CBSE Class 12 Chemistry Question Paper 2016 with Solution PDF-Set 056-3 - South

Question Paper with Solutions

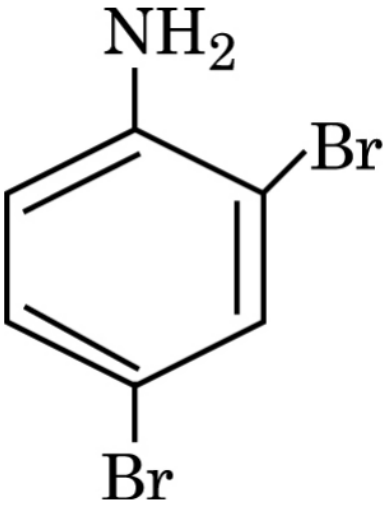
Conducted by the Central Board of Secondary Education (CBSE)

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



Solution:

Concept:

- The amino group is the principal functional group; its benzene carbon is numbered 1.
- Identical halogen substituents are named using locants and the multiplicative prefix di-.

Step 1: Choose the parent The ring bearing the amino group is aniline, the retained IUPAC parent name. Assign carbon 1 to the carbon attached to NH_2, rather than to either bromine atom.

Step 2: Locate the substituents Numbering towards the adjacent bromine gives bromine atoms at positions 2 and 4. Numbering in the other direction gives 4 and 6, so the lowest set of locants is 2,4. Both substituents are bromo groups, giving the prefix 2,4-dibromo-.

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

Quick Tip to Solve: Number an aniline ring from the carbon bearing the amino group, then choose the lower bromine locants.

2. 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 moments add vectorially; equal antiparallel moments cancel.
- Antiferromagnetism involves equal opposing magnetic contributions.

Step 1: Compare the opposing contributions The stated arrangement has the same number of domains pointing in each of two opposite directions. Their magnetic contributions therefore cancel, producing zero resultant magnetic moment in the ideal arrangement.

Step 2: Identify the magnetic behaviour Such equal antiparallel alignment is characteristic of antiferromagnetism. In ferrimagnetism the opposing contributions are unequal and leave a net moment; in ferromagnetism the moments align parallel and reinforce one another.

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

Quick Tip to Solve: Equal opposite magnetic contributions indicate antiferromagnetism; unequal opposite contributions indicate ferrimagnetism.

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

Solution:

Concept:

- Concentrated nitric acid oxidises zinc and is reduced to nitrogen dioxide.
- Brown NO_2 dimerises to colourless N_2O_4 on cooling.

Step 1: Identify the brown product Zinc reacts with concentrated nitric acid according to

$$Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O.$$

The brown gaseous product is nitrogen dioxide, in which nitrogen has oxidation state +4.

Step 2: Check the cooling observation Nitrogen dioxide undergoes reversible dimerisation:

$$2NO_2 \rightleftharpoons N_2O_4.$$

Cooling favours the dimer, dinitrogen tetroxide, and the brown colour fades. This confirms the identification; nitric oxide is colourless and does not match the initial observation.

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

Quick Tip to Solve: Use both clues together: brown gas plus dimerisation on cooling identifies nitrogen dioxide.

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

Solution:

Concept:

- Colloidal particles in a given sol carry charges of the same sign.
- Electrostatic repulsion opposes aggregation and precipitation.

Step 1: Identify the charge on particles Particles of a particular colloidal sol generally acquire the same kind of charge, for example by selective adsorption of ions. The sol as a whole remains electrically neutral because counter-ions are present in the dispersion medium.

Step 2: Explain why the sol persists Like-charged particles repel one another. This repulsion prevents their close approach and aggregation into larger particles that would settle out. Thus the dispersed particles remain separated, accounting for the stability of the sol against coagulation.

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

Quick Tip to Solve: Link sol stability to mutual repulsion of like charges, and coagulation to loss of that repulsion.

5. 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 a carbocation in its slow ionisation step.
- Resonance stabilisation of the carbocation facilitates this ionisation.

