CBSE Class 12 Chemistry Question Paper 2016 with Solution PDF-Set 056-1 - South

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. Out of CH_2=CH-CH_2Cl and CH_3-CH_2-CH_2Cl, which is more reactive towards S_N1 reaction? [1 mark]

Solution:

Concept:

- The rate of an S_N1 reaction depends on formation of a carbocation by ionisation of the carbon-chlorine bond.
- A carbocation stabilised by resonance forms more readily than an ordinary primary alkyl carbocation.

Step 1: Compare the intermediates Allyl chloride, $CH_2 = CH - CH_2Cl$, loses chloride to form the allyl carbocation. Its positive charge is delocalised:

$$CH_2 = CH - CH_2^+ \leftrightarrow {}^+CH_2 - CH = CH_2.$$

Step 2: Compare ionisation Propyl chloride, $CH_3CH_2CH_2Cl$, would form an unstable primary propyl carbocation without resonance stabilisation. Hence its ionisation is less favourable.

Step 3: Conclusion $CH_2 = CH - CH_2Cl$ (allyl chloride) is more reactive towards S_N1 because it forms a resonance-stabilised allyl carbocation.

Quick Tip to Solve: For an S_N1 comparison, draw the carbocation first and look for resonance stabilisation.

2. On heating Zn granules with conc. HNO_3, a brown gas is evolved which undergoes dimerization on cooling. Identify this gas. [1 mark]

Solution:

Concept:

- Concentrated nitric acid acts as an oxidising acid and is reduced to nitrogen dioxide on reaction with zinc.
- Brown NO_2 molecules associate reversibly to form colourless N_2O_4.

Step 1: Identify the reaction product The reaction is

$$Zn + 4HNO_3(\text{conc.}) \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O.$$

The brown gaseous product is therefore nitrogen dioxide.

Step 2: Check the cooling observation On cooling, the equilibrium

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

shifts towards the dimer. The brown colour becomes lighter, which confirms the identification.

Step 3: Conclusion The gas is nitrogen dioxide, NO_2.

Quick Tip to Solve: Remember the linked colour clue: brown NO_2 forms colourless N_2O_4 on cooling.

3. What type of magnetism is shown by a substance if its domains are arranged in equal number and in opposite directions? [1 mark]

Solution:

Concept:

- Magnetic behaviour depends on the relative directions and magnitudes of magnetic moments in the material.
- Equal magnetic moments aligned in opposite directions cancel, giving zero resultant magnetic moment.

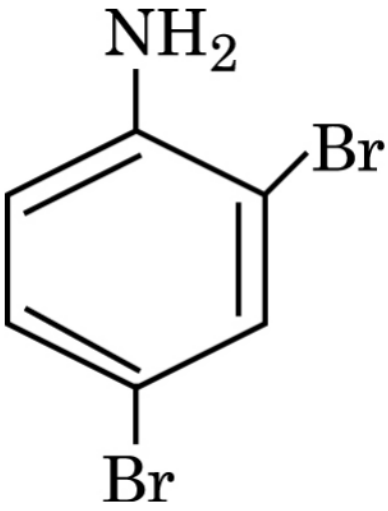
Step 1: Combine the opposing moments The stated arrangement has equal numbers of oppositely directed domains. Their moments cancel pairwise, so the resultant magnetic moment is zero.

Step 2: Identify the magnetic ordering This equal and opposite alignment is characteristic of antiferromagnetism. In ferrimagnetism, opposing moments are unequal and leave a net moment; in ferromagnetism they align in the same direction.

Step 3: Conclusion The substance shows antiferromagnetism.

Quick Tip to Solve: Equal opposite moments mean antiferromagnetism; unequal opposite moments mean ferrimagnetism.

4. Write the IUPAC name of the given compound: [1 mark]



Solution:

Concept:

- For an aromatic amine, aniline is the retained parent name, and the carbon bearing $-NH_2$ is carbon 1.
- The ring is numbered to give the substituents the lowest possible set of locants.

Step 1: Choose the parent and numbering The structure contains a benzene ring directly bonded to an amino group. Take aniline as the parent and assign position 1 to the carbon bonded to $-NH_2$.

Step 2: Locate both bromine substituents One bromine is adjacent to the amino group, at carbon 2, and the other is opposite it, at carbon 4. Numbering the other way would give 4 and 6, so the lower set 2 and 4 is selected. Two bromine substituents require the prefix dibromo.

Step 3: Conclusion The IUPAC name is 2,4-dibromoaniline.

Quick Tip to Solve: Fix the amino-bearing carbon as carbon 1, then choose the direction giving bromines locants 2 and 4.

5. What is the reason for the stability of colloidal sols? [1 mark]

Solution:

Concept:

- Particles in a stable colloidal sol usually carry an electric charge of the same sign.
- Electrostatic repulsion between similarly charged particles opposes their aggregation and coagulation.

Step 1: Identify the stabilising feature Colloidal particles acquire charge, often by preferential adsorption of ions from the dispersion medium. In a given sol the particles normally carry charges of the same sign.

Step 2: Explain resistance to aggregation Like charges repel. This repulsion prevents particles from coming close enough to combine into larger aggregates and settle out. The dispersed state is therefore maintained; neutralising this charge can cause coagulation.

Step 3: Conclusion Colloidal sols are stable mainly because similarly charged colloidal particles repel one another and resist aggregation.

Quick Tip to Solve: Link sol stability to like-charge repulsion, and coagulation to loss or neutralisation of that charge.

6. For the given cells: Lead storage cell, Mercury cell, Fuel cell and Dry cell.

Answer the following:

(i) Which cell is used in hearing aids?

(ii) Which cell was used in Apollo space programme?

(iii) Which cell is used in automobiles and inverters?

(iv) Which cell does not have long life? [2 marks]

Solution:

Concept:

- The application of a cell depends on its size, voltage stability, rechargeability and the manner in which reactants are supplied.
- Primary cells are not ordinarily recharged, whereas a lead storage cell is a rechargeable secondary cell.

Step 1: (i) Hearing aids The mercury cell is used in hearing aids. Its compact size and nearly constant potential during use suit small devices requiring a steady supply.

Step 2: (ii) Apollo space programme The hydrogen-oxygen fuel cell was used in the Apollo space programme. Hydrogen and oxygen supplied continuously to the electrodes generate electrical energy; the overall reaction is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l).$$

The water produced was useful to the astronauts.

Step 3: (iii) Automobiles and inverters The lead storage cell is used in automobiles and inverters. It can supply substantial current and can be recharged by reversing its discharge reaction using an external electrical source.

Step 4: (iv) Limited life The dry cell does not have a long life. Its reactants are gradually consumed during use, and the common zinc-carbon dry cell cannot be effectively recharged for repeated service.

Step 5: Conclusion (i) Mercury cell; (ii) fuel cell; (iii) lead storage cell; (iv) dry cell.

Quick Tip to Solve: Associate miniature devices with mercury cells, space missions with fuel cells, and rechargeable backup with lead storage cells.

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7. When pyrolusite ore MnO_2 is fused with KOH in presence of air, a green coloured compound (A) is obtained which undergoes disproportionation reaction in acidic medium to give a purple coloured compound (B).

(i) Write the formulae of the compounds (A) and (B).

(ii) What happens when compound (B) is heated? [2 marks]

Solution:

Concept:

- Potassium manganate contains the green manganate ion, MnO_4^{2-}, with manganese in oxidation state +6.

- In acid, manganate disproportionates: manganese(+6) is both oxidised to +7 and reduced to +4.

Step 1: Identify compounds (A) and (B) Fusion of pyrolusite with potassium hydroxide in air oxidises manganese from +4 to +6:

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O.$$

Thus green (A) is potassium manganate, K_2MnO_4. In acidic solution,

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O.$$

The purple compound (B) is potassium permanganate, $KMnO_4$.

Step 2: Heat compound (B) Potassium permanganate decomposes on heating and liberates oxygen, leaving potassium manganate and manganese dioxide:

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2 \uparrow .$$

The equation conserves potassium, manganese and all eight oxygen atoms.

Step 3: Conclusion (i) (A): K_2MnO_4; (B): $KMnO_4$. (ii) On heating, (B) forms K_2MnO_4, MnO_2 and oxygen.

Quick Tip to Solve: Remember green manganate has Mn(+6), whereas purple permanganate has Mn(+7).

8. When a coordination compound $PdCl_2.4NH_3$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write:

(i) Structural formula of the complex

(ii) IUPAC name of the complex [2 marks]

Solution:

Concept:

- Only ionisable chloride ions outside the coordination sphere precipitate immediately as $AgCl$ with silver nitrate.
- Ammonia is a neutral ligand named ammine; counter-ions balance the charge of the complex ion.

Step 1: Locate the chloride ions Two moles of silver chloride per mole of compound mean that both chloride ions are outside the coordination sphere. All four ammonia molecules therefore coordinate to palladium:

$$PdCl_2 \cdot 4NH_3 = [Pd(NH_3)_4]Cl_2.$$

In water it gives $[Pd(NH_3)_4]^{2+}$ and $2Cl^-$. Hence

$$[Pd(NH_3)_4]Cl_2 + 2AgNO_3 \longrightarrow 2AgCl \downarrow + [Pd(NH_3)_4](NO_3)_2.$$

Step 2: Name the complex Each coordinated ammonia is neutral. Since the complex cation has charge +2, palladium has oxidation state +2. Four ammine ligands give the prefix tetraammine. Name the

complex cation first, followed by the chloride counter-ion; the metal name remains palladium because this is a cationic complex.

