CBSE Class 12 Chemistry Question Paper 2016 with Solution PDF-Set 056-2 - 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. 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 agent; its reduction product with zinc is nitrogen dioxide.
- Brown nitrogen dioxide, NO_2, dimerises to colourless dinitrogen tetroxide, N_2O_4, on cooling.

Step 1: Identify the gas from the reaction Zinc is oxidised to zinc nitrate while concentrated nitric acid is reduced:

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

The evolved nitrogen dioxide is brown.

Step 2: Check the cooling observation The gas undergoes the equilibrium

$$2NO_2 \rightleftharpoons N_2O_4.$$

Cooling favours formation of the dimer and the brown colour becomes lighter, confirming the identification.

Step 3: Conclusion The gas is nitrogen dioxide, $\boxed{NO_2}$.

Quick Tip to Solve: Use both clues together: brown colour and dimerisation on cooling identify nitrogen dioxide.

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

Solution:

Concept:

- Colloidal particles in a given sol generally carry charges of the same sign.
- Electrostatic repulsion between similarly charged particles opposes their aggregation into larger particles.

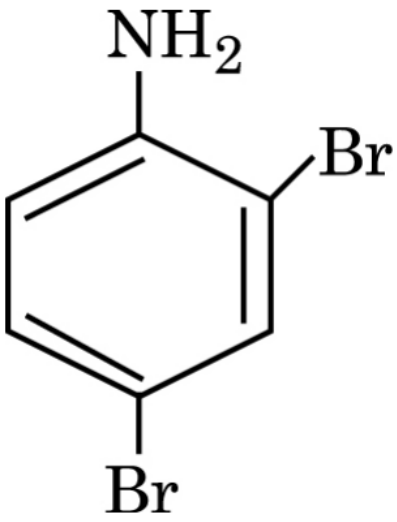
Step 1: Recognise the interaction between particles Particles of a sol acquire a common positive or negative charge, often through selective adsorption of ions at their surfaces. Since like charges repel, neighbouring particles resist close approach.

Step 2: Relate repulsion to stability This repulsion prevents particles from combining and coagulating into large aggregates that would separate from the dispersion medium. Thus the dispersed particles remain distributed through the sol.

Step 3: Conclusion Colloidal sols are stable mainly because like charges on their particles cause mutual electrostatic repulsion and prevent coagulation.

Quick Tip to Solve: For sol stability, connect common surface charge to repulsion and then to prevention of coagulation.

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



Solution:

Concept:

- The $-NH_2$ group is the principal functional group, so the parent is aniline (benzenamine).
- Number the amino-bearing ring carbon as carbon 1 and choose the direction that gives substituents the lowest locants.

Step 1: Choose the parent and numbering The diagram contains an amino group directly attached to benzene. Use aniline as the retained IUPAC parent name and assign position 1 to the carbon bearing $-NH_2$.

Step 2: Locate the bromo substituents One bromine is adjacent to the amino group and the other is opposite it. Numbering towards the adjacent bromine gives locants 2 and 4, rather than 4 and 6. Two identical bromo substituents require the prefix dibromo.

Step 3: Conclusion The IUPAC name is $\boxed{\text{2,4-dibromoaniline}}$ (also 2,4-dibromobenzenamine).

Quick Tip to Solve: Start ring numbering at the amino-bearing carbon, then choose 2,4 rather than 4,6 for bromine.

4. 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:

- An S_N1 reaction proceeds through slow ionisation of the carbon-halogen bond to form a carbocation.
- A more stable carbocation lowers the barrier to ionisation and generally increases the S_N1 reaction rate.

Step 1: Examine the allylic compound Ionisation of $CH_2{=}CH{-}CH_2Cl$ gives the allyl carbocation. Its

positive charge is delocalised by resonance:

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

Step 2: Compare the propyl compound Ionisation of $CH_3{-}CH_2{-}CH_2Cl$ would produce an ordinary primary propyl carbocation without resonance stabilisation. Its formation is less favourable than formation of the allylic ion.

Step 3: Conclusion $\boxed{CH_2{=}CH{-}CH_2Cl}$ is more reactive towards S_N1, because its carbocation is resonance-stabilised.

Quick Tip to Solve: For an SN1 comparison, draw the carbocations first; allylic resonance outweighs the primary label.

5. 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 both the directions and the magnitudes of the magnetic moments.
- In an antiferromagnetic arrangement, equal magnetic moments align antiparallel and cancel each other.

Step 1: Interpret the given arrangement The question describes equal populations of domains directed oppositely. In the stated antiferromagnetic arrangement the moments in the two opposite directions have equal resultant magnitudes.

Step 2: Find the resultant magnetisation Adding equal and opposite magnetic moments gives zero resultant magnetic moment. This cancellation distinguishes the arrangement from ferromagnetism, where moments reinforce, and ferrimagnetism, where opposing moments are unequal.

Step 3: Conclusion The substance shows $\boxed{\text{antiferromagnetism}}$.

Quick Tip to Solve: Equal and opposite moments cancel: identify antiferromagnetism; unequal opposing moments indicate ferrimagnetism.

6. When a coordination compound $PdCl_2 \cdot 4NH_3$ 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 with $AgNO_3$ as $AgCl$.
- Ammonia is a neutral ligand named ammine; four ammonia ligands use the prefix tetraammine.

Step 1: Locate the chloride ions Two moles of $AgCl$ per mole of compound show that both chloride ions are outside the coordination sphere. All four ammonia molecules are coordinated to palladium. Therefore the structural coordination formula is

$$\boxed{[Pd(NH_3)_4]Cl_2}.$$

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

Step 2: Determine the oxidation state and name The two chloride counterions require a complex cation of charge $+2$. Since each ammonia ligand is neutral, palladium has oxidation state $+2$. Name the complex cation before the anion: tetraamminepalladium(II) chloride. Palladium remains palladium rather than palladate because the complex is cationic.

Step 3: Verify the precipitation result The proposed formula gives the observed reaction:

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

Thus both chloride ions are accounted for as ionisable counterions, consistent with the given composition.

Step 4: Conclusion (i) $[Pd(NH_3)_4]Cl_2$. (ii) Tetraamminepalladium(II) chloride.

Quick Tip to Solve: Count AgCl first to locate outer-sphere chloride, then use neutral NH3 to obtain the metal oxidation state.

7(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 amalgamated zinc and concentrated hydrochloric acid.
- The Hell-Volhard-Zelinsky reaction replaces an α-hydrogen of a carboxylic acid by halogen; the acid must contain at least one α-hydrogen.

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

$$\mathrm{RCOR' + 4[H] \xrightarrow{Zn(Hg),\,conc.\ HCl} RCH_2R' + H_2O.}$$

Here R and R' are alkyl or aryl groups. For example,

$$\mathrm{CH_3COCH_3 + 4[H] \longrightarrow CH_3CH_2CH_3 + H_2O.}$$

Thus the carbonyl oxygen is removed, while the carbon skeleton remains intact.

Step 2: Write the Hell-Volhard-Zelinsky equation A representative equation, with bromine and red phosphorus followed by hydrolysis, is

$$\mathrm{CH_3COOH + Br_2 \xrightarrow[(ii)\ H_2O]{(i)\ red\ P} BrCH_2COOH + HBr.}$$

Bromination occurs at the carbon adjacent to the carboxyl group, giving bromoacetic acid. The carboxyl group is retained.