Step 1: Compare the intermediates Allyl chloride gives an allylic carbocation on breaking the carbon-chlorine bond:

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

The positive charge is delocalised over the two terminal carbon atoms by resonance.

Step 2: Relate stability to reactivity The other compound, 1-chloropropane, would form the primary carbocation $CH_3CH_2CH_2^+$, which has no resonance stabilisation. Formation of the allylic carbocation is therefore easier, making allyl chloride more reactive by the unimolecular substitution pathway.

Step 3: Conclusion $\boxed{CH_2 = CH - CH_2Cl}$, allyl chloride, is more reactive towards S_N1.

Quick Tip to Solve: For an SN1 comparison, draw the carbocation after chloride leaves and check for resonance stabilisation.

6. 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:

- Oxidative fusion converts manganese(IV) oxide to green manganate(VI).
- Acidic manganate disproportionates into permanganate(VII) and manganese(IV) oxide.
- Potassium permanganate decomposes on heating, releasing oxygen.

Step 1: Identify the green compound (A) Fusion of pyrolusite with potassium hydroxide in air gives potassium manganate:

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

Thus (A) is K_2MnO_4, containing manganese in oxidation state +6.

Step 2: Identify the purple compound (B) In acidic medium manganate ions disproportionate:

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

Some manganese is oxidised from +6 to +7 and the rest is reduced to +4. The purple compound (B) is potassium permanganate, $KMnO_4$.

Step 3: Describe heating of (B) Potassium permanganate undergoes thermal decomposition to green potassium manganate, manganese dioxide and oxygen:

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

The equation balances potassium, manganese and oxygen atoms, and accounts for evolution of oxygen gas.

Step 4: Conclusion $\boxed{(A) = K_2MnO_4, \quad (B) = KMnO_4}$. On heating, (B) gives K_2MnO_4, MnO_2 and O_2.

Quick Tip to Solve: Remember the colour sequence: manganate is green, permanganate is purple; heating permanganate releases oxygen.

7. 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 chloride ions outside the coordination sphere are freely ionisable and precipitate with silver nitrate: $Ag^+ + Cl^- \rightarrow AgCl(s)$.
- Ammonia is a neutral ligand. The charge of the complex ion therefore gives the oxidation state of palladium.

Step 1: Identify the coordination sphere 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. Thus the structural (coordination) formula is

$$[Pd(NH_3)_4]Cl_2.$$

Its ionisation is $[Pd(NH_3)_4]Cl_2 \rightarrow [Pd(NH_3)_4]^{2+} + 2Cl^-$.

Step 2: Name the complex The complex cation has charge +2, and each NH_3 ligand has zero charge,

so palladium is in oxidation state $+2$. Four ammonia ligands are named tetraammine. Name the cation first and then the chloride counterion: tetraamminepalladium(II) chloride.

Step 3: Conclusion (i) $[Pd(NH_3)_4]Cl_2$. (ii) Tetraamminepalladium(II) chloride.

Quick Tip to Solve: Count the moles of AgCl first: they directly count chloride ions outside the square brackets.

8. 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 voltage stability, rechargeability and supply of reactants.
- Primary cells are used once, secondary cells can be recharged, and fuel cells operate while fuel and oxidant are supplied.

Step 1: (i) Cell used in hearing aids Among the listed cells, the mercury cell is used in hearing aids. It is compact and supplies a nearly constant potential during its working life, making it suitable for small electronic devices.

Step 2: (ii) Cell used in the Apollo programme The hydrogen–oxygen fuel cell was used in the Apollo space programme. Hydrogen and oxygen react electrochemically to generate electrical energy; water is the reaction product.

Step 3: (iii) Cell used in automobiles and inverters The lead storage cell is used in automobiles and inverters. It is a secondary cell, so the discharge reaction can be reversed by charging. It can deliver the substantial current needed in these applications.

Step 4: (iv) Cell with a short life The dry cell does not have a long life. It is a primary cell and its reactants are consumed during use; its paste electrolyte also deteriorates with time, including during storage.

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

Quick Tip to Solve: Link mercury with steady voltage, fuel with Apollo, lead storage with recharging, and dry cell with limited life.