Step 3: Conclusion Structural formula: $[Pd(NH_3)_4]Cl_2$. IUPAC name: tetraamminepalladium(II) chloride.

Quick Tip to Solve: Count the moles of AgCl first: they directly reveal the number of chloride counter-ions.

9. For a reaction: $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$, Rate = k.

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k. [2 marks]

Solution:

Concept:

- The order is the sum of concentration exponents in the experimental rate law; a constant rate corresponds to zero order.
- The molecularity used for the stated reaction counts the reacting ammonia molecules; the unit of a zero-order rate constant equals the unit of rate.

Step 1: Determine order and molecularity The given law can be written as $r = k[NH_3]^0 = k$. Its concentration exponent is zero, so the reaction is of zero order. The written reaction involves two molecules of ammonia, so its molecularity, as asked from this reaction equation, is two (bimolecular). Order is obtained from the rate law and need not equal this count. In a rigorous mechanistic description molecularity refers to an elementary step, so the overall surface reaction alone does not establish its elementary mechanism.

Step 2: Find the unit of the rate constant Since $r = k$, the dimensions of k are those of reaction rate: concentration divided by time. With concentration in moles per litre and time in seconds,

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

A unit of inverse seconds would correspond to a first-order rate constant and is inappropriate for the given constant-rate law.

Step 3: Conclusion (i) Order = 0; molecularity = 2 (bimolecular, for the stated reaction). (ii) $[k] = \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Quick Tip to Solve: Read order from the rate law, not the coefficient 2 in front of ammonia.

10(a). Write the chemical equations involved in the following reactions:

(i) Clemmensen reduction

(ii) Hell-Volhard-Zelinsky reaction [2 marks]

Solution:

Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen using chlorine or bromine and red phosphorus.

Step 1: Write Clemmensen reduction For a ketone, the general equation is

$$\mathrm{R{-}CO{-}R' + 4[H] \xrightarrow{Zn(Hg),\ conc.\ HCl} R{-}CH_2{-}R' + H_2O.}$$

For example, propanone yields propane:

$$\mathrm{CH_3COCH_3 + 4[H] \xrightarrow{Zn(Hg),\ conc.\ HCl} CH_3CH_2CH_3 + H_2O.}$$

Here [H] denotes reducing hydrogen equivalents; the carbonyl oxygen is removed as water.

Step 2: Write Hell-Volhard-Zelinsky reaction A carboxylic acid having an alpha hydrogen reacts with bromine in the presence of a small amount of red phosphorus:

$$\mathrm{RCH_2COOH + Br_2 \xrightarrow{red\ P} RCHBrCOOH + HBr.}$$

For example, ethanoic acid gives bromoethanoic acid. Halogenation occurs on the carbon adjacent to the carboxyl group; it does not replace the hydroxyl group of the acid.

Step 3: Conclusion Clemmensen: $\mathrm{RCOR' \to RCH_2R'}$ using Zn(Hg)/concentrated HCl. HVZ: $\mathrm{RCH_2COOH \to RCHBrCOOH}$ using bromine/red P.

Quick Tip to Solve: For HVZ first check for an alpha hydrogen; for Clemmensen show Zn(Hg) and concentrated HCl on the arrow.

OR

10(b). How do you convert:

(i) Toluene to benzaldehyde

(ii) Ethanoyl chloride to ethanal [2 marks]

Solution:

Concept:

- Controlled oxidation of a benzylic methyl group gives an aldehyde. In the Etard reaction, chromyl chloride, $\mathrm{CrO_2Cl_2}$, forms a complex that yields benzaldehyde on hydrolysis.

- Rosenmund reduction converts an acyl chloride to an aldehyde using hydrogen and palladium supported on barium sulphate, $\mathrm{Pd/BaSO_4}$.

Step 1: (i) Convert toluene to benzaldehyde Treat toluene with chromyl chloride in a non-aqueous solvent such as carbon disulphide, then hydrolyse the resulting chromium complex. This controlled side-chain oxidation is the Etard reaction:

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

The aromatic ring remains intact while the methyl carbon becomes the aldehyde carbon. Strong oxidation with hot alkaline permanganate would continue to the carboxylic acid, so it is unsuitable for isolating benzaldehyde.

Step 2: (ii) Convert ethanoyl chloride to ethanal Pass hydrogen over ethanoyl chloride in the presence of the poisoned catalyst palladium on barium sulphate. The Rosenmund reduction is

$$\mathrm{CH_3COCl + H_2} \xrightarrow{\mathrm{Pd/BaSO_4}} \mathrm{CH_3CHO + HCl}.$$

Replacement of the acyl chlorine by hydrogen produces ethanal without changing the two-carbon skeleton. The reduced activity of the supported, poisoned catalyst prevents further reduction of the aldehyde to ethanol.

Step 3: Conclusion (i) Use $\mathrm{CrO_2Cl_2/CS_2}$, followed by hydrolysis (Etard reaction). (ii) Use $\mathrm{H_2,\ Pd/BaSO_4}$ (Rosenmund reduction).

Quick Tip to Solve: For an aldehyde target, choose a controlled reagent: Etard oxidation of a methyl side chain or Rosenmund reduction of an acyl chloride.

11. An element crystallizes in a f.c.c. lattice with cell edge of 400 pm. The density of the element is 7 g cm^{-3}. How many atoms are present in 280 g of the element? [3 marks]

Solution:

Concept:

- An f.c.c. unit cell contains $Z = 8(1/8) + 6(1/2) = 4$ atoms, counting corner and face-centre contributions.
- For cell edge a and density ρ, cell mass is ρa^3. Thus a sample of mass m contains $N = Zm/(\rho a^3)$ atoms.

Step 1: Convert the cell edge and calculate cell volume The density is given in $\mathrm{g\,cm^{-3}}$, so convert the cell edge into centimetres before cubing. Since $1\,\mathrm{pm} = 10^{-10}\,\mathrm{cm}$,

$$a = 400 \times 10^{-10} = 4.00 \times 10^{-8}\,\mathrm{cm}.$$

Therefore the volume of one cubic unit cell is

$$V_{\text{cell}} = a^3 = (4.00 \times 10^{-8})^3 = 6.40 \times 10^{-23}\,\mathrm{cm^3}.$$

The exponent is multiplied by three when the edge length is cubed.

Step 2: Calculate the number of unit cells in the sample The sample volume is its mass divided by its density:

$$V_{\text{sample}} = \frac{280\,\text{g}}{7\,\text{g cm}^{-3}} = 40\,\text{cm}^3.$$

Dividing by the volume of one unit cell gives

$$n_{\text{cells}} = \frac{40}{6.40 \times 10^{-23}} = 6.25 \times 10^{23}.$$

This is a count of unit cells, not a count of atoms.

Step 3: Use the f.c.c. occupancy Each corner atom is shared among eight cells and each face-centre atom among two cells. Therefore

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

Multiplying the number of cells by four gives

$$N = 4 \times 6.25 \times 10^{23} = 2.50 \times 10^{24}.$$

No molar mass is needed because the density and cell dimensions already determine the mass per unit cell.

Step 4: Conclusion The $280\,\text{g}$ sample contains $\boxed{2.50 \times 10^{24}\ \text{atoms}}$.

Quick Tip to Solve: Find sample volume first, divide by cell volume, then multiply by four for f.c.c.; keep all lengths in centimetres.

12. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:
$\log k = 14.2 - (1.0 \times 10^4\ \text{K})/T$
Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes. (Given: R = 8.314 $\text{JK}^{-1}\ \text{mol}^{-1}$) [3 marks]

Solution:

Concept:

- The base-10 Arrhenius equation is $\log k = \log A - E_a/(2.303RT)$, where A is the pre-exponential factor, E_a activation energy, R the gas constant and T absolute temperature.
- For first-order kinetics, $t_{1/2} = \ln 2/k = 0.693/k$. The time unit chosen for the half-life determines the reciprocal-time unit of k.

Step 1: Compare the given equation with the Arrhenius form The printed relation is

$$\log k = 14.2 - \frac{1.0 \times 10^4\,\text{K}}{T}.$$

Compare it term by term with

$$\log k = \log A - \frac{E_a}{2.303R}\frac{1}{T}.$$

Thus the constant term is $\log A = 14.2$, while the magnitude of the coefficient of $1/T$ is

$$\frac{E_a}{2.303R} = 1.0 \times 10^4\,\text{K}.$$

The minus sign describes the negative slope of the Arrhenius plot; the activation energy itself is positive.

Step 2: Calculate the activation energy Using $R = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1}$,

$$\begin{aligned} E_a &= 2.303R(1.0 \times 10^4\,\text{K}) \\ &= 2.303 \times 8.314 \times 10^4\,\text{J mol}^{-1} \\ &= 1.9147 \times 10^5\,\text{J mol}^{-1} \\ &\simeq 191.5\,\text{kJ mol}^{-1}. \end{aligned}$$

The kelvin unit in the coefficient cancels the reciprocal kelvin in the gas constant.

