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

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 carry **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. Write one similarity between Physisorption and Chemisorption. [1 mark]

Solution:

Concept:

- Adsorption is the accumulation of molecules of an adsorbate on the surface of an adsorbent.
- Both physical adsorption and chemical adsorption involve attraction between the surface and the adsorbed species.

Step 1: Identify the shared process In both cases, molecules are retained at the surface of the adsorbent, so their concentration at the surface exceeds that in the bulk.

Step 2: State one common energetic feature Both processes release heat when the adsorbate is attracted to the surface. Physical adsorption involves intermolecular forces, whereas chemical adsorption involves bond formation; the nature of the attraction differs, but both processes are exothermic.

Step 3: Conclusion Both physisorption and chemisorption are exothermic processes.

Quick Tip to Solve: For a similarity, select a shared property such as heat release; the type of bonding is a difference.

2. Write the structure of 2,4-dinitrochlorobenzene. [1 mark]

Solution:

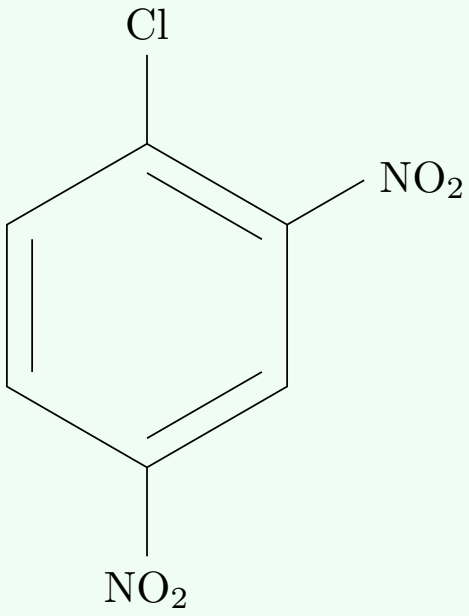
Concept:

- Chlorobenzene has a chlorine atom attached directly to a benzene-ring carbon.
- Ring numbering assigns the chlorine-bearing carbon position 1; the locants 2 and 4 specify the two nitro groups.

Step 1: Fix the chlorine position Start with a benzene ring and attach Cl at carbon 1. Number the remaining carbons consecutively around the ring.

Step 2: Place the two nitro groups Attach NO_2 at carbon 2 (ortho to chlorine) and carbon 4 (para to chlorine). The remaining positions, 3, 5 and 6, each carry one hydrogen. The nitro group is bonded to the ring through its nitrogen atom.

Quick Tip to Solve: Use chlorine as position 1, then put nitro groups at the adjacent carbon and the opposite carbon.



Structure of 2,4-dinitrochlorobenzene

Step 3: Conclusion The required structure is 1-chloro-2,4-dinitrobenzene, $C_6H_3Cl(NO_2)_2$, with the substituents at positions 1, 2 and 4.

Quick Tip to Solve: Use chlorine as position 1, then put nitro groups at the adjacent carbon and the opposite carbon.

3. For a reaction $R \to P$, half-life $t_{1/2}$ is observed to be independent of the initial concentration of reactants. What is the order of reaction? [1 mark]

Solution:

Concept:

- The half-life $t_{1/2}$ is the time required for the reactant concentration to become half its initial value.
- For a first-order reaction, $t_{1/2} = \ln 2/k$, where k is the first-order rate constant.

Step 1: Use the first-order rate equation For a first-order reaction, $kt = \ln([R]_0/[R]_t)$. At the half-life, $[R]_t = [R]_0/2$, so the ratio inside the logarithm becomes 2.

Step 2: Check the dependence on concentration Thus $t_{1/2} = \ln 2/k = 0.693/k$. The initial concentration cancels, agreeing with the observation. In contrast, a zero-order half-life is proportional to initial concentration, and a second-order half-life is inversely proportional to it.

Step 3: Conclusion The reaction is first order (order = 1).

Quick Tip to Solve: When the half-life stays constant as initial concentration changes, recognise first-order kinetics.

4. Write IUPAC name of the following compound:

$CH_3NHCH(CH_3)_2$ [1 mark]

Solution:

Concept:

- Name an amine from the carbon chain bearing the amino group, with its attachment position included.
- A substituent attached to the nitrogen atom is indicated by the prefix N-, rather than a carbon locant.

Step 1: Choose the parent chain Rewrite the structure as $CH_3 - CH(NHCH_3) - CH_3$. The carbon chain is propane, and the amino nitrogen is attached to carbon 2, so the parent name is propan-2-amine.

Step 2: Identify the nitrogen substituent The nitrogen also bears a methyl group, CH_3, in addition to hydrogen. This methyl group is attached to nitrogen rather than to the propane chain, so its prefix is N-methyl.

Step 3: Conclusion The IUPAC name is N-methylpropan-2-amine.

Quick Tip to Solve: Separate the two groups on nitrogen first; the longer carbon chain supplies the parent amine name.

5. Write the formula of an oxo-anion of Chromium (Cr) in which it shows the oxidation state equal to its group number. [1 mark]

Solution:

Concept:

- Chromium belongs to group 6, so the required chromium oxidation state is $+6$.
- For an oxo-anion, the sum of the oxidation states equals the overall ionic charge; oxygen has oxidation state -2.

Step 1: Choose a chromium oxo-anion Chromate, CrO_4^{2-}, contains one chromium atom and four oxygen atoms. Let the chromium oxidation state be x.

Step 2: Verify its oxidation state The charge balance gives $x + 4(-2) = -2$, hence $x = +6$. This equals the group number of chromium. Dichromate, $Cr_2O_7^{2-}$, also has chromium in the $+6$ oxidation state, but only one example is required.

Step 3: Conclusion An appropriate oxo-anion is the chromate ion, $\boxed{CrO_4^{2-}}$.

Quick Tip to Solve: Choose chromate and check the charge balance; four oxygens contribute a total oxidation state of -8.

6. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is $39.05\,\mathrm{S\,cm^2\,mol^{-1}}$.

Given: $\lambda^\circ(\mathrm{H^+}) = 349.6\,\mathrm{S\,cm^2\,mol^{-1}}$ **and** $\lambda^\circ(\mathrm{CH_3COO^-}) = 40.9\,\mathrm{S\,cm^2\,mol^{-1}}$**.** [2 marks]

Solution:

Concept:

- For a weak electrolyte, degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m is molar conductivity at the given concentration.
- By Kohlrausch's law, limiting molar conductivity is the sum of the limiting ionic conductivities: $\Lambda_m^\circ = \lambda^\circ(\mathrm{H^+}) + \lambda^\circ(\mathrm{CH_3COO^-})$.

Step 1: Calculate limiting molar conductivity Acetic acid dissociates as $\mathrm{CH_3COOH \rightleftharpoons H^+ + CH_3COO^-}$. One mole gives one mole of each ion, so

$$\Lambda_m^\circ = 349.6 + 40.9 = 390.5\,\mathrm{S\,cm^2\,mol^{-1}}.$$

At infinite dilution, the weak acid is effectively completely dissociated.

Step 2: Calculate the degree of dissociation Using the measured molar conductivity,

$$\alpha = \frac{39.05}{390.5} = 0.100.$$

The same conductivity units occur in numerator and denominator and cancel. Therefore the degree of dissociation is dimensionless. It represents the fraction of acetic acid molecules that produce ions under the stated conditions.

Step 3: Conclusion $\boxed{\alpha = 0.100}$, or $\boxed{10.0\%}$ dissociation.

Quick Tip to Solve: First add the two ionic conductivities; divide the measured conductivity by that sum, then multiply by 100 for percent.

7. Draw the structures of the following:

(i) $\mathrm{H_3PO_2}$

(ii) $\mathrm{XeF_4}$ [2 marks]

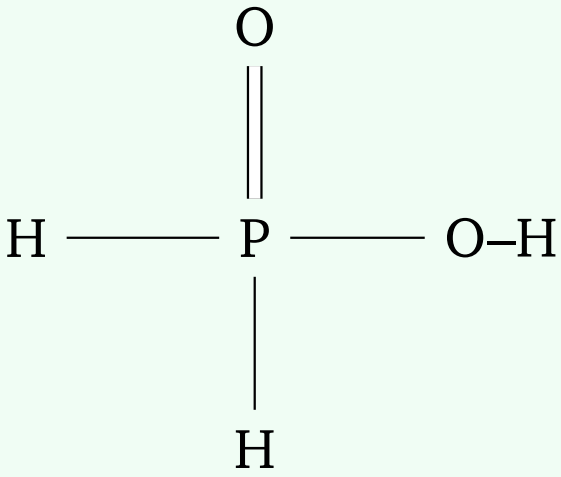
Solution:

Concept:

- Hypophosphorous acid, $\mathrm{H_3PO_2}$, has a central phosphorus atom with one $\mathrm{P=O}$ bond, one $\mathrm{P-OH}$ bond and two $\mathrm{P-H}$ bonds.
- In VSEPR theory, four bond pairs and two lone pairs around xenon give six electron-pair domains. The electron-pair arrangement is octahedral; opposite lone pairs leave a square-planar molecule.

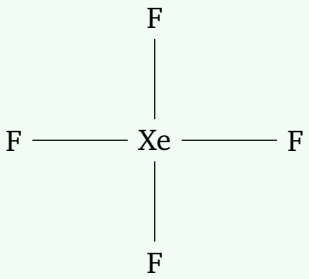
Step 1: (i) Structure of hypophosphorous acid The connectivity is $\mathrm{H_2P(=O)OH}$. Of its three hydrogen atoms, two are directly bonded to phosphorus and the third is attached to oxygen. Only the hydrogen in the hydroxyl group is ionisable, so this acid is monobasic. Count the atoms in the drawing: one phosphorus, two oxygens and three hydrogens, as required by $\mathrm{H_3PO_2}$.

