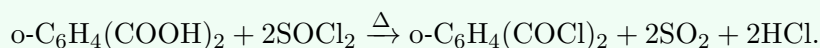
**Step 3: (b)(i) Oxidation of ethylbenzene** Hot alkaline permanganate oxidises a side chain containing a benzylic hydrogen completely to a carboxylate group, irrespective of its initial length. The aromatic ring is retained:



The organic product under the printed alkaline conditions is potassium benzoate. On subsequent acidification, it yields benzoic acid; acidification is a separate work-up.

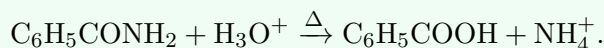
**Step 4: (b)(ii) Action of thionyl chloride** Thionyl chloride replaces the hydroxyl group of each

carboxyl group by chlorine. Thus phthalic acid gives phthaloyl chloride, with gaseous sulphur dioxide and hydrogen chloride:



Both adjacent carboxyl groups are converted, so two equivalents of thionyl chloride are required.

**Step 5: (b)(iii) Acidic hydrolysis of benzamide** Heating benzamide with aqueous acid hydrolyses the amide group to a carboxylic acid. In the acidic medium, the nitrogen-containing product is ammonium ion:



This balanced equation represents acidic hydrolysis, rather than dehydration of the amide to a nitrile.

**Step 6: Conclusion** Cannizzaro reaction is aldehyde disproportionation, and soda-lime decarboxylation gives an alkane with one fewer carbon. The organic products in (b) are (i) potassium benzoate (benzoic acid after acidification), (ii) phthaloyl chloride and (iii) benzoic acid.

**Quick Tip to Solve:** Read the reagent before choosing the product: alkaline permanganate gives a carboxylate,  $\text{SOCl}_2$  gives an acid chloride, and hot aqueous acid hydrolyses an amide.

**30(a). Explain the following:**

(i)  $\text{NF}_3$  is an exothermic compound whereas  $\text{NCl}_3$  is not.

(ii)  $\text{F}_2$  is most reactive of all the four common halogens.

(b) Complete the following chemical equations:

(i)  $\text{C} + \text{H}_2\text{SO}_4(\text{conc.}) \rightarrow$

(ii)  $\text{P}_4 + \text{NaOH} + \text{H}_2\text{O} \rightarrow$

(iii)  $\text{Cl}_2 + \text{F}_2(\text{excess}) \rightarrow$

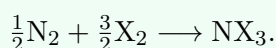
[5 marks]

**Solution:**

**Concept:**

- The enthalpy of formation depends on energy consumed in breaking reactant bonds and energy released on forming product bonds; stronger product bonds favour exothermic formation.
- Fluorine is a strong oxidising agent because its weak F-F bond and the high hydration enthalpy of fluoride favour its reduction. Redox equations must conserve atoms as well as oxidation-number changes.

**Step 1: (a)(i) Compare formation of nitrogen trifluoride and nitrogen trichloride** Formation from the elements requires breaking the very strong nitrogen triple bond and halogen bonds, followed by formation of three nitrogen-halogen bonds per molecule:

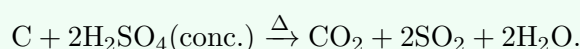


The N-F bonds are sufficiently strong that their formation releases more energy than is consumed in breaking the reactant bonds. Hence the enthalpy of formation of  $\text{NF}_3$  is negative, and it is an

exothermic compound. The N–Cl bonds are much weaker; their formation does not compensate for the energy needed to break the reactant bonds. NCl<sub>3</sub> therefore has a positive enthalpy of formation and is not an exothermic compound.

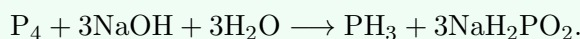
**Step 2: (a)(ii) Explain fluorine's exceptional reactivity** The small fluorine atoms bring their nonbonding electron pairs very close together. Strong lone-pair repulsions weaken the F–F bond, so relatively little energy is needed to dissociate F<sub>2</sub>. Fluorine also has a very strong tendency to accept an electron, and the small fluoride ion has a large, favourable hydration enthalpy. Together these effects make fluorine the strongest oxidising agent among the common halogens and account for its exceptionally high reactivity. Its behaviour should not be attributed to electron-gain enthalpy alone, since chlorine has a more negative electron-gain enthalpy than fluorine.

**Step 3: (b)(i) Carbon with concentrated sulphuric acid** Hot concentrated sulphuric acid acts as an oxidising agent. Carbon is oxidised from oxidation state zero to +4 in carbon dioxide, and sulphur is reduced from +6 to +4 in sulphur dioxide:



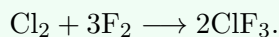
The four electrons lost by carbon correspond to two sulphur atoms each gaining two electrons. The balanced equation also conserves hydrogen and oxygen.

**Step 4: (b)(ii) Phosphorus with aqueous sodium hydroxide** White phosphorus disproportionates in hot aqueous alkali, producing phosphine and sodium hypophosphite:



One phosphorus atom is reduced from zero to -3 in phosphine, while the other three are each oxidised from zero to +1 in hypophosphite. Thus the electron gain and loss balance.

**Step 5: (b)(iii) Chlorine with excess fluorine** With excess fluorine, chlorine forms chlorine trifluoride:



Each chlorine is bonded to three fluorine atoms. The excess-fluorine condition selects ClF<sub>3</sub>, whereas a limited supply of fluorine can yield chlorine monofluoride, ClF.