Step 3: Use the specified first-order half-life For $t_{1/2} = 200\,\text{min}$,

$$k = \frac{0.693}{200} = 3.465 \times 10^{-3}\,\text{min}^{-1}.$$

Equivalently, the half-life is $200 \times 60 = 12000\,\text{s}$, so

$$k = \frac{0.693}{12000} = 5.775 \times 10^{-5}\,\text{s}^{-1}.$$

These are the same rate constant expressed in two time units. The half-life relation gives this value directly; no temperature needs to be determined.

Step 4: Conclusion $\boxed{E_a \simeq 191.5\,\text{kJ mol}^{-1}}$, and $\boxed{k = 3.465 \times 10^{-3}\,\text{min}^{-1} = 5.775 \times 10^{-5}\,\text{s}^{-1}}$.

Quick Tip to Solve: When the equation uses log rather than ln, retain the factor 2.303; use the half-life separately to calculate k.

13. (i) Out of silica gel and anhydrous $CaCl_2$, which will adsorb the water vapours more?
(ii) Out of H_2SO_4 and H_3PO_4, which one is more effective in causing coagulation of positively charged sol? Give reason.
(iii) Out of sulphur sol and proteins, which one forms macromolecular colloids? [3 marks]

Solution:

Concept:

- Adsorption concentrates molecules on a surface, whereas absorption distributes a substance throughout the bulk. A large specific surface area favours adsorption.

- By the Hardy–Schulze rule, the coagulating power of a counter-ion increases with its charge. A positive sol is coagulated by anions.
- A macromolecular colloid contains individual large molecules of colloidal dimensions; a multi-molecular colloid contains aggregates of many small molecules.

Step 1: (i) Compare removal of water vapour Silica gel adsorbs more water vapour. Its porous structure provides a large surface area on which water molecules accumulate. Anhydrous $CaCl_2$ is also a drying agent, but it takes up water mainly by absorption and hydrate formation. Thus its ability to remove moisture should not be confused with the surface phenomenon specifically asked about here.

Step 2: (ii) Identify the more effective coagulating acid For a positively charged sol, the active coagulating species is the negative ion. In the standard Hardy–Schulze comparison, H_3PO_4 supplies phosphate, PO_4^{3-}, whereas H_2SO_4 supplies sulphate, SO_4^{2-}. The trivalent phosphate counter-ion has greater coagulating power than the divalent sulphate counter-ion and neutralises the positive colloidal charge more effectively.

Step 3: (iii) Classify the colloids Proteins form macromolecular colloids because a single protein molecule is sufficiently large to have colloidal dimensions. Sulphur sol is multimolecular: its dispersed particles are aggregates of many small sulphur molecules, rather than individual giant molecules.

Step 4: Conclusion (i) Silica gel. (ii) H_3PO_4, since PO_4^{3-} has greater coagulating power than SO_4^{2-}. (iii) Proteins.

Quick Tip to Solve: For a positive sol compare anion charge; distinguish silica surface adsorption from the bulk uptake of water by calcium chloride.

14. (i) Name the method of refining Zirconium.

(ii) In the extraction of Al, impure Al_2O_3 is dissolved in conc. NaOH to form sodium aluminate and leaving impurities behind. What is the name of this process?

(iii) What is the function of limestone in the extraction of iron from its oxides? [3 marks]

Solution:

Concept:

- Refining removes impurities from a crude metal; volatile-compound refining exploits formation and decomposition of a volatile metal compound.
- Leaching selectively dissolves the desired ore constituent while leaving insoluble impurities behind.
- A flux reacts with gangue to form a fusible slag. Basic calcium oxide removes acidic silica gangue.

Step 1: (i) Refining zirconium Zirconium is refined by the van Arkel or iodide process. Impure zirconium reacts with iodine to form volatile zirconium tetraiodide; this vapour decomposes on a hot tungsten filament, depositing pure zirconium. The two stages are represented by

$$Zr + 2I_2 \longrightarrow ZrI_4, \qquad ZrI_4 \xrightarrow{\text{hot filament}} Zr + 2I_2.$$

Impurities that do not undergo this volatile-compound cycle are separated.

Step 2: (ii) Dissolving alumina selectively This process is leaching, specifically the alkaline leaching used in Bayer's process. Alumina is amphoteric and dissolves in concentrated sodium hydroxide as sodium aluminate, while insoluble impurities can be filtered off. In aqueous solution the reaction can be written as

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4].$$

Step 3: (iii) Role of limestone in iron extraction Limestone acts as a source of the basic flux calcium oxide. On heating,

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2.$$

The calcium oxide reacts with acidic silica gangue to form calcium silicate slag:

$$CaO + SiO_2 \longrightarrow CaSiO_3.$$

The molten slag separates from molten iron, removing the silica impurity.

Step 4: Conclusion (i) van Arkel (iodide) process. (ii) Leaching (Bayer's process). (iii) Limestone provides CaO flux, which converts silica into calcium silicate slag.

Quick Tip to Solve: Link limestone to CaO first, then combine CaO with acidic silica; limestone itself is not the reducing agent for iron oxide.

15. Calculate E°_{cell} for the following reaction at 298 K:

$$2Cr(s) + 3Fe^{2+}(0.01\,M) \longrightarrow 2Cr^{3+}(0.01\,M) + 3Fe(s)$$

Given: $E_{cell} = 0.261$ **V.** [3 marks]

Solution:

Concept:

- At 298 K, the Nernst equation is $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log_{10} Q$, where n is the number of electrons transferred in the balanced reaction and Q is the reaction quotient.
- Pure solids have unit activity and are omitted from Q. For this dilute-solution calculation, ionic activities are approximated by their molar concentrations relative to the standard concentration.

Step 1: Count the electrons transferred The oxidation and reduction half-reactions for the reaction as written are

$$2Cr(s) \longrightarrow 2Cr^{3+} + 6e^-,$$
$$3Fe^{2+} + 6e^- \longrightarrow 3Fe(s).$$

Therefore the balanced reaction transfers $n = 6$ electrons. The chromium and iron solids do not contribute concentration factors to the reaction quotient.

Step 2: Calculate the reaction quotient Use the stoichiometric coefficients as exponents:

$$Q = \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} = \frac{(0.01)^2}{(0.01)^3} = 100.$$

Thus $\log_{10} Q = 2$. Although both ionic concentrations are equal, the quotient is not unity because their powers differ.

Step 3: Find the standard cell potential The printed given value is the cell potential $E_{\text{cell}} = 0.261\,\text{V}$, and the required quantity is E°_{cell}. Rearranging the Nernst equation gives

$$\begin{aligned} E^\circ_{\text{cell}} &= E_{\text{cell}} + \frac{0.0591}{6}\log_{10} 100 \\ &= 0.261 + \frac{0.0591}{6}(2) \\ &= 0.261 + 0.0197 = 0.2807\,\text{V}. \end{aligned}$$

Since $Q > 1$, the non-standard potential is lower than the standard potential, consistent with the positive correction just obtained.

Step 4: Conclusion

$$\boxed{E^\circ_{\text{cell}} = 0.2807\,\text{V} \approx 0.281\,\text{V}}$$

Quick Tip to Solve: Read the superscript zero carefully: here the unknown is the standard potential, so add the Nernst correction to the given cell potential.

16. Give reasons:

(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.

(ii) Zn is soft whereas Cr is hard.

(iii) Eu^{2+} is a good reducing agent. [3 marks]

Solution:

Concept:

- High oxidation states are stabilised by strong metal-ligand bonding; oxygen can form multiple bonds with a transition metal.
- Metallic hardness depends on the strength of metallic bonding, to which unpaired valence electrons can contribute.
- A reducing agent donates an electron and is itself oxidised; the stability of the resulting ion helps determine this tendency.

Step 1: (i) Compare bonding with oxygen and fluorine Oxygen can stabilise the high oxidation state of manganese by forming strong multiple bonds, as in Mn_2O_7, where Mn has oxidation state $+7$. Fluorine forms only single bonds with manganese and cannot provide this multiple-bond stabilisation. Consequently, the highest oxidation state displayed by Mn with fluorine is $+4$, as in MnF_4. Thus electronegativity alone does not decide the maximum oxidation state.

Step 2: (ii) Compare metallic bonding in Zn and Cr Zinc has the configuration $[\text{Ar}]3d^{10}4s^2$, with a filled $3d$ subshell and no unpaired electrons in the free atom. Chromium has $[\text{Ar}]3d^5 4s^1$, with six unpaired valence electrons available for strong metallic bonding. Metallic bonding is therefore much

stronger in chromium than in zinc, making Cr hard and Zn comparatively soft.

Step 3: (iii) Examine oxidation of the europium ion Europium(II), Eu^{2+}, readily loses an electron to form Eu^{3+}, the common and more stable oxidation state in aqueous solution:

$$Eu^{2+} \longrightarrow Eu^{3+} + e^{-}.$$

The released electron reduces another species, so Eu^{2+} acts as a good reducing agent. Although Eu^{2+} has the half-filled $4f^7$ configuration, the overall energetics in solution favour its oxidation to the trivalent ion.

Step 4: Conclusion Oxygen stabilises Mn(VII) by multiple bonding; Cr has stronger metallic bonding than Zn; and Eu^{2+} reduces other species by oxidation to Eu^{3+}.

Quick Tip to Solve: For these reasons, identify the controlling factor separately: ligand bonding, metallic bonding, and stability of the oxidised ion.

17. What happens when:

(i) 2, 4, 6-trinitrochlorobenzene is treated with warm water.