Quick Tip to Solve: For phosphorus oxyacids, count O-H bonds to find basicity; do not count P-H bonds.



Structure of hypophosphorous acid

Step 2: (ii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Forming four single bonds to fluorine leaves two lone pairs on xenon. These lone pairs occupy opposite axial sites to minimise repulsion. All four fluorine atoms lie in one plane at the corners of a square around xenon, with adjacent $\mathrm{F-Xe-F}$ angles of 90° and opposite angles of 180°. Each fluorine additionally carries three lone pairs, omitted from the molecular-shape sketch for clarity.



Xe lone pairs:
one above the plane,
one below the plane

Square-planar XeF4; the two Xe lone pairs are above and below the molecular plane

Step 3: Conclusion $\mathrm{H_3PO_2}$ has structure $\mathrm{H_2P(=O)OH}$; $\mathrm{XeF_4}$ is square planar with two opposite lone pairs on Xe.

Quick Tip to Solve: For phosphorus oxyacids, count O-H bonds to find basicity; do not count P-H bonds.

8. Define the following terms:

(i) Ideal solution

(ii) Molarity (M) [2 marks]

Solution:

Concept:

- An ideal solution obeys Raoult's law for every component throughout the full composition range at a specified temperature.

Quick Tip to Solve: In a molarity calculation, convert the final solution volume to litres before dividing.

- Molarity measures amount of solute per volume of solution; the denominator is the volume of the final solution, not the volume of the solvent.

Step 1: (i) Define ideal solution An ideal solution is a solution that obeys Raoult's law at all concentrations (compositions). For a binary solution of volatile components A and B,

$$p_A = x_A p_A^\circ, \qquad p_B = x_B p_B^\circ.$$

Here x_A, x_B are liquid-phase mole fractions and p_A°, p_B° are the vapour pressures of the pure components at the same temperature. Mixing causes neither heat absorption nor evolution and no volume change: $\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$.

Step 2: (ii) Define molarity Molarity M is the number of moles of solute dissolved per litre of solution:

$$M = \frac{n_{\text{solute}}}{V_{\text{solution}}\,(\text{in litres})}.$$

Its unit is $\text{mol}\,\text{L}^{-1}$. If the measured volume is in millilitres, multiply the number of moles by 1000 before dividing by that volume. Since liquid volume changes with temperature, molarity is temperature dependent.

Step 3: Conclusion Ideal solution: obeys Raoult's law at every composition. Molarity: moles of solute per litre of solution.

Quick Tip to Solve: In a molarity calculation, convert the final solution volume to litres before dividing.

9(a). Complete the following reactions:

(i) Cl_2 + H_2O $\longrightarrow$

(ii) XeF_6 + $3H_2O$ $\longrightarrow$ [2 marks]

Solution:

Concept:

- Chlorine disproportionates in water: the same element is simultaneously reduced and oxidised.
- Complete hydrolysis of xenon hexafluoride replaces all six fluorine atoms and produces xenon trioxide and hydrogen fluoride.

Step 1: (i) Chlorine with water Chlorine reacts with water to form hydrochloric acid and hypochlorous acid:

$$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HCl} + \text{HOCl}.$$

Chlorine has oxidation state zero in Cl_2. It becomes -1 in HCl and $+1$ in HOCl, confirming disproportionation. The equation contains two chlorine atoms, two hydrogen atoms and one oxygen atom on each side. The reaction in chlorine water is reversible; the arrow completes the equation as requested.

Step 2: (ii) Complete hydrolysis of xenon hexafluoride Three molecules of water supply the three oxygen atoms needed for xenon trioxide. Their six hydrogen atoms combine with all six fluorine

Quick Tip to Solve: Use the given three water molecules to distinguish complete XeF6 hydrolysis from partial hydrolysis.

atoms to form hydrogen fluoride:

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF.$$

This is complete hydrolysis, rather than the partial hydrolysis that forms xenon oxyfluorides. Xenon remains in oxidation state $+6$ in both XeF_6 and XeO_3, so this hydrolysis does not change its oxidation state.

Step 3: Conclusion (i) $HCl + HOCl$. (ii) $XeO_3 + 6HF$.

Quick Tip to Solve: Use the given three water molecules to distinguish complete XeF6 hydrolysis from partial hydrolysis.

OR

9(b). What happens when

(i) conc. H_2SO_4 is added to Cu?

(ii) SO_3 is passed through water?

Write the equations. [2 marks]

Solution:

Concept:

- Hot concentrated sulphuric acid acts as an oxidising agent: copper is oxidised to copper(II), and sulphur in the acid is reduced to sulphur dioxide.
- Sulphur trioxide is the acid anhydride of sulphuric acid; reaction with water forms H_2SO_4.

Step 1: (i) Concentrated sulphuric acid with copper Copper reacts with hot concentrated sulphuric acid to form copper(II) sulphate, sulphur dioxide gas and water:

$$Cu + 2H_2SO_4(\text{conc.}) \xrightarrow{\Delta} CuSO_4 + SO_2 \uparrow + 2H_2O.$$

Copper changes from oxidation state zero to $+2$. Sulphur in the portion of acid reduced changes from $+6$ to $+4$ in SO_2. Thus concentrated acid supplies the oxidising action, and the gas evolved is sulphur dioxide, not hydrogen. The reaction is promoted by heating.

Step 2: (ii) Sulphur trioxide passed through water Sulphur trioxide reacts with water to give sulphuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

This hydration is strongly exothermic. Sulphur remains in oxidation state $+6$, so there is no oxidation-state change in this second reaction. The balanced equation has one sulphur, four oxygen and two hydrogen atoms on each side; one water molecule is required per molecule of sulphur trioxide.

Step 3: Conclusion (i) Hot concentrated H_2SO_4 gives $CuSO_4$, SO_2 and water. (ii) SO_3 and water give H_2SO_4.

Quick Tip to Solve: Read the sulphur oxide formula carefully: SO3 forms sulphuric acid on hydration.

10. Write the reactions involved in the following:

(i) Hell-Volhard Zelinsky reaction

(ii) Decarboxylation reaction [2 marks]

Solution:

Concept:

- The Hell-Volhard-Zelinsky (HVZ) reaction replaces an alpha-hydrogen of a carboxylic acid by halogen in the presence of red phosphorus.
- Decarboxylation of a sodium carboxylate with soda lime gives an alkane with one carbon atom fewer.

Step 1: (i) Hell-Volhard-Zelinsky reaction A carboxylic acid having at least one alpha-hydrogen undergoes halogenation at the carbon next to its carboxyl group. With bromine and red phosphorus, followed by hydrolysis, the reaction is

$$\mathrm{RCH_2COOH} + \mathrm{Br_2} \xrightarrow[\text{then } \mathrm{H_2O}]{\text{red P}} \mathrm{RCHBrCOOH} + \mathrm{HBr}.$$

For example, ethanoic acid gives bromoethanoic acid, $\mathrm{CH_2BrCOOH}$. The hydrogen replaced is attached to the alpha-carbon, not the acidic hydrogen of $-\mathrm{COOH}$.

Step 2: (ii) Decarboxylation reaction Heating a sodium carboxylate with soda lime, a mixture of sodium hydroxide and calcium oxide, removes the carboxyl carbon from the organic molecule:

$$\mathrm{RCOONa} + \mathrm{NaOH} \xrightarrow[\mathrm{CaO}]{\Delta} \mathrm{RH} + \mathrm{Na_2CO_3}.$$

For example, sodium ethanoate gives methane:

$$\mathrm{CH_3COONa} + \mathrm{NaOH} \xrightarrow[\mathrm{CaO}]{\Delta} \mathrm{CH_4} + \mathrm{Na_2CO_3}.$$

The removed carboxyl carbon appears in sodium carbonate under these basic conditions.

Step 3: Conclusion HVZ gives an alpha-halo carboxylic acid; soda-lime decarboxylation gives an alkane containing one fewer carbon atom than the parent acid.

Quick Tip to Solve: Locate the alpha-hydrogen for HVZ; remove the carboxyl carbon when counting the alkane carbons in decarboxylation.

11. Write one difference in each of the following:

(i) Lyophobic sol and Lyophilic sol

(ii) Solution and Colloid

(iii) Homogeneous catalysis and Heterogeneous catalysis [3 marks]

Solution:

Concept:

- Colloids are classified by the affinity of the dispersed phase for the dispersion medium; lyophilic means solvent-loving and lyophobic means solvent-hating.
- Particle size distinguishes a true solution from a colloid, whereas the phases of reactants and catalyst distinguish homogeneous from heterogeneous catalysis.

Step 1: (i) Lyophobic sol and lyophilic sol In a lyophobic sol, the dispersed phase has little affinity for the dispersion medium. In a lyophilic sol, the dispersed phase has strong affinity for the dispersion medium. For example, a gold sol in water is lyophobic, whereas a starch sol in water is lyophilic. This difference concerns the interaction of the particles with the liquid surrounding them; the words do not describe the size of the particles.

Step 2: (ii) Solution and colloid A true solution has solute particles smaller than about $1\,\text{nm}$, while a colloid has dispersed particles in the approximate size range 1–$1000\,\text{nm}$. Dissolved salt in water is an example of a true solution, and starch dispersed in water is an example of a colloid. Although both may appear uniform to the unaided eye, the larger colloidal particles form a dispersed phase distinct from the dispersion medium.