Step 3: Conclusion Clemmensen reduction: carbonyl compound $\rightarrow$ corresponding hydrocarbon using $\mathrm{Zn(Hg)/conc.\ HCl}$. HVZ reaction: $\mathrm{CH_3COOH \rightarrow BrCH_2COOH}$ using $\mathrm{Br_2/red\ P}$, followed by water.

Quick Tip to Solve: Write the reagent above each arrow: acidic zinc amalgam reduces C=O, whereas bromine/red phosphorus substitutes an alpha hydrogen.

OR

7(b). How do you convert:

(i) Toluene to benzaldehyde

(ii) Ethanoyl chloride to ethanal [2 marks]

Solution:

Concept:

- A selective oxidation of the methyl side chain of toluene gives benzaldehyde. Strong oxidation with hot permanganate would instead give benzoic acid.
- Rosenmund reduction converts an acid chloride to an aldehyde using hydrogen over poisoned palladium on barium sulphate.

Step 1: Convert toluene into benzaldehyde Use the Etard reaction: treat toluene with chromyl chloride in carbon disulphide, then hydrolyse the resulting complex.

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

This controlled oxidation changes the side-chain $-\mathrm{CH_3}$ into $-\mathrm{CHO}$, without converting it further into $-\mathrm{COOH}$. The benzene ring and its attachment to the side chain remain unchanged.

Step 2: Convert ethanoyl chloride into ethanal Carry out Rosenmund reduction:

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

The palladium catalyst is poisoned, for example with sulphur or quinoline, to reduce its activity. This allows the reduction to stop at the aldehyde stage instead of proceeding to ethanol. The acid chloride loses chlorine as hydrogen chloride.

Step 3: Conclusion (i) Use CrO_2Cl_2/CS_2, then hydrolysis (Etard reaction). (ii) Use H_2 with poisoned $Pd/BaSO_4$ (Rosenmund reduction).

Quick Tip to Solve: For an aldehyde target, choose a selective reagent: Etard oxidation for toluene and poisoned Pd/BaSO4 for an acid chloride.

8. 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 experimentally determined rate law. Here Rate $= k = k[NH_3]^0$.
- Molecularity counts the reacting species participating in an elementary event; in the usual school-level treatment here, the two ammonia molecules give molecularity two.

Step 1: Determine order and molecularity Since no concentration occurs in the stated rate law, changing ammonia concentration does not change the rate under these conditions. Therefore the reaction has order zero. The printed reaction involves two molecules of ammonia, so the expected molecularity is two, i.e. bimolecular. The platinum catalyst is written above the arrow and is not counted as a reactant molecule. More strictly, molecularity belongs to an elementary step; the overall equation alone does not establish a detailed mechanism.

Step 2: Determine the unit of the rate constant For a zero-order reaction,

$$k = \text{Rate}.$$

Rate has dimensions concentration divided by time. Taking concentration in $\text{mol}\,\text{L}^{-1}$ and time in seconds gives

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

The unit is not s^{-1}, which would correspond to a first-order rate constant. The concentration-independent law is characteristic of the stated surface-catalysed conditions.

Step 3: Conclusion Order $= 0$; expected molecularity $= 2$ (bimolecular). The unit of k is $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Quick Tip to Solve: Read order from the rate law, not the balanced equation; for Rate = k, copy the rate units directly onto k.

9. 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:

- A primary cell is used until its reactants are depleted, whereas a secondary cell can be recharged by reversing its chemical reaction.
- A fuel cell generates electricity while fuel and oxidant are continuously supplied; cell selection depends on size, current demand and rechargeability.

Step 1: Identify the cells for hearing aids and the Apollo programme (i) A mercury cell is used in hearing aids. Its small size and nearly constant potential during operation make it suitable for such low-current devices.

(ii) A hydrogen-oxygen fuel cell was used in the Apollo space programme. It converts the chemical energy of hydrogen and oxygen into electrical energy, with water as the reaction product. Continuous supply of the gases sustains operation.

Step 2: Identify the cells for automobiles and limited service life (iii) A lead storage cell is used in automobiles and inverters. It is a secondary cell, so it can deliver substantial current and then be recharged for repeated use.

(iv) A dry cell does not have a long life. It is a primary cell whose active materials are gradually consumed, and it is not restored by ordinary recharging. Its limited service life distinguishes it from the rechargeable lead storage cell in this list.

Step 3: Conclusion (i) Mercury cell; (ii) hydrogen-oxygen fuel cell; (iii) lead storage cell; (iv) dry cell.

Quick Tip to Solve: Match the four uses in order: tiny constant-voltage device, spacecraft fuel supply, rechargeable power source, then disposable dry cell.

10. 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:

- Fusion of manganese dioxide with alkali in air oxidises manganese from $+4$ to $+6$, forming green manganate ions, MnO_4^{2-}.
- Disproportionation means that the same species undergoes oxidation and reduction. Manganate(VI) forms permanganate(VII) and manganese dioxide(IV) in acidic medium.

Step 1: (i) Identify the green and purple compounds The green compound is potassium manganate, $A = K_2MnO_4$. Its formation is represented by

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

In acidic medium, the manganate ion disproportionates:

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

Hence the purple compound is potassium permanganate, $B = KMnO_4$.

Step 2: (ii) Heat potassium permanganate On heating, potassium permanganate decomposes to potassium manganate, manganese dioxide and oxygen gas:

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

Thus oxygen is evolved and a solid residue containing manganate and manganese dioxide remains.

Step 3: Conclusion $A = K_2MnO_4$ and $B = KMnO_4$. Heating B gives K_2MnO_4, MnO_2 and O_2.

Quick Tip to Solve: Use the colours to distinguish green manganate(VI) from purple permanganate(VII).

11. Calculate E^0_{cell} for the following reaction at 298K:

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

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

Solution:

Concept:

- At $298\,K$, the Nernst equation is $E_{cell} = E^\circ_{cell} - (0.0591/n)\log_{10} Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Pure solids have unit activity and are omitted from Q. The powers of the dissolved-ion concentrations equal their coefficients in the balanced reaction.

Step 1: Determine the electron transfer The oxidation and reduction half-reactions for the reaction as written are

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

Therefore, $n = 6$. Although each chromium atom loses three electrons, there are two chromium atoms in the balanced cell reaction.

Step 2: Evaluate the reaction quotient Chromium and iron are pure solids, so neither appears in the reaction quotient. Using the given ionic concentrations,

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

Thus $\log_{10} Q = 2$. Concentrations are used relative to the standard concentration of $1\,\mathrm{mol\,L^{-1}}$.

Step 3: Calculate the standard cell potential Rearranging the Nernst equation before substituting gives

$$\begin{aligned} E^\circ_{\text{cell}} &= E_{\text{cell}} + \frac{0.0591}{n}\log_{10} Q \\ &= 0.261 + \frac{0.0591}{6} \times 2 \\ &= 0.2807\,\mathrm{V}. \end{aligned}$$

Since $Q > 1$, the concentration correction lowers the observed potential below its standard value, consistent with this result.

Step 4: Conclusion The standard cell potential is $\boxed{E^\circ_{\text{cell}} = 0.2807\,\mathrm{V} \approx 0.281\,\mathrm{V}}$.

Quick Tip to Solve: Count electrons for the complete balanced reaction: here n is 6, and the unequal ion powers make Q equal to 100.