(ii) 2-chlorobutane is treated with alcoholic KOH.

(iii) Ethyl chloride is treated with Na metal in presence of dry ether.

Write the equations involved in the above reactions. [3 marks]

Solution:

Concept:

- Nitro groups at ortho and para positions strongly activate an aryl halide towards nucleophilic substitution by stabilising the anionic intermediate.
- Alcoholic KOH favours beta-elimination of hydrogen halide. According to Saytzeff's rule, the more substituted alkene is the major product.
- In the Wurtz reaction, two alkyl halide molecules couple with sodium in dry ether to form an alkane.

Step 1: (i) Hydrolyse 2,4,6-trinitrochlorobenzene The chlorine atom is replaced by a hydroxyl group on warming with water, giving 2,4,6-trinitrophenol, also called picric acid:

$$C_6H_2(NO_2)_3Cl + H_2O \xrightarrow{\text{warm}} C_6H_2(NO_2)_3OH + HCl.$$

The three nitro groups at positions 2, 4 and 6 withdraw electrons and facilitate this nucleophilic aromatic substitution. The nitro groups retain their positions in the product.

Step 2: (ii) Eliminate HCl from 2-chlorobutane Alcoholic KOH removes a beta-hydrogen while chlorine leaves the adjacent carbon. Dehydrohalogenation gives but-2-ene as the major product:

$$CH_3CH(Cl)CH_2CH_3 + KOH \xrightarrow{\text{alcoholic}} CH_3CH{=}CHCH_3 + KCl + H_2O.$$

Removal of a hydrogen from the other beta-carbon also gives a smaller amount of but-1-ene, $CH_2{=}CHCH_2CH_3$. But-2-ene predominates because its double bond is more substituted and more stable.

Step 3: (iii) Couple ethyl chloride by the Wurtz reaction Sodium couples two ethyl groups in dry ether, producing n-butane:

$$2CH_3CH_2Cl + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_3 + 2NaCl.$$

The carbon chain therefore doubles from two to four carbon atoms. Dry ether provides the anhydrous medium required for the reaction.

Step 4: Conclusion The products are (i) picric acid, (ii) mainly but-2-ene with some but-1-ene, and (iii) n-butane, respectively.

Quick Tip to Solve: Read the reagent and solvent first: warm water gives substitution here, alcoholic KOH gives elimination, and Na/dry ether gives coupling.

18. Give reasons for the following:

(a) Aldehydes (R-CHO) are more reactive than ketones (R-CO-R) towards nucleophilic addition reaction.

(b) Benzaldehyde does not undergo aldol condensation reaction.

(c) Benzoic acid does not give Friedel-Crafts reaction. [3 marks]

Solution:

Concept:

- Nucleophiles attack the electrophilic carbonyl carbon. Electron donation and steric crowding decrease the ease of this attack.
- Aldol condensation requires at least one alpha-hydrogen so that an enolate or enol can form from the carbonyl compound.
- Friedel-Crafts reactions are electrophilic aromatic substitutions and require a sufficiently electron-rich aromatic ring.

Step 1: (a) Compare aldehydes and ketones An aldehyde, $RCHO$, has one alkyl group and one hydrogen attached to its carbonyl carbon, whereas a ketone, $RCOR$, has two alkyl groups. Alkyl groups release electron density by the $+I$ effect. The two alkyl groups of a ketone therefore decrease the partial positive charge on the carbonyl carbon more than the single alkyl group of an aldehyde does, reducing its susceptibility to nucleophilic attack. Also, the two alkyl groups cause greater steric hindrance in a ketone, obstructing the approaching nucleophile and the formation of the tetrahedral addition product. Aldehydes consequently undergo nucleophilic addition more readily than comparable ketones because of both electronic and steric factors.

Step 2: (b) Check for an alpha-hydrogen in benzaldehyde In benzaldehyde, C_6H_5CHO, the carbon adjacent to the carbonyl group is a carbon of the benzene ring and bears no hydrogen. Thus benzaldehyde has no alpha-hydrogen and cannot form the enolate needed for self-aldol condensation.

The hydrogen directly attached to the carbonyl carbon is an aldehydic hydrogen, not an alpha-hydrogen, so it does not satisfy this requirement.

Step 3: (c) Examine the effect of the carboxyl group In benzoic acid, C_6H_5COOH, the $-COOH$ group withdraws electron density from the benzene ring through both the negative inductive and negative resonance effects. The ring is therefore strongly deactivated towards electrophilic substitution and does not undergo the usual Friedel-Crafts alkylation or acylation. Interaction of the carboxyl group with the Lewis acid catalyst, such as $AlCl_3$, further hinders the reaction.

Step 4: Conclusion Aldehydes are less hindered and more electrophilic than ketones; benzaldehyde cannot undergo self-aldol condensation because it lacks an alpha-hydrogen; and the carboxyl group strongly deactivates the ring of benzoic acid towards Friedel-Crafts reaction.

Quick Tip to Solve: Distinguish the hydrogen on the carbonyl carbon from an alpha-hydrogen on the adjacent carbon before deciding whether aldol condensation is possible.

19. Complete the following reactions:

(i) $\mathbf{C_6H_5-COO^-NH_4^+ \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow{CH_3COCl/pyridine} C}$

(ii) $\mathbf{C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow[\Delta]{CHCl_3+alc.\,KOH} C}$ [3 marks]

Solution:

Concept:

- Heating an ammonium carboxylate eliminates water to form an amide. Hofmann bromamide degradation converts a primary amide into a primary amine with one fewer carbon atom.
- Diazonium salts undergo replacement of the diazonium group; nitro compounds are reduced to amines. Primary amines give isocyanides in the carbylamine reaction.

Step 1: (i) Form benzamide and then aniline On heating, ammonium benzoate loses water:

$$C_6H_5COONH_4 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O.$$

Thus A is benzamide. Bromine and aqueous KOH cause Hofmann degradation:

$$C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Thus B is aniline; the carbonyl carbon is lost during this step.

Step 2: (i) Acetylate aniline Acetyl chloride acylates the amino group of aniline. Pyridine takes up the hydrogen chloride produced:

$$C_6H_5NH_2 + CH_3COCl \xrightarrow{\text{pyridine}} C_6H_5NHCOCH_3 + HCl.$$

C is acetanilide; the benzene ring remains unchanged.

Step 3: (ii) Replace, reduce and form the isocyanide With sodium nitrite and copper on heating, the diazonium group is replaced by a nitro group, so A is nitrobenzene, $C_6H_5NO_2$. Tin and hydrochloric

acid reduce it:

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

The free amine B is aniline (obtained after the usual alkaline work-up of the acidic reduction mixture). Heating this primary amine with chloroform and alcoholic KOH gives phenyl isocyanide:

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O.$$

Here nitrogen is bonded to the phenyl group in the product; the product is an isocyanide, not benzonitrile.

Step 4: Conclusion (i) $\boxed{A = C_6H_5CONH_2,\ B = C_6H_5NH_2,\ C = C_6H_5NHCOCH_3}$.

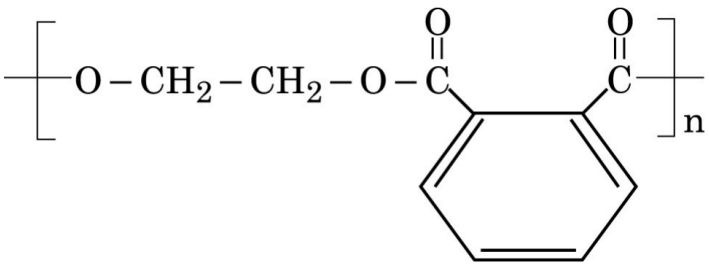
(ii) $\boxed{A = C_6H_5NO_2,\ B = C_6H_5NH_2,\ C = C_6H_5NC}$.

Quick Tip to Solve: For Hofmann degradation remove the carbonyl carbon; for carbylamine retain the amine nitrogen between phenyl and carbon.

20(a). (i) What is the role of t-butyl peroxide in the polymerization of ethene?

(ii) Identify the monomers in the following polymer:

(iii) Arrange the following polymers in the increasing order of their intermolecular forces: PVC, Nylon-6, Buna-N [3 marks]



Solution:

Concept:

- Peroxides initiate addition polymerisation by forming free radicals through homolytic cleavage of the weak oxygen–oxygen bond.
- A polyester can be traced back to its diol and dicarboxylic acid by breaking its ester links. Polymer intermolecular attraction increases from elastomers to thermoplastics to hydrogen-bonded fibres.

Step 1: (i) Role of t-butyl peroxide t-Butyl peroxide acts as a free-radical initiator. Its peroxide bond undergoes homolysis on heating:

$$(CH_3)_3CO{-}OC(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO^{\bullet}.$$

A radical attacks the double bond of ethene, producing a new carbon-centred radical that adds further ethene molecules. Thus the peroxide starts the chain reaction; it is not the monomer.

Step 2: (ii) Identify the two monomers from the printed structure The segment $-OCH_2CH_2O-$ comes from ethane-1,2-diol (ethylene glycol), $HOCH_2CH_2OH$. The two carbonyl substituents in the printed benzene ring are on adjacent carbon atoms, so the acid component is benzene-1,2-dicarboxylic acid (phthalic acid), $o-C_6H_4(COOH)_2$.