Step 3: (iii) Homogeneous and heterogeneous catalysis In homogeneous catalysis, the catalyst and reactants are in the same phase; in heterogeneous catalysis, the catalyst and reactants are in different phases. For example, oxidation of gaseous sulphur dioxide by oxygen using gaseous nitric oxide as catalyst is homogeneous. Hydrogenation of a liquid vegetable oil with hydrogen in the presence of solid nickel is heterogeneous because the solid catalyst is in a different phase from the reactants.

Step 4: Conclusion The respective distinctions are: little versus strong affinity for the medium; particles below $1\,\text{nm}$ versus approximately 1–$1000\,\text{nm}$; and catalyst in the same phase as the reactants versus a different phase.

Quick Tip to Solve: Compare the same property on both sides: affinity, particle size, and phase are the three direct distinctions here.

12. Following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-elimination reaction. [3 marks]

Solution:

Concept:

- An S_N2 reaction requires backside attack at the carbon bearing the leaving group; increasing crowding reduces its rate.
- A tetrahedral carbon bonded to four different groups is a chiral centre. A single enantiomer of such a compound can show optical activity.
- In the usual comparison of alkyl halides under beta-elimination conditions, reactivity follows tertiary greater than secondary greater than primary.

Step 1: Classify the three bromides The carbon bonded to bromine is primary in 1-bromopentane, secondary in 2-bromopentane, and tertiary in 2-bromo-2-methylbutane. Their condensed structures are respectively $BrCH_2CH_2CH_2CH_2CH_3$, $CH_3CH(Br)CH_2CH_2CH_3$, and $CH_3C(Br)(CH_3)CH_2CH_3$. The degree of substitution is assessed at the carbon carrying bromine, not from the total number of carbon atoms in the molecule.

Step 2: (i) Greatest reactivity towards substitution 1-Bromopentane is most reactive towards S_N2. Its primary carbon offers the least steric obstruction to the incoming nucleophile. The secondary carbon of 2-bromopentane is more crowded, and the tertiary carbon of 2-bromo-2-methylbutane strongly obstructs backside attack.

Step 3: (ii) Optical activity 2-Bromopentane has a chiral centre at carbon 2: this carbon is attached to Br, H, CH_3, and $CH_2CH_2CH_3$, which are four different groups. It is therefore the compound capable of optical activity. In 1-bromopentane, the bromine-bearing carbon has two hydrogen atoms; in 2-bromo-2-methylbutane it has two identical methyl groups. Neither is a chiral centre. Optical rotation requires an enantiomerically enriched sample; a racemic mixture of 2-bromopentane has zero net rotation.

Step 4: (iii) Greatest reactivity towards beta-elimination 2-Bromo-2-methylbutane is most reactive towards beta-elimination. It is a tertiary halide and has beta-hydrogens available for removal. The usual elimination reactivity order is tertiary greater than secondary greater than primary, and its elimination can give the more substituted alkene 2-methylbut-2-ene as the major product under ordinary alcoholic-base conditions.

Step 5: Conclusion (i) 1-Bromopentane; (ii) 2-bromopentane; (iii) 2-bromo-2-methylbutane.

Quick Tip to Solve: Classify the bromine-bearing carbon first, then count its distinct attached groups to identify the chiral compound.

13. Write the principles of the following methods:

(i) Vapour phase refining

(ii) Zone refining

(iii) Chromatography [3 marks]

Solution:

Concept:

- Refining separates impurities from a metal by exploiting a difference in volatility, solubility or adsorption.
- A suitable refining method must transfer the desired substance selectively while leaving impurities behind.

Step 1: (i) Vapour phase refining The impure metal is converted into a volatile compound by reaction with a suitable reagent. The volatile compound is separated from non-volatile impurities and then decomposed to obtain pure metal. Thus the metal must form a volatile compound, and that compound must decompose readily to regenerate the metal. For example, in the Mond process nickel forms volatile nickel tetracarbonyl, $\mathrm{Ni(CO)_4}$, which decomposes on heating to give pure nickel.

Step 2: (ii) Zone refining This method rests on the principle that impurities are more soluble in the molten metal than in the solid metal. A narrow molten zone is moved along an impure metal rod. As the melt solidifies behind the heater, relatively pure metal crystallises, while impurities remain in the melt and travel with the molten zone. Repeated passage concentrates the impurities at one end, which is cut off. It is used to obtain very pure silicon and germanium.

Step 3: (iii) Chromatography The components of a mixture are adsorbed to different extents on an adsorbent, the stationary phase. A suitable solvent, the mobile phase, carries the mixture through the adsorbent. Strongly adsorbed components move more slowly, while weakly adsorbed components move faster; consequently the components separate into different bands and can be collected separately.

Step 4: Conclusion Vapour phase refining uses formation and decomposition of a volatile compound; zone refining uses the greater solubility of impurities in the melt; chromatography uses differential adsorption.

Quick Tip to Solve: For each method, state the property that causes separation before describing the operation.

14. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.

Given: (Molar mass of sucrose = 342 g mol^{-1})

(Molar mass of glucose = 180 g mol^{-1}) [3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = K_f m$, where K_f is the solvent cryoscopic constant and m is the solute molality.

Quick Tip to Solve: For equal solute and solvent masses, freezing-point depressions are inversely proportional to solute molar masses.

- Sucrose and glucose are non-electrolytes, so their van't Hoff factors are $i = 1$. Equal mass percentages give equal solute and solvent masses, but not equal numbers of solute particles.

Step 1: Find the depression for sucrose The freezing point of pure water is $273.15\,\text{K}$, while that of the sucrose solution is $269.15\,\text{K}$. Hence

$$\Delta T_{f,\text{sucrose}} = 273.15 - 269.15 = 4.00\,\text{K}.$$

Take $100\,\text{g}$ of each solution. A 10% solution by mass contains $10\,\text{g}$ of solute and $90\,\text{g} = 0.090\,\text{kg}$ of water. The solvent mass is therefore identical for the two solutions.

Step 2: Compare the molalities Using the supplied molar masses,

$$m_{\text{sucrose}} = \frac{10/342}{0.090},$$
$$m_{\text{glucose}} = \frac{10/180}{0.090}.$$

Since both solutions have the same solvent, K_f cancels in their depression ratio. Thus

$$\frac{\Delta T_{f,\text{glucose}}}{4.00} = \frac{m_{\text{glucose}}}{m_{\text{sucrose}}} = \frac{342}{180} = 1.90.$$

Glucose has a smaller molar mass, so the same solute mass provides more particles and a larger freezing-point depression.

Step 3: Calculate the glucose freezing point The glucose solution has depression

$$\Delta T_{f,\text{glucose}} = 4.00 \times 1.90 = 7.60\,\text{K}.$$

Subtract this depression from the freezing point of pure water:

$$T_{f,\text{glucose}} = 273.15 - 7.60 = 265.55\,\text{K}.$$

The decrease is measured relative to pure water, not relative to the freezing point of the sucrose solution.

Step 4: Conclusion The freezing point of the 10% glucose solution is $\boxed{265.55\,\text{K}}$.

Quick Tip to Solve: For equal solute and solvent masses, freezing-point depressions are inversely proportional to solute molar masses.

15. Define the following:

(i) Cationic detergents

(ii) Narrow spectrum antibiotics

(iii) Disinfectants [3 marks]

Solution:

Concept:

- Detergents are surface-active cleaning agents; their ionic classification depends on the charge of the active organic ion.
- Antibiotics are classified by the range of microorganisms against which they act; disinfectants are classified by their use on non-living objects.

Step 1: (i) Cationic detergents Cationic detergents are quaternary ammonium salts having a long hydrocarbon chain and a positively charged organic part. Their anions are generally chloride, bromide or acetate ions. The long-chain cation is the surface-active part, while its hydrocarbon chain interacts with greasy dirt and its charged head interacts with water. Cetyltrimethylammonium bromide, $[C_{16}H_{33}N(CH_3)_3]^+Br^-$, is an example and is used in hair conditioners.

Step 2: (ii) Narrow spectrum antibiotics Narrow spectrum antibiotics are antibiotics effective mainly against a limited range of bacteria, for example primarily Gram-positive or primarily Gram-negative bacteria. They do not act effectively against the wide variety of bacteria targeted by broad spectrum antibiotics. Penicillin G is a standard example of a narrow spectrum antibiotic. The word spectrum refers to the range of susceptible microorganisms, rather than to the strength or dose of the drug.

Step 3: (iii) Disinfectants Disinfectants are chemical substances used to kill microorganisms on non-living objects such as floors, drains and instruments. They are generally unsuitable for application to living tissues in the concentrations used for disinfection. For example, a 1% phenol solution acts as a disinfectant. This distinguishes their use from antiseptics, which are applied to living tissues in suitable concentrations to control microorganisms.

Step 4: Conclusion Cationic detergents contain a surface-active positive ion; narrow spectrum antibiotics act against a limited bacterial range; disinfectants kill microorganisms on non-living objects.

Quick Tip to Solve: Identify the defining feature: charge for detergent, bacterial range for antibiotic, and non-living surface for disinfectant.

16. (a) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $AgNO_3$ for 15 minutes.

(Given: Molar mass of Ag = 108 g mol^{-1}, 1F = 96500 C mol^{-1})

(b) Define fuel cell. [3 marks]

Solution:

Concept:

- Faraday's law gives $m = MIt/(nF)$, where M is molar mass, I is current, t is time in seconds, and n is the electrons required per metal ion.
- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy by redox reactions.

