CBSE Class 12 Chemistry Question Paper 2017 with Solution PDF-Set 56-2-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) **All** questions are compulsory.
(ii) Questions number **1 to 5** are very short-answer questions and carry **1** mark each.
(iii) Questions number **6 to 10** are short-answer questions and carry **2** marks each.
(iv) Questions number **11 to 22** are also short-answer questions and carry **3** marks each.
(v) Question number **23** is a value based question and carries **4** marks.
(vi) Questions number **24 to 26** are long-answer questions and carry **5** marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. What is the formula of a compound in which the element P forms ccp lattice and atoms of Q occupy 2/3rd of tetrahedral voids? [1 mark]

Solution:

Concept:

- For N atoms in a close-packed lattice, there are $2N$ tetrahedral voids.
- The formula gives the simplest whole-number ratio of the atoms of the two elements.

Step 1: Count the occupied voids Let the ccp lattice contain N atoms of P. It has $2N$ tetrahedral voids. Since Q occupies two-thirds of these voids, the number of Q atoms is $\frac{2}{3}(2N) = \frac{4N}{3}$.

Step 2: Reduce the atomic ratio Thus $\mathrm{P} : \mathrm{Q} = N : \frac{4N}{3} = 3 : 4$. Multiplying both entries by the same factor gives the smallest integral subscripts; the void fraction is not itself the Q subscript.

Step 3: Conclusion The formula of the compound is $\boxed{\mathrm{P_3Q_4}}$.

Quick Tip to Solve: First double the number of ccp atoms to count tetrahedral voids, then apply their occupancy fraction.

2. Arrange the following hydrides of Group-16 elements in the increasing order of their thermal stability:

H_2O, H_2S, H_2Se, H_2Te [1 mark]

Solution:

Concept:

- Thermal stability of a hydride depends mainly on the strength of its element-hydrogen bonds.
- Down Group 16, increasing atomic size weakens the overlap with the hydrogen orbital and lowers bond strength.

Step 1: Compare the bonds From oxygen to tellurium, the central atom becomes larger and the E–H bond becomes longer. Its bond dissociation enthalpy generally decreases, so progressively less energy is needed to break the bond.

Step 2: Translate bond strength into stability The O–H bond is strongest among these bonds, so water is most resistant to thermal decomposition. The Te–H bond is weakest, so hydrogen telluride is least stable. Sulfur and selenium occupy the intermediate positions in their group order.

Step 3: Conclusion The increasing order is $\boxed{\mathrm{H_2Te < H_2Se < H_2S < H_2O}}$.

Quick Tip to Solve: For these hydrides, move upward in Group 16 to obtain increasing thermal stability.

3. What is the role of desorption in the process of catalysis? [1 mark]

Solution:

Concept:

- Desorption is the release of an adsorbed species from a surface.
- A heterogeneous catalyst provides surface active sites on which reactants adsorb and undergo reaction.

Step 1: Identify what leaves the surface After the adsorbed reactants have reacted on the catalyst surface, the product molecules must detach. Their release into the surrounding gas or liquid phase is product desorption.

Step 2: Explain why release is necessary Desorption removes products from the active sites and makes those sites available for fresh reactant molecules. If products remained strongly bound, they would occupy the surface and obstruct further adsorption and reaction. Thus desorption permits repeated catalytic cycles.

Step 3: Conclusion Desorption releases the products from the catalyst surface and frees active sites for further catalysis.

Quick Tip to Solve: Remember the last surface-catalysis stage: products leave so fresh reactants can occupy the same sites.

4. Write the IUPAC name of the following compound:

C_6H_5 - CH_2 - CH_2 - OH [1 mark]

Solution:

Concept:

- The parent chain must contain the carbon bonded to the principal functional group, $-OH$.
- Number the parent chain to give the hydroxyl group the lowest possible locant.

Step 1: Choose and number the parent The chain containing the hydroxyl group has two carbon atoms: $HO-CH_2-CH_2-$. Its parent is ethan-1-ol. Numbering begins at the CH_2OH end, which places the hydroxyl group on carbon 1.

Step 2: Locate the aromatic substituent The C_6H_5 group is a phenyl substituent attached to carbon 2 of that chain. Combining its locant and name with the alcohol parent gives the systematic name. The oxygen is on the side chain, so this is an alcohol rather than a phenol.

Step 3: Conclusion The IUPAC name is $\boxed{\text{2-phenylethan-1-ol}}$.

Quick Tip to Solve: Start numbering at the hydroxyl end; the phenyl group is then on the second carbon.

5. Among the isomers of pentane (C_5H_{12}), write the one which on photochemical chlorination yields a single monochloride. [1 mark]

Solution:

Concept:

- Photochemical chlorination replaces a hydrogen atom by chlorine through a free-radical substitution.
- Only one constitutional monochloride is formed when all hydrogen positions in the starting alkane are equivalent.

Step 1: Choose the symmetric isomer Neopentane has the structure $C(CH_3)_4$. Its four methyl groups are identical and symmetrically arranged around the central carbon. Therefore all twelve hydrogen atoms belong to equivalent positions.

Step 2: Check the monochlorination product Replacement of any one of those hydrogens gives the same structure, $(CH_3)_3CCH_2Cl$. The other pentane isomers, pentane and 2-methylbutane, have more than one type of hydrogen position and therefore can give different monochlorides.

Step 3: Conclusion The required isomer is $\boxed{\text{2,2-dimethylpropane (neopentane)}}$, $C(CH_3)_4$.

Quick Tip to Solve: Count distinct hydrogen environments, not just carbon atoms, when asked for a single monochloride.

6(a). Do the following conversions in not more than two steps:

(a) Propene to Acetone

(b) Propanoic acid to 2-hydroxypropanoic acid [2 marks]

Solution:

Concept:

- Markovnikov hydration of propene gives propan-2-ol; oxidation of a secondary alcohol gives a ketone.
- The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen.
- Hydrolysis of an alpha-bromo acid replaces bromine by a hydroxyl group.

Step 1: Part (a): hydrate propene Treat propene with water in the presence of dilute sulfuric acid. Markovnikov addition places the hydroxyl group on the middle carbon:

$$CH_3CH{=}CH_2 \xrightarrow{H_2O/\text{dil. } H_2SO_4} CH_3CH(OH)CH_3.$$

Step 2: Part (a): oxidise the secondary alcohol Use acidified potassium dichromate to oxidise propan-2-ol to acetone:

$$CH_3CH(OH)CH_3 \xrightarrow{K_2Cr_2O_7/H^+} CH_3COCH_3.$$

The three-carbon skeleton is retained in both steps.

Step 3: Part (b): brominate at the alpha carbon Treat propanoic acid with bromine in the presence of

Quick Tip to Solve: To introduce OH next to COOH, first use HVZ alpha-bromination, then hydrolyse the C–Br bond.

red phosphorus, followed by the usual hydrolytic work-up. The HVZ reaction gives 2-bromopropanoic acid:

$$CH_3CH_2COOH \xrightarrow{Br_2/\text{red P}} CH_3CHBrCOOH.$$

Step 4: Part (b): replace bromine by hydroxyl Heat the alpha-bromo acid with aqueous alkali and then acidify the carboxylate formed:

$$CH_3CHBrCOOH \xrightarrow[\text{then acidify}]{\text{aq. KOH}} CH_3CH(OH)COOH.$$

Aqueous alkali effects substitution of bromine by hydroxyl; acidification restores the free carboxylic acid.

Step 5: Conclusion (a) Propene $\rightarrow$ propan-2-ol $\rightarrow$ acetone. (b) Propanoic acid $\rightarrow$ 2-bromopropanoic acid $\rightarrow$ 2-hydroxypropanoic acid.

Quick Tip to Solve: To introduce OH next to COOH, first use HVZ alpha-bromination, then hydrolyse the C–Br bond.

OR

6(b). Write the reaction involved in the following:

(a) Etard reaction

(b) Wolff-Kishner reduction [2 marks]

Solution:

Concept:

- Etard oxidation converts the methyl group attached to a benzene ring into an aldehyde group using chromyl chloride, followed by hydrolysis.
- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine and strong base on heating.

Step 1: (a) Etard reaction Toluene is treated with chromyl chloride, CrO_2Cl_2, in a non-aqueous solvent such as CS_2. It first forms the Etard complex; hydrolysis of this intermediate gives benzaldehyde:

$$C_6H_5CH_3 \xrightarrow[CS_2]{CrO_2Cl_2} \text{Etard complex} \xrightarrow{H_2O} C_6H_5CHO.$$

Thus the side-chain methyl group is oxidised to $-CHO$, while the benzene ring remains intact.

Step 2: (b) Wolff-Kishner reduction A ketone first reacts with hydrazine to give its hydrazone. Heating the hydrazone with KOH in ethylene glycol eliminates nitrogen and reduces the carbonyl carbon to $-CH_2-$:

$$R_2C{=}O + H_2NNH_2 \longrightarrow R_2C{=}NNH_2 + H_2O,$$

$$R_2C{=}NNH_2 \xrightarrow[\text{ethylene glycol},\,\Delta]{\text{KOH}} R_2CH_2 + N_2.$$

For example, acetone gives propane. The reaction also reduces an aldehyde RCHO to RCH_3.

Quick Tip to Solve: Remember Etard as side-chain oxidation to an aldehyde, and Wolff-Kishner as removal of carbonyl oxygen under basic conditions.

Step 3: Conclusion Etard reaction: toluene $\rightarrow$ benzaldehyde using CrO_2Cl_2, then hydrolysis. Wolff-Kishner reduction: aldehyde or ketone $\rightarrow$ hydrocarbon using NH_2NH_2/KOH and heat.

Quick Tip to Solve: Remember Etard as side-chain oxidation to an aldehyde, and Wolff-Kishner as removal of carbonyl oxygen under basic conditions.

7. What are colligative properties? Write the colligative property which is used to find the molecular mass of macromolecules. [2 marks]

Solution:

Concept:

- Colligative properties depend on the number of solute particles relative to solvent particles, rather than on the chemical identity of the solute, in a dilute solution.
- Osmotic pressure obeys $\pi = CRT$ for a dilute solution of a non-electrolyte, where C is molar concentration, R the gas constant and T absolute temperature.