12. (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 purifies a metal. In the van Arkel method, a volatile metal iodide is formed and then decomposed on a hot filament to deposit pure metal.
- Leaching selectively dissolves a desired ore constituent in a suitable reagent. A flux removes gangue by forming a fusible slag.

Step 1: (i) Refining zirconium Zirconium is refined by the **van Arkel method**, also called the iodide or crystal-bar process. Impure zirconium reacts with iodine to form volatile zirconium tetraiodide:

$$\mathrm{Zr} + 2\mathrm{I_2} \longrightarrow \mathrm{ZrI_4}.$$

The vapour decomposes on an electrically heated tungsten filament, depositing pure zirconium:

$$ZrI_4 \longrightarrow Zr + 2I_2.$$

Non-volatile impurities are left behind during iodide formation.

Step 2: (ii) Dissolving alumina selectively This process is **leaching**, specifically the alkaline leaching used in the Bayer process. Amphoteric alumina dissolves in concentrated sodium hydroxide to give soluble sodium aluminate, while insoluble impurities are separated by filtration. A conventional equation is

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O.$$

In aqueous solution, the aluminate may also be represented as $[Al(OH)_4]^-$.

Step 3: (iii) Function of limestone Limestone acts as a **flux**. It first decomposes in the furnace:

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

The basic calcium oxide combines with acidic silica gangue to form fusible calcium silicate slag:

$$CaO + SiO_2 \longrightarrow CaSiO_3.$$

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

Step 4: Conclusion (i) Van Arkel (iodide) method. (ii) Leaching (Bayer process). (iii) Limestone supplies CaO, which removes silica as $CaSiO_3$ slag.

Quick Tip to Solve: For limestone, always write both reactions: thermal decomposition supplies CaO, and CaO then binds silica as slag.

13. (i) Out of silica gel and anhydrous $CaCl_2$, which will adsorb the water vapours?

(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 is the accumulation of molecules at a surface; absorption involves their entry into the bulk of a substance.
- For coagulation of a charged sol, the effective ion has the opposite charge. The Hardy-Schulze rule relates greater coagulating power to greater valency of this counter-ion.
- Macromolecular colloids contain individual giant molecules of colloidal dimensions, whereas multimolecular colloids contain aggregates of many small molecules.

Step 1: (i) Identify the adsorbent Silica gel adsorbs water vapours. Its porous structure provides a large surface area on which water molecules accumulate. Anhydrous $CaCl_2$ also acts as a drying agent, but it takes up water through hydration rather than serving as the surface adsorbent in this

comparison.

Step 2: (ii) Compare the coagulating ions A positively charged sol is coagulated by negatively charged ions. The relevant ions from the two acids are sulphate, SO_4^{2-}, and phosphate, PO_4^{3-}. By the Hardy-Schulze rule, the trivalent phosphate ion has greater coagulating power than the divalent sulphate ion. Therefore H_3PO_4 is more effective in causing coagulation of the positively charged sol.

Step 3: (iii) Identify the macromolecular colloid Proteins form macromolecular colloids because a protein molecule is itself a giant molecule with dimensions in the colloidal range. Sulphur sol is a multimolecular colloid: many small sulphur molecules aggregate to form a colloidal particle.

Step 4: Conclusion (i) Silica gel; (ii) H_3PO_4, because PO_4^{3-} has higher counter-ion valency; (iii) proteins.

Quick Tip to Solve: For a positive sol compare the anions: phosphate has charge magnitude 3, whereas sulphate has 2.

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

Solution:

Concept:

- The base-10 Arrhenius equation is $\log k = \log A - E_a/(2.303RT)$, where A is the frequency factor, E_a the activation energy and T the absolute temperature.
- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$. The time unit used for the half-life determines the inverse-time unit of k.

Step 1: Compare the temperature coefficient with the Arrhenius equation The given equation is

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

Comparing its coefficient of $1/T$ with the base-10 Arrhenius form gives

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

The constant 14.2 is $\log A$; it is not the activation energy. The factor 2.303 is essential because the question uses a common logarithm.

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

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

The kelvin in the temperature coefficient cancels the inverse kelvin in R. The negative slope of $\log k$ against $1/T$ therefore corresponds to a positive activation energy.

Step 3: Use the specified half-life to determine the rate constant For the stated first-order reaction with $t_{1/2} = 200\,\text{min}$,

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

Equivalently, dividing this value by 60 gives $k = 5.775 \times 10^{-5}\,\text{s}^{-1}$. This calculation uses the half-life directly, so the reaction temperature need not be found.

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

Quick Tip to Solve: Multiply the coefficient of 1/T by 2.303R, and keep minutes in k when the half-life is in minutes.

15. 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 the shared corner and face-centre atoms.
- For a cubic unit cell of edge a, its volume is a^3 and its mass is ρa^3, where ρ is the density. Thus a sample of mass m contains $m/(\rho a^3)$ unit cells.

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

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

Therefore

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

Cube both the numerical factor and the power of ten when calculating the volume.

Step 2: Find the number of unit cells in the sample The mass of one cell is

$$m_{\text{cell}} = \rho a^3 = (7)(6.40 \times 10^{-23}) = 4.48 \times 10^{-22}\,\text{g}.$$

Consequently, the number of unit cells in $280\,\text{g}$ is

$$N_{\text{cell}} = \frac{280}{4.48 \times 10^{-22}} = 6.25 \times 10^{23}.$$

The sample mass divided by the mass per cell gives a dimensionless count of cells.

Step 3: Count atoms using the f.c.c. occupancy Each face-centred cubic unit cell contributes four atoms: the eight corners together contribute one atom and the six face centres together contribute

three. Hence

$$N = 4N_{\text{cell}} = 4(6.25 \times 10^{23}) = 2.50 \times 10^{24}.$$

This direct density-and-volume method avoids finding the molar mass or introducing Avogadroś constant as an intermediate quantity.

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

Quick Tip to Solve: Use N = 4m/(density times edge cubed) for f.c.c.; convert pm to cm before cubing the edge.

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16. (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:

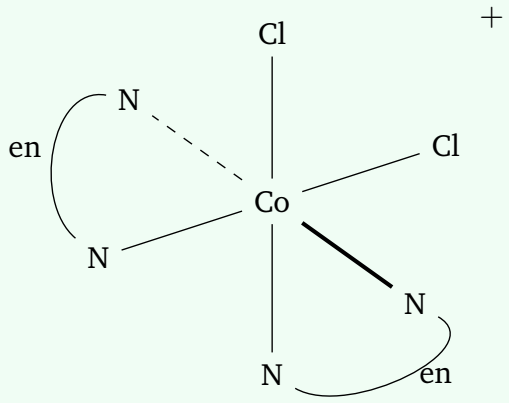
Concept:

- The oxidation state determines the metal-ion electronic configuration. Fluoride is a weak-field ligand, so it does not force pairing of the cobalt $3d$ electrons.
- An octahedral high-spin complex uses outer-orbital sp^3d^2 hybridization. Each unpaired electron contributes spin $s = \frac{1}{2}$.
- Ethylenediamine, en, is a bidentate ligand. Its two nitrogen donor atoms occupy adjacent coordination sites and form a chelate ring.

Step 1: Determine the cobalt configuration in part (a) In $[CoF_6]^{3-}$, let the cobalt oxidation state be x. Then $x + 6(-1) = -3$, so $x = +3$. Neutral cobalt has configuration $[Ar]3d^74s^2$; removing three electrons gives Co^{3+} : $[Ar]3d^6$.