Step 1: (a) Find the charge passed The cathode reaction is $\mathrm{Ag^+ + e^- \longrightarrow Ag}$. Thus, one mole of electrons deposits one mole of silver, so $n = 1$. The nitrate ion is a spectator and does not affect this electron requirement. Since an ampere is a coulomb per second, first convert the time:

$$t = 15 \times 60 = 900\,\mathrm{s}, \qquad Q = It = 2 \times 900 = 1800\,\mathrm{C}.$$

The amount of electrons passed is therefore $1800/96500\,\mathrm{mol}$, which equals the amount of silver deposited.

Step 2: (a) Calculate the deposited mass Substitute the supplied molar mass and Faraday constant:

$$m = \frac{MQ}{nF} = \frac{108 \times 1800}{1 \times 96500} = 2.0145\,\mathrm{g}.$$

This uses the usual assumption that the supplied current produces silver at the cathode. The units also agree: multiplying moles of silver by grams per mole gives grams. Substituting 15 directly for time would wrongly use minutes in a formula requiring seconds.

Step 3: (b) Define fuel cell A fuel cell is an electrochemical cell that directly converts the chemical energy of a fuel and an oxidant, continuously supplied to the electrodes, into electrical energy. For example, a hydrogen–oxygen fuel cell consumes hydrogen and oxygen, forms water and supplies an electric current. Its operation continues while the reactants are supplied; their redox reaction provides the electrical energy.

Step 4: Conclusion (a) The deposited silver mass is $\boxed{2.01\,\mathrm{g}}$. (b) A fuel cell converts chemical energy of continuously supplied fuel and oxidant directly into electrical energy.

Quick Tip to Solve: Use one electron per Ag ion, and convert the 15-minute duration to 900 seconds before calculating the charge.

17. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?

(ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless? (At. no. of Ni = 28)

(iii) Write the IUPAC name of the following complex: $[Co(NH_3)_5(CO_3)]Cl$. [3 marks]

Solution:

Concept:

- Coordination isomerism arises when ligands exchange between the complex cation and the complex anion of a coordination compound.
- Ligand field splitting and electronic transitions determine the colour of transition-metal complexes; ligand strength also controls pairing and geometry.
- In naming a complex, name ligands alphabetically before the metal and specify the metal oxidation state in Roman numerals.

Step 1: (i) Identify the isomerism Both the cation and anion in $[Co(NH_3)_6][Cr(CN)_6]$ are coordination entities. Interchanging ligands between cobalt and chromium gives $[Cr(NH_3)_6][Co(CN)_6]$, with the same overall composition. This is coordination isomerism, arising from a different distribution of ligands between the two metal centres.

Step 2: (ii) Explain the colours of the nickel complexes Nickel has configuration $[Ar]3d^8 4s^2$; hence Ni^{2+} is $3d^8$ in both complexes. Water is a weak-field ligand. The octahedral aqua complex has configuration $t_{2g}^6 e_g^2$, with two unpaired electrons, and its ligand-field transitions absorb visible light. The remaining transmitted light gives the solution its green colour. Cyanide is a strong-field ligand, producing pairing and a square-planar dsp^2 complex. Its relevant electronic excitations require greater energy and do not absorb visible light appreciably, so its solution is colourless. Pairing describes its diamagnetism; the absence of visible absorption explains its colour.

Step 3: (iii) Name the cobalt complex The chloride counter-ion has charge -1, so the complex cation has charge $+1$. Ammonia is neutral and carbonato has charge -2. Therefore the cobalt oxidation state x satisfies $x + 5(0) - 2 = +1$, giving $x = +3$. Name the five ammonia ligands as pentaammine, followed alphabetically by carbonato, then cobalt(III), and finally the counter-ion chloride.

Step 4: Conclusion (i) Coordination isomerism. (ii) The aqua complex absorbs visible light and is green; the strong-field square-planar cyanide complex has no appreciable visible absorption and is colourless. (iii) Pentaamminecarbonatocobalt(III) chloride.

Quick Tip to Solve: Use the external chloride to find the complex charge first; neutral ammonia and divalent carbonato then give cobalt the oxidation state +3.

18(a). Write structures of compounds A, B and C in each of the following reactions:

(i) $C_6H_5Br \xrightarrow{Mg/\text{dry ether}} A \xrightarrow[(b)\ H_3O^+]{(a)\ CO_2} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[(b)\ H_3O^+]{(a)\ SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$ [3 marks]

Solution:

Concept:

- A Grignard reagent reacts with carbon dioxide and then undergoes acidic hydrolysis to give a carboxylic acid with one additional carbon atom.
- Stephen reduction gives an aldehyde from a nitrile using $SnCl_2/HCl$, then hydrolysis.
- Dilute base gives a beta-hydroxy aldehyde by aldol addition; heating eliminates water to give an unsaturated aldehyde.

Step 1: (i) Identify the Grignard reagent and carboxylic acid Magnesium inserts into the carbon–bromine bond in dry ether, forming phenylmagnesium bromide. Thus $A = C_6H_5-MgBr$. The phenyl group attacks carbon dioxide to give a magnesium carboxylate, which yields benzoic acid on acidic hydrolysis:

$$C_6H_5MgBr \xrightarrow{CO_2} C_6H_5COOMgBr \xrightarrow{H_3O^+} C_6H_5COOH.$$

Hence $B = C_6H_5-C(=O)-OH$.

Step 2: (i) Identify the product of phosphorus pentachloride Phosphorus pentachloride replaces the acid hydroxyl group by chlorine, without changing the phenyl group or the carbonyl carbon:

$$C_6H_5COOH + PCl_5 \longrightarrow C_6H_5COCl + POCl_3 + HCl.$$

Therefore $C = C_6H_5-C(=O)-Cl$, benzoyl chloride.

Step 3: (ii) Identify the aldehyde and aldol product Stephen reduction and subsequent hydrolysis convert acetonitrile into ethanal, so $A = CH_3-C(=O)H$. Ethanal contains alpha hydrogen atoms; two molecules undergo aldol addition in dilute sodium hydroxide:

$$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO.$$

Thus $B = CH_3-CH(OH)-CH_2-C(=O)H$, 3-hydroxybutanal.

Step 4: (ii) Identify the heated product Heating removes water from the beta-hydroxy aldehyde, forming a double bond between the alpha and beta carbon atoms:

$$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3CH{=}CHCHO + H_2O.$$

Hence $C = CH_3-CH{=}CH-C(=O)H$, but-2-enal (crotonaldehyde).

Step 5: Conclusion (i) A: phenylmagnesium bromide; B: benzoic acid; C: benzoyl chloride. (ii) A: ethanal; B: 3-hydroxybutanal; C: but-2-enal. Their structures are given in the steps above.

Quick Tip to Solve: Carbon dioxide adds one carbon in the Grignard sequence; in the ethanal sequence, dilute base gives the hydroxy aldol and heat gives the alkene.

OR

18(b). Do the following conversions in not more than two steps:

(i) Benzoic acid to benzaldehyde

(ii) Ethyl benzene to Benzoic acid

(iii) Propanone to Propene [3 marks]

Solution:

Concept:

- An acid chloride can be selectively reduced to an aldehyde by Rosenmund reduction using hydrogen and poisoned palladium on barium sulphate.
- Hot alkaline potassium permanganate oxidises an alkyl side chain containing a benzylic hydrogen to a carboxylate; acidification gives the carboxylic acid.
- Reduce a ketone to its secondary alcohol, then dehydrate the alcohol to obtain an alkene.

Step 1: (i) Convert benzoic acid through benzoyl chloride First replace the acid hydroxyl group with chlorine using thionyl chloride. Then reduce the acid chloride by the Rosenmund method:

$$C_6H_5COOH \xrightarrow{SOCl_2} C_6H_5COCl$$

$$C_6H_5COCl \xrightarrow{H_2,\,Pd/BaSO_4} C_6H_5CHO$$

The poisoned catalyst limits the reduction to benzaldehyde. Direct reduction of the acid with a strong hydride would instead give benzyl alcohol, so the acid chloride intermediate is essential for this route.

Step 2: (ii) Oxidise the side chain of ethylbenzene Ethylbenzene has benzylic hydrogen atoms, so strong oxidation converts its entire side chain into the benzoate group while retaining the benzene ring:

$$C_6H_5CH_2CH_3 \xrightarrow{KMnO_4,\,OH-,heat} C_6H_5COO^-$$

$$C_6H_5COO^- \xrightarrow{H_3O^+} C_6H_5COOH$$

Acidification of the benzoate formed in the alkaline medium is the second step and yields benzoic acid.

Step 3: (iii) Reduce propanone and dehydrate the alcohol Sodium borohydride reduces the carbonyl group to give propan-2-ol. Heat this alcohol with concentrated sulphuric acid to eliminate water:

$$CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3$$

$$CH_3CH(OH)CH_3 \xrightarrow{\text{conc}\cdot H_2SO_4,\,443\,K} CH_3CH{=}CH_2 + H_2O$$

The carbon skeleton is unchanged in both operations, and dehydration produces propene.

Step 4: Conclusion The required two-step routes are acid chloride formation followed by Rosenmund reduction; alkaline side-chain oxidation followed by acidification; and ketone reduction followed by alcohol dehydration, respectively.

Quick Tip to Solve: For acid-to-aldehyde conversion use the acid chloride; for ketone-to-alkene conversion insert the corresponding alcohol as the intermediate.

19. Write the structures of the monomers used for getting the following polymers:

(i) Neoprene

(ii) Melamine-formaldehyde polymer

(iii) Buna-S [3 marks]

Solution:

Concept:

- Addition polymers are formed by joining unsaturated monomers. Their monomers retain the carbon skeleton and substituents that identify the polymer.
- A copolymer uses two different monomers, whereas a condensation polymer forms through reactions of functional groups with elimination of small molecules.