Step 1: Define colligative properties Colligative properties are properties of dilute solutions that depend only on the number of dissolved solute particles, and not on their nature. The four such properties are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. When comparing solutions, dissociation or association must be accounted for because it changes the number of particles.

Step 2: Select the property for macromolecules Osmotic pressure is used to determine the molecular mass of macromolecules such as proteins and polymers. Their high molar masses give very small boiling-point elevations and freezing-point depressions, whereas osmotic pressure remains measurable even in very dilute solutions. It can also be measured at room temperature, avoiding possible decomposition on heating. For mass w dissolved to solution volume V,

$$\pi = \frac{wRT}{MV}, \qquad M = \frac{wRT}{\pi V},$$

where M is the molar mass; consistent units are used for R, V and π.

Step 3: Conclusion Colligative properties depend on the number of solute particles, not their nature. The property used for determining the molecular mass of macromolecules is $\boxed{\text{osmotic pressure}}$.

Quick Tip to Solve: For a protein or polymer, choose osmotic pressure: it is measurable in dilute solution at room temperature.

8. (a) Write the IUPAC name of the isomer of the following complex:

$[Pt(NH_3)_2Cl_2]$

(b) Write the formula for the following:

Tetraammineaquachloridocobalt(III) nitrate [2 marks]

Solution:

Concept:

- A square-planar complex of the type MA_2B_2 has cis and trans geometrical isomers: identical ligands are adjacent in cis and opposite in trans.
- Neutral ammine and aqua ligands carry zero charge; chlorido carries -1. The charge of the coordination entity determines the number of counterions.

Step 1: (a) Name the geometrical isomers In $[Pt(NH_3)_2Cl_2]$, the two ammine ligands are neutral and the two chlorido ligands contribute -2, so platinum is in oxidation state $+2$. Platinum(II) gives a square-planar complex. With the two chlorido ligands adjacent, the name is cis-diamminedichloridoplatinum(II); with them opposite, it is trans-diamminedichloridoplatinum(II). The printed formula does not specify a geometry, so both geometrical isomers are identified. In the name, ammine precedes chlorido alphabetically, ignoring the multiplicative prefixes.

Step 2: (b) Build the cobalt complex formula Tetraammine supplies four NH_3 ligands, aqua supplies one H_2O, and chlorido supplies one Cl^-. Cobalt is $+3$, so the coordination entity has charge $+3 - 1 = +2$:

$$[Co(NH_3)_4(H_2O)Cl]^{2+}.$$

Each nitrate counterion has charge -1, hence two nitrate ions are needed outside the coordination brackets to make an electrically neutral compound.

Step 3: Conclusion (a) cis-Diamminedichloridoplatinum(II) and trans-diamminedichloridoplatinum(II). (b) $\boxed{[Co(NH_3)_4(H_2O)Cl](NO_3)_2}$.

Quick Tip to Solve: Determine the bracket charge before adding counterions: cobalt(III) plus one chlorido ligand gives a dication and needs two nitrates.

9. In a galvanic cell, the following cell reaction occurs:

Zn (s) + 2 Ag^+ (aq) $\rightarrow$ Zn^{2+} (aq) + 2 Ag (s); $E^\circ_{cell} = +1.56\,V$

(a) Is the direction of flow of electrons from zinc to silver or silver to zinc?

(b) How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions? [2 marks]

Solution:

Concept:

- In a galvanic cell, oxidation occurs at the anode and reduction at the cathode. Electrons flow through the external circuit from the anode to the cathode.
- The balanced half-reactions show which dissolved ions are produced and which are consumed while the cell delivers current.

Quick Tip to Solve: Read the ionic species directly from the reaction: the product ion increases and the reactant ion decreases.

Step 1: (a) Identify the direction of electron flow Zinc is oxidised in the given spontaneous reaction:

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

Therefore the zinc electrode is the anode and supplies electrons to the external circuit. Silver ions are reduced at the silver cathode:

$$2\mathrm{Ag^+(aq)} + 2\mathrm{e^-} \longrightarrow 2\mathrm{Ag(s)}.$$

The electrons released at zinc are used at silver, so electron flow is from zinc to silver through the external wire. The positive standard cell potential is consistent with the reaction proceeding in the stated direction.

Step 2: (b) Track the concentrations of the ions As the cell functions, zinc metal dissolves and produces $\mathrm{Zn^{2+}}$ ions in the anode compartment; thus their concentration increases. At the cathode, $\mathrm{Ag^+}$ ions leave the solution as metallic silver is deposited; thus their concentration decreases. For every mole of zinc oxidised, one mole of $\mathrm{Zn^{2+}}$ is produced and two moles of $\mathrm{Ag^+}$ are consumed. The salt bridge maintains electrical neutrality and does not reverse these reaction-driven changes.

Step 3: Conclusion (a) Electrons flow from $\boxed{\text{zinc to silver}}$. (b) $\boxed{[\mathrm{Zn^{2+}}] \text{ increases; } [\mathrm{Ag^+}] \text{ decreases}}$ as the cell functions.

Quick Tip to Solve: Read the ionic species directly from the reaction: the product ion increases and the reactant ion decreases.

10. In the following ions:

$\mathrm{Mn^{3+}}$, $\mathrm{V^{3+}}$, $\mathrm{Cr^{3+}}$, $\mathrm{Ti^{4+}}$

(Atomic no.: Mn = 25, V = 23, Cr = 24, Ti = 22)

(a) Which ion is most stable in an aqueous solution?

(b) Which ion is the strongest oxidizing agent?

(c) Which ion is colourless?

(d) Which ion has the highest number of unpaired electrons? [2 marks]

Solution:

Concept:

- Form a transition-metal cation by removing the $4s$ electrons before the $3d$ electrons. The resulting d-electron configuration controls its magnetic and optical properties.
- The stability of an ion in water depends on its electronic configuration and hydration. In an octahedral aqueous environment, d^3 has the stable t_{2g}^3 arrangement.
- An oxidizing agent accepts electrons. Reduction of $\mathrm{Mn^{3+}}$ produces the especially stable half-filled $3d^5$ configuration of $\mathrm{Mn^{2+}}$.

Quick Tip to Solve: First write the four ionic d-electron counts: 4, 2, 3, 0; use d3 stability, reduction to d5 and the absence of d electrons to identify the answers.

Step 1: Compare the ionic configurations Removing the appropriate number of electrons gives

$$\begin{aligned} \mathrm{Mn}^{3+} &: [\mathrm{Ar}]\, 3d^4, \\ \mathrm{V}^{3+} &: [\mathrm{Ar}]\, 3d^2, \\ \mathrm{Cr}^{3+} &: [\mathrm{Ar}]\, 3d^3, \\ \mathrm{Ti}^{4+} &: [\mathrm{Ar}]\, 3d^0. \end{aligned}$$

In their usual aqueous environments, the corresponding numbers of unpaired electrons are $4, 2, 3, 0$. Thus manganese(III) has the greatest number, namely four.

Step 2: Explain stability, oxidation and colour (a) Cr^{3+} is the most stable aqueous ion among the given ions; its d^3 configuration has three electrons in the lower-energy t_{2g} orbitals and appreciable crystal-field stabilization. (b) Mn^{3+} is the strongest oxidizing agent: it readily accepts an electron according to $\mathrm{Mn}^{3+} + \mathrm{e}^- \rightarrow \mathrm{Mn}^{2+}$, producing stable half-filled $3d^5$. (c) Ti^{4+} is colourless because its d^0 configuration has no d electron available for a d-d transition. (d) Mn^{3+}, with $3d^4$, has four unpaired electrons.

Step 3: Conclusion (a) Cr^{3+}; (b) Mn^{3+}; (c) Ti^{4+}; (d) Mn^{3+}, with four unpaired electrons.

Quick Tip to Solve: First write the four ionic d-electron counts: 4, 2, 3, 0; use d3 stability, reduction to d5 and the absence of d electrons to identify the answers.

11. The electrical resistance of a column of 0.05 M KOH solution of diameter 1 cm and length 45.5 cm is $4.55 \times 10^3\,\Omega$. Calculate its molar conductivity. [3 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$. For a uniform cylindrical column, conductivity is $\kappa = G(l/A) = l/(RA)$, where l is the length and A the cross-sectional area.
- Molar conductivity is $\Lambda_m = 1000\kappa/C$ when κ is in S cm^{-1} and concentration C is in mol L^{-1}. Its unit is S cm^2 mol^{-1}.

Step 1: Determine the area and cell constant The diameter is $1\,\mathrm{cm}$, so the radius is $r = 0.5\,\mathrm{cm}$, not $1\,\mathrm{cm}$. Hence

$$A = \pi r^2 = \pi(0.5)^2 = 0.7854\,\mathrm{cm}^2.$$

For the length $l = 45.5\,\mathrm{cm}$, the cell constant is

$$\frac{l}{A} = \frac{45.5}{0.7854} = 57.93\,\mathrm{cm}^{-1}.$$

Using centimetres throughout allows us to obtain conductivity directly in S cm^{-1}.

Quick Tip to Solve: Halve the stated diameter before calculating area; keep length in centimetres and then apply the factor 1000 in the molar-conductivity formula.

Step 2: Calculate conductivity from resistance The measured resistance is $R = 4.55 \times 10^3\ \Omega$. Therefore,

$$G = \frac{1}{4.55 \times 10^3} = 2.198 \times 10^{-4}\ \text{S},$$
$$\kappa = \frac{45.5}{(4.55 \times 10^3)(0.7854)}$$
$$= 1.273 \times 10^{-2}\ \text{S cm}^{-1}.$$

The factor l/A converts the conductance of this particular column into the conductivity of the solution.

Step 3: Convert conductivity into molar conductivity Substitute the molarity $C = 0.05\ \text{mol L}^{-1}$:

$$\Lambda_m = \frac{1000\kappa}{C}$$
$$= \frac{1000(1.273 \times 10^{-2})}{0.05}$$
$$= 254.6\ \text{S cm}^2\ \text{mol}^{-1}.$$

The factor 1000 converts litres into cubic centimetres. Equivalently, this value is $2.546 \times 10^{-2}\ \text{S m}^2\ \text{mol}^{-1}$ in SI units.