Condensation of the two hydroxyl groups of the diol with carboxyl groups of the diacid forms ester links and eliminates water. The adjacent positions shown in the diagram must be preserved when naming the acid; they do not represent the para arrangement of terephthalic acid.

Step 3: (iii) Compare the intermolecular forces Buna-N is an elastomer, whose chains have comparatively weak intermolecular attractions and can uncoil on stretching. PVC is a thermoplastic with stronger intermolecular attractions, including dipolar interactions due to its polar carbon–chlorine bonds. Nylon-6 is a fibre with strong interchain hydrogen bonding between its amide groups. Therefore the increasing order follows elastomer, thermoplastic, then polyamide fibre.

Step 4: Conclusion (i) Free-radical initiator. (ii) Ethane-1,2-diol and phthalic acid, $HOCH_2CH_2OH$ and $o-C_6H_4(COOH)_2$. (iii) $\boxed{\text{Buna-N} < \text{PVC} < \text{Nylon-6}}$.

Quick Tip to Solve: Trace each ester bond back to an alcohol and acid, and check the positions of both carbonyl groups on the ring.

OR

20(b). Write the mechanism of free radical polymerization of ethene. [3 marks]

Solution:

Concept:

- Free-radical addition polymerisation converts ethene into polyethene without elimination of a small molecule. The double bond opens while the carbon backbone grows.
- The mechanism has initiation, propagation and termination. A peroxide supplies the initiating radical; the unpaired electron remains at the growing chain end until termination.

Step 1: Initiation Let ROOR denote a peroxide initiator. Heat or light cleaves its weak oxygen–oxygen bond homolytically:

$$ROOR \longrightarrow 2RO^{\bullet}.$$

An alkoxy radical adds to one carbon of ethene and leaves the unpaired electron on the other carbon:

$$RO^{\bullet} + CH_2{=}CH_2 \longrightarrow RO{-}CH_2{-}CH_2^{\bullet}.$$

This carbon-centred radical is the first growing chain. Each dot denotes one unpaired electron.

Step 2: Propagation The radical end successively attacks more ethene molecules:

$$RO{-}CH_2{-}CH_2^{\bullet} + CH_2{=}CH_2 \longrightarrow RO{-}CH_2{-}CH_2{-}CH_2{-}CH_2^{\bullet}.$$

More generally, with P representing the existing chain,

$$\mathrm{P{-}CH_2{-}CH_2^{\bullet} + CH_2{=}CH_2 \longrightarrow P{-}CH_2{-}CH_2{-}CH_2{-}CH_2^{\bullet}.}$$

Each addition consumes one double bond and extends the chain by an ethylene unit, while preserving a radical at the new end. Repetition builds a long saturated carbon chain.

Step 3: Termination by combination Two growing radical chains combine, pairing their unpaired electrons to form a covalent bond:

$$\mathrm{P{-}CH_2{-}CH_2^{\bullet} + {}^{\bullet}CH_2{-}CH_2{-}Q \longrightarrow P{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}Q.}$$

Here P and Q denote the remaining portions of the two chains. The resulting molecule has no radical end, so growth by this radical mechanism stops. The chain contains repeating $-\mathrm{CH_2-CH_2-}$ units.

Step 4: Conclusion The three stages are initiation by peroxide radicals, repeated addition of ethene in propagation, and combination of growing radicals in termination. Overall,

$$\boxed{\mathrm{nCH_2{=}CH_2 \longrightarrow [-CH_2-CH_2-]_n}}$$

with initiator-derived end groups omitted in the repeat-unit formula.

Quick Tip to Solve: Keep the radical dot at the chain end after every propagation step; remove both dots only when chains terminate.

21. (i) Write the name of two monosaccharides obtained on hydrolysis of maltose sugar.
(ii) Name the vitamin whose deficiency causes convulsions.
(iii) Write one example each for Fibrous protein and Globular protein. [3 marks]

Solution:

Concept:

- Hydrolysis breaks a disaccharide's glycosidic linkage by addition of water, giving its constituent monosaccharide units.
- Vitamins are required in small amounts for normal metabolism; a characteristic deficiency disorder identifies the vitamin concerned.
- Fibrous proteins have extended, thread-like structures, whereas globular proteins have compact, folded structures.

Step 1: (i) Identify the hydrolysis products of maltose Maltose contains two glucose units joined by an $\alpha(1 \to 4)$ glycosidic linkage. Hydrolysis cleaves this linkage and yields two molecules of D-glucose:

$$\mathrm{Maltose + H_2O \longrightarrow D\text{-}glucose + D\text{-}glucose.}$$

Thus the two monosaccharides named in the question are both glucose; they are not two different types of sugar. Glucose and fructose would instead be the products of sucrose hydrolysis.

Step 2: (ii) Identify the vitamin Deficiency of vitamin $\mathrm{B_6}$, also called pyridoxine, causes convulsions.

This is the characteristic vitamin-deficiency association required here.

Step 3: (iii) Give examples of the two protein classes Keratin is a fibrous protein, found in hair and wool, whose extended polypeptide chains provide structural strength. Insulin is a globular protein: its polypeptide chains fold into a compact structure. These examples distinguish a structural, fibre-forming protein from a compact functional protein.

Step 4: Conclusion (i) Glucose and glucose (two molecules of D-glucose). (ii) Vitamin B_6 (pyridoxine). (iii) Fibrous protein: keratin; globular protein: insulin.

Quick Tip to Solve: Remember maltose as glucose plus glucose; sucrose, rather than maltose, yields glucose plus fructose.

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22. (a) For the complex $[CoF_6]^{3-}$, write the hybridization, magnetic character and spin of the complex. (At. number: Co = 27)

(b) Draw one of the geometrical isomers of the complex $[Co(en)_2Cl_2]^+$ which is optically active.

[3 marks]

Solution:

Concept:

- The oxidation state of cobalt determines its d-electron count. Fluoride is a weak-field ligand, so an octahedral fluoride complex has a high-spin configuration.
- An octahedral outer-orbital complex uses sp^3d^2 hybridization. Unpaired electrons cause paramagnetism, and each contributes spin $\frac{1}{2}$.
- Ethane-1,2-diamine, en, is bidentate. The cis form of $[Co(en)_2Cl_2]^+$ exists as non-superimposable mirror images and is optically active.

Step 1: (a) Determine the metal ion and electron configuration Let cobalt have oxidation state x. Since each fluoride ligand has charge -1,

$$x + 6(-1) = -3 \quad \Rightarrow \quad x = +3.$$

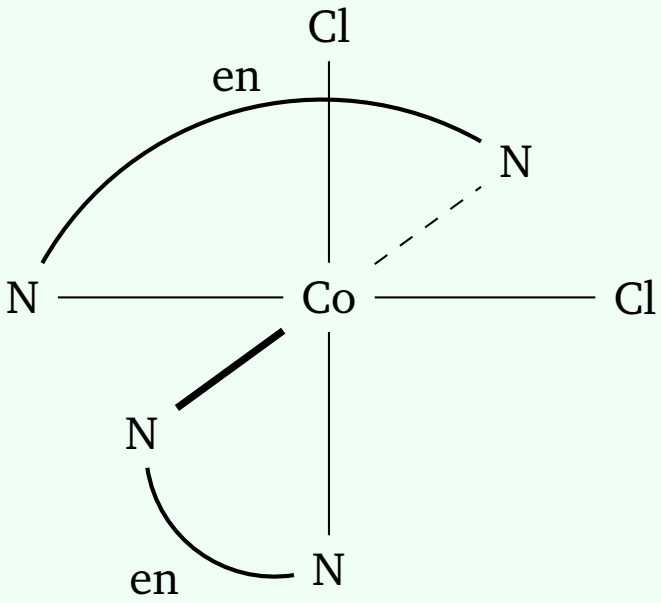
Cobalt has atomic number 27, so its atom is $[Ar]3d^7 4s^2$, and Co^{3+} is $[Ar]3d^6$. With weak-field F^-, electrons remain unpaired as far as possible; the octahedral configuration is $t_{2g}^4 e_g^2$, containing four unpaired electrons.

Step 2: (a) State hybridization, magnetic character and spin Pairing does not create two vacant inner $3d$ orbitals. In the valence-bond description the complex uses the outer $4d$ orbitals along with $4s$ and $4p$, giving sp^3d^2 hybridization. Four unpaired electrons make the complex paramagnetic and high spin. Its total spin is

$$S = 4\left(\frac{1}{2}\right) = 2.$$

Step 3: (b) Draw the optically active geometrical isomer Draw the cis isomer, in which the two chloride ligands occupy adjacent positions with a 90° angle at cobalt. Each pair of N donor atoms joined by a curved line belongs to one en ligand. The chelate arrangement shown is one optical form;

its mirror image is the other. The trans geometrical isomer is optically inactive.



One optical form of cis-$[Co(en)_2Cl_2]^+$; curved links join the N donors of each en ligand.

Step 4: Conclusion (a) $[CoF_6]^{3-}$: sp^3d^2, paramagnetic with four unpaired electrons, high spin with $S = 2$. (b) The cis form of $[Co(en)_2Cl_2]^+$, drawn above, is optically active.

Quick Tip to Solve: For cobalt(III), count six d electrons first; weak-field fluoride leaves four unpaired, while cis dichloro bis-chelate geometry permits optical isomerism.