Step 2: Find hybridization, magnetism and spin Because F^- is weak-field, the six d electrons adopt the high-spin octahedral arrangement $t_{2g}^4e_g^2$. There are four unpaired electrons: two in t_{2g} and two in e_g. Thus the complex is paramagnetic and uses outer-orbital sp^3d^2 hybridization. Its total spin is $S = 4(\frac{1}{2}) = 2$, with multiplicity $2S + 1 = 5$.

Step 3: Draw the optically active geometrical isomer in part (b) The optically active geometrical isomer is cis-$[Co(en)_2Cl_2]^+$. The two chloride ligands occupy adjacent octahedral sites. In the sketch, the four nitrogen donor atoms are joined in pairs by the two en ligands; each curved link denotes one chelate ligand. This cis arrangement has non-superimposable mirror images, whereas the trans form is optically inactive.



One optically active cis isomer; curved en links join paired nitrogen donors.

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

Quick Tip to Solve: For octahedral cobalt(III), decide weak or strong ligand field before pairing the six d electrons.

17. (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:

- A disaccharide yields two monosaccharide units when its glycosidic bond undergoes hydrolysis. These two units can be identical.
- Vitamin deficiencies produce characteristic disorders; vitamin $\mathrm{B_6}$ is also called pyridoxine.
- Fibrous proteins have extended, strand-like structures, whereas globular proteins fold into compact shapes.

Step 1: Identify the hydrolysis products of maltose Maltose consists of two glucose units linked through an $\alpha(1 \rightarrow 4)$ glycosidic bond. Hydrolysis cleaves this bond with the addition of water, producing two molecules of D-glucose. Thus the two monosaccharides requested have the same name: glucose and glucose. The reaction is

$$\mathrm{C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6}.$$

Step 2: Identify the deficient vitamin Convulsions are associated with deficiency of vitamin $\mathrm{B_6}$, or pyridoxine. This is a water-soluble B-group vitamin involved, through its coenzyme forms, in amino-acid metabolism and normal nervous-system function.

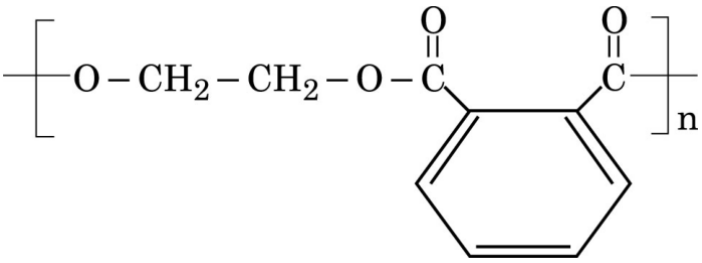
Step 3: Give one example of each protein class Keratin, present in hair and wool, is a fibrous protein: its elongated chains provide structural strength. Insulin is a globular protein: its polypeptide chains adopt a compact, specific conformation needed for its hormonal function. These examples distinguish

the structural class from the biological role of the protein.

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

Quick Tip to Solve: Maltose gives glucose twice; reserve glucose plus fructose for sucrose hydrolysis.

18(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:

- An organic peroxide initiates addition polymerization by homolytic cleavage of its weak $O-O$ bond to generate free radicals.
- A polyester can be traced back to its diol and dicarboxylic acid by replacing the ester connections with hydroxyl and carboxyl groups.
- In the standard polymer classification, elastomers have weaker intermolecular attractions than thermoplastics, while fibres have strong interchain attractions such as hydrogen bonding.

Step 1: Explain the role of t-butyl peroxide t-Butyl peroxide acts as a free-radical initiator. On heating, its peroxide bond undergoes homolysis, giving radicals which attack the $C=C$ bond of ethene. This produces a new carbon-centred radical and starts the chain reaction. It therefore initiates polymerization; it is neither the ethene monomer nor a chain-linking reagent.

Step 2: Identify both monomers from the printed structure The fragment $-OCH_2CH_2O-$ comes from ethane-1,2-diol (ethylene glycol), $HOCH_2CH_2OH$. The two carbonyl groups attached to adjacent carbon atoms of the benzene ring come from benzene-1,2-dicarboxylic acid (phthalic acid), o-$C_6H_4(COOH)_2$. The adjacency of these groups in the printed ring is essential: it identifies the ortho acid. Condensation of the diol and this diacid forms the polyester ester linkages with elimination of water.

Step 3: Arrange the polymers by intermolecular forces Buna-N is an elastomer and has relatively weak interchain forces, allowing extension and recovery. PVC is a thermoplastic with intermediate intermolecular attraction. Nylon-6 is a fibre whose amide groups form strong interchain hydrogen

bonds. Hence the required increasing order is

$$\text{Buna}-\text{N} < \text{PVC} < \text{Nylon}-6.$$

Step 4: Conclusion (i) Free-radical initiator. (ii) Ethane-1,2-diol and phthalic acid (benzene-1,2-dicarboxylic acid). (iii) Buna-N < PVC < Nylon-6.

Quick Tip to Solve: Trace the actual ring attachment positions before naming a polyester diacid: adjacent groups mean phthalic acid.

OR

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

Solution:

Concept:

- Free radical addition polymerisation converts the carbon-carbon double bonds of ethene into single bonds in a long chain, without eliminating a small molecule.
- A peroxide initiator supplies radicals by homolytic bond cleavage. Initiation, chain propagation and termination are the three stages.

Step 1: Initiation: produce radicals and start the chain On heating, an organic peroxide undergoes homolytic cleavage of its weak oxygen-oxygen bond. Using ROOR for the peroxide:

$$\text{ROOR} \xrightarrow{\Delta} 2\text{RO}^{\bullet}.$$

The radical attacks the double bond of ethene, forming a new bond and leaving an unpaired electron at the other carbon:

$$\text{RO}^{\bullet} + \text{CH}_2{=}\text{CH}_2 \longrightarrow \text{RO}{-}\text{CH}_2{-}\text{CH}_2{}^{\bullet}.$$

Step 2: Propagation: repeatedly add ethene The chain-end radical adds to another ethene molecule; the radical centre moves to the new chain end:

$$\text{RO}{-}\text{CH}_2{-}\text{CH}_2{}^{\bullet} + \text{CH}_2{=}\text{CH}_2 \longrightarrow \text{RO}{-}\text{CH}_2{-}\text{CH}_2{-}\text{CH}_2{-}\text{CH}_2{}^{\bullet}.$$

Repeated additions give a long radical chain. In general,

$$\text{RO}{-}(\text{CH}_2{-}\text{CH}_2)_n{}^{\bullet} + \text{CH}_2{=}\text{CH}_2 \longrightarrow \text{RO}{-}(\text{CH}_2{-}\text{CH}_2)_{n+1}{}^{\bullet}.$$

Each addition consumes a double bond but retains an active radical, allowing rapid chain growth.

Step 3: Termination: remove the radical centres Two growing chain radicals can combine, pairing their unpaired electrons to form a covalent bond:

$$\text{P}^{\bullet} + \text{P}'^{\bullet} \longrightarrow \text{P}{-}\text{P}'.$$

Here $P^{\bullet}$ and $P'^{\bullet}$ represent growing polyethylene chains. The joined chain has no radical centre, so this chain stops growing. The initiator-derived groups occur only at chain ends; the repeating unit is $-CH_2-CH_2-$.