Step 4: Conclusion The molar conductivity of the KOH solution is approximately $\boxed{254.6\ \text{S cm}^2\ \text{mol}^{-1}}$.

Quick Tip to Solve: Halve the stated diameter before calculating area; keep length in centimetres and then apply the factor 1000 in the molar-conductivity formula.

12(a). Define the following terms with an example in each:

(a) Lyophobic colloids

(b) Homogeneous catalysis

(c) O/W emulsion [3 marks]

Solution:

Concept:

- A colloid contains a dispersed phase distributed through a dispersion medium. The interaction between these two phases determines whether a sol is lyophilic or lyophobic.
- Catalysis changes the rate of a reaction through an alternative pathway. Homogeneous catalysis means that the catalyst and the reactants occupy the same phase.
- An emulsion is a colloidal dispersion of one liquid in another immiscible liquid. Its name identifies which liquid forms droplets and which forms the continuous medium.

Step 1: Define lyophobic colloids and give an example Lyophobic colloids are colloidal systems in which the dispersed particles have little affinity for the dispersion medium. The term means solvent-hating. They do not form merely by mixing the substance with the medium, so special preparation methods are required. Such sols are comparatively less stable and are readily coagulated by adding electrolytes. A gold sol in water is an example: gold is the dispersed phase and water is the dispersion medium.

Quick Tip to Solve: Read O/W as oil dispersed in water: the liquid after the slash is the continuous dispersion medium, so milk supplies a suitable example.

Step 2: Define homogeneous catalysis and give an example Homogeneous catalysis is catalysis in which the catalyst and the reactants are in the same phase. For example, aqueous acid catalyses the hydrolysis of an ester such as methyl acetate:

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH.$$

In the aqueous reaction mixture, the reactants and the acid catalyst are in the liquid phase. The hydrogen ion accelerates hydrolysis and is regenerated during the catalytic process.

Step 3: Define an oil-in-water emulsion and give an example An O/W, or oil-in-water, emulsion is a colloidal system in which small droplets of oil form the dispersed phase and water forms the continuous dispersion medium. Milk is an example: droplets of liquid fat are dispersed in an aqueous medium. Here oil is the internal droplet phase; water surrounds those droplets. This distinguishes O/W emulsions from W/O emulsions, where water droplets are dispersed in oil.

Step 4: Conclusion (a) Lyophobic colloids have little affinity for their medium, for example gold sol in water. (b) Homogeneous catalysis uses a catalyst in the same phase as the reactants, for example acid-catalysed ester hydrolysis. (c) An O/W emulsion consists of oil droplets in water, for example milk.

Quick Tip to Solve: Read O/W as oil dispersed in water: the liquid after the slash is the continuous dispersion medium, so milk supplies a suitable example.

OR

12(b). Write three differences between Physisorption and Chemisorption. [3 marks]

Solution:

Concept:

- Adsorption is the accumulation of an adsorbate on the surface of an adsorbent. The nature of the attractive force determines whether adsorption is physical or chemical.
- Physisorption involves weak van der Waals forces, whereas chemisorption involves formation of chemical bonds between the adsorbate and the surface.

Step 1: Compare the forces and specificity In physisorption, adsorbate particles are held by weak van der Waals attractions. These forces can act between many different substances, so physisorption is not highly specific. In chemisorption, the adsorbate forms chemical bonds with suitable surface sites. It is therefore highly specific: the adsorbate and adsorbent must be capable of forming those bonds. Thus, weak physical attraction and strong chemical bonding constitute the first difference.

Step 2: Compare the enthalpy of adsorption Physisorption has a relatively low magnitude of enthalpy of adsorption, typically about 20–$40\,\text{kJ mol}^{-1}$. Chemisorption has a much larger magnitude, typically about 80–$240\,\text{kJ mol}^{-1}$, because chemical bonds are formed. These values describe the magnitude of the energy released; adsorption itself is generally exothermic.

Step 3: Compare the number of adsorbed layers Physisorption can produce several layers of adsorbate. After the first layer forms, further particles can be attracted to particles already adsorbed by van der

Quick Tip to Solve: Organise the three paired differences under force, adsorption enthalpy and number of layers; keep the physical and chemical properties in the same order.

Waals forces. Chemisorption normally forms only a single layer because chemical bonding requires direct contact with available sites on the adsorbent surface. Once those sites are occupied, additional layers cannot bond directly to them.

Step 4: Conclusion The three differences are: weak van der Waals forces versus chemical bonds; low versus high magnitude of adsorption enthalpy; and possible multilayer adsorption versus monolayer adsorption, for physisorption and chemisorption respectively.

Quick Tip to Solve: Organise the three paired differences under force, adsorption enthalpy and number of layers; keep the physical and chemical properties in the same order.

13. A solution of glucose (Molar mass = 180 g mol^{-1}) in water has a boiling point of 100.20°C. Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are 1.86 K kg mol^{-1} and 0.512 K kg mol^{-1} respectively. [3 marks]

Solution:

Concept:

- For a dilute solution of a non-volatile solute, elevation of boiling point is $\Delta T_b = K_b m$ and depression of freezing point is $\Delta T_f = K_f m$, where m is molality and K_b, K_f are the solvent's molal constants.
- Glucose is a non-electrolyte: it does not dissociate into ions in water, so its van't Hoff factor is $i = 1$. The same solution has the same molality in both calculations.

Step 1: Find the elevation of boiling point The normal boiling point of pure water is $100.00\,^\circ$C. Hence the rise due to dissolved glucose is

$$\Delta T_b = 100.20 - 100.00 = 0.20\,\text{K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius. Use this rise, rather than the absolute boiling temperature, in the colligative-property formula.

Step 2: Calculate the molality and freezing-point depression Using $K_b = 0.512\,\text{K kg mol}^{-1}$,

$$m = \frac{\Delta T_b}{K_b} = \frac{0.20}{0.512} = 0.390625\,\text{mol kg}^{-1}.$$

Now use $K_f = 1.86\,\text{K kg mol}^{-1}$ for the same solution:

$$\Delta T_f = K_f m = 1.86 \times 0.390625 = 0.7265625\,\text{K}.$$

The supplied molar mass is not needed, since molality has already been obtained from boiling-point elevation; no solute mass or solvent mass is required.

Step 3: Obtain the solution's freezing point Pure water freezes at $0.00\,^\circ$C. Dissolved glucose lowers that temperature, so subtract the depression:

$$T_f(\text{solution}) = 0.00 - 0.7265625 = -0.7265625\,^\circ\text{C}.$$

Quick Tip to Solve: For the same glucose solution, eliminate molality using $\Delta T_f = (K_f/K_b)\Delta T_b$, then subtract the depression from $0\,^\circ$C.

Rounding to two decimal places gives the required freezing temperature below zero.

Step 4: Conclusion The freezing point of the glucose solution is $\boxed{-0.73\,^\circ\text{C}}$.

Quick Tip to Solve: For the same glucose solution, eliminate molality using $\Delta T_f = (K_f/K_b)\Delta T_b$, then subtract the depression from $0\,^\circ$C.

---

14. (a) Write the principle of vapour phase refining.

(b) What is the role of depressant in froth floatation process?

(c) Write the name of reducing agent to obtain iron from Fe_2O_3 at high temperature. [3 marks]

Solution:

Concept:

- Refining separates a metal from impurities; vapour phase refining achieves this through a volatile compound that can subsequently yield the pure metal.
- Froth floatation separates sulphide ores by differences in wetting and flotation behaviour. A depressant selectively prevents one sulphide from entering the froth.
- Reduction removes oxygen from a metal oxide. The effective reducing agent depends on temperature and the thermodynamic feasibility of the reaction.

Step 1: (a) State the principle of vapour phase refining The impure metal is converted into a volatile compound by reaction with a suitable reagent. The volatile compound is separated from the non-volatile impurities and is then decomposed to deposit pure metal. Therefore, two conditions are essential: the metal must form a volatile compound, and that compound must be readily decomposable to recover the metal. For example, in Mond refining, nickel forms volatile nickel tetracarbonyl, which decomposes on heating:

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

Step 2: (b) Explain the role of a depressant A depressant prevents a selected sulphide ore from forming froth, thereby enabling separation of two sulphide ores present together. For example, in a mixture of ZnS and PbS, sodium cyanide acts as a depressant for ZnS. It prevents ZnS from floating with the froth, while PbS is carried into the froth and collected. Its role is selective suppression of flotation, rather than production or stabilisation of the froth.

Step 3: (c) Identify the reducing agent at high temperature At high temperature, carbon in the form of coke is the reducing agent used to obtain iron from its oxide. Carbon removes oxygen from the iron oxide and is oxidised to carbon monoxide. The overall reduction can be represented as

$$\mathrm{Fe_2O_3} + 3\mathrm{C} \longrightarrow 2\mathrm{Fe} + 3\mathrm{CO}.$$

In the high-temperature region of the blast furnace, coke also directly reduces FeO to iron: $\mathrm{FeO} + \mathrm{C} \longrightarrow \mathrm{Fe} + \mathrm{CO}$. Carbon monoxide contributes to the indirect reduction in the cooler regions.

Step 4: Conclusion (a) Form a volatile metal compound and decompose it to recover pure metal. (b) Selectively prevent one sulphide from forming froth so the ores can be separated. (c) The high-temperature reducing agent is carbon (coke).

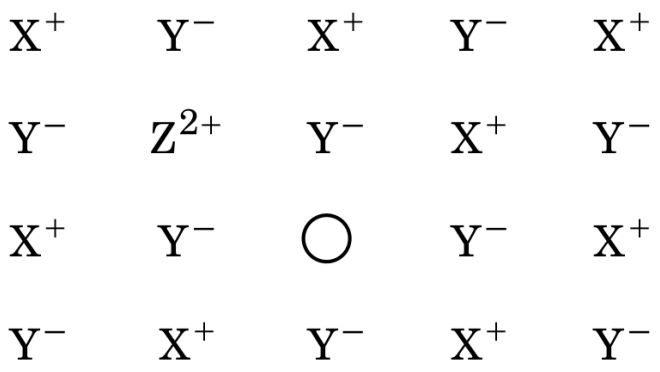
Quick Tip to Solve: In part (c), use the phrase "high temperature" to identify coke; in part (b), name the sulphide suppressed by the depressant, not just the reagent.