23. Due to hectic and busy schedule, Mr. Awasthi made his life full of tensions and anxiety. He started taking sleeping pills to overcome the depression without consulting the doctor. Mr. Roy, a close friend of Mr. Awasthi, advised him to stop taking sleeping pills and suggested to change his lifestyle by doing Yoga, meditation and some physical exercise. Mr. Awasthi followed his friend's advice and after few days he started feeling better.

After reading the above passage, answer the following:

(i) What are the values (at least two) displayed by Mr. Roy?

(ii) Why it is not advisable to take sleeping pills without consulting doctor?

(iii) What are tranquilizers? Give two examples. [4 marks]

Solution:

Concept:

- Tranquilizers are drugs used to treat stress and mild or severe mental diseases. They act on the central nervous system and help relieve anxiety and tension.
- Medicines affecting the nervous system must be used in the appropriate dose under medical supervision; self-medication can cause harmful effects and dependence.

Step 1: (i) Values displayed by Mr. Roy Mr. Roy shows care and concern for his friend's health, helpfulness and a sense of responsibility. He also displays scientific awareness by discouraging unsupervised use of medicines. His suggestion of Yoga, meditation and physical exercise reflects an appreciation of a healthy and balanced lifestyle. Any two of these values answer the question; for example, concern for others and responsible helpfulness.

Step 2: (ii) Need for a doctor's advice Sleeping pills act on the central nervous system. Repeated or uncontrolled use may produce tolerance, dependence or addiction, while an excessive dose may cause dangerous depression of the nervous system, including impaired breathing. They may also interact with other medicines. Therefore, a doctor should assess the condition and prescribe the suitable drug, dose and duration. Taking such pills merely because one feels depressed does not establish that they are the appropriate treatment.

Step 3: (iii) Meaning and examples of tranquilizers Tranquilizers are a class of drugs used in the treatment of stress and mild or severe mental diseases. They reduce anxiety and tension and may produce a calming effect. Two examples are diazepam and chlordiazepoxide. Both are examples of medicines whose use requires medical supervision. The term tranquilizer describes their therapeutic action; it does not imply that every such medicine should be used as a sleeping pill or that different drugs can be substituted freely.

Step 4: Conclusion (i) Mr. Roy shows concern, helpfulness and responsibility. (ii) Unsupervised sleeping-pill use can cause dependence and harmful nervous-system depression. (iii) Tranquilizers relieve stress and anxiety; examples are diazepam and chlordiazepoxide.

Quick Tip to Solve: Link the values to Roy's actions, then distinguish the risks of self-medication from the definition and two examples of tranquilizers.

24(a). Account for the following:

(i) H_2Te is more acidic than H_2S.

(ii) PCl_5 is more covalent than PCl_3.

(iii) Boiling points of interhalogens are little higher as compared to pure halogens.

(b) Draw the structures of: (i) $HClO_4$ (ii) $XeOF_4$ [5 marks]

Solution:

Concept:

- For group 16 hydrides, acidity increases down the group as the larger central atom forms a longer, weaker bond to hydrogen, making proton release easier.
- Fajans' rule relates covalent character to polarisation: a central atom in a higher positive oxidation state has greater polarising power towards the surrounding anions.
- Boiling requires overcoming intermolecular attractions. Unlike homonuclear halogens, interhalogens contain unlike atoms and generally have polar bonds, giving additional dipolar attractions.
- In VSEPR theory, each bond, whether single or multiple, counts as one electron domain. Four bond domains give tetrahedral geometry; five bond domains and one lone pair give square pyramidal molecular geometry.

Step 1: (a)(i) Compare the hydride bond strengths Tellurium lies below sulphur in group 16 and has a larger atomic size. Consequently the $\mathrm{H-Te}$ bond is longer and weaker than the $\mathrm{H-S}$ bond. It is therefore easier for $\mathrm{H_2Te}$ to release a proton in water:

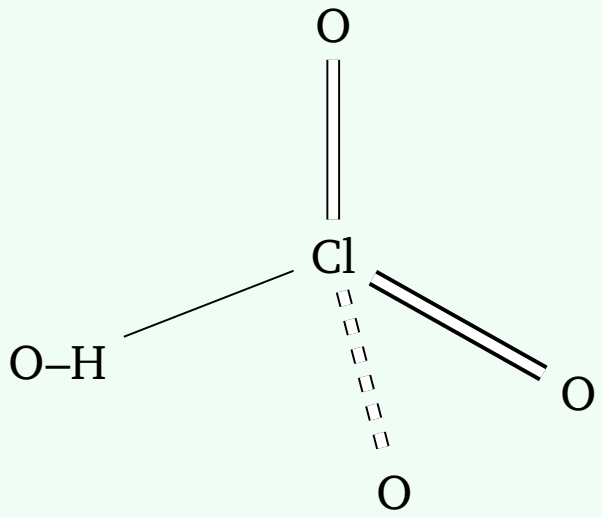
$$\mathrm{H_2E + H_2O \rightleftharpoons H_3O^+ + HE^-}, \qquad E = \mathrm{S, Te}.$$

The decrease in bond strength down this group outweighs the decrease in electronegativity. Hence $\mathrm{H_2Te}$ is more acidic than $\mathrm{H_2S}$.

Step 2: (a)(ii) Explain the greater covalent character The oxidation state of phosphorus is $+5$ in $\mathrm{PCl_5}$, compared with $+3$ in $\mathrm{PCl_3}$. In the Fajans' rule comparison, the higher positive charge gives phosphorus greater polarising power: it distorts the electron cloud of chloride more strongly. The greater distortion increases electron sharing, and hence the covalent character of $\mathrm{PCl_5}$. This is the usual comparison of the molecular chlorides in the question.

Step 3: (a)(iii) Relate boiling point to molecular attractions A pure halogen molecule, $\mathrm{X_2}$, contains identical atoms and is nonpolar; its intermolecular attractions are mainly London dispersion forces. An interhalogen contains different halogens with different electronegativities and has polar bonds. Dipole attractions, in addition to dispersion forces, generally strengthen its intermolecular attractions compared with a comparable halogen. More heat is then needed to separate the molecules into the vapour, explaining the slightly higher boiling points stated in the question. Comparisons should be made between species of comparable size rather than arbitrary members of the two classes.

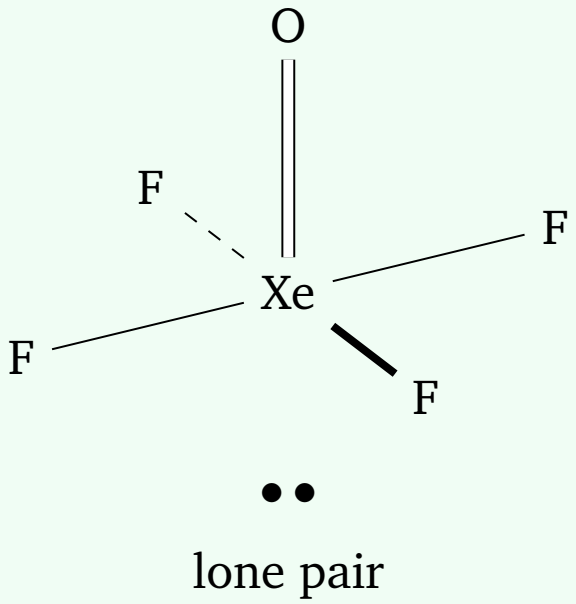
Step 4: (b)(i) Construct the structure of perchloric acid In $\mathrm{HClO_4}$, chlorine is the central atom bonded to four oxygen atoms. Its conventional structural formula is $\mathrm{HO-Cl(=O)_3}$: three terminal $\mathrm{Cl=O}$ bonds and one $\mathrm{Cl-O-H}$ group. Hydrogen is attached to oxygen, not directly to chlorine. The four oxygen atoms lie approximately at the corners of a tetrahedron around chlorine; there is no lone pair on the central chlorine in this representation.



HClO4: tetrahedral arrangement of oxygen atoms around chlorine (perspective sketch).

Step 5: (b)(ii) Construct the structure of xenon oxytetrafluoride Xenon is bonded to one oxygen through a double bond and to four fluorine atoms through single bonds. One lone pair remains on

Xe. Thus there are six electron domains: five bonding domains and one lone pair. They have an octahedral electron-domain arrangement. The four fluorines form a square plane; oxygen is at one axial position and the lone pair occupies the opposite axial position. Omitting the lone pair when naming the molecular shape gives a square pyramid, with O at its apex and Xe at the centre of the square base.



XeOF4: square pyramidal shape; the lone pair lies opposite the oxygen apex.

Step 6: Conclusion H_2Te is more acidic because its H–Te bond is weaker; PCl_5 has greater covalent character by the polarisation argument; and interhalogens have stronger dipolar attractions. $HClO_4$ has tetrahedral $HO-Cl(=O)_3$ connectivity, while $XeOF_4$ is square pyramidal with the lone pair opposite oxygen.

Quick Tip to Solve: Count a double bond as one VSEPR domain: XeOF4 has five bond domains plus one lone pair, so its molecular shape is square pyramidal.

OR

24(b). (i) Arrange the following in the increasing order of their reducing character: H_3PO_3, H_3PO_4, H_3PO_2.

(ii) Out of He and Xe, which one can easily form compound and why?

(iii) Write the conditions to maximize the yield of ammonia in Haber's process.

(iv) Write two uses of Chlorine gas.