Step 4: Conclusion Thus ethene forms polyethene by radical initiation, propagation and termination: $nCH_2{=}CH_2 \longrightarrow [-CH_2-CH_2-]_n$.

Quick Tip to Solve: Keep a radical dot at the growing chain end in every propagation equation; remove both dots only in termination.

19. Complete the following reactions:

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

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

Solution:

Concept:

- Heating an ammonium carboxylate gives an amide. Hofmann bromamide degradation then produces a primary amine containing one carbon atom fewer.
- A diazonium group can be replaced by a nitro group using sodium nitrite and copper. Nitro reduction yields a primary amine, which gives an isocyanide in the carbylamine reaction.

Step 1: Identify A, B and C in sequence (i) Ammonium benzoate loses water on heating to form benzamide:

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

Thus $A = C_6H_5CONH_2$. Bromine and potassium hydroxide cause Hofmann degradation:

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

Hence B is aniline, $C_6H_5NH_2$. Acetyl chloride acylates its amino group:

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

C is acetanilide. Pyridine removes the hydrogen chloride formed.

Step 2: Identify A, B and C in sequence (ii) Heating benzenediazonium tetrafluoroborate with sodium nitrite and copper replaces the diazonium group by $-NO_2$:

$$C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} C_6H_5NO_2.$$

Thus A is nitrobenzene. Tin and hydrochloric acid reduce the nitro group:

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2 + 2H_2O.$$

B is aniline (obtained as its salt in the acidic medium and liberated on work-up). Being a primary amine, it gives the carbylamine reaction:

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow[\Delta]{\text{alcohol}} C_6H_5NC + 3KCl + 3H_2O.$$

Therefore C is phenyl isocyanide; its ring is bonded to nitrogen, not to the terminal carbon.

Step 3: Conclusion (i) A: benzamide; B: aniline; C: acetanilide. (ii) A: nitrobenzene; B: aniline; C: phenyl isocyanide.

Quick Tip to Solve: Track the carbonyl carbon in Hofmann degradation: it is lost, while carbylamine adds a terminal isocyanide carbon.

20. 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:

- Nucleophilic addition is favoured by a more electrophilic and less sterically hindered carbonyl carbon.
- Aldol condensation requires at least one alpha hydrogen. Friedel-Crafts reactions require an aromatic ring sufficiently reactive towards electrophilic substitution.

Step 1: Explain the greater reactivity of aldehydes In RCHO, the carbonyl carbon is attached to one alkyl group and one hydrogen; in RCOR, it is attached to two alkyl groups. Alkyl groups release electron density by the positive inductive effect. The two alkyl groups of a ketone reduce the partial positive charge on its carbonyl carbon more than the single alkyl group in an aldehyde. The ketone therefore attracts a nucleophile less strongly. There is also a steric effect: two alkyl groups hinder the approach of the nucleophile more than one alkyl group and a small hydrogen atom. Both electronic and steric factors consequently favour nucleophilic addition to aldehydes.

Step 2: Explain why benzaldehyde does not undergo aldol condensation The initial step of aldol condensation is removal of an alpha hydrogen to form an enolate ion (or formation of the corresponding enol). In benzaldehyde, C_6H_5CHO, the carbon adjacent to the carbonyl group belongs to the benzene ring and has no alpha hydrogen. The hydrogen of the $-CHO$ group is attached to the carbonyl carbon itself, so it is not an alpha hydrogen. Benzaldehyde therefore cannot form the required enolate and does not undergo self-aldol condensation.

Step 3: Explain why benzoic acid does not give Friedel-Crafts reaction The $-COOH$ group withdraws electron density from the benzene ring through both the negative inductive and negative resonance effects. This strongly deactivates the ring towards electrophilic substitution. Friedel-Crafts alkylation

and acylation consequently fail on benzoic acid under the usual conditions. In addition, the oxygen atoms of the carboxyl group can coordinate with the Lewis acid catalyst, such as $AlCl_3$, further interfering with the reaction. The decisive reason is the strong deactivation of the aromatic ring by $-COOH$.

Step 4: Conclusion (a) Aldehydes have less electron donation and steric hindrance. (b) Benzaldehyde has no alpha hydrogen. (c) The carboxyl group strongly deactivates the ring towards Friedel-Crafts substitution.

Quick Tip to Solve: For aldol eligibility, inspect the carbon next to the carbonyl; the aldehydic hydrogen never counts as an alpha hydrogen.

21. 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:

- Electron-withdrawing nitro groups at ortho and para positions activate an aryl chloride towards nucleophilic substitution.
- Alcoholic KOH favours beta-elimination; sodium in dry ether couples alkyl halides in the Wurtz reaction.

Step 1: (i) Hydrolysis of the activated aryl chloride The three nitro groups withdraw electron density and stabilise the intermediate formed during nucleophilic substitution. Consequently warm water replaces chlorine by a hydroxyl group, forming 2,4,6-trinitrophenol (picric acid):

$$C_6H_2Cl(NO_2)_3 + H_2O \xrightarrow{\text{warm}} C_6H_2(OH)(NO_2)_3 + HCl.$$

The nitro groups remain at positions 2, 4 and 6 relative to the substituted group.

Step 2: (ii) Elimination from 2-chlorobutane Alcoholic KOH removes a beta-hydrogen while chlorine leaves from the adjacent carbon. According to Saytzeff's rule, the more substituted alkene, but-2-ene, is the major product:

$$CH_3CHClCH_2CH_3 + KOH \xrightarrow[\Delta]{\text{alcohol}} CH_3CH{=}CHCH_3 + KCl + H_2O.$$

But-1-ene, $CH_2{=}CHCH_2CH_3$, is a minor product. Alcoholic KOH therefore favours alkene formation, unlike aqueous KOH which favours substitution.

Step 3: (iii) Wurtz coupling of ethyl chloride Two ethyl groups couple in the presence of sodium metal and dry ether. Their carbon chains join to produce n-butane:

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

This is the Wurtz reaction. The equation requires two molecules of ethyl chloride and two sodium atoms for each molecule of butane formed.

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

Quick Tip to Solve: Use warm water for substitution, alcoholic KOH for elimination, and Na/dry ether for joining two alkyl groups.

22. 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 bonds to oxygen; oxygen can form multiple bonds with transition metals.
- Metallic bond strength depends on the electrons available for bonding. Lanthanoids generally favour the +3 oxidation state.

Step 1: (i) Highest oxidation states of manganese Oxygen stabilises the very high oxidation state of manganese by forming multiple bonds with the metal. Thus manganese reaches $+7$ in Mn_2O_7, where $2x + 7(-2) = 0$ gives $x = +7$. Fluorine can form only single bonds, so it does not provide comparable stabilisation of this high oxidation state; the highest fluoride is MnF_4, containing manganese in $+4$. The ability of oxygen to form multiple bonds explains the difference despite fluorine's greater electronegativity.

Step 2: (ii) Soft zinc and hard chromium Zinc has the configuration $[Ar]3d^{10}4s^2$, with a completely filled d subshell. Its d electrons contribute little to metallic bonding, which is relatively weak. Chromium has configuration $[Ar]3d^5 4s^1$, with several unpaired electrons available for strong metallic bonding. The stronger interatomic bonding makes chromium hard, whereas the weaker metallic bonding makes zinc soft.

Step 3: (iii) Reducing behaviour of europium(II) Although Eu^{2+} has a half-filled $4f^7$ configuration, it readily loses an electron to form the usual, more stable trivalent lanthanoid state in aqueous solution:

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

The released electron reduces another species. Hence Eu^{2+} is a good reducing agent; the common stability of the +3 state outweighs the special half-filled-shell consideration here.