15. (a) What is the radius of sodium atom if it crystallises in bcc structure with the cell edge of 400 pm?

(b) Examine the given defective crystal:

(i) Write the term used for this type of defect.

(ii) What is the result when XY crystal is doped with divalent (Z^{2+}) impurity? [3 marks]



Solution:

Concept:

- In a body-centred cubic (bcc) unit cell, atoms touch along the body diagonal. If a is the cell edge and r the atomic radius, $\sqrt{3}a = 4r$.
- An impurity defect occurs when a foreign ion occupies a lattice site. Replacing a monovalent cation with a divalent cation requires a cation vacancy to maintain electrical neutrality.

Step 1: (a) Relate the radius to the body diagonal The body diagonal passes through a corner atom, the central atom and the opposite corner atom. Their contacting radii add to $r + 2r + r = 4r$. Therefore, for the given cell edge $a = 400\,\text{pm}$,

$$r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 400}{4}\,\text{pm} = 100\sqrt{3}\,\text{pm} \approx 173.2\,\text{pm}.$$

Contact along the body diagonal, rather than the cell edge, is the defining geometrical relation for bcc.

Step 2: (b)(i) Identify the defect in the figure The figure shows a foreign Z^{2+} ion occupying a site normally occupied by X^{+}, together with an empty X^{+} site. This is an impurity defect, specifically a substitutional impurity accompanied by a cation vacancy. The displayed defect is identified by the foreign ion and the compensating vacancy.

Step 3: (b)(ii) Explain the result of divalent doping Each Z^{2+} ion contributes one extra positive charge relative to the X^{+} ion it replaces. Leaving another X^{+} site vacant removes one positive charge and compensates this excess. Thus two original X^{+} sites are represented by one Z^{2+} ion and one vacancy, with total charge still $+2$. The anion lattice remains unchanged and the crystal stays electrically neutral. One cation vacancy is produced for each divalent impurity ion incorporated.

Step 4: Conclusion (a) $r = 100\sqrt{3}\,\text{pm} \approx 173.2\,\text{pm}$. (b)(i) Impurity defect. (ii) Doping creates one X^{+} vacancy per Z^{2+} ion to preserve electrical neutrality.

Quick Tip to Solve: For bcc use the body diagonal, $4r = \sqrt{3}a$; for divalent doping, balance charge before counting the vacancies.

16. Give reasons:

(a) Propanone is less reactive than ethanal towards nucleophilic addition reactions.

(b) O_2N - CH_2 - COOH has lower pKa value than CH_3COOH.

(c) $(CH_3)_2CH$ - CHO undergoes aldol condensation whereas $(CH_3)_3C$ - CHO does not. [3 marks]

Solution:

Concept:

- Nucleophilic addition begins with attack on the electron-deficient carbonyl carbon. Electron-releasing groups decrease its electrophilicity, while bulky groups hinder the approaching nucleophile.
- An electron-withdrawing group stabilises a carboxylate conjugate base by its negative inductive effect. Greater acid strength means larger K_a and lower $pK_a = -\log K_a$.
- Aldol reactions require at least one α-hydrogen: a hydrogen attached to the carbon immediately adjacent to the carbonyl carbon.

Step 1: (a) Compare propanone with ethanal Propanone, CH_3COCH_3, has two electron-releasing methyl groups attached to its carbonyl carbon, whereas ethanal, CH_3CHO, has only one. Their positive inductive effect reduces the partial positive charge on the carbonyl carbon more in propanone, so it is less susceptible to nucleophilic attack. Also, two methyl groups cause greater steric hindrance than a methyl group and a hydrogen. Both electronic and steric effects therefore make propanone less reactive.

Step 2: (b) Explain the lower pKa of nitroacetic acid The NO_2 group in O_2NCH_2COOH is strongly electron-withdrawing. Its negative inductive effect stabilises the negative charge of the conjugate base $O_2NCH_2COO^-$, favouring dissociation of the acid. In acetic acid, the methyl group has a positive inductive effect and destabilises the carboxylate ion relative to this nitro-substituted carboxylate. Hence nitroacetic acid has the larger K_a and the lower pK_a.

Step 3: (c) Check the alpha-hydrogens In $(CH_3)_2CHCHO$, the carbon adjacent to $-CHO$ is a CH group and bears one α-hydrogen. A base can remove it to form an enolate, which attacks another carbonyl molecule and gives the aldol product. In $(CH_3)_3CCHO$, the adjacent carbon is bonded to three methyl groups and the carbonyl carbon, so it bears no hydrogen. It cannot form the required enolate and does not undergo the usual aldol reaction. Hydrogens on its methyl groups are not α-hydrogens.

Step 4: Conclusion (a) Two methyl groups reduce electrophilicity and increase steric hindrance in propanone. (b) The $-I$ effect of NO_2 stabilises the conjugate base and lowers pK_a. (c) $(CH_3)_2CHCHO$ has an α-hydrogen; $(CH_3)_3CCHO$ has none.

Quick Tip to Solve: Locate the carbon directly next to the carbonyl before counting alpha-hydrogens; methyl hydrogens farther away do not qualify.

17. Write the names and structures of the monomers of the following polymers:

(a) Terylene

(b) Teflon

(c) Nylon-6,6 [3 marks]

Solution:

Concept:

- A monomer is a small molecule that combines with other molecules to form a polymer. Condensation polymers use bifunctional monomers that form ester or amide linkages with loss of small molecules.
- Addition polymerisation opens a monomer's carbon-carbon double bond without eliminating a small molecule. The atoms attached to those carbons remain attached in the repeating unit.

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

$$\mathrm{HO-CH_2-CH_2-OH} \qquad \text{and} \qquad \mathrm{HOOC-C_6H_4-COOH}\ (1,4\text{-positions}).$$

The two hydroxyl groups of the diol react with carboxyl groups of the diacid to form ester linkages with elimination of water. In terephthalic acid the carboxyl groups occupy opposite positions on the benzene ring; this specifies the para isomer.

Step 2: (b) Monomer of Teflon The monomer is tetrafluoroethene (tetrafluoroethylene), with structure

$$\mathrm{CF_2=CF_2}.$$

Addition polymerisation opens its double bond to give repeating $-\mathrm{CF_2-CF_2}-$ units. All four substituents on the two alkene carbons are fluorine atoms, distinguishing this monomer from ethene and chloroethene.

Step 3: (c) Monomers of Nylon-6,6 Nylon-6,6 is made from hexamethylenediamine (hexane-1,6-diamine) and adipic acid (hexanedioic acid). Their structures are

$$\mathrm{H_2N-(CH_2)_6-NH_2} \qquad \text{and} \qquad \mathrm{HOOC-(CH_2)_4-COOH}.$$

Amino and carboxyl groups condense to form amide linkages with loss of water. The diamine has six carbon atoms, and the diacid also has six: four methylene carbons plus the two carboxyl carbons. These counts explain the two sixes in the polymer's name.

Step 4: Conclusion Terylene: ethylene glycol and terephthalic acid; Teflon: tetrafluoroethene; Nylon-6,6: hexamethylenediamine and adipic acid, with the structures given above.

Quick Tip to Solve: For Nylon-6,6 count the carboxyl carbons too: adipic acid has four methylene groups but six carbon atoms in total.

18. (a) Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$.

(b) $[Ni(CN)_4]^{2-}$ is colourless whereas $[Ni(H_2O)_6]^{2+}$ is green. Why? (At. no. of Ni = 28) [3 marks]

Solution:

Concept:

- Crystal field splitting energy is the energy separation between the two sets of metal d orbitals produced by the ligand field. In an octahedral field it is denoted by Δ_o.
- The pairing energy P is the energy needed to pair two electrons in an orbital. Comparing Δ_o with P determines whether electrons pair or occupy the higher set.
- Colour depends on absorption of visible light during electronic transitions between separated energy levels. Ligand strength and complex geometry affect that separation.

Step 1: Define the octahedral splitting In an octahedral complex, the d_{xy}, d_{yz}, d_{xz} orbitals form the lower-energy t_{2g} set, while $d_{x^2-y^2}, d_{z^2}$ form the higher-energy e_g set. Thus

$$\Delta_o = E(e_g) - E(t_{2g}).$$

This is the crystal field splitting energy asked for in part (a).

Step 2: Place the four d electrons When $\Delta_o < P$, promotion to an e_g orbital costs less energy than pairing in a t_{2g} orbital. The first three electrons occupy the three t_{2g} orbitals singly; the fourth occupies an e_g orbital. The high-spin configuration is therefore

$$t_{2g}^3 e_g^1,$$

with four unpaired electrons.

Step 3: Compare the nickel complexes Nickel has configuration $[Ar]3d^8 4s^2$, so Ni^{2+} is $3d^8$. The strong-field ligand CN^- produces substantial splitting and a square-planar complex, $[Ni(CN)_4]^{2-}$, with paired electrons. Its relevant d-level excitation does not absorb visible light in the description given, so it is colourless. Water is a weaker-field ligand: $[Ni(H_2O)_6]^{2+}$ is octahedral with $t_{2g}^6 e_g^2$ and two unpaired electrons. Its d-d transitions absorb visible light, and the transmitted complementary light makes it appear green. The direct cause of colour is the wavelength absorbed; electron pairing alone is not a general colour test.

Step 4: Conclusion Δ_o is the octahedral d-level separation; for d^4 with $\Delta_o < P$, the configuration is $t_{2g}^3 e_g^1$. The cyanide and aqua complexes have different ligand-field splitting and hence different visible-light absorption.

Quick Tip to Solve: For d-electron placement, compare splitting with pairing energy first; for colour, ask whether the transition absorbs visible light.

19. What happens when

(a) $(CH_3)_3C$ - OH is treated with Cu at 573 K,

(b) Anisole is treated with CH_3Cl/anhydrous $AlCl_3$,

(c) Phenol is treated with Zn dust?