9(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 halogenates the alpha carbon of a carboxylic acid containing an alpha hydrogen, using halogen and red phosphorus.

Step 1: (i) Clemmensen reduction The carbonyl oxygen is removed by reduction, while the carbon skeleton remains unchanged. For example, propanone gives propane:

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

Here $[H]$ denotes reducing hydrogen equivalents supplied by the reagent. An aldehyde similarly gives $RCHO \rightarrow RCH_3$.

Step 2: (ii) Hell–Volhard–Zelinsky reaction An alpha hydrogen of the carboxylic acid is replaced by bromine in the presence of red phosphorus. For example, ethanoic acid gives bromoethanoic acid:

$$CH_3COOH + Br_2 \xrightarrow{red\ P} BrCH_2COOH + HBr.$$

The substitution occurs at the carbon next to the carboxyl group; the acid must possess an alpha hydrogen.

Step 3: Conclusion Clemmensen: $CH_3COCH_3 \rightarrow CH_3CH_2CH_3$ with $Zn(Hg)/HCl$. HVZ: $CH_3COOH \rightarrow BrCH_2COOH$ with $Br_2/\text{red P}$.

Quick Tip to Solve: For Clemmensen replace C=O by CH2; for HVZ replace an alpha hydrogen by halogen and retain COOH.

OR

9(b). How do you convert:

(i) Toluene to benzaldehyde

(ii) Ethanoyl chloride to ethanal [2 marks]

Solution:

Concept:

- Controlled oxidation of the benzylic methyl group can produce an aldehyde without proceeding to the carboxylic acid.
- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen over palladium supported on barium sulphate.

Step 1: (i) Toluene to benzaldehyde Use the Etard reaction: treat toluene with chromyl chloride in carbon disulphide, then hydrolyse the intermediate chromium complex. The conversion is

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

This controlled oxidation changes the side-chain methyl group into $-CHO$, preserving the benzene ring. Strong aqueous oxidants would instead give benzoic acid.

Step 2: (ii) Ethanoyl chloride to ethanal Carry out Rosenmund reduction by passing hydrogen over palladium supported on barium sulphate:

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

The moderated catalyst permits reduction of the acyl chloride to the aldehyde and limits further reduction to the alcohol. The two-carbon skeleton is retained.

Step 3: Conclusion (i) Etard oxidation: CrO_2Cl_2/CS_2, followed by hydrolysis. (ii) Rosenmund reduction: H_2, $Pd/BaSO_4$.

Quick Tip to Solve: Choose controlled Etard oxidation for the benzylic methyl group and Rosenmund reduction for an acyl chloride.

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10. 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:

- Reaction order is the sum of concentration exponents in the experimentally determined rate law. A constant rate means zero order.
- In the stated reaction representation, two ammonia molecules participate, giving molecularity two; molecularity and reaction order need not be equal.

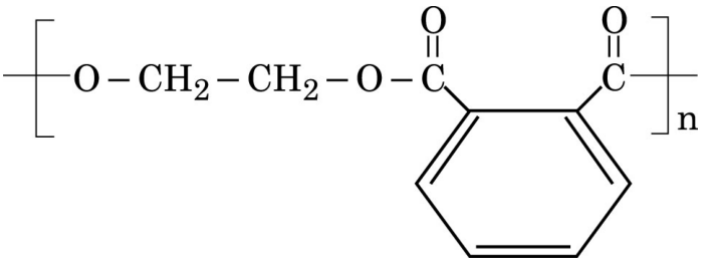
Step 1: (i) Read the rate law and reaction The given law is Rate $= k = k[NH_3]^0$. Hence the exponent of ammonia concentration is zero and the order is zero. The equation shows two molecules of ammonia on the reactant side, so the molecularity asked for is two (bimolecular). The coefficient 2 must not be used as the order: order comes from the rate law, whereas molecularity counts reacting particles in the stated reaction step. In general, molecularity is defined for an elementary step rather than inferred for an arbitrary multistep overall reaction.