Step 4: Conclusion Oxygen stabilises Mn(VII) through multiple bonding; stronger metallic bonding makes Cr harder than Zn; oxidation to Eu^{3+} accounts for the reducing action of Eu^{2+}.

Quick Tip to Solve: For Eu(II), write its oxidation to Eu(III); do not conclude that a half-filled f subshell prevents reducing behaviour.

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 a 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 is it 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 reduce anxiety and produce a sense of well-being.
- Drugs acting on the central nervous system require medical supervision: their appropriate choice and dose depend on the patient's condition.

Step 1: (i) Values displayed by Mr. Roy Mr. Roy displays care and concern for his friend's health, empathy towards a person experiencing stress, and a sense of responsibility. His advice also shows health awareness and a scientific attitude: he encourages yoga, meditation and physical exercise as healthy habits instead of supporting unsupervised use of medicines. Any two of these values, explained in the context of the passage, answer this part.

Step 2: (ii) Need for a doctor's advice Sleeping pills act on the central nervous system. Taking them without a doctor's advice can lead to harmful side effects, dependence and addiction; excessive doses can be dangerous. A doctor must assess the underlying cause of the symptoms and prescribe the appropriate drug, dose and duration where needed. Thus a person should not choose or repeatedly take such pills on their own merely to cope with stress or depression.

Step 3: (iii) Definition and examples of tranquilizers Tranquilizers are a class of drugs used for the treatment of stress and mild or even severe mental diseases. They relieve anxiety and tension and induce a sense of well-being. Two examples are diazepam and chlordiazepoxide. Their calming action explains their medical use, but it does not make them suitable for self-medication; they must be used under medical supervision.

Step 4: Conclusion Mr. Roy shows empathy, concern and responsibility. Sleeping pills can cause adverse effects and dependence and therefore require a doctor's advice. Tranquilizers relieve anxiety and stress; diazepam and chlordiazepoxide are examples.

Quick Tip to Solve: Link the values to Mr. Roy's actions, then give both the definition of tranquilizers and two named examples.

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

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

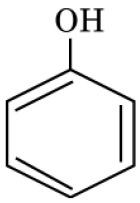
(ii) Phenol $\xrightarrow{Zn\ dust}$ **?**

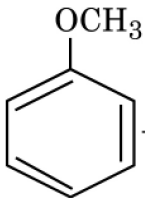
(iii) Anisole + $CH_3COCl \xrightarrow{anhyd.\ AlCl_3}$ **?**

(b) Write the mechanism of the following reaction:

$2CH_3CH_2OH \xrightarrow{Conc.\ H_2SO_4/413\,K} CH_3CH_2\text{-}O\text{-}CH_2CH_3$ [5 marks]

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

(ii)  $\xrightarrow{Zn\ dust}$

(iii)  $+ CH_3COCl \xrightarrow{anhyd.AlCl_3}$

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

Solution:

Concept:

- PCC (pyridinium chlorochromate) oxidises a primary alcohol to an aldehyde under anhydrous conditions, without further oxidation to the acid.
- Zinc dust removes oxygen from phenol as zinc oxide. The methoxy group in anisole activates the aromatic ring and directs electrophilic substitution to the ortho and para positions.
- At $413\,K$, concentrated sulphuric acid catalyses intermolecular dehydration of ethanol. Protonation converts the poor leaving group $-OH$ into water; another ethanol molecule acts as the nucleophile.

Step 1: (a)(i) Oxidise the allylic primary alcohol The terminal $-CH_2OH$ group becomes $-CHO$, while the carbon-carbon double bond remains intact:

$$CH_2=CHCH_2OH \xrightarrow{PCC} CH_2=CHCHO.$$

The product is prop-2-enal (acrolein). Since PCC is a mild oxidising agent, the required product is the aldehyde, rather than prop-2-enoic acid.

Step 2: (a)(ii) Heat phenol with zinc dust Zinc takes up the oxygen of the phenolic hydroxyl group,

giving benzene:

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

Thus the organic product is benzene and the inorganic product is zinc oxide. The aromatic ring remains intact during this reduction.

Step 3: (a)(iii) Carry out Friedel-Crafts acylation of anisole Anhydrous $AlCl_3$ activates acetyl chloride to generate the acyl electrophile. The methoxy group directs its attack to the ortho and para positions:

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

These are 2-methoxyacetophenone and 4-methoxyacetophenone. Each substitution also liberates HCl. The para product is major because attack there encounters less steric hindrance than attack next to the methoxy group.

Step 4: (b) Protonate ethanol A lone pair on oxygen accepts a proton from the acid, forming an ethyloxonium ion:

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2^+.$$

This activation is essential: water can leave much more readily than a hydroxide ion.

Step 5: Attack by a second ethanol molecule The oxygen lone pair of a second ethanol molecule attacks the primary carbon bonded to OH_2^+. Simultaneously the carbon-oxygen bond to water breaks, giving protonated ether through an S_N2 substitution:

$$CH_3CH_2OH + CH_3CH_2OH_2^+ \longrightarrow (CH_3CH_2)_2OH^+ + H_2O.$$

No free primary ethyl carbocation is required in this mechanism.

Step 6: Remove a proton and regenerate the catalyst Loss of a proton from the oxonium ion gives diethyl ether and regenerates the acid catalyst:

$$(CH_3CH_2)_2OH^+ \longrightarrow CH_3CH_2OCH_2CH_3 + H^+.$$

Adding the steps gives $2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$. The stated temperature favours intermolecular ether formation from this primary alcohol.

Step 7: Conclusion (a) The products are (i) prop-2-enal, (ii) benzene with ZnO, and (iii) ortho- and para-methoxyacetophenone, with the para isomer major. (b) Ethanol forms diethyl ether by protonation, nucleophilic substitution by a second ethanol molecule, and deprotonation.

Quick Tip to Solve: Preserve the C=C bond in PCC oxidation, and use the methoxy group's ortho/para direction in anisole acylation. For ether formation, show water leaving only after protonating ethanol.

OR

24(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 $-OH$ group activates phenol towards electrophilic substitution and directs the incoming group to the ortho and para positions.
- Phenol undergoes the Reimer–Tiemann reaction with chloroform and aqueous alkali to introduce a formyl group, principally at the ortho position.
- Hydrogen iodide cleaves anisole at its alkyl–oxygen bond. Free alcoholic hydroxyl groups and the different rates of substitution of primary and tertiary alcohols provide distinguishing tests.

Step 1: (a)(i) Bromination of phenol in carbon disulphide In the non-polar solvent CS_2, controlled bromination of phenol gives a mixture of ortho- and para-bromophenol. The para product predominates because substitution there suffers less steric hindrance.

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

Here BrC_6H_4OH represents the two positional isomers, *o*-bromophenol and *p*-bromophenol (major). These conditions differ from bromine water, which produces 2,4,6-tribromophenol.

Step 2: (a)(ii) Reimer–Tiemann reaction Heating phenol with chloroform and aqueous sodium hydroxide, followed by acidification, gives 2-hydroxybenzaldehyde (salicylaldehyde) as the principal product. The balanced overall equation, with acid work-up understood, is

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

Alkali generates the reactive intermediate dichlorocarbene from chloroform. Its reaction with the activated phenoxide ring, followed by hydrolysis and acidification, replaces an ortho ring hydrogen with $-CHO$. A small amount of the para isomer may also form.