Write chemical equations in support of your answer. [3 marks]

Solution:

Concept:

- Heated copper dehydrogenates primary and secondary alcohols, but a tertiary alcohol lacks a hydrogen on the carbon bearing OH and undergoes dehydration.
- The methoxy group activates the benzene ring and directs electrophilic substitution to its ortho and para positions.
- Zinc dust removes the oxygen of phenol as zinc oxide, converting phenol into benzene.

Step 1: Dehydrate tert-butanol in part (a) The carbon attached to OH in $(CH_3)_3COH$ is bonded to three carbon atoms and has no hydrogen. It cannot undergo the usual copper-catalysed dehydrogenation to a carbonyl compound. At $573\,K$, it loses water to form 2-methylpropene:

$$(CH_3)_3COH \xrightarrow[573\,K]{Cu} CH_2 = C(CH_3)_2 + H_2O.$$

A hydrogen is removed from an adjacent methyl group as the double bond forms.

Step 2: Methylate anisole in part (b) Anisole undergoes Friedel-Crafts alkylation with methyl chloride and anhydrous aluminium chloride. Donation of electron density by the methoxy group favours ortho and para substitution. The para product is major because it is less sterically crowded.

$$C_6H_5OCH_3 + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} o\text{-}CH_3C_6H_4OCH_3 + HCl.$$

The corresponding para substitution is

$$C_6H_5OCH_3 + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} p\text{-}CH_3C_6H_4OCH_3 + HCl.$$

These are 2-methylanisole and 4-methylanisole, respectively; the equations describe alternative products, not simultaneous stoichiometric products.

Step 3: Reduce phenol in part (c) On heating phenol with zinc dust, zinc takes up its oxygen and forms zinc oxide. The aromatic ring is retained and OH is replaced by hydrogen:

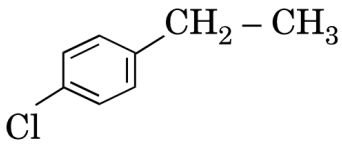
$$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO.$$

Thus benzene is obtained, with the hydrogen count unchanged overall.

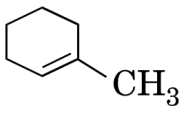
Step 4: Conclusion (a) 2-Methylpropene forms by dehydration. (b) Ortho- and para-methylanisole form, with the para isomer major. (c) Phenol gives benzene and zinc oxide.

Quick Tip to Solve: Before applying the heated-copper rule, check for a hydrogen on the OH-bearing carbon; tert-butanol has none.

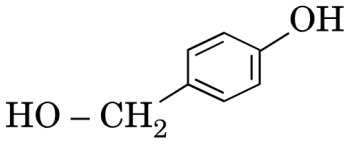
20. Draw the structures of the major monohalo product for each of the following reactions: [3 marks]

(a) 

$\xrightarrow{Br_2,\ heat}$?

(b) 

+ HBr $\longrightarrow$?

(c) 

$\xrightarrow{HCl,\ heat}$?

Solution:

Concept:

- Bromination with heat follows a free-radical pathway and strongly favours the benzylic position because a benzylic radical is resonance stabilised.
- HBr adds to an unsymmetrical alkene by Markovnikov addition in the absence of peroxide: the more stable carbocation determines the major product.
- HCl replaces the OH group of a benzylic alcohol with chlorine. Phenolic OH is not replaced by HCl under these conditions.

Step 1: Brominate the side chain in (a) The substrate is para-chloroethylbenzene, p-$ClC_6H_4CH_2CH_3$. Heat promotes homolytic cleavage of bromine. Removal of a benzylic hydrogen gives a radical whose unpaired electron is delocalised into the aromatic ring; removal from the terminal methyl group would give a less stable primary radical. Bromine therefore replaces one hydrogen on the carbon next to the ring:

$$p\text{-}ClC_6H_4CH_2CH_3 + Br_2 \xrightarrow{\text{heat}} p\text{-}ClC_6H_4CH(Br)CH_3 + HBr.$$

The pre-existing aryl chlorine remains attached to the ring. Here monohalogenation means introduction of one new halogen atom.

Step 2: Apply Markovnikov addition in part (b) In 1-methylcyclohexene, one carbon of the double bond bears a methyl group. Addition of hydrogen to the other alkene carbon leaves a tertiary carbocation at the methyl-bearing carbon; the opposite orientation would give a secondary carbocation. Bromide attacks the tertiary centre. Thus Br and the original methyl group lie on the same ring carbon, giving 1-bromo-1-methylcyclohexane. The double bond becomes a single bond, and only one bromine atom is added.

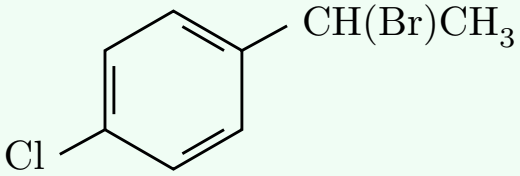
Step 3: Distinguish the two OH groups in part (c) The substrate is p-$HOC_6H_4CH_2OH$. The side-chain OH is an alcohol group bonded to an sp3 carbon, while the other OH is phenolic. In hot HCl, protonation of the benzylic OH allows water to leave and chloride replaces it. The phenolic C-O bond has partial double-bond character through resonance and resists this substitution. Hence

$$p\text{-}HOC_6H_4CH_2OH + HCl \xrightarrow{\text{heat}} p\text{-}HOC_6H_4CH_2Cl + H_2O.$$

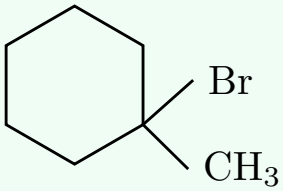
Quick Tip to Solve: Use the reagent conditions to choose the reaction site: heat with bromine selects the benzylic C-H bond; hot HCl replaces benzylic alcohol OH.

The product is 4-(chloromethyl)phenol; its ring OH remains intact.

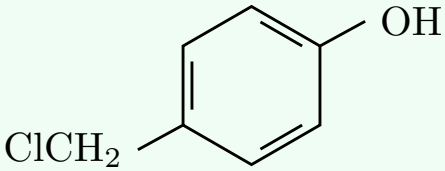
(a)



(b)



(c)



Structures of the three major products, labelled (a), (b) and (c).

Step 4: Conclusion The labelled structures show the major products: (a) benzylic bromination, (b) 1-bromo-1-methylcyclohexane, and (c) 4-(chloromethyl)phenol. The ring chlorine in (a) and the phenolic OH in (c) remain unchanged.

Quick Tip to Solve: Use the reagent conditions to choose the reaction site: heat with bromine selects the benzylic C-H bond; hot HCl replaces benzylic alcohol OH.

21. Account for the following:

(a) $CuCl_2$ is more stable than Cu_2Cl_2.

(b) Atomic radii of 4d and 5d series elements are nearly same.

(c) Hydrochloric acid is not used in permanganate titrations. [3 marks]

Solution:

Concept:

- Stability of an oxidation state in aqueous solution depends on the overall energy change, including hydration enthalpy, and cannot be predicted from electronic configuration alone.
- Poor shielding by $4f$ electrons produces lanthanoid contraction, while acidified permanganate is a strong oxidising agent capable of oxidising chloride ions.

Step 1: (a) Compare copper(I) and copper(II) stability In Cu_2Cl_2, copper is in the $+1$ oxidation state; in $CuCl_2$, it is in the $+2$ state. Although Cu^+ has the filled $3d^{10}$ configuration, Cu^{2+} has a much more negative hydration enthalpy because of its greater charge density. This hydration energy compensates for the energy needed to remove the second electron. Consequently, Cu^{2+} is more stable in aqueous

Quick Tip to Solve: Link the three reasons to hydration enthalpy, poor shielding by 4f electrons, and unwanted oxidation of chloride, respectively.

solution and Cu^{+} tends to disproportionate:

$$2Cu^{+}(aq) \longrightarrow Cu^{2+}(aq) + Cu(s).$$

Step 2: (b) Explain the similar radii of the two transition series The $5d$ series follows the lanthanoids, across which electrons fill the $4f$ subshell. These electrons shield the increasing nuclear charge poorly, so the effective nuclear charge rises and the atoms contract. This lanthanoid contraction largely offsets the increase in size expected from the extra shell in the $5d$ series. Thus corresponding $4d$ and $5d$ elements, such as Zr and Hf, have nearly the same atomic radii.

Step 3: (c) Identify the interfering reaction in a permanganate titration Hydrochloric acid supplies Cl^{-} ions, which acidified permanganate oxidises to chlorine. Permanganate is therefore consumed in a side reaction in addition to reacting with the substance being titrated:

$$2MnO_4^{-} + 16H^{+} + 10Cl^{-} \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2.$$

This extra consumption gives an inaccurate titre. Dilute sulphuric acid is used to provide the acidic medium instead.

Step 4: Conclusion (a) Greater hydration of Cu^{2+} favours $CuCl_2$ in aqueous solution. (b) Lanthanoid contraction makes corresponding $4d$ and $5d$ radii nearly equal. (c) HCl is avoided because permanganate oxidises chloride to chlorine.

Quick Tip to Solve: Link the three reasons to hydration enthalpy, poor shielding by 4f electrons, and unwanted oxidation of chloride, respectively.

22. Define the following terms:

(a) Tranquilizer

(b) Anionic detergent

(c) Disinfectant [3 marks]

Solution:

Concept:

- Medicinal drugs and cleansing agents are classified by their biological action or by the charge on the active species responsible for their action.
- A disinfectant destroys microorganisms on non-living objects; an antiseptic is suitable for application to living tissues at an appropriate concentration.

Step 1: (a) Define a tranquilizer A tranquilizer is a drug used to treat stress and mild or severe mental disorders by relieving anxiety and tension. It acts on the central nervous system and produces a calming effect. Such drugs can help relieve irritability or mental agitation. Diazepam is an example of a tranquilizer. The defining feature is its calming action in the treatment of mental disorders, rather than an action against microorganisms.