Step 2: (ii) Obtain the unit of the rate constant Since Rate $= k$, the rate constant has the same dimensions as reaction rate, namely concentration divided by time. Taking concentration in mol L^{-1} and time in seconds gives $[k] = \text{mol L}^{-1}\,\text{s}^{-1}$. There is no concentration factor in the rate law to divide out.

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

Quick Tip to Solve: When the rate law is simply rate = k, immediately assign zero order and give k the units of reaction rate.

11(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 homolytic cleavage of the weak oxygen–oxygen bond, producing free radicals.
- Ester linkages in a polyester reveal the alcohol and carboxylic acid monomers; the ring positions of substituents must be preserved.
- Elastomers have relatively weak interchain attractions, thermoplastics have intermediate attractions, and polyamide fibres have strong hydrogen bonding.

Step 1: (i) Role of t-butyl peroxide It acts as a free-radical initiator. On heating, its peroxide bond undergoes homolytic fission to generate radicals. A radical attacks the carbon–carbon double bond of ethene, forming a new carbon radical that adds further ethene molecules. Thus it starts chain polymerisation; it is not the ethene monomer itself.

Step 2: (ii) Identify both monomers from the printed structure The segment $-OCH_2CH_2O-$ 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), $HOOC-C_6H_4-COOH$, with the two $-COOH$ groups in the ortho positions. Condensation between the diol and diacid forms the ester links with elimination of water. The adjacent ring attachments are crucial: the printed structure gives phthalic acid, not the para isomer terephthalic acid.

Step 3: (iii) Compare intermolecular forces Buna-N is an elastomer whose chains have relatively weak attractions, allowing stretching. PVC is a thermoplastic with stronger interchain attractions, including dipolar interactions associated with its polar carbon–chlorine bonds. Nylon-6 is a polyamide fibre; its repeated $-CONH-$ groups form strong hydrogen bonds between chains. Hence the required increasing order is $\text{Buna}-\text{N} < \text{PVC} < \text{Nylon}-6$.

Step 4: Conclusion (i) t-Butyl peroxide is a 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 ring attachments in the polyester before naming its diacid: adjacent carbonyl groups indicate phthalic acid.

OR

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

Solution:

Concept:

- Free-radical polymerisation converts ethene's carbon–carbon double bonds into single bonds joining a polyethylene chain.
- The mechanism has initiation, propagation and termination stages. A dot denotes an unpaired electron; R denotes the organic group of a peroxide initiator.

Step 1: Initiation: generate radicals and attack ethene Heating an organic peroxide cleaves its weak oxygen–oxygen bond homolytically:

$$\mathrm{RO{-}OR} \xrightarrow{\Delta} 2\mathrm{RO}^{\bullet}.$$

Each radical can add across an ethene double bond, making a new carbon–oxygen bond and leaving a carbon radical at the chain end:

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

This starts a chain; the radical is transferred to the terminal carbon rather than destroyed.

Step 2: Propagation: extend the chain repeatedly The terminal carbon radical attacks another ethene molecule. One bond of the double bond opens and the radical centre moves to the newly added terminal carbon:

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

Many repetitions produce a long chain. If $P_n^{\bullet}$ denotes an active chain containing n ethene units, the growth step is $P_n^{\bullet} + \mathrm{CH_2{=}CH_2} \longrightarrow P_{n+1}^{\bullet}$. Each added molecule contributes the unit $-\mathrm{CH_2{-}CH_2}-$.

Step 3: Termination: combine two growing radicals Two active chain ends combine by pairing their unpaired electrons to form a carbon–carbon bond:

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

Here P and Q represent the remaining polymer chain portions. The resulting molecule has no radical at the joined ends, so growth by this route stops. This illustrates termination by combination.

Step 4: Conclusion Peroxide-initiated radical addition of ethene proceeds through initiation, repeated propagation and termination, giving polyethene with repeating unit $[-\mathrm{CH_2{-}CH_2}-]_n$.

Quick Tip to Solve: Put a radical dot on the terminal carbon after every propagation step; remove both dots only when two chains terminate by combination.

12. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$\log k = 14.2 - (1.0 \times 10^4\ K)/T$

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 Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the pre-exponential factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For a first-order reaction, $t_{1/2} = \ln 2/k$; the time unit chosen for the half-life fixes the reciprocal-time unit of k.