Step 3: (a)(iii) Cleavage of anisole by HI

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

The products are phenol and methyl iodide. Protonation of ether oxygen is followed by attack of iodide on the methyl carbon. The aryl–oxygen bond is retained because its partial double-bond character and the nature of the aryl carbon prevent the usual substitution cleavage there.

Step 4: (b)(i) Distinguish ethanol from diethyl ether Add a small piece of sodium metal to separate

dry samples. Ethanol evolves bubbles of hydrogen, whereas dry diethyl ether shows no such reaction under these conditions:

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

Ethanol contains an $O - H$ hydrogen that sodium can replace; the ether has no $O - H$ bond. Dry samples are essential because moisture itself reacts with sodium and would obscure the distinction.

Step 5: (b)(ii) Distinguish propanol from tert-butyl alcohol Use Lucas reagent, concentrated hydrochloric acid containing anhydrous $ZnCl_2$, at room temperature. Tert-butyl alcohol gives immediate turbidity due to the formation of insoluble tert-butyl chloride:

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

Propan-1-ol, a primary alcohol, gives no turbidity at room temperature during the usual test period. The tertiary alcohol reacts rapidly through its relatively stable tertiary carbocation. If propanol is taken as propan-2-ol, it gives turbidity only after a few minutes, so the immediate response of tert-butyl alcohol still distinguishes the samples.

Step 6: Conclusion (a) The products are (i) ortho- and para-bromophenol, with para predominant; (ii) salicylaldehyde after acidification; and (iii) phenol plus methyl iodide. (b) Sodium gives hydrogen with ethanol but not dry diethyl ether; Lucas reagent gives immediate turbidity with tert-butyl alcohol, unlike propanol.

Quick Tip to Solve: Check the bromination solvent first: bromine in CS2 gives monobromophenols, whereas bromine water gives the tribromo derivative.

25(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: $\Delta T_b = iK_bm$, where i is the van't Hoff factor, K_b is the molal elevation constant and m is the molality of the dissolved formula units.
- Complete dissociation of one formula unit of Na_2SO_4 gives three ions. Hence its ideal van't Hoff factor is $i = 3$.
- An ideal solution obeys Raoult's law over the entire composition range; mixing has zero enthalpy change and zero volume change.

Step 1: (a) Determine the number of solute particles Sodium sulphate undergoes complete ionisation as stated:

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

Thus one mole of dissolved sodium sulphate yields three moles of ions, giving $i = 2+1 = 3$. The factor must multiply the elevation because boiling point depends on the total number of solute particles, rather than just the number of formula units added.

Step 2: (a) Calculate molality and boiling point The mass of the solvent is $50\,\text{g} = 0.050\,\text{kg}$. Therefore,

$$n = \frac{2}{142}\,\text{mol},$$
$$m = \frac{2/142}{0.050} = 0.28169\,\text{mol kg}^{-1},$$
$$\Delta T_b = 3 \times 0.52 \times 0.28169 = 0.43944\,\text{K}.$$

Taking the normal boiling point of water as $100\,^\circ\text{C}$, the solution boils at

$$T_b = 100 + 0.43944 = 100.43944\,^\circ\text{C} \approx 100.44\,^\circ\text{C}.$$

A temperature interval has the same numerical value in kelvin and degrees Celsius. The boiling point rises because the nonvolatile solute lowers the solvent's vapour pressure.

Step 3: (b)(i) Define colligative properties Colligative properties are properties of dilute solutions that depend only on the number of solute particles relative to the number of solvent particles, and not on the chemical identity of the solute. Examples are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. When a solute dissociates, its ions must be counted as separate particles.

Step 4: (b)(ii) Define an ideal solution An ideal solution is one that obeys Raoult's law throughout the entire range of composition at a given temperature. For each volatile component j, its partial vapour pressure is $p_j = x_j p_j^\circ$, where x_j is its mole fraction and p_j° is its pure-component vapour pressure. Such a solution has $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$, since the unlike intermolecular interactions are comparable to the like interactions.

Step 5: Conclusion (a) The boiling point is $\boxed{100.44\,^\circ\text{C}}$ 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, with zero enthalpy and volume changes on mixing.

Quick Tip to Solve: Count the three ions from each sodium sulphate formula unit, and use the solvent mass in kilograms before substituting into $iK_b m$.

OR

25(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 K_f is the cryoscopic constant and m is the number of moles of solute per kilogram of solvent.
- The molar mass M connects solute mass w and amount n through $n = w/M$. For sulphur molecules S_x, $M = 32x$ g mol^{-1}.
- Osmosis is movement of solvent across a semipermeable membrane towards the solution of higher osmotic pressure. At the same temperature, a more concentrated solution of the same solute has higher osmotic pressure.

Step 1: (a) Calculate the molality of dissolved sulphur The lowering of freezing point is given directly, so the freezing point of pure carbon disulphide is not needed. Using the stated value of K_f,

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

The solvent mass is $100\,\text{g} = 0.100\,\text{kg}$. Hence the amount of sulphur molecules present is

$$n = m \times 0.100 = 0.0100 \text{ mol}.$$

The solvent mass, rather than the total solution mass, enters the definition of molality.

Step 2: (a) Obtain the molecular formula The mass of these sulphur molecules is $2.56\,\text{g}$, so their molar mass is

$$M = \frac{w}{n} = \frac{2.56}{0.0100} = 256 \text{ g mol}^{-1}.$$

Since each sulphur atom contributes $32\,\text{g mol}^{-1}$,

$$x = \frac{M}{32} = \frac{256}{32} = 8.$$

As a check, $2.56/256 = 0.0100$ mole in 0.100 kg solvent gives $\Delta T_f = 3.83(0.100) = 0.383\,\text{K}$, exactly the stated lowering.

Step 3: (b)(i) Place blood cells in 1.2 percent sodium chloride The cells are isotonic with 0.9% sodium chloride solution, meaning that this reference solution has the same osmotic pressure as the cell contents. The 1.2% solution is more concentrated and is therefore hypertonic relative to the cells. Water moves out of the cells through their semipermeable membranes by exosmosis. The cells lose

water and shrink, a change called crenation.

Step 4: (b)(ii) Place blood cells in 0.4 percent sodium chloride The 0.4% solution is less concentrated than the isotonic 0.9% solution, so it is hypotonic relative to the cell contents. Water enters the cells by endosmosis. The cells swell and may burst; rupture of red blood cells is called haemolysis. It is the direction of water movement, rather than movement of the cells themselves, that explains both observations.

Step 5: Conclusion (a) The molar mass of sulphur is $256\,\text{g mol}^{-1}$, and its molecular formula is $\boxed{S_8}$. (b)(i) In 1.2% NaCl, blood cells lose water and shrink. (ii) In 0.4% NaCl, they gain water, swell and may undergo haemolysis.

Quick Tip to Solve: Divide the measured molar mass by 32 to find the sulphur atom count; compare each salt concentration directly with 0.9 percent to predict water movement.

26(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:

- The acidity of group 16 hydrides increases down the group because the element-hydrogen bond becomes weaker as the central atom becomes larger.
- A higher positive oxidation state of a central atom generally increases its polarising power and hence the covalent character of its bonds.
- Molecular polarity adds dipole-dipole attractions to dispersion forces. VSEPR theory predicts molecular shape from bonding regions and lone pairs around the central atom.