Step 2: (b) Define an anionic detergent Anionic detergents are cleansing agents in which the anionic,

Quick Tip to Solve: For each definition state the distinguishing feature: calming action, a negatively charged cleansing ion, or use on non-living surfaces.

or negatively charged, part of the molecule is responsible for the cleansing action. They are commonly sodium salts of sulphonated long-chain alcohols or hydrocarbons. An example is sodium lauryl sulphate:

$$CH_3(CH_2)_{11}OSO_3^-Na^+.$$

Its long hydrocarbon chain interacts with grease, while its negatively charged head interacts with water. Thus the active detergent ion is an anion; the sodium ion is the counter-ion.

Step 3: (c) Define a disinfectant A disinfectant is a chemical substance used to kill or destroy microorganisms on non-living objects such as floors, drains and instruments. It is generally unsuitable for application to living tissues at the concentration used for disinfection. For example, a 1% phenol solution acts as a disinfectant. Its use on inanimate surfaces distinguishes it from an antiseptic, which is applied to living tissues at a suitable concentration.

Step 4: Conclusion A tranquilizer relieves anxiety and mental tension; an anionic detergent cleans through its negatively charged active ion; and a disinfectant destroys microorganisms on non-living objects.

Quick Tip to Solve: For each definition state the distinguishing feature: calming action, a negatively charged cleansing ion, or use on non-living surfaces.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Veena, a class XII student, decided to make others aware about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct the canteen contractor to stop selling sandwiches, pizzas, burgers and other bakery products to the students. The principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins-rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and students.

After reading the above passage, answer the following questions:

(a) What are the values (at least two) displayed by Veena?

(b) Which polysaccharide component of carbohydrates is commonly present in bread?

(c) Write the two types of secondary structures of proteins.

(d) Give two examples of water soluble vitamins. [4 marks]

Solution:

Concept:

- Responsible use of scientific information includes concern for others' health and taking constructive action through the appropriate authority.
- Starch is a plant storage polysaccharide made of glucose units; cereal flour is a major source of starch.
- Secondary protein structure describes regular folding of the polypeptide backbone, stabilised by hydrogen bonds between peptide groups.
- Vitamins are classified by solubility: the B-group vitamins and vitamin C are water soluble.

Quick Tip to Solve: Match each part to its category: values from actions, starch in cereal flour, helix/sheet for secondary protein structure, and B or C for water-soluble vitamins.

Step 1: (a) Identify Veena's values from her actions Veena displays **social responsibility** and **concern for the health and welfare of others**. She does not keep the information to herself: she tries to protect fellow students from the harmful substances described in the programme. Approaching the principal also shows initiative and scientific awareness.

Step 2: (b) Identify the polysaccharide in bread Bread is commonly prepared from cereal flour, which contains **starch**. Starch is a polysaccharide consisting of glucose units and has two components, amylose and amylopectin. Glucose itself is a monosaccharide, not the required polysaccharide.

Step 3: (c) Name the secondary structures of proteins The two standard secondary structures are the α-helix and the β-pleated sheet. In an α-helix the polypeptide chain coils regularly, while in a β-pleated sheet extended chain segments lie beside one another. Hydrogen bonding involving the backbone $\mathrm{C=O}$ and $\mathrm{N-H}$ groups stabilises these arrangements.

Step 4: (d) Give two water-soluble vitamins Two examples are **vitamin $\mathrm{B_1}$ (thiamine)** and **vitamin C (ascorbic acid)**. Both dissolve in water; vitamins A, D, E and K instead belong to the fat-soluble category.

Step 5: Conclusion (a) Social responsibility and concern for others' health; (b) starch; (c) α-helix and β-pleated sheet; (d) vitamin $\mathrm{B_1}$ and vitamin C.

Quick Tip to Solve: Match each part to its category: values from actions, starch in cereal flour, helix/sheet for secondary protein structure, and B or C for water-soluble vitamins.

24(a). A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.

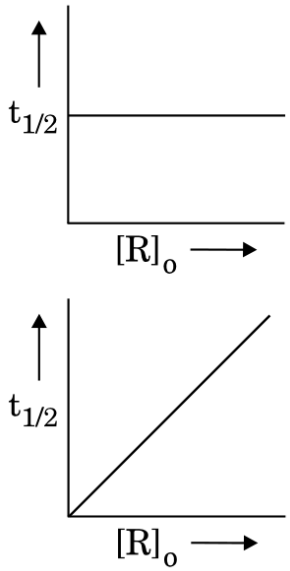
(b) Predict the order of the reaction in the given plots:

(i)

(ii)

where $[R]_0$ is the initial concentration of reactant.

(Given: log 2 = 0.3010, log 4 = 0.6021) [5 marks]



Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are the initial and remaining reactant concentrations and k is the rate constant.
- The first-order half-life is $t_{1/2} = \dfrac{2.303\log 2}{k}$. It is independent of the initial concentration.
- For a zero-order reaction, $[R]_t = [R]_0 - kt$, so $t_{1/2} = \dfrac{[R]_0}{2k}$. At fixed k, the half-life is directly proportional to the initial concentration.

Step 1: (a) Convert completion into the fraction remaining Completion of 75% means that 25% of the initial reactant remains after 40 min. Therefore,

$$[R]_{40} = 0.25[R]_0, \qquad \frac{[R]_0}{[R]_{40}} = 4.$$

The concentration ratio in the integrated rate equation uses the amount remaining, rather than the amount consumed. Substituting this ratio gives

$$k = \frac{2.303}{40}\log 4 = \frac{2.303 \times 0.6021}{40} = 0.03467\,\text{min}^{-1}.$$

Step 2: (a) Calculate the half-life and check the result Using the supplied logarithm of 2,

$$t_{1/2} = \frac{2.303 \times 0.3010}{0.03467} \simeq 20.0\,\text{min}.$$

Equivalently, eliminating k directly gives

$$t_{1/2} = 40\frac{\log 2}{\log 4} = 40\frac{0.3010}{0.6021} \simeq 20.0\,\text{min}.$$

This agrees with the successive-halving interpretation: the reactant falls from its initial concentration to one-half after one half-life, and to one-quarter after two half-lives. Thus the given time spans two half-lives; the tiny difference from exactly 20 in the logarithmic calculation is due to rounding of the supplied logarithms.

Step 3: (b)(i) Interpret the horizontal half-life plot The vertical axis is $t_{1/2}$, and the horizontal axis is $[R]_0$. The horizontal line shows that changing the initial concentration does not change the half-life. This is the characteristic dependence for a first-order reaction, because $t_{1/2} = 2.303\log 2/k$ contains no concentration term. The plot is of half-life against initial concentration; it should not be mistaken for a reactant concentration against time plot.

Step 4: (b)(ii) Interpret the straight line through the origin Here $t_{1/2}$ increases linearly with $[R]_0$, and the straight line passes through the origin. For a zero-order reaction, setting $[R]_t = [R]_0/2$ in $[R]_t = [R]_0 - kt$ gives

$$\frac{[R]_0}{2} = [R]_0 - kt_{1/2} \quad \Longrightarrow \quad t_{1/2} = \frac{[R]_0}{2k}.$$

The slope of this plot is therefore $1/(2k)$. Its direct proportionality identifies the zero-order reaction; a first-order reaction would instead give the horizontal line seen in plot (i).

Quick Tip to Solve: For a first-order reaction, 75 percent completion leaves one-quarter of the reactant, so the elapsed time equals two half-lives. Always identify both graph axes before using a straight line to infer order.

Step 5: Conclusion (a) $\boxed{t_{1/2} = 20\,\text{min}}$. (b) Plot (i): $\boxed{\text{first order}}$; plot (ii): $\boxed{\text{zero order}}$.

Quick Tip to Solve: For a first-order reaction, 75 percent completion leaves one-quarter of the reactant, so the elapsed time equals two half-lives. Always identify both graph axes before using a straight line to infer order.

OR

24(b). The following data were obtained for the reaction:

$2\,NO + O_2 \rightarrow 2\,NO_2$

Experiment	[NO]/M	[O_2]/M	Initial rate of formation of NO_2 / M min^{-1}
1	0.3	0.2	7.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.40×10^{-2}

(a) Find the order of reaction with respect to NO and O_2.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k). [5 marks]

Solution:

Concept:

- The experimental rate law is $r_f = k[\text{NO}]^m[\text{O}_2]^n$, where r_f is the given initial rate of formation of NO_2, m and n are the orders with respect to the two reactants, and k is the rate constant.
- Compare experiments in which one reactant concentration is unchanged. The ratio of the measured rates then isolates the exponent of the reactant whose concentration changes. Reaction orders must be obtained from these data, rather than from the stoichiometric coefficients.
- The overall order is $m+n$. For an overall order p, the units of k are $\text{M}^{1-p}\,\text{min}^{-1}$ when concentration is in molarity and time in minutes.

Step 1: (a) Determine the order with respect to oxygen Compare experiments 1 and 3. The concentration of NO remains $0.3\,\text{M}$, while the oxygen concentration doubles from $0.2\,\text{M}$ to $0.4\,\text{M}$. The measured rate increases by a factor of four:

$$\frac{r_3}{r_1} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = 4 = \left(\frac{0.4}{0.2}\right)^n = 2^n.$$

Thus $n = 2$: the reaction is second order with respect to O_2.

Step 2: (a) Determine the order with respect to nitric oxide Compare experiments 2 and 4. The concentration of oxygen remains $0.1\,\text{M}$, while the NO concentration increases fourfold from $0.1\,\text{M}$ to $0.4\,\text{M}$. Consequently,

$$\frac{r_4}{r_2} = \frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = 4 = \left(\frac{0.4}{0.1}\right)^m = 4^m.$$

Quick Tip to Solve: Use experiments 1 and 3 for oxygen, and 2 and 4 for NO: each pair keeps the other reactant fixed, so no simultaneous equations are needed.

Hence $m = 1$: the reaction is first order with respect to NO.

Step 3: (b) Write the rate law and determine the overall order Substitution of the experimentally determined exponents into the general rate expression gives

$$r_f = \frac{d[\mathrm{NO_2}]}{dt} = k[\mathrm{NO}][\mathrm{O_2}]^2, \qquad m + n = 1 + 2 = 3.$$

The reaction is therefore third order overall. Here the rate law uses the product-formation rate explicitly supplied in the table; the numerical constant must be calculated using that same rate convention.