(v) How can you detect the presence of SO_2 gas? [5 marks]

Solution:

Concept:

- The reducing character of phosphorus oxoacids depends on their hydrogen atoms bonded directly to phosphorus, rather than their total hydrogen content.
- A noble gas with lower ionisation enthalpy loses or shares its valence electrons more readily. Equilibrium yields respond to pressure and temperature according to Le Chatelier's principle.
- Chlorine is an effective disinfectant and bleaching agent. Sulphur dioxide is a reducing agent and reduces acidified permanganate to nearly colourless manganese(II) ions.

Step 1: (i) Compare the phosphorus-hydrogen bonds The structures are represented by $OP(OH)_3$, $HP(O)(OH)_2$ and $H_2P(O)(OH)$ for H_3PO_4, H_3PO_3 and H_3PO_2, respectively. Thus, they contain zero, one and two P–H bonds. Phosphoric acid has no P–H bond and is non-reducing, while hypophosphorous acid has the strongest reducing character of the three. The increasing order is

$$H_3PO_4 < H_3PO_3 < H_3PO_2.$$

Step 2: (ii) Compare helium and xenon Xenon forms compounds more easily. Its larger size and greater shielding make its outer electrons less tightly held than those of helium, so its first ionisation enthalpy is much lower. Highly electronegative elements such as fluorine and oxygen can therefore combine with xenon; XeF_2 is an example. Helium has a compact, completely filled $1s^2$ shell and exceptionally high ionisation enthalpy.

Step 3: (iii) Apply equilibrium principles to the Haber process The synthesis equilibrium is

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g), \qquad \Delta H < 0.$$

High pressure favours ammonia because the number of gaseous moles decreases from four to two. Low temperature favours the exothermic forward reaction. In practice, about $700\,K$ and $200\,atm$, with a finely divided iron catalyst and suitable promoters, provide a useful compromise between yield and reaction rate. Remove ammonia by cooling and condensation, and recycle unreacted nitrogen and hydrogen, supplied in a $1:3$ molar ratio. A catalyst speeds attainment of equilibrium but does not change its equilibrium yield.

Step 4: (iv) State two uses of chlorine Chlorine is used to disinfect drinking water, killing disease-causing microorganisms. It is also used to bleach wood pulp and textiles such as cotton and linen. In moist conditions it forms hypochlorous acid, which accounts for its oxidising, disinfecting and bleaching action.

Step 5: (v) Test for sulphur dioxide Pass the gas through acidified potassium permanganate solution. Sulphur dioxide decolourises the purple solution by reducing permanganate ions to manganese(II), while itself being oxidised to sulphate:

$$2\,MnO_4^- + 5\,SO_2 + 2\,H_2O \longrightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 4\,H^+.$$

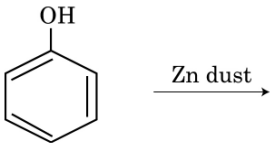
The disappearance of the purple colour is the required observation. The gas should be passed through the reagent rather than identified by directly smelling it.

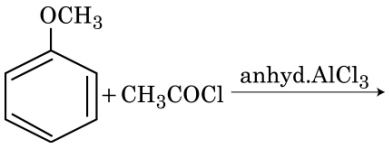
Step 6: Conclusion (i) $H_3PO_4 < H_3PO_3 < H_3PO_2$; (ii) Xe, owing to its lower ionisation enthalpy; (iii) high pressure, a suitably low temperature, an iron catalyst for rate, and continuous removal of ammonia; (iv) water disinfection and bleaching; (v) decolourisation of acidified potassium permanganate.

Quick Tip to Solve: Count P–H bonds to order these oxoacids: zero, one, two gives increasing reducing strength. For Haber equilibrium, use the gas-mole decrease and exothermicity separately.

25(a). Write the product(s) in each of the following reactions: [5 marks]

(i) $CH_2=CH-CH_2OH \xrightarrow{PCC}$

(ii) 

(iii) 

(b) Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow{Conc.H_2SO_4\,/\,413K} CH_3CH_2 - O - CH_2CH_3$$

Solution:

Concept:

- PCC (pyridinium chlorochromate) converts a primary alcohol into an aldehyde without oxidising an isolated carbon-carbon double bond under these conditions.
- Heating phenol with zinc dust removes its oxygen as zinc oxide. The methoxy group in anisole

activates the benzene ring and directs electrophilic substitution to the ortho and para positions.

- At $413\,\mathrm{K}$, concentrated sulphuric acid catalyses intermolecular dehydration of ethanol. Protonation changes its poor leaving group, $-\mathrm{OH}$, into the good leaving group water.

Step 1: (a)(i) Oxidation of allyl alcohol The primary alcohol group changes from $-\mathrm{CH_2OH}$ to $-\mathrm{CHO}$, while the double bond remains intact:

$$\mathrm{CH_2{=}CH{-}CH_2OH} \xrightarrow{\mathrm{PCC}} \mathrm{CH_2{=}CH{-}CHO}.$$

The organic product is prop-2-enal (acrolein). PCC stops the oxidation at the aldehyde stage; acrylic acid is therefore not the product.

Step 2: (a)(ii) Reduction of phenol with zinc dust Zinc removes the oxygen of phenol on heating, forming zinc oxide and benzene:

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

Thus, the organic product is benzene. The hydroxyl group is replaced by hydrogen, rather than being converted into a different oxygen-containing group.

Step 3: (a)(iii) Friedel-Crafts acylation of anisole Acetyl chloride and anhydrous aluminium chloride generate the acetyl electrophile. Electrophilic substitution occurs at the positions ortho and para to the methoxy group:

$$\mathrm{C_6H_5OCH_3 + CH_3COCl} \xrightarrow{\text{anhyd. } \mathrm{AlCl_3}} \mathrm{o{-}CH_3OC_6H_4COCH_3 + p{-}CH_3OC_6H_4COCH_3}.$$

This expression shows the two possible organic products; each substitution also liberates HCl. They are 2-methoxyacetophenone and 4-methoxyacetophenone. The para isomer is the major product because substitution there experiences less steric hindrance.

Step 4: (b) Protonation of ethanol An oxygen lone pair of ethanol accepts a proton supplied by the acid:

$$\mathrm{CH_3CH_2OH + H^+} \rightleftharpoons \mathrm{CH_3CH_2OH_2^+}.$$

The protonated alcohol can lose a neutral water molecule. This activation is necessary because hydroxide itself would be a poor leaving group in acidic solution.

Step 5: Nucleophilic attack by a second ethanol molecule The oxygen lone pair of a second ethanol molecule attacks the primary ethyl carbon of protonated ethanol. The carbon-oxygen bond to water breaks simultaneously, giving protonated diethyl ether:

$$\begin{aligned}&\mathrm{CH_3CH_2OH + CH_3CH_2OH_2^+}\\ &\longrightarrow \mathrm{(C_2H_5)_2OH^+ + H_2O}.\end{aligned}$$

This is an $S_\mathrm{N}2$ displacement: attack and departure occur in the same step. A free primary ethyl carbocation is not required.

Step 6: Deprotonation regenerates the catalyst The oxonium ion loses a proton to give the neutral ether:

$$\mathrm{(C_2H_5)_2OH^+} \rightleftharpoons \mathrm{C_2H_5OC_2H_5 + H^+}.$$

Adding the three steps gives the overall intermolecular dehydration:

$$2C_2H_5OH \xrightarrow[413\,K]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O.$$

The acid is regenerated, so it acts as a catalyst. The specified temperature favours ether formation from the primary alcohol.

Step 7: Conclusion (a) The products are (i) prop-2-enal, (ii) benzene, and (iii) ortho- and para-methoxyacetophenone, with the para isomer major. (b) Diethyl ether forms by protonation of ethanol, attack by a second ethanol molecule with loss of water, and deprotonation.

Quick Tip to Solve: For ethanol at 413 K, show attack by a second alcohol molecule on protonated ethanol; do not introduce a primary carbocation into the ether mechanism.

OR

25(b). (a) Write equations of the following reactions:

(i) Bromine in CS_2 with phenol

(ii) Treating phenol with chloroform in the presence of aq. NaOH

(iii) Anisole reacts with HI

(b) Distinguish between:

(i) Ethanol and Diethyl ether

(ii) Propanol and t-butyl alcohol [5 marks]

Solution:

Concept:

- The hydroxyl group activates the benzene ring of phenol and directs electrophilic substitution to the ortho and para positions. The solvent and amount of bromine control the extent of substitution.
- Reimer–Tiemann formylation introduces a $-CHO$ group mainly ortho to phenolic $-OH$. Aryl–alkyl ethers undergo cleavage of the alkyl–oxygen bond with HI.
- Alcohols contain an active hydroxyl hydrogen, whereas ethers do not. The Lucas test uses concentrated HCl and anhydrous $ZnCl_2$ to distinguish alcohols by the rate of formation of an insoluble alkyl chloride.

Step 1: (a)(i) Bromination of phenol in carbon disulphide With bromine in a non-polar solvent such as CS_2, under controlled conditions, phenol gives monobrominated products: ortho-bromophenol and para-bromophenol, with the para isomer predominating because it is less sterically hindered.

$$C_6H_5OH + Br_2 \xrightarrow{CS_2} BrC_6H_4OH + HBr.$$

Here BrC_6H_4OH denotes the mixture of 2-bromophenol and 4-bromophenol. This is distinct from bromine water, which readily produces $2,4,6$-tribromophenol.