Step 1: (i) Identify the monomer of neoprene Neoprene is the addition polymer of chloroprene, whose systematic name is 2-chlorobuta-1,3-diene. Its condensed structural formula is

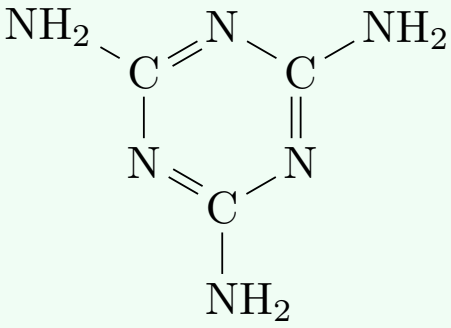
$$\mathrm{CH_2{=}C(Cl){-}CH{=}CH_2}.$$

Chlorine is attached to the second carbon of the conjugated diene chain. This distinguishes chloroprene from unsubstituted buta-1,3-diene and from isoprene, which has a methyl substituent instead of chlorine.

Step 2: (ii) Identify both monomers of melamine-formaldehyde polymer The monomers are melamine and formaldehyde (methanal). Melamine is 2,4,6-triamino-1,3,5-triazine: its six-membered ring has alternating carbon and nitrogen atoms, and each ring carbon bears an amino group, as shown below. Formaldehyde has the structure

$$\mathrm{H{-}C(=O){-}H}.$$

The amino groups of melamine react with formaldehyde during condensation to produce the cross-linked resin; both monomers must therefore be specified.



Melamine: 2,4,6-triamino-1,3,5-triazine

Step 3: (iii) Identify both monomers of Buna-S Buna-S is a copolymer of buta-1,3-diene and styrene (phenylethene). Their condensed structural formulae are

$$\text{Buta-1,3-diene:}\quad \mathrm{CH_2{=}CH{-}CH{=}CH_2},$$
$$\text{Styrene:}\quad \mathrm{C_6H_5{-}CH{=}CH_2}.$$

Styrene contains a vinyl group attached directly to the benzene ring. It supplies the styrene component

Quick Tip to Solve: Remember neoprene's chlorine substituent and Buna-S's styrene unit; for melamine draw alternating ring nitrogen atoms and three amino groups.

represented by S in the polymer name; acrylonitrile would instead be used in Buna-N.

Step 4: Conclusion Neoprene uses chloroprene; melamine-formaldehyde polymer uses melamine and methanal; Buna-S uses buta-1,3-diene and styrene. The structures given above identify every required monomer.

Quick Tip to Solve: Remember neoprene's chlorine substituent and Buna-S's styrene unit; for melamine draw alternating ring nitrogen atoms and three amino groups.

20. Following data are obtained for the reaction:

$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

t/s: 0, 300, 600

$[N_2O_5]$/mol L^{-1}: 1.6×10^{-2}, 0.8×10^{-2}, 0.4×10^{-2}

(a) Show that it follows first order reaction.

(b) Calculate the half-life.

(Given log 2 = 0.3010, log 4 = 0.6021) [3 marks]

Solution:

Concept:

- For first-order disappearance of a reactant, $k = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are its initial concentration and concentration after time t.
- A first-order reaction has a concentration-independent half-life: $t_{1/2} = \dfrac{0.693}{k}$. Equal successive halving times support first-order kinetics.

Step 1: (a) Calculate the rate constant at 300 seconds Use the concentration of N_2O_5, the reactant whose disappearance is measured. At $t = 300\,\text{s}$, its concentration has fallen from 1.6×10^{-2} to $0.8 \times 10^{-2}\,\text{mol L}^{-1}$. Substitution in the first-order integrated equation gives

$$\begin{aligned} k_1 &= \frac{2.303}{300} \log \left(\frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} \right) \\ &= \frac{2.303 \times 0.3010}{300} \\ &= 2.311 \times 10^{-3}\,\text{s}^{-1}. \end{aligned}$$

Concentration units cancel in the ratio, leaving inverse seconds as the unit of k.

Step 2: (a) Verify the same constant at 600 seconds For the second observation, the initial concentration is still the value at zero time, whereas the elapsed time is now $600\,\text{s}$:

$$\begin{aligned} k_2 &= \frac{2.303}{600} \log \left(\frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} \right) \\ &= \frac{2.303 \times 0.6021}{600} \\ &= 2.311 \times 10^{-3}\,\text{s}^{-1}. \end{aligned}$$

Quick Tip to Solve: Successive halving in equal time intervals immediately gives the half-life; show first order by calculating the same rate constant from both observations.

Thus k_1 and k_2 agree to the precision of the supplied logarithms. The data therefore satisfy the first-order integrated rate law. The concentration also halves during each successive interval of $300\,\text{s}$, confirming the constant halving time.

Step 3: (b) Calculate the half-life Substitute the common rate constant in the first-order half-life relation:

$$t_{1/2} = \frac{0.693}{2.311 \times 10^{-3}} \approx 300\,\text{s}.$$

This agrees directly with the table: the concentration decreases to half its initial value at $300\,\text{s}$, and halves again by $600\,\text{s}$. The small rounding in the calculated result is due to the quoted logarithms and the use of 0.693 for $\ln 2$.

Step 4: Conclusion The reaction follows first-order kinetics, with $k \approx 2.31 \times 10^{-3}\,\text{s}^{-1}$, and its half-life is $t_{1/2} = 300\,\text{s}$.

Quick Tip to Solve: Successive halving in equal time intervals immediately gives the half-life; show first order by calculating the same rate constant from both observations.

21. Give reasons:

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Although -NH_2 is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline. [3 marks]

Solution:

Concept:

- An amino group activates a benzene ring by donating the nitrogen lone pair through resonance; competition for this lone pair reduces ring activation.
- Basicity depends on the availability of a lone pair to accept a proton. Electron-releasing alkyl groups increase availability, whereas resonance delocalisation into an aromatic ring decreases it.
- The directing effect depends on the group actually present under the reaction conditions: $-\text{NH}_2$ is ortho/para directing, whereas $-\text{NH}_3^+$ is meta directing.

Step 1: (i) Effect of acetylation on activation Acetylation converts aniline, $\text{C}_6\text{H}_5\text{NH}_2$, into acetanilide, $\text{C}_6\text{H}_5\text{NHCOCH}_3$. In the latter, the nitrogen lone pair is delocalised towards the carbonyl group as well as towards the benzene ring. The amide resonance contribution may be represented as

$$\text{C}_6\text{H}_5 - \text{NH} - \text{C}(=\text{O}) - \text{CH}_3 \longleftrightarrow \text{C}_6\text{H}_5 - \text{N}^+\text{H} = \text{C}(-\text{O}^-) - \text{CH}_3.$$

Consequently, the lone pair is less available for donation into the ring. The acetylamino group therefore activates the ring less strongly than the amino group, although it remains ortho/para directing.

Step 2: (ii) Comparison of methylamine and aniline In methylamine, the methyl group exerts a positive inductive effect, increasing electron density on nitrogen. Its lone pair is localised and readily accepts H^+. In aniline, the lone pair is delocalised into the benzene ring by resonance and is less available for protonation. Protonation also removes this lone pair from ring conjugation. Thus

Quick Tip to Solve: Track the nitrogen lone pair in each case: carbonyl conjugation, ring conjugation and protonation respectively explain all three observations.

methylamine accepts a proton more readily and is more basic than aniline.

Step 3: (iii) Meta product during nitration The strongly acidic nitrating mixture protonates a substantial fraction of aniline:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3^+.$$

The anilinium ion has no nitrogen lone pair available to donate to the ring; its positively charged group withdraws electron density and is meta directing. Nitration of this protonated species therefore gives meta-nitroaniline after work-up. The unprotonated aniline gives ortho and para products, explaining why a significant meta product accompanies them.

Step 4: Conclusion Acetylation diverts the nitrogen lone pair towards the carbonyl group; methylamine has a more available lone pair than aniline; and protonation to meta-directing anilinium ions explains the significant meta product in nitration.

Quick Tip to Solve: Track the nitrogen lone pair in each case: carbonyl conjugation, ring conjugation and protonation respectively explain all three observations.

22. Give reasons:

(i) Thermal stability decreases from H_2O to H_2Te.

(ii) Fluoride ion has higher hydration enthalpy than chloride ion.

(iii) Nitrogen does not form pentahalide. [3 marks]

Solution:

Concept:

- Thermal stability of a hydride depends on the strength of its element-hydrogen bonds; stronger bonds require more energy to break.
- Hydration is the stabilisation of gaseous ions by water molecules. For ions of equal charge, a smaller radius gives a greater charge density and stronger ion-dipole attraction.
- Nitrogen is a second-period element whose valence shell contains only $2s$ and $2p$ orbitals; it cannot expand its octet to form five ordinary covalent bonds.

Step 1: (i) Thermal stability of Group 16 hydrides On moving from oxygen to tellurium, the atomic size of the central atom increases. The $E-H$ bond becomes longer, and overlap between hydrogen's $1s$ orbital and the increasingly larger valence orbital of E becomes less effective. Hence the bond dissociation enthalpy decreases down the group. The weaker bonds are broken more readily on heating, so thermal stability decreases in the order

$$H_2O > H_2S > H_2Se > H_2Te.$$

The especially strong $O-H$ bonds make water the most thermally stable member of this series.