Step 4: (c) Calculate and check the rate constant Using experiment 2,

$$k = \frac{r_f}{[\mathrm{NO}][\mathrm{O_2}]^2} = \frac{6.0 \times 10^{-3}}{(0.1)(0.1)^2} = 6.0\,\mathrm{M^{-2}\,min^{-1}}.$$

The units follow from dividing $\mathrm{M\,min^{-1}}$ by $\mathrm{M^3}$; equivalently they are $\mathrm{L^2\,mol^{-2}\,min^{-1}}$. Check the result using the other three experiments:

$$r_1 = 6.0(0.3)(0.2)^2 = 0.072,$$
$$r_3 = 6.0(0.3)(0.4)^2 = 0.288,$$
$$r_4 = 6.0(0.4)(0.1)^2 = 0.024.$$

Each calculated value, in $\mathrm{M\,min^{-1}}$, agrees with the corresponding initial rate in the printed table.

Step 5: Conclusion (a) Order with respect to NO: 1; order with respect to $\mathrm{O_2}$: 2. (b) $r_f = k[\mathrm{NO}][\mathrm{O_2}]^2$, and overall order $= 3$. (c) $k = 6.0\,\mathrm{L^2\,mol^{-2}\,min^{-1}}$.

Quick Tip to Solve: Use experiments 1 and 3 for oxygen, and 2 and 4 for NO: each pair keeps the other reactant fixed, so no simultaneous equations are needed.

25(a). Account for the following:

(i) BiH_3 is the strongest reducing agent in Group 15 elements hydrides.

(ii) Cl_2 acts as a bleaching agent.

(iii) Noble gases have very low boiling points.

(b) Draw the structures of the following:

(i) $H_4P_2O_7$

(ii) $XeOF_4$ [5 marks]

Solution:

Concept:

- Reducing power of Group 15 hydrides increases as the element–hydrogen bond weakens down the group; a less stable hydride is more readily oxidised.
- Chlorine bleaches moist coloured substances by oxidation. Noble gases are monatomic, nonpolar species held together only by weak London dispersion forces.

Quick Tip to Solve: Count oxygen neighbours around each P, and count Xe=O as one VSEPR domain: XeOF4 has five bonds plus one lone pair.

- A phosphorus atom in pyrophosphoric acid has a tetrahedral oxygen environment. In $XeOF_4$, five bonding domains and one lone pair around xenon give a square-pyramidal molecular shape.

Step 1: (a)(i) Explain the reducing power of bismuthine Down Group 15, atomic size increases and overlap between the hydrogen orbital and the central atom's orbital becomes poorer. Consequently, the element–hydrogen bond strength and the thermal stability of the hydrides decrease. The Bi–H bond in BiH_3 is the weakest among these hydrides, making bismuthine the least stable and most readily oxidised. Thus it most readily reduces another substance. The trend in reducing power is

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

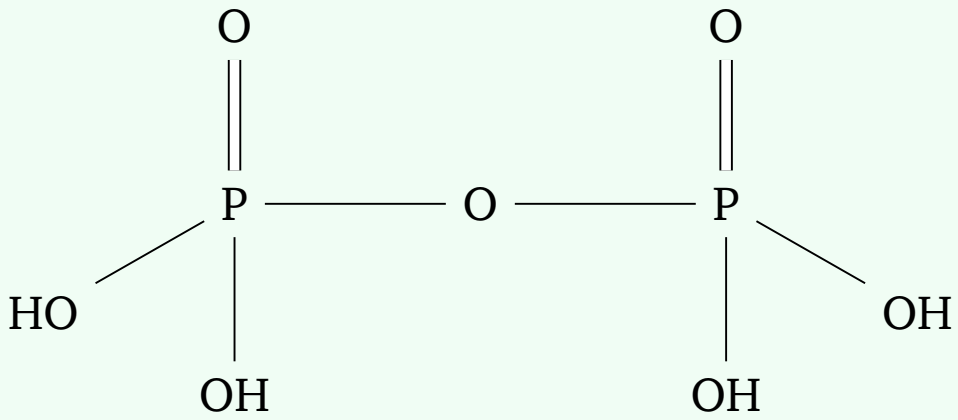
Step 2: (a)(ii) Explain chlorine bleaching Chlorine reacts with water to form hydrochloric acid and hypochlorous acid. Hypochlorous acid supplies oxidising oxygen, conventionally represented as $[O]$:

$$Cl_2 + H_2O \longrightarrow HCl + HOCl,$$
$$HOCl \longrightarrow HCl + [O].$$

This oxygen oxidises the coloured substance to a colourless product. Moisture is therefore essential for bleaching by chlorine, and the bleaching is permanent because it involves a chemical oxidation of the colouring material.

Step 3: (a)(iii) Explain the low boiling points of noble gases Noble gases have completely filled valence shells and exist as individual atoms. Their atoms are nonpolar, so they do not experience permanent dipole–dipole attraction or hydrogen bonding. Only weak London dispersion forces act between them. Very little thermal energy is needed to overcome these attractions on boiling; hence their boiling points are very low. The forces become stronger with increasing atomic size and polarizability down the group, but remain weak compared with ordinary chemical bonds.

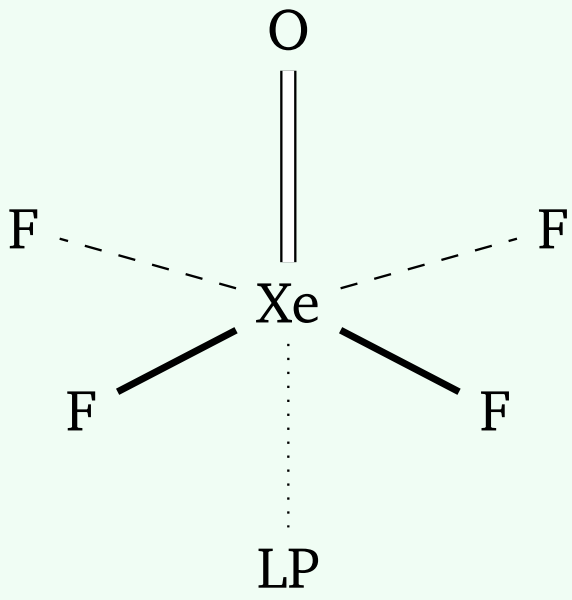
Step 4: (b)(i) Draw pyrophosphoric acid Pyrophosphoric acid, $H_4P_2O_7$, contains two phosphorus atoms connected through a bridging oxygen atom. Each phosphorus is attached to one doubly bonded oxygen and two hydroxyl groups. Its connectivity is $(HO)_2P(=O)-O-P(=O)(OH)_2$. The four O–H bonds account for its four acidic hydrogen atoms; no P–H bond is present. Each phosphorus has a tetrahedral arrangement of its four oxygen neighbours.



Pyrophosphoric acid: two tetrahedral phosphorus centres joined by oxygen

Quick Tip to Solve: Count oxygen neighbours around each P, and count Xe=O as one VSEPR domain: XeOF4 has five bonds plus one lone pair.

Step 5: (b)(ii) Draw xenon oxytetrafluoride Xenon has four Xe–F single bonds, one Xe=O double bond and one lone pair. The double bond counts as one electron domain, giving six domains in all and an octahedral electron-domain arrangement. The oxygen occupies one axial position and the lone pair occupies the opposite axial position. Four fluorine atoms form the square base, so the molecular geometry is square pyramidal. The drawing indicates the lone pair below xenon and oxygen above the square of fluorine atoms.



Square-pyramidal XeOF4; LP denotes the lone pair opposite oxygen

Step 6: Conclusion BiH_3 is the strongest reducing hydride because its Bi–H bonds are weakest; chlorine bleaches by oxidation in the presence of moisture; noble gases boil at low temperatures because their interatomic dispersion forces are weak. The structures are the P–O–P bridged $H_4P_2O_7$ and square-pyramidal $XeOF_4$, as drawn.

Quick Tip to Solve: Count oxygen neighbours around each P, and count Xe=O as one VSEPR domain: XeOF4 has five bonds plus one lone pair.

OR

25(b). (a) Although nitrogen and chlorine have nearly same electronegativity yet nitrogen forms hydrogen bonding while chlorine does not. Why?

(b) What happens when F_2 reacts with water?

(c) Write the name of the gas evolved when Ca_3P_2 is dissolved in water.

(d) Write the formula of a noble gas species which is isostructural with IBr_2^-.

(e) Complete the equation: $[Fe(H_2O)_6]^{2+} + NO \longrightarrow ?$ [5 marks]

Solution:

Concept:

- Strong hydrogen bonding requires hydrogen bonded to a small, highly electronegative atom, especially nitrogen, oxygen or fluorine. Atomic size affects charge density as well as electronegativity.
- Fluorine is a strong oxidising agent and oxidises water to oxygen while forming hydrogen fluoride. Metal phosphides undergo hydrolysis to release phosphine.
- VSEPR predicts molecular shape from bond pairs and lone pairs on the central atom. Ligand substitution replaces a coordinated water molecule by another ligand without changing the number of coordination sites.

Step 1: (a) Compare the atomic sizes of nitrogen and chlorine Nitrogen is much smaller than chlorine. Its small size and high electronegativity make the $N-H$ bond strongly polar, and the lone pair on nitrogen has a high charge density. Hence nitrogen forms appreciable hydrogen bonds, as between ammonia molecules. Chlorine has a larger, more diffuse electron cloud; although its electronegativity is similar, its charge density is lower and it does not form appreciable hydrogen bonding of this kind. Electronegativity alone is therefore insufficient to decide whether strong hydrogen bonding occurs.

Step 2: (b) Describe the reaction of fluorine with water Fluorine reacts vigorously with water, producing hydrogen fluoride and oxygen. The balanced equation is

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2.$$

Oxygen in water changes from oxidation state -2 to 0, whereas fluorine changes from 0 to -1. Thus water is oxidised and fluorine is reduced. The products account for all four fluorine atoms, four hydrogen atoms and two oxygen atoms.