**Step 6: Conclusion** NF<sub>3</sub> is exothermic because strong N–F bond formation outweighs the bond-breaking energy, unlike NCl<sub>3</sub>. Fluorine's weak F–F bond and favourable reduction energetics explain its high reactivity. The products are (i) CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O, (ii) PH<sub>3</sub> and NaH<sub>2</sub>PO<sub>2</sub>, and (iii) ClF<sub>3</sub>, as balanced above.

**Quick Tip to Solve:** In phosphorus disproportionation, balance one P atom at -3 against three P atoms at +1; excess fluorine selects ClF<sub>3</sub> rather than ClF.

**30(b).** (a) Account for the following:

- (i) The acidic strength decreases in the order  $\text{HCl} > \text{H}_2\text{S} > \text{PH}_3$   
 (ii) Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

(b) Complete the following chemical equations:

- (i)  $\text{P}_4 + \text{SO}_2\text{Cl}_2 \rightarrow$   
 (ii)  $\text{XeF}_2 + \text{H}_2\text{O} \rightarrow$   
 (iii)  $\text{I}_2 + \text{HNO}_3(\text{conc.}) \rightarrow$

[5 marks]

### Solution:

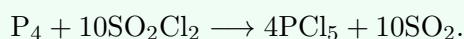
#### Concept:

- Across the third period, increasing electronegativity of the atom bonded to hydrogen increases the polarity of its H–X bond and favours release of  $\text{H}^+$ .
- In group 15, the inert-pair effect increases down the group: the valence  $ns^2$  pair participates less readily in bonding, so the +3 state becomes more stable relative to +5.
- Complete an equation by identifying the products and conserving every element. Hydrolysis of  $\text{XeF}_2$  is a redox reaction: xenon is reduced to its elemental state while water is oxidised to oxygen.

**Step 1: (a)(i) Explain the acidity order** Phosphorus, sulphur and chlorine belong to the same period, and their electronegativities increase in the order  $\text{P} < \text{S} < \text{Cl}$ . Consequently, the hydrogen bonded to chlorine has the greatest positive character and is most readily released as a proton. Hydrogen sulphide releases a proton less readily, while phosphine is an extremely weak proton donor. Thus the increase in electronegativity across this period accounts for the given decrease in acidic strength,  $\text{HCl} > \text{H}_2\text{S} > \text{PH}_3$ .

**Step 2: (a)(ii) Explain the trend in pentahalide formation** Formation of a pentahalide requires the group 15 element to use all five valence electrons and attain the +5 oxidation state. On moving down the group, the valence  $ns^2$  pair becomes increasingly reluctant to participate in bonding because of the inert-pair effect. The +5 state therefore becomes less stable relative to +3, so the tendency to form pentahalides decreases. This trend concerns the heavier members capable of forming pentahalides; nitrogen itself cannot form a pentahalide because its compact second-shell valence orbitals cannot accommodate five bonds.

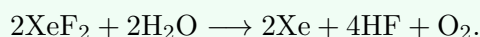
**Step 3: (b)(i) Reaction of phosphorus with sulphuryl chloride** Sulphuryl chloride chlorinates phosphorus, yielding phosphorus pentachloride and sulphur dioxide. Balancing first the four phosphorus atoms and then the chlorine atoms gives



The ten sulphuryl chloride molecules supply the twenty chlorine atoms required for four molecules of  $\text{PCl}_5$ ; their sulphur and oxygen appear in ten molecules of  $\text{SO}_2$ .

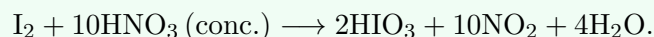
**Step 4: (b)(ii) Hydrolysis of xenon difluoride** Xenon difluoride reacts with water to produce xenon, hydrogen fluoride and oxygen. Xenon is reduced from +2 in  $\text{XeF}_2$  to zero, whereas oxygen is oxidised

from  $-2$  in water to zero in  $O_2$ . The balanced equation is



Two xenon atoms gain four electrons in total and the two oxygen atoms lose four electrons in total. Four fluorine atoms combine with the four hydrogen atoms to form four molecules of hydrogen fluoride. Both atom balance and electron balance are therefore satisfied.

**Step 5: (b)(iii) Oxidation of iodine by concentrated nitric acid** Concentrated nitric acid oxidises iodine from oxidation state zero to  $+5$  in iodic acid, while nitrogen is reduced from  $+5$  to  $+4$  in nitrogen dioxide. Two iodine atoms lose ten electrons, so ten nitrate nitrogen atoms each gain one electron:



The equation conserves iodine, nitrogen, hydrogen and oxygen as well as the electron transfer.

**Step 6: Conclusion** The acidity order follows increasing electronegativity across the period; the decreasing tendency to form pentahalides follows the increasing inert-pair effect. The products in (b) are respectively  $PCl_5 + SO_2$ ,  $Xe + HF + O_2$ , and  $HIO_3 + NO_2 + H_2O$ , with coefficients as balanced above.

**Quick Tip to Solve:** In  $XeF_2$  hydrolysis, balance the redox change first: two  $Xe(+2)$  atoms gain the four electrons lost when two water oxygen atoms form  $O_2$ .