Step 2: (ii) Hydration of fluoride and chloride ions Both ions carry the same charge, -1, but F^- is smaller than Cl^-. Fluoride therefore has greater charge density and attracts the positively polarised hydrogen ends of surrounding water molecules more strongly. This stronger ion-dipole interaction releases more energy when fluoride is hydrated. Its hydration enthalpy is consequently larger in

Quick Tip to Solve: Use bond strength for hydride stability, ionic charge density for hydration, and the second-shell octet limit for nitrogen pentahalides.

magnitude, that is, more negative than that of chloride. Thus the printed expression "higher hydration enthalpy" refers to the greater magnitude of the energy released, rather than a more positive numerical enthalpy.

Step 3: (iii) Absence of nitrogen pentahalides Nitrogen has valence-shell configuration $2s^2 2p^3$. Its second shell has no d orbitals and accommodates at most eight electrons. A pentahalide with five ordinary covalent $\mathrm{N-X}$ bonds would place ten bonding electrons around nitrogen, exceeding this octet. Nitrogen cannot expand its valence shell in this way and therefore does not form a pentahalide. This explains why nitrogen forms trihalides such as $\mathrm{NF_3}$, while heavier Group 15 elements can form pentahalides such as $\mathrm{PCl_5}$.

Step 4: Conclusion The hydrides become less stable as $\mathrm{E-H}$ bonds weaken down Group 16; smaller $\mathrm{F^-}$ has a more negative hydration enthalpy than $\mathrm{Cl^-}$; and nitrogen cannot expand its octet to form five covalent bonds.

Quick Tip to Solve: Use bond strength for hydride stability, ionic charge density for hydration, and the second-shell octet limit for nitrogen pentahalides.

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, Ritu a class XII student decided to aware others about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contractor to stop selling sandwiches, pizza, burgers and other bakery products to the students. 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:

(i) What are the values (at least two) displayed by Ritu?

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

(iii) Write the two types of secondary structure of proteins.

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

Solution:

Concept:

- Responsible action combines awareness of a possible food hazard with concern for the health of others and a practical way of improving their food choices.
- Starch is a plant storage polysaccharide built from glucose units. It contains amylose and amylopectin and is abundant in cereal flour.
- The secondary structure of a protein describes regular arrangements of its polypeptide backbone, stabilised mainly by hydrogen bonds between peptide groups.
- Vitamins are classified as water soluble or fat soluble. The B-group vitamins and vitamin C belong to the water-soluble class.

Step 1: (i) Identify the values shown by Ritu Ritu displays **social responsibility** and **concern for the health and welfare of others**. She uses the information in the programme to help protect fellow

Quick Tip to Solve: Associate cereal flour with starch, protein secondary structure with helix and sheet, and water-soluble vitamins with the B group and C.

students instead of keeping it to herself. Her approach to the principal also shows **initiative** and **health awareness**: she seeks a practical change in the canteen menu through the appropriate school authority. Any two of these values answer this part.

Step 2: (ii) Identify the polysaccharide in bread Bread is generally prepared using cereal flour, such as wheat flour, whose principal storage carbohydrate is **starch**. Starch consists of the two components amylose and amylopectin, both polymers of glucose. Thus the polysaccharide asked for is starch; glucose itself is a monosaccharide and is not the required answer.

Step 3: (iii) Name the two secondary structures of proteins The two common types are the α**-helix** and the β**-pleated sheet**. In an α-helix, the polypeptide backbone coils into a helix stabilised by hydrogen bonds within the chain. In a β-pleated sheet, extended backbone segments lie alongside one another and are linked by hydrogen bonds. These are arrangements of the backbone, whereas the amino-acid sequence defines primary structure.

Step 4: (iv) Give two water-soluble vitamins Two specific examples are **vitamin** B_1 **(thiamine)** and **vitamin C (ascorbic acid)**. Both are water soluble. More generally, B-group vitamins and vitamin C constitute the water-soluble class, whereas vitamins A, D, E and K are fat soluble and would not answer this part.

Step 5: Conclusion (i) Social responsibility and concern for others' health; (ii) starch; (iii) α-helix and β-pleated sheet; (iv) vitamin B_1 and vitamin C.

Quick Tip to Solve: Associate cereal flour with starch, protein secondary structure with helix and sheet, and water-soluble vitamins with the B group and C.

24(a). Write the product(s) in the following reactions:

(i) The reaction of salicylic acid shown below with $(CH_3CO)_2O$ **in the presence of** H^+**.**

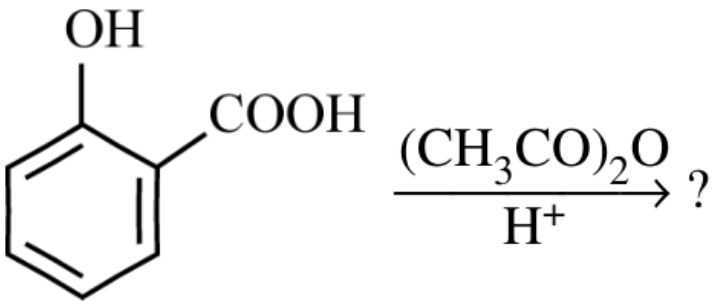
(ii) $CH_3-CH(CH_3)-O-CH_2-CH_3 \xrightarrow{HI} ? + ?$

(iii) $CH_3-CH=CH-CH_2-OH \xrightarrow{PCC} ?$

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Ethanol and Phenol

(ii) Propanol and 2-methylpropan-2-ol [5 marks]



Solution:

Concept:

- Acetic anhydride acetylates the phenolic hydroxyl group of salicylic acid. The adjacent carboxyl group remains unchanged in the aspirin product.
- Hydrogen iodide protonates an ether oxygen; iodide attacks the less hindered alkyl carbon by nucleophilic substitution when both groups are primary or secondary.
- PCC (pyridinium chlorochromate) oxidises a primary alcohol to an aldehyde without normally oxidising its carbon-carbon double bond.
- Phenols give a coloured complex with neutral ferric chloride. The Lucas reagent, concentrated HCl and anhydrous $ZnCl_2$, distinguishes alcohol classes through the rate of formation of insoluble alkyl chlorides.

Step 1: Acetylate the phenolic group in (a)(i) The printed benzene ring has adjacent OH and $COOH$ groups: the substrate is salicylic acid (2-hydroxybenzoic acid). Acid-catalysed reaction with acetic anhydride replaces the hydrogen of the phenolic hydroxyl group by an acetyl group, CH_3CO. Thus the ring bears $OCOCH_3$ adjacent to $COOH$. The product is 2-acetoxybenzoic acid, commonly called aspirin or acetylsalicylic acid; acetic acid is the accompanying product.

$$\text{o-}HOC_6H_4COOH + (CH_3CO)_2O \xrightarrow{H^+} \text{o-}CH_3COOC_6H_4COOH + CH_3COOH$$

This is ester formation at the phenolic oxygen, so the carbon skeleton and the position of the carboxyl group are preserved.

Step 2: Cleave the unsymmetrical ether in (a)(ii) The ether contains an ethyl group and an isopropyl group. After oxygen is protonated by HI, I^- attacks the primary ethyl carbon more readily than the secondary isopropyl carbon. Breaking the ethyl-oxygen bond therefore gives ethyl iodide and propan-2-ol:

$$CH_3CH(CH_3)OCH_2CH_3 + HI \longrightarrow CH_3CH(OH)CH_3 + CH_3CH_2I$$

The two products for the indicated cleavage are propan-2-ol and iodoethane. An excess of HI with heating can subsequently convert the alcohol to its iodide, but that further reaction is not specified here.

Step 3: Oxidise the primary alcohol in (a)(iii) The terminal CH_2OH group is primary. PCC removes two hydrogen atoms to form CHO, while leaving the existing $C{=}C$ bond intact. The product is but-2-enal:

$$CH_3CH{=}CHCH_2OH \xrightarrow{PCC} CH_3CH{=}CHCHO$$

Because PCC is a mild oxidising agent used under nonaqueous conditions, the aldehyde is the expected product rather than the corresponding carboxylic acid.

Step 4: Distinguish ethanol from phenol in (b)(i) Add a few drops of neutral aqueous ferric chloride to separate samples. Phenol gives a violet colour through formation of a ferric phenolate complex. Ethanol gives no characteristic violet colour. The positive colour identifies phenol; the absence of that colour identifies ethanol in this pair. This test directly exploits the phenolic hydroxyl group attached to the benzene ring.

Step 5: Distinguish propanol from the tertiary alcohol in (b)(ii) Add Lucas reagent at room tempera-

Quick Tip to Solve: In HI cleavage of this ether, attach iodine to the less hindered ethyl group. For the tests, look for violet colour with phenol and immediate Lucas turbidity with the tertiary alcohol.

ture and observe the time required for turbidity. 2-Methylpropan-2-ol is tertiary and gives immediate turbidity because insoluble 2-chloro-2-methylpropane forms rapidly:

$$(CH_3)_3COH + HCl \xrightarrow{ZnCl_2} (CH_3)_3CCl + H_2O$$

Propanol, meaning propan-1-ol here, is a primary alcohol and remains clear at room temperature during the usual test period. Primary alcohol substitution is much slower, whereas the tertiary alcohol readily forms a stabilised carbocation. Compare the two samples under identical room-temperature conditions.

Step 6: Conclusion (a)(i) Aspirin, o-$CH_3COOC_6H_4COOH$, with CH_3COOH; (ii) $CH_3CH(OH)CH_3$ and CH_3CH_2I; (iii) $CH_3CH{=}CHCHO$. (b)(i) Neutral ferric chloride gives a violet colour with phenol but not ethanol. (ii) Lucas reagent gives immediate turbidity with 2-methylpropan-2-ol, while propanol remains clear at room temperature.