Step 2: (a)(ii) Reaction with chloroform and aqueous sodium hydroxide On heating phenol with chloroform and aqueous NaOH, followed by acidification, the major product is 2-hydroxybenzaldehyde

(salicylaldehyde). This is the Reimer–Tiemann reaction; a small amount of the para isomer may also form.

$$C_6H_5OH + CHCl_3 + 3NaOH \longrightarrow o\text{–}HOC_6H_4CHO + 3NaCl + 2H_2O.$$

The equation expresses the overall transformation after acid work-up; acidification liberates the free phenolic aldehyde from the alkaline mixture.

Step 3: (a)(iii) Cleavage of anisole by HI Anisole gives phenol and methyl iodide on heating with HI:

$$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I.$$

After oxygen is protonated, iodide attacks the methyl carbon by an S_N2 process. The aryl–oxygen bond is retained because it has partial double-bond character; substitution at the aromatic sp^2 carbon is not the usual ether-cleavage pathway.

Step 4: (b)(i) Distinguish ethanol from diethyl ether Add a small piece of sodium metal to separate dry samples. Ethanol gives effervescence of hydrogen, whereas dry diethyl ether gives no such reaction.

$$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2 \uparrow.$$

Ethanol has an $O-H$ hydrogen that sodium can replace. Diethyl ether, $C_2H_5OC_2H_5$, has no $O-H$ bond. Dry samples are essential since water itself reacts with sodium.

Step 5: (b)(ii) Distinguish propanol from tert-butyl alcohol Add Lucas reagent (concentrated HCl and anhydrous $ZnCl_2$) at room temperature. Tert-butyl alcohol gives immediate turbidity due to insoluble tert-butyl chloride:

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

Propan-1-ol, the primary alcohol, gives no turbidity at room temperature under the test conditions. The tertiary alcohol reacts rapidly because it forms a stable tertiary carbocation. If the name propanol is used for propan-2-ol, it is secondary and gives turbidity only after a few minutes, still distinguishing it from the immediate response of tert-butyl alcohol.

Step 6: Conclusion (a) The products are ortho- and para-bromophenol (para major); salicylaldehyde after acidification; and phenol plus methyl iodide, respectively. (b) Ethanol evolves hydrogen with sodium but diethyl ether does not; tert-butyl alcohol gives immediate turbidity with Lucas reagent, whereas propanol does not give an immediate response.

Quick Tip to Solve: Check the bromination solvent first: CS_2 gives monobromophenols, while bromine water gives the tribromo product. Use the timing of Lucas turbidity to identify the tertiary alcohol.

26(a). Calculate the boiling point of solution when 2 g of Na_2SO_4 (M = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionization.

(K_b for water = 0.52 K kg mol^{-1})

(b) Define the following terms:

(i) Colligative properties (ii) Ideal solution [5 marks]

Solution:

Concept:

- Elevation of boiling point is a colligative property. For an electrolyte, $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b is the molal elevation constant and m is molality in moles of solute per kilogram of solvent.
- Complete dissociation of one formula unit of $\mathrm{Na_2SO_4}$ gives three ions. Thus its ideal van't Hoff factor is $i = 3$.
- An ideal solution obeys Raoult's law throughout the entire composition range and has zero enthalpy and volume changes on mixing.

Step 1: (a) Determine the particle factor and molality Complete ionization gives

$$\mathrm{Na_2SO_4(aq) \longrightarrow 2Na^+(aq) + SO_4^{2-}(aq).}$$

Each formula unit produces three independently moving solute particles, so $i = 2 + 1 = 3$. The amount of sodium sulphate and mass of solvent are

$$n = \frac{2\,\mathrm{g}}{142\,\mathrm{g\ mol^{-1}}} = 0.0140845\,\mathrm{mol}, \qquad w_{\mathrm{water}} = 0.050\,\mathrm{kg}.$$

Hence the molality of the dissolved salt, before applying its particle factor, is

$$m = \frac{0.0140845}{0.050} = 0.28169\,\mathrm{mol\ kg^{-1}}.$$

The denominator is the mass of water, not the combined mass of salt and water, because molality is defined per kilogram of solvent.

Step 2: (a) Calculate the elevation and the boiling point Substituting the data into the electrolyte form of the boiling-point equation,

$$\begin{aligned}\Delta T_b &= iK_b m \\ &= 3 \times 0.52 \times 0.28169 \\ &= 0.43944\,\mathrm{K}.\end{aligned}$$

A nonvolatile dissolved solute lowers the vapour pressure, so the solution must be heated above the boiling point of pure water. At normal atmospheric pressure, pure water boils at $100\,^\circ$C. Thus

$$T_b = 100 + 0.43944 = 100.43944\,^\circ\mathrm{C}.$$

A temperature rise of one kelvin equals a rise of one degree Celsius; no conversion factor is needed for the elevation.

Step 3: (b)(i) Define colligative properties Colligative properties are properties of dilute solutions that depend on the number of solute particles relative to the solvent particles, and not on the chemical nature of the solute. Examples are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. For an electrolyte, dissociation changes the particle count, which is why i is included in part (a).

Step 4: (b)(ii) Define an ideal solution An ideal solution is one that obeys Raoult's law over the entire range of composition at a given temperature. For each volatile component j,

$$p_j = x_j p_j^0,$$

where p_j is its partial vapour pressure, x_j its mole fraction and p_j^0 the vapour pressure of the pure component. Such a solution has $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$, reflecting comparable interactions between like and unlike molecules.

Step 5: Conclusion (a) The solution boils at approximately $\boxed{100.44\,^\circ\text{C}}$ at normal atmospheric pressure. (b) Colligative properties depend on the relative number of solute particles; an ideal solution obeys Raoult's law at every composition.

Quick Tip to Solve: Count the three ions from sodium sulphate before using the boiling-point formula, and convert the 50 g of solvent into 0.050 kg.

OR

26(b). (a) When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x).

(K_f for CS_2 = 3.83 K kg mol^{-1}; Atomic mass of Sulphur = 32 g mol^{-1})

(b) Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing?

(i) 1.2% sodium chloride solution

(ii) 0.4% sodium chloride solution [5 marks]

Solution:

Concept:

- Depression of freezing point is a colligative property: $\Delta T_f = K_f m$, where m is the molality of dissolved solute particles and K_f is the solvent's molal freezing-point depression constant.
- For solute mass w, molar mass M and solvent mass W in grams, $m = 1000w/(MW)$. The molecular formula S_x has molar mass $32x\,\text{g mol}^{-1}$.
- Osmosis is the movement of solvent through a semipermeable membrane toward the solution with greater osmotic pressure. At the same temperature, a more concentrated solution of the same solute has greater osmotic pressure.

Step 1: (a) Find the molality of sulphur in carbon disulphide The observed depression is $\Delta T_f =$

$0.383\,\mathrm{K}$, and $K_f = 3.83\,\mathrm{K\,kg\,mol^{-1}}$. Hence

$$m = \frac{\Delta T_f}{K_f} = \frac{0.383}{3.83} = 0.100\,\mathrm{mol\,kg^{-1}}.$$

The solvent mass is $100\,\mathrm{g} = 0.100\,\mathrm{kg}$, so the number of moles of dissolved sulphur molecules is $n = m \times 0.100 = 0.0100\,\mathrm{mol}$. Here the colligative measurement counts sulphur molecules, rather than the individual atoms within a molecule.

Step 2: (a) Determine the molecular formula Using the given solute mass, the molecular molar mass is

$$M = \frac{2.56\,\mathrm{g}}{0.0100\,\mathrm{mol}} = 256\,\mathrm{g\,mol^{-1}}.$$

Each sulphur atom contributes $32\,\mathrm{g\,mol^{-1}}$; therefore $32x = 256$, giving $x = 8$. As a check, $2.56/256 = 0.0100\,\mathrm{mol}$ in $0.100\,\mathrm{kg}$ of solvent gives $\Delta T_f = 3.83 \times 0.100 = 0.383\,\mathrm{K}$, agreeing with the observation.

Step 3: (b)(i) Place the cells in 1.2 percent sodium chloride The reference 0.9% sodium chloride solution is isotonic with the blood cells: its osmotic pressure equals that of the cell contents, so it causes no net movement of water. A 1.2% sodium chloride solution is more concentrated than this reference and is hypertonic to the cells. Water therefore passes out through their semipermeable membranes by exosmosis. The cells lose water and shrink; this shrinking of red blood cells is called crenation.

Step 4: (b)(ii) Place the cells in 0.4 percent sodium chloride A 0.4% sodium chloride solution is less concentrated than the isotonic 0.9% solution and is hypotonic to the cells. Its osmotic pressure is lower than that of the cell contents. Water consequently enters the cells by endosmosis. The cells swell and can burst because red blood cells lack a rigid cell wall; their rupture is called haemolysis.

Step 5: Conclusion (a) The molecular formula of sulphur is $\boxed{\mathrm{S_8}}$. (b)(i) In 1.2% sodium chloride solution, blood cells lose water and shrink. (ii) In 0.4% sodium chloride solution, they gain water, swell and may undergo haemolysis.

Quick Tip to Solve: Convert the solvent mass to kilograms first; compare both salt concentrations directly with the isotonic value of 0.9 percent to predict water flow.