Step 1: Express the Arrhenius equation in common logarithms Taking logarithms to base ten gives

$$\log k = \log A - \frac{E_a}{2.303RT}.$$

The factor 2.303 converts the natural logarithm to the common logarithm. Compare this with the printed relation

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

Thus the intercept is $\log A = 14.2$, while the coefficient of $1/T$ gives $E_a/(2.303R) = 1.0 \times 10^4\,\text{K}$. The negative sign is already included in both equations; the activation energy itself is positive.

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

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

The kelvin units cancel. Dividing by 10^3 converts this value to $191.47\,\text{kJ mol}^{-1}$.

Step 3: Use the half-life to obtain the rate constant The decomposition is first order, so its half-life is independent of the initial concentration. With $t_{1/2} = 200\,\text{min}$,

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

Equivalently, $200\,\text{min} = 12000\,\text{s}$, giving $k = 5.775 \times 10^{-5}\,\text{s}^{-1}$. No concentration factor is required in this first-order half-life formula.

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: When the given equation uses $\log$, multiply the coefficient of $1/T$ by $2.303R$, not just R.

13. 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 involves attack on the electron-deficient carbonyl carbon; both its electrophilicity and steric accessibility affect reactivity.
- Aldol condensation requires an α-hydrogen to generate an enolate, whereas Friedel–Crafts reactions require an aromatic ring sufficiently reactive towards electrophilic substitution.

Step 1: (a) Compare the carbonyl groups An aldehyde RCHO has one alkyl group and one small hydrogen attached to its carbonyl carbon. A ketone RCOR has two alkyl groups. Alkyl groups release electron density through their $+I$ effect, decreasing the partial positive charge on the carbonyl carbon. Two such groups in a ketone reduce its electrophilicity more than the single group in an aldehyde. Moreover, the two alkyl groups cause greater steric hindrance to the approaching nucleophile and to formation of the tetrahedral addition product. Both electronic and steric effects therefore favour nucleophilic addition to aldehydes.

Step 2: (b) Check the requirement for aldol condensation In benzaldehyde, $\mathrm{C_6H_5CHO}$, the carbonyl group is bonded directly to a phenyl group. It has no α-hydrogen: the carbon adjacent to the carbonyl carbon is the substituted ring carbon and bears no hydrogen. The hydrogen on $-\mathrm{CHO}$ is attached to the carbonyl carbon itself and is not an α-hydrogen. Consequently benzaldehyde cannot form the enolate needed to undergo self-aldol condensation.

Step 3: (c) Examine the effect of the carboxyl group The $-\mathrm{COOH}$ group of benzoic acid withdraws electron density from the benzene ring by both inductive and resonance effects. This strongly deactivates the ring towards electrophilic substitution. Friedel–Crafts alkylation and acylation therefore do not occur under the usual conditions. Interaction of the oxygen atoms with the Lewis acid catalyst, such as $\mathrm{AlCl_3}$, also interferes with the reaction.

Step 4: Conclusion (a) Aldehydes have less electron donation and less steric hindrance. (b) Benzaldehyde lacks an α-hydrogen. (c) The $-\mathrm{COOH}$ group strongly deactivates the aromatic ring.

Quick Tip to Solve: For aldol questions, locate the carbon adjacent to the carbonyl carbon; the aldehydic hydrogen does not count as an α-hydrogen.

14. (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 concentrates molecules at a surface. A porous solid with a large internal surface area can adsorb appreciable amounts of vapour.
- According to the Hardy–Schulze rule, the coagulating power increases with the valency of the counter-ion, whose charge is opposite to that of the sol.
- Macromolecular colloids contain individual large molecules of colloidal dimensions; multimolecular colloids contain aggregates of many smaller molecules.

Step 1: (i) Identify the adsorbent for water vapour Silica gel adsorbs water vapour on its extensive porous surface. Water molecules accumulate at the surface, so silica gel acts as an adsorbent and is widely used as a desiccant. Anhydrous $CaCl_2$ also removes moisture, but its drying action involves hydration and eventual deliquescence rather than the surface-adsorption process being tested here.