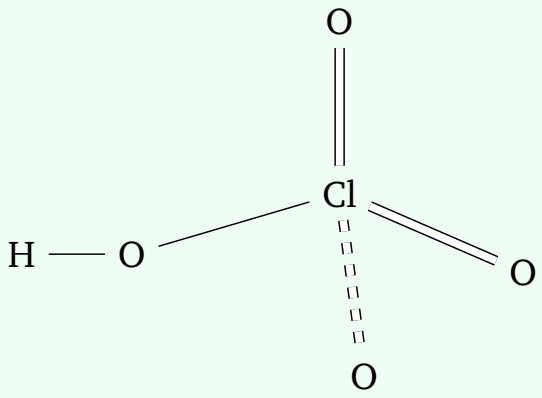
Step 1: (a)(i) Compare the strengths of the hydride bonds Tellurium is larger than sulphur, so the $H-Te$ bond is longer and weaker than the $H-S$ bond. It is therefore easier for H_2Te to release a proton in water. The decrease in bond strength dominates the trend, making H_2Te more acidic than H_2S.

Step 2: (a)(ii) Compare the covalent character of the chlorides The oxidation state of phosphorus is $+5$ in PCl_5, compared with $+3$ in PCl_3. The higher oxidation state gives the central atom greater polarising power: it distorts the electron cloud of chlorine more strongly. According to Fajans' rule, increased polarisation increases covalent character. Thus the printed comparison follows from the higher oxidation state of phosphorus in PCl_5.

Step 3: (a)(iii) Compare intermolecular attractions An interhalogen contains different halogen atoms, which have different electronegativities, so its bonds are polar. Pure diatomic halogen molecules are non-polar. In addition to dispersion attractions, polar interhalogen molecules experience dipole-dipole

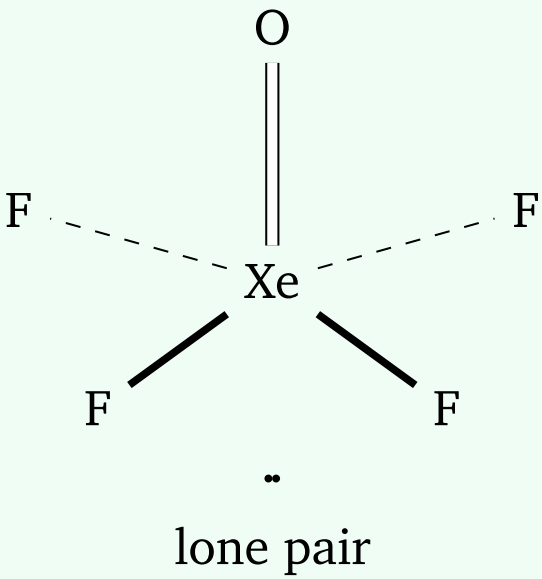
attractions. For comparable molecules, these stronger intermolecular forces require more heat to overcome, accounting for the slightly higher boiling points of interhalogens.

Step 4: (b)(i) Structure of perchloric acid In $HClO_4$, chlorine is bonded to four oxygen atoms: three terminal $Cl = O$ bonds and one $Cl - O - H$ group. The four bonding regions around chlorine give a tetrahedral arrangement. Hydrogen is attached to oxygen, not directly to chlorine. The drawing represents the conventional structural formula $HO - Cl(= O)_3$.



Tetrahedral arrangement about chlorine in perchloric acid.

Step 5: (b)(ii) Structure of xenon oxytetrafluoride Xenon has four $Xe - F$ bonds, one $Xe = O$ bond and one lone pair. A double bond counts as one electron domain, so there are six domains with an octahedral electron-pair arrangement. The lone pair lies opposite oxygen; the four fluorine atoms form the square base and oxygen occupies the apex. Thus $XeOF_4$ has a square-pyramidal molecular shape.



Square-pyramidal XeOF4; the lone pair is opposite oxygen.

Step 6: Conclusion H_2Te has the weaker element-hydrogen bond; phosphorus in PCl_5 has greater polarising power; and interhalogens have additional polar intermolecular attractions. The structures

are tetrahedral about Cl in $HClO_4$ and square pyramidal about Xe in $XeOF_4$.

Quick Tip to Solve: For XeOF4, count the Xe=O double bond as one electron domain, then place the lone pair opposite oxygen before naming the shape.

OR

26(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 is associated with their P–H bonds. Bonds between phosphorus and hydroxyl oxygen do not provide this reducing behaviour.
- Noble-gas compound formation becomes easier when the atom can lose or share its outer electrons more readily; ionisation enthalpy decreases substantially from He to Xe.
- Le Chatelier's principle predicts that high pressure favours the side with fewer gaseous moles and low temperature favours an exothermic reaction.

Step 1: (i) Compare the phosphorus oxoacids The structures may be represented as $O=P(OH)_3$, $O=P(H)(OH)_2$, and $O=P(H)_2(OH)$. Thus H_3PO_4, H_3PO_3, and H_3PO_2 have zero, one and two P–H bonds, respectively. Phosphoric acid therefore does not show the reducing behaviour of the other two, and hypophosphorous acid has the strongest reducing character of the three.

Step 2: (ii) Compare helium and xenon Xenon forms compounds more readily. Its larger atomic size and greater shielding make its outer electrons less tightly bound, so its ionisation enthalpy is much lower than that of helium. Highly electronegative elements such as fluorine and oxygen can therefore form compounds with Xe. The very small He atom has a tightly held, complete $1s^2$ shell and an exceptionally high ionisation enthalpy.

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

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

Four moles of gaseous reactants form two moles of gaseous product, so high pressure increases the equilibrium yield. Since the reaction is exothermic, a lower temperature favours ammonia at equilibrium, but an excessively low temperature makes the reaction too slow. Industrially, a pressure of about 200 atm and a moderate temperature of about 700 K are used with finely divided iron catalyst and suitable promoters. A $1:3$ nitrogen-to-hydrogen feed is supplied, ammonia is removed by cooling, and unreacted gases are recycled. Removal of ammonia shifts the equilibrium towards further production; the catalyst speeds attainment of equilibrium without changing its position.

Step 4: (iv) State two uses of chlorine Chlorine is used to disinfect drinking water by destroying harmful microorganisms. It is also used as a bleaching agent for wood pulp, cotton and textiles. In the presence of moisture, chlorine forms hypochlorous acid, whose oxidising action is responsible for these applications.

Step 5: (v) Detect sulphur dioxide chemically Pass the gas through acidified potassium permanganate solution. Sulphur dioxide reduces purple permanganate ions to nearly colourless manganese(II) ions, while it is itself oxidised to sulphate:

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

Decolourisation of the acidified purple solution is the characteristic observation for this test in the stated context.

Step 6: Conclusion (i) $\mathrm{H_3PO_4} < \mathrm{H_3PO_3} < \mathrm{H_3PO_2}$ in reducing character. (ii) Xe forms compounds more easily owing to its lower ionisation enthalpy. (iii) Use high pressure, a suitably low operating temperature, iron catalyst and continuous removal of ammonia. (iv) Chlorine is used for water disinfection and bleaching. (v) $\mathrm{SO_2}$ decolourises acidified potassium permanganate.

Quick Tip to Solve: For phosphorus oxoacids, count P–H bonds, not the total hydrogen atoms; for the Haber equilibrium, count gas molecules and note the negative enthalpy change.