Quick Tip to Solve: In HI cleavage of this ether, attach iodine to the less hindered ethyl group. For the tests, look for violet colour with phenol and immediate Lucas turbidity with the tertiary alcohol.

OR

24(b). (a) Write the formula of reagents used in the following reactions:

(i) Bromination of phenol to 2,4,6-tribromophenol

(ii) Hydroboration of propene and then oxidation to propanol.

(b) Arrange the following compound groups in the increasing order of their property indicated:

(i) p-nitrophenol, ethanol, phenol (acidic character)

(ii) Propanol, Propane, Propanal (boiling point)

(c) Write the mechanism (using curved arrow notation) of the following reaction:

$CH_3CH_2OH_2^+ \xrightarrow{CH_3CH_2OH} CH_3CH_2O^+(H)CH_2CH_3 + H_2O$. [5 marks]

Solution:

Concept:

- Phenol activates its ortho and para positions towards electrophilic bromination; aqueous bromine substitutes at all three positions.
- Hydroboration followed by alkaline peroxide oxidation adds water across an alkene in the anti-Markovnikov orientation, giving the alcohol at the less substituted carbon.
- Acidity increases when the conjugate base is stabilised. Boiling point increases with stronger intermolecular attraction for molecules of comparable size.
- In acid-catalysed ether formation, protonation turns the alcohol's poor leaving group into water. An alcohol oxygen supplies its lone pair to form the new carbon–oxygen bond.

Step 1: (a)(i) Reagent for bromination Use bromine water, $Br_2(aq)$. The hydroxyl group activates the phenol ring, so bromination occurs at both ortho positions and the para position, producing a

Quick Tip to Solve: For the mechanism, start each curved arrow at electrons: the ethanol oxygen lone pair attacks carbon while the leaving C–O bond pair goes to oxygen.

white precipitate of 2,4,6-tribromophenol:

$$C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3HBr.$$

Aqueous bromine is essential here: bromination under controlled non-polar conditions need not give the tribromo product.

Step 2: (a)(ii) Reagents for hydroboration and oxidation First use B_2H_6 (diborane, a source of BH_3); then use H_2O_2 with OH^-, commonly aqueous $NaOH$. Boron attaches to the terminal carbon of propene and oxidation replaces the carbon–boron bond by a carbon–oxygen bond. The product is propan-1-ol:

$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2/OH^-]{1.\ B_2H_6} CH_3CH_2CH_2OH.$$

Acid-catalysed direct hydration would instead favour propan-2-ol, so it is not the required reagent sequence.

Step 3: (b)(i) Increasing acidic character The order is

$$\boxed{\text{ethanol} < \text{phenol} < p\text{-nitrophenol}}.$$

Ethoxide has no resonance delocalisation of its negative charge, whereas phenoxide is resonance stabilised. The para nitro group further stabilises the conjugate base by its electron-withdrawing inductive and resonance effects. Hence loss of a proton is most favourable for p-nitrophenol.

Step 4: (b)(ii) Increasing boiling point The order is

$$\boxed{\text{propane} < \text{propanal} < \text{propanol}}.$$

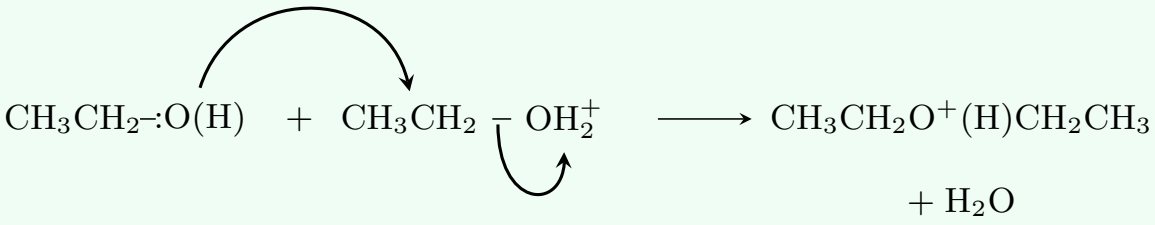
Propane is non-polar and has only London dispersion forces. Propanal has a polar carbonyl group and therefore additional dipole–dipole attraction. Propanol molecules form intermolecular hydrogen bonds through their hydroxyl groups, requiring the greatest energy to separate them into vapour.

Step 5: (c) Curved-arrow mechanism of ether formation The starting alcohol is already protonated, $CH_3CH_2OH_2^+$. The oxygen lone pair of a second, neutral ethanol molecule attacks the primary carbon bonded to OH_2^+. At the same time, the old carbon–oxygen bond electron pair moves onto the leaving oxygen, releasing neutral water. This concerted substitution forms the protonated ether shown in the question:

$$CH_3CH_2OH_2^+ + CH_3CH_2OH \longrightarrow CH_3CH_2O^+(H)CH_2CH_3 + H_2O.$$

Both curved arrows below start at an electron pair: one at the attacking oxygen's lone pair and one at the departing carbon–oxygen bond. No primary carbocation is required. Subsequent removal of the oxonium proton gives diethyl ether and regenerates the acid catalyst, although the printed reaction stops at the protonated ether.

Quick Tip to Solve: For the mechanism, start each curved arrow at electrons: the ethanol oxygen lone pair attacks carbon while the leaving C–O bond pair goes to oxygen.



Concerted attack of ethanol and departure of water; the product is an oxonium ion.

Step 6: Conclusion The reagents are $Br_2(aq)$, and then B_2H_6 followed by H_2O_2/OH^-. The increasing orders are ethanol $<$ phenol $<$ p-nitrophenol for acidity, and propane $<$ propanal $<$ propanol for boiling point. Ethanol attacks protonated ethanol with simultaneous loss of water to give protonated diethyl ether.

Quick Tip to Solve: For the mechanism, start each curved arrow at electrons: the ethanol oxygen lone pair attacks carbon while the leaving C–O bond pair goes to oxygen.

25(a). Account for the following:

(i) Transition metals form large number of complex compounds.

(ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.

(iii) E° value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

[5 marks]

Solution:

Concept:

- Complex formation involves donation of lone pairs by ligands to a central metal ion; small ionic size and high charge density favour metal-ligand bonding.
- Increasing the oxidation state increases the polarising power of a metal ion, increasing covalent character and generally changing its oxides from basic towards acidic.
- A positive standard reduction potential indicates a favourable reduction under standard conditions; the relative stability of the two oxidation states affects this potential.
- Lanthanoids involve filling of the $4f$ subshell, whereas actinoids involve filling of the $5f$ subshell.

Step 1: (a)(i) Explain complex formation Transition-metal ions are relatively small and have a high ionic charge, so they strongly attract ligands carrying lone pairs. They also have suitable vacant orbitals that can accept these electron pairs to form coordinate bonds. Consequently, they form many complexes with ligands such as water, ammonia and cyanide. For example, $[Cu(NH_3)_4]^{2+}$ contains ammonia ligands bonded to a copper ion through nitrogen lone pairs.

Step 2: (a)(ii) Explain the nature of the oxides In a low oxidation state, the metal has relatively low polarising power and its oxide is predominantly ionic. The oxide ions accept protons, so the oxide is basic. In a high oxidation state, the metal strongly polarises the oxygen electron cloud, giving greater covalent character and acidic behaviour; intermediate higher oxides may be amphoteric. For example,

Quick Tip to Solve: For a reduction-potential explanation, write both ion configurations first and identify whether reduction creates or destroys a particularly stable configuration.

CrO is basic, Cr_2O_3 is amphoteric and CrO_3 is acidic. Thus the change in oxidation state explains the change in oxide character.

Step 3: (a)(iii) Compare the manganese and chromium reductions The relevant electronic configurations are

$$Mn^{3+} : 3d^4, \quad Mn^{2+} : 3d^5,$$
$$Cr^{3+} : 3d^3, \quad Cr^{2+} : 3d^4.$$

Reduction of Mn^{3+} gives Mn^{2+}, which has the particularly stable half-filled $3d^5$ configuration. Hence Mn^{3+} readily accepts an electron and its reduction potential is strongly positive, $+1.57\,V$. In contrast, Cr^{3+} has a stable $3d^3$ configuration (t_{2g}^3 in an octahedral environment); its reduction to Cr^{2+} produces the less stable $3d^4$ configuration. This reduction is much less favourable, so the chromium couple has a much lower reduction potential.

Step 4: (b) State one similarity and one difference **Similarity:** Both lanthanoids and actinoids commonly show the $+3$ oxidation state. Their trivalent ionic radii also decrease progressively across their respective series because the added f electrons shield the increasing nuclear charge poorly.

Difference: Lanthanoids predominantly show $+3$, with relatively few exceptions such as Ce^{4+} and Eu^{2+}. Actinoids exhibit a wider range of oxidation states because the energies of the $5f$, $6d$ and $7s$ orbitals are comparable, allowing different numbers of electrons to participate in bonding.

Step 5: Conclusion Transition metals form complexes through ligand electron-pair acceptance; increasing oxidation state raises oxide covalency and acidity. The stable $3d^5$ product makes the Mn^{3+}/Mn^{2+} reduction especially favourable. Both inner-transition series commonly show $+3$, but actinoids show a wider range of oxidation states.

Quick Tip to Solve: For a reduction-potential explanation, write both ion configurations first and identify whether reduction creates or destroys a particularly stable configuration.

OR

25(b). (a) (i) How is the variability in oxidation states of transition metals different from that of the p-block elements?

(ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why?

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?