Step 2: (ii) Compare the counter-ions for the positive sol A positively charged sol is coagulated by negatively charged ions, which neutralise the charge responsible for keeping its particles dispersed. In the standard Hardy–Schulze comparison, H_2SO_4 supplies sulphate ions, SO_4^{2-}, whereas H_3PO_4 supplies phosphate ions, PO_4^{3-}. The phosphate ion has the higher negative valency. Hence H_3PO_4 is more effective in causing coagulation in this comparison. The relevant ions are the anions, since the sol is positively charged.

Step 3: (iii) Distinguish macromolecular and multimolecular colloids Proteins form macromolecular colloids: each protein molecule is a high-molar-mass molecule whose dimensions can lie in the colloidal range. In a suitable medium, these large molecules constitute the dispersed particles. Sulphur sol, on the other hand, is a multimolecular colloid: many comparatively small sulphur molecules associate to form particles of colloidal size. Thus the molecular nature of the dispersed particle distinguishes the two choices.

Step 4: Conclusion (i) Silica gel. (ii) H_3PO_4, since PO_4^{3-} has higher counter-ion valency than SO_4^{2-}. (iii) Proteins.

Quick Tip to Solve: First determine the sign of the sol: a positive sol requires comparison of anion valencies in the Hardy–Schulze rule.

15. 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:

- Oxidation states are stabilised by suitable bonding: oxygen can form multiple bonds with transition metals, whereas fluorine forms only single bonds.
- Metallic bond strength depends on the number of valence electrons available for delocalisation; stronger bonding makes a metal harder.
- A reducing agent loses electrons and is itself oxidised. For europium, the usual stable oxidation state in compounds is $+3$.

Step 1: (i) Highest oxidation state of manganese Manganese has the valence configuration $3d^5 4s^2$, so it can use seven valence electrons in bonding. Oxygen stabilises the high oxidation state by forming multiple bonds with manganese, as in Mn_2O_7, where $2x + 7(-2) = 0$ gives $x = +7$. Fluorine cannot form such multiple bonds; it forms single bonds only. Hence the highest oxidation state shown by Mn with fluorine is $+4$, in MnF_4. High electronegativity alone therefore does not explain the difference.

Step 2: (ii) Soft zinc and hard chromium Zinc has configuration $[Ar]3d^{10}4s^2$. Its filled $3d$ subshell contributes little to metallic bonding, giving relatively weak metal-metal bonding and a soft metal. Chromium has configuration $[Ar]3d^5 4s^1$, with many unpaired valence electrons available for metallic bonding. The stronger metallic bonding and greater enthalpy of atomisation make chromium hard.

Step 3: (iii) Reducing action of europium(II) Europium readily attains its common $+3$ oxidation state by donating an electron:

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

The released electron reduces another species, so Eu^{2+} acts as a good reducing agent. Although Eu^{2+} has a half-filled $4f^7$ configuration, that does not prevent its oxidation to the thermodynamically favoured trivalent state in solution.

Step 4: Conclusion Oxygen stabilises Mn(VII) through 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 reducing agents, write the electron-loss half-reaction first; do not infer inertness solely from a half-filled subshell.

16. 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:

- Ortho and para nitro groups activate an aryl chloride towards nucleophilic substitution by stabilising the anionic intermediate.
- Alcoholic KOH favours beta-elimination of HCl; the more substituted alkene is the major product according to Saytzeffś rule.
- In the Wurtz reaction, sodium couples two alkyl halide molecules in dry ether to give a higher alkane.

Step 1: (i) Hydrolysis of the activated aryl chloride The three electron-withdrawing nitro groups at positions 2, 4 and 6 strongly activate the carbon bearing chlorine. Warm water therefore replaces chlorine by a hydroxyl group, forming 2,4,6-trinitrophenol (picric acid):

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

The nitro groups remain at the same positions. This unusually easy hydrolysis results from nitro-group activation; ordinary chlorobenzene does not hydrolyse readily with warm water.