Step 3: (c) Identify the gas from calcium phosphide Calcium phosphide undergoes hydrolysis with water and evolves phosphine, PH_3. The balanced reaction is

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3 \uparrow .$$

The three calcium atoms form calcium hydroxide, while the two phosphorus atoms give two molecules of phosphine. The gas asked for is phosphine.

Step 4: (d) Find the isostructural noble gas species In IBr_2^-, iodine has two bond pairs and three lone pairs. Its five electron pairs have a trigonal bipyramidal arrangement, with the three lone pairs occupying equatorial positions and the two bonds occupying axial positions. The molecular shape is therefore linear. XeF_2 also has two bond pairs and three lone pairs on its central atom, so it is linear

Quick Tip to Solve: For the linear species, count three equatorial lone pairs and two axial bonds; for the nitrosyl complex, replace exactly one coordinated water and release it as a product.

and isostructural with IBr_2^-.

Step 5: (e) Complete the coordination reaction with nitric oxide Nitric oxide replaces one water ligand in the hexaaquairon(II) ion, forming the brown nitrosyl complex responsible for the brown-ring test for nitrate. The completed equation is

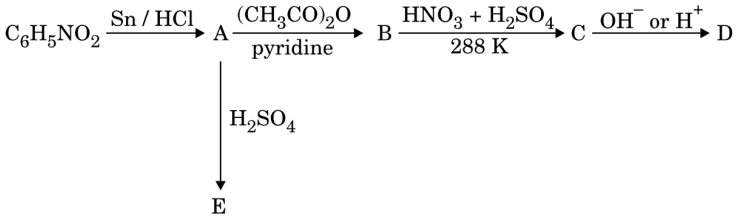
$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O.$$

The released water must be included to balance the reaction. The complex retains six coordination sites: five occupied by water and one by nitric oxide.

Step 6: Conclusion (a) Nitrogen's smaller size and greater charge density favour hydrogen bonding. (b) Fluorine gives HF and O_2 with water. (c) The gas is phosphine, PH_3. (d) The species is XeF_2. (e) The products are $[Fe(H_2O)_5(NO)]^{2+}$ and H_2O.

Quick Tip to Solve: For the linear species, count three equatorial lone pairs and two axial bonds; for the nitrosyl complex, replace exactly one coordinated water and release it as a product.

26(a). Write the structures of A, B, C, D and E in the following reactions: [5 marks]



Solution:

Concept:

- Tin and hydrochloric acid reduce the nitro group of nitrobenzene to an amino group. The aromatic ring remains unchanged.
- Acetylation converts $-NH_2$ into $-NHCOCH_3$. This protects the amino group during nitration; the acetamido group directs substitution mainly to the para position.
- Hydrolysis removes the acetyl protecting group. Sulphuric acid protonates aniline to form an anilinium salt when no heating for sulphonation is specified.

Step 1: Identify A by reduction Reduction of the nitro group gives aniline, whose condensed structural formula is $C_6H_5 - NH_2$:

$$C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O.$$

Thus A is aniline. In the acidic reaction mixture it is protonated, but the amine used in the subsequent acetylation is conventionally represented by its free-base structure.

Step 2: Identify B by acetylation Aniline reacts with acetic anhydride in pyridine to form acetanilide:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

Quick Tip to Solve: Follow the nitrogen group through reduction, acetylation and hydrolysis; retain the para nitro group once introduced. For the separate sulphuric-acid arrow, check for a heating condition before assigning sulphonation.

Therefore B has the structure $C_6H_5 - NH - C(=O) - CH_3$. The acetyl group reduces the strongly activating effect of the free amino group and prevents its direct protonation from controlling nitration.

Step 3: Identify C by nitration at 288 K The $-NHCOCH_3$ group is ortho/para directing. Nitration with the mixture of nitric and sulphuric acids at $288\,K$ gives predominantly para-nitroacetanilide, since the para position is less sterically hindered:

$$C_6H_5NHCOCH_3 + HNO_3 \longrightarrow p\text{-}NO_2 - C_6H_4 - NHCOCH_3 + H_2O.$$

Thus C is $p\text{-}NO_2 - C_6H_4 - NH - C(=O) - CH_3$, with the nitro and acetamido groups opposite each other on the benzene ring.

Step 4: Identify D by hydrolysis Acidic or alkaline hydrolysis cleaves the amide bond and restores the amino group, without removing the ring's nitro group. The neutral organic product is para-nitroaniline:

$$p\text{-}NO_2 - C_6H_4 - NHCOCH_3 + H_2O \longrightarrow p\text{-}NO_2 - C_6H_4 - NH_2 + CH_3COOH.$$

In alkaline medium the acid product is acetate; in acidic medium the amine is initially protonated. D is represented after work-up as $p\text{-}NO_2 - C_6H_4 - NH_2$.

Step 5: Identify E by the acid-base reaction The separate arrow from A specifies sulphuric acid without heating. The nitrogen lone pair accepts a proton, forming anilinium hydrogen sulphate:

$$C_6H_5NH_2 + H_2SO_4 \longrightarrow [C_6H_5NH_3]^+[HSO_4]^-.$$

Hence E is the salt $[C_6H_5 - NH_3]^+[HSO_4]^-$. Conversion of this salt into sulphanilic acid requires further heating at about 453–$473\,K$, which is not indicated on the printed arrow.

Step 6: Conclusion The required structures are:

$$\begin{aligned} A &= C_6H_5NH_2 && \text{(aniline)},\\ B &= C_6H_5NHCOCH_3 && \text{(acetanilide)},\\ C &= p\text{-}NO_2 - C_6H_4 - NHCOCH_3, &&\\ D &= p\text{-}NO_2 - C_6H_4 - NH_2, &&\\ E &= [C_6H_5NH_3]^+[HSO_4]^-. && \end{aligned}$$

C is para-nitroacetanilide, D is para-nitroaniline and E is anilinium hydrogen sulphate.

Quick Tip to Solve: Follow the nitrogen group through reduction, acetylation and hydrolysis; retain the para nitro group once introduced. For the separate sulphuric-acid arrow, check for a heating condition before assigning sulphonation.

OR

26(b). (a) Write the structures of the main products when benzene diazonium chloride reacts with the following reagents:

(i) CuCN

(ii) CH_3CH_2OH

(iii) Cu/HCl

(b) Arrange the following in the increasing order of their basic strength:

CH_3NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

(c) Write one chemical test to distinguish between Aniline and Ethyl amine. [5 marks]

Solution:

Concept:

- Aromatic diazonium salts undergo replacement of the diazonium group, $-N_2^+$, with elimination of nitrogen gas. CuCN replaces it by $-CN$, while Cu/HCl replaces it by $-Cl$.
- Ethanol reduces an aromatic diazonium group to hydrogen; ethanol itself is oxidised to ethanal.
- Basic strength depends on the availability of the nitrogen lone pair and stabilisation of the conjugate acid. Resonance reduces the basicity of aniline, whereas alkyl groups increase electron density on nitrogen through their positive inductive effect.

Step 1: (a)(i) Reaction with CuCN The diazonium group is replaced by a cyano group in the Sandmeyer reaction:

$$C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5 - C \equiv N + N_2.$$

The main organic product is benzonitrile. Its structural formula is $C_6H_5 - C \equiv N$: the benzene ring bonds to the carbon of the cyano group, not its nitrogen.

Step 2: (a)(ii) Reaction with ethanol Ethanol acts as a reducing agent and replaces the diazonium group with hydrogen:

$$C_6H_5N_2^+Cl^- + CH_3CH_2OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

The requested main product from the diazonium salt is benzene, $C_6H_5 - H$. Ethanal is the oxidation product of ethanol. This reaction removes the amino group after its conversion into the diazonium salt.

Step 3: (a)(iii) Reaction with Cu/HCl Copper in hydrochloric acid replaces the diazonium group by chlorine in the Gattermann reaction:

$$C_6H_5N_2^+Cl^- \xrightarrow{Cu/HCl} C_6H_5 - Cl + N_2.$$

The main product is chlorobenzene, with chlorine directly bonded to the benzene ring.

Step 4: (b) Compare the basic strengths In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring by resonance and is consequently less available to accept a proton. Aniline is therefore the weakest base of the four. In benzylamine, $C_6H_5CH_2NH_2$, the intervening $-CH_2-$ group prevents this direct conjugation. Benzylamine is thus stronger than aniline, but weaker than

Quick Tip to Solve: Identify the replacing group from the diazonium reagent first; for basicity, check whether nitrogen is directly attached to the benzene ring or separated by a methylene group.

methylamine because the phenyl group exerts an electron-withdrawing inductive influence through the carbon chain. Methyl groups donate electron density to nitrogen. In the usual aqueous comparison, dimethylamine is stronger than methylamine because its two methyl groups increase the availability of the lone pair, with favourable stabilisation of the protonated amine. The increasing order is

$$C_6H_5NH_2 < C_6H_5CH_2NH_2 < CH_3NH_2 < (CH_3)_2NH.$$

Step 5: (c) Distinguish aniline from ethylamine Add bromine water separately to the two samples at room temperature. Aniline decolourises bromine water and gives a white precipitate of 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2\,(2,4,6) + 3HBr.$$

The amino group strongly activates the benzene ring towards substitution at its two ortho positions and its para position. Ethylamine does not give this characteristic white precipitate of 2,4,6-tribromoaniline. Formation of this precipitate therefore identifies aniline.

Step 6: Conclusion (a) The main products are (i) benzonitrile, $C_6H_5 - C \equiv N$; (ii) benzene, C_6H_6; and (iii) chlorobenzene, $C_6H_5 - Cl$. (b) Increasing basic strength: $C_6H_5NH_2 < C_6H_5CH_2NH_2 < CH_3NH_2 < (CH_3)_2NH$. (c) Bromine water gives a white precipitate of 2,4,6-tribromoaniline with aniline; ethylamine does not give this precipitate.

Quick Tip to Solve: Identify the replacing group from the diazonium reagent first; for basicity, check whether nitrogen is directly attached to the benzene ring or separated by a methylene group.