(b) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons. [5 marks]

Solution:

Concept:

- Transition metals have closely spaced $(n-1)d$ and ns energy levels, so different numbers of electrons can participate in bonding.
- Stability of an ion in water depends on the total energy balance, including ionisation and hydration; a filled subshell alone does not determine aqueous stability.
- Chromate and dichromate ions are related by an acid-base equilibrium. A change in pH changes their relative concentrations without changing the oxidation state of chromium.

Quick Tip to Solve: For dichromate-to-chromate conversion, write the equilibrium with hydrogen ions first; adding alkali removes them and immediately predicts the yellow chromate product.

- The comparable energies of $5f$, $6d$ and $7s$ orbitals give actinoids a wider range of oxidation states than lanthanoids.

Step 1: (a)(i) Compare the variation in oxidation states Transition metals commonly show oxidation states differing by one unit because both ns and $(n-1)d$ electrons can take part in bonding. For example, manganese shows $+2, +3, +4, +5, +6$ and $+7$ states. In p-block elements, the commonly encountered oxidation states generally differ by two units. For example, tin shows $+2$ and $+4$, while phosphorus shows $+3$ and $+5$. This difference arises because the participation or non-participation of the outer ns^2 electron pair changes the oxidation state by two. Thus, the typical variation is successive one-unit changes in transition metals and two-unit changes in p-block elements.

Step 2: (a)(ii) Identify the unstable aqueous copper ion Cu^+ is unstable in aqueous solution and undergoes disproportionation:

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

Although Cu^+ has a filled $3d^{10}$ configuration, Cu^{2+} has a much more favourable hydration enthalpy because of its greater charge density. This hydration energy more than compensates for the energy required to remove an additional electron in the overall disproportionation process. Hence Cu^{2+} is stabilised in water, and the filled d subshell does not prevent aqueous Cu^+ from disproportionating.

Step 3: (a)(iii) Explain the orange-to-yellow colour change Orange dichromate ions and yellow chromate ions are in equilibrium:

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+.$$

An alkali supplies OH^-, which removes H^+ by forming water. By Le Chatelier's principle, the equilibrium shifts towards chromate ions. The net reaction is

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O.$$

The solution therefore becomes yellow. Chromium remains in oxidation state $+6$ in both ions; this is an acid-base conversion, rather than a redox reaction.

Step 4: (b) Give two reasons for the more complicated chemistry of actinoids First, actinoids exhibit a much wider range of oxidation states because their $5f$, $6d$ and $7s$ orbitals have comparable energies and can participate in bonding. Lanthanoids predominantly show the $+3$ state, with fewer exceptions. The larger number of possible ionic states makes actinoid reactions and compounds more varied.

Second, all actinoids are radioactive. Their radioactive decay and the associated transformations complicate the study, isolation and handling of their compounds. Most lanthanoids are not radioactive, so this complication is much less prominent in lanthanoid chemistry.

Step 5: Conclusion (a)(i) Transition-metal oxidation states typically differ by one unit, whereas p-block states generally differ by two. (ii) Cu^+ disproportionates in water because hydration strongly stabilises Cu^{2+}. (iii) Alkali converts orange dichromate into yellow chromate. (b) Actinoid chemistry is more complicated because of their wider range of oxidation states and their radioactivity.

Quick Tip to Solve: For dichromate-to-chromate conversion, write the equilibrium with hydrogen ions first; adding alkali removes them and immediately predicts the yellow chromate product.

26(a). An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell.

(b) Write any two differences between amorphous solids and crystalline solids. [5 marks]

Solution:

Concept:

- The density of a cubic crystal is $\rho = \dfrac{ZM}{N_A a^3}$, where Z is the number of atoms per unit cell, M is molar mass, a is edge length and N_A is Avogadro's constant. The units of mass and volume must match the given density.
- For elemental cubic crystals, simple cubic, body-centred cubic and face-centred cubic unit cells contain 1, 2 and 4 atoms respectively. Crystalline solids have long-range order, whereas amorphous solids have only short-range order.

Step 1: (a) Convert the edge length and calculate the cell volume Since the density is given in g cm^{-3}, express the edge in centimetres. Using $1\,\text{pm} = 10^{-10}\,\text{cm}$,

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

The mass of one unit cell is therefore ρa^3, while the mass of one atom is M/N_A. Their ratio gives the number of atoms in the cell.

Step 2: (a) Calculate the number of atoms per unit cell Rearranging the density equation and substituting $M = 93\,\text{g mol}^{-1}$ and $N_A = 6.022 \times 10^{23}\,\text{mol}^{-1}$,

$$Z = \frac{\rho a^3 N_A}{M} = \frac{11.5 \times 2.70 \times 10^{-23} \times 6.022 \times 10^{23}}{93} = 2.01 \simeq 2.$$

The small departure from an integer is due to rounding of the supplied data. A body-centred cubic cell has eight corner atoms, each shared among eight cells, and one atom wholly inside the cell: $8(1/8) + 1 = 2$. Thus the computed atom count corresponds to this arrangement.

Step 3: (b) Compare the internal arrangement In a crystalline solid, constituent particles occupy a regular repeating arrangement throughout the solid, giving long-range order. In an amorphous solid, the arrangement is irregular over large distances; order exists only over short distances. This is the first difference.

Step 4: (b) Compare melting behaviour A crystalline solid melts at a sharp, definite temperature because its regular structure is disrupted at a characteristic temperature. An amorphous solid softens gradually over a range of temperatures and has no sharp melting point. This is the second difference.

Step 5: Conclusion (a) $Z \simeq 2$, so the unit cell is $\boxed{\text{body-centred cubic (bcc)}}$. (b) Crystalline solids have long-range order and a sharp melting point; amorphous solids have only short-range order and soften over a temperature range.

Quick Tip to Solve: Convert pm to cm before cubing the edge; then compare the calculated atom count with 1, 2 and 4 for simple cubic, bcc and fcc.

OR

26(b). (a) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a f.c.c. structure. (Atomic mass of Al = 27 g mol^{-1})

(b) Give reasons:

(i) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.

(ii) Silicon on doping with Phosphorus forms n-type semiconductor.

(iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances. [5 marks]

Solution:

Concept:

- In a face-centred cubic (f.c.c.) unit cell, eight corner atoms contribute $8 \times \frac{1}{8} = 1$ atom and six face-centred atoms contribute $6 \times \frac{1}{2} = 3$ atoms. Thus each unit cell contains effectively four atoms.
- The number of atoms in a sample is $N = (m/M)N_A$, where m is its mass, M its molar mass and $N_A = 6.022 \times 10^{23}\,\text{mol}^{-1}$ is Avogadro's constant.
- Stoichiometric defects preserve the cation-to-anion ratio. Doping supplies mobile charge carriers, while the net magnetism of a solid depends on the vector sum of its magnetic moments.

Step 1: (a) Calculate the number of aluminium atoms The amount of aluminium present in the sample is

$$n = \frac{8.1\,\text{g}}{27\,\text{g mol}^{-1}} = 0.300\,\text{mol}.$$

Therefore, its number of atoms is

$$N = 0.300 \times 6.022 \times 10^{23} = 1.8066 \times 10^{23}.$$

This counts atoms in the whole sample, including the fractional contributions assigned to individual unit cells.

Step 2: (a) Convert atoms into f.c.c. unit cells Since each f.c.c. unit cell accounts for four atoms, divide the total number of atoms by four:

$$N_{\text{cells}} = \frac{N}{4} = \frac{1.8066 \times 10^{23}}{4} = 4.5165 \times 10^{22}.$$

No density or edge length is needed because the crystal structure directly gives the number of atoms associated with each cell.

Step 3: (b)(i) Explain the defect in sodium chloride NaCl has a high coordination number, and its cations and anions have comparable sizes. Formation of vacancies is favoured: equal numbers of Na^+ and Cl^- ions are missing from their normal lattice sites, producing a Schottky defect while preserving electrical neutrality and stoichiometry. A Frenkel defect requires a sufficiently small ion to leave its lattice site and occupy an interstitial position. In NaCl, the cation is not sufficiently small relative to the anion to favour this displacement, so NaCl exhibits Schottky rather than Frenkel defects.

Step 4: (b)(ii) Explain n-type conduction in phosphorus-doped silicon Silicon has four valence electrons and forms four covalent bonds with neighbouring silicon atoms. A phosphorus atom has five valence electrons. When it replaces a silicon atom, four electrons form these bonds, while the fifth is

Quick Tip to Solve: For an f.c.c. sample, use $N_{\text{cells}} = mN_A/(4M)$; for magnetic ordering, check whether the opposing moments cancel completely.

only weakly bound and can become mobile. Phosphorus therefore acts as an electron donor. Electrons are the majority charge carriers, so the doped crystal is an n-type semiconductor. The sample remains electrically neutral overall; n-type describes the charge of the dominant mobile carriers.

Step 5: (b)(iii) Compare ferrimagnetic and antiferromagnetic order In both types of substances, magnetic moments on different sets of sites are aligned in opposite directions. In an antiferromagnetic substance, the opposing moments are equal and cancel, giving zero net magnetic moment in the ideal ordered state. In a ferrimagnetic substance, the opposing moments are unequal and do not cancel completely. The residual net magnetic moment makes its magnetism stronger than that of an antiferromagnetic substance.

Step 6: Conclusion (a) The sample contains approximately $\boxed{4.52 \times 10^{22}}$ f.c.c. unit cells. (b) NaCl favours paired ion vacancies; phosphorus supplies extra mobile electrons in silicon; and unequal opposing moments in ferrimagnetic substances leave a nonzero net magnetic moment.

Quick Tip to Solve: For an f.c.c. sample, use $N_{\text{cells}} = mN_A/(4M)$; for magnetic ordering, check whether the opposing moments cancel completely.