Step 2: (ii) Elimination from 2-chlorobutane Alcoholic KOH removes a beta-hydrogen while chloride leaves the neighbouring carbon, producing an alkene:

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

But-2-ene is the major product because it is more substituted and more stable. Removal of a hydrogen from the terminal beta-carbon also gives a minor amount of but-1-ene, $CH_2{=}CHCH_2CH_3$. Thus the reaction is dehydrohalogenation rather than substitution to an alcohol.

Step 3: (iii) Wurtz coupling of ethyl chloride Two ethyl groups join through their carbon atoms in the presence of sodium and dry ether:

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

The organic product is n-butane. The carbon count doubles from two in each ethyl group to four in the coupled product, and two sodium atoms remove the two chlorine atoms as sodium chloride.

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

Quick Tip to Solve: Distinguish the reagent medium: alcoholic KOH favours an alkene, while sodium in dry ether couples two alkyl groups.

17. Complete the following reactions:

(i) $C_6H_5COO^-NH_4^+ \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow{CH_3COCl/pyridine} C$

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

Solution:

Concept:

- Heating an ammonium carboxylate gives an amide by loss of water; Hofmann bromamide degradation then gives a primary amine with one fewer carbon atom.
- Acylation converts aniline into an amide, while nitrobenzene is reduced to aniline by tin and hydrochloric acid.
- The carbylamine reaction of a primary amine with chloroform and alcoholic KOH gives an isocyanide, whose connectivity is $R - N{\equiv}C$.

Step 1: (i) Identify A: thermal dehydration Ammonium benzoate loses water on heating to form benzamide:

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

Thus A in sequence (i) is benzamide, $C_6H_5CONH_2$. The carbonyl carbon is retained at this stage.

Step 2: (i) Identify B and C: degradation and acylation Bromine and KOH convert benzamide into aniline through Hofmann degradation:

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

Therefore B is aniline. Acetyl chloride in pyridine acylates its amino group:

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

Pyridine accepts the liberated HCl. C is acetanilide; the acetyl group attaches to nitrogen.

Step 3: (ii) Identify A and B: nitro substitution and reduction Heating benzenediazonium tetrafluoroborate with sodium nitrite and copper replaces the diazonium group by a nitro group, with nitrogen evolution:

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

Thus A in sequence (ii) is nitrobenzene. Reduction with Sn/HCl gives aniline (as its salt in the acidic medium), conventionally shown after work-up as B:

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

Step 4: (ii) Identify C: carbylamine reaction Aniline, a primary amine, reacts with chloroform and alcoholic KOH on heating to form phenyl isocyanide:

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

Hence C is phenyl isocyanide, with the phenyl group bonded to nitrogen. It is not benzonitrile, in

which the phenyl group would be bonded to the nitrile carbon.

Step 5: 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 and the N-C connectivity in the carbylamine product to avoid the common product errors.

18. (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:

- Maltose is a reducing disaccharide made of two D-glucose units joined by an $\alpha(1 \rightarrow 4)$ glycosidic linkage. Hydrolysis breaks this linkage by addition of water.
- Vitamins are essential dietary micronutrients; characteristic deficiency symptoms help identify the missing vitamin.
- Fibrous proteins have elongated chains and mainly structural roles, whereas globular proteins fold into compact shapes and often perform metabolic functions.

Step 1: Identify the products of maltose hydrolysis Both monosaccharide units in maltose are glucose. Therefore, hydrolysis produces two molecules of D-glucose, not a glucose-fructose pair. The reaction is

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

The two products have the same monosaccharide name because maltose consists of two glucose residues.

Step 2: Identify the vitamin Deficiency of vitamin B_6, also called pyridoxine, causes convulsions. This identifies the required member of the vitamin B group specifically; naming only vitamin B would be incomplete.

Step 3: Give one example of each protein type Keratin is a fibrous protein, present in hair and nails; its long structural chains give mechanical strength. Insulin is a globular protein: its polypeptide chains fold into a compact functional structure. These provide one example of each requested class.

Step 4: Conclusion (i) 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 + glucose; sucrose, by contrast, gives glucose + fructose.

19. (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; the van Arkel method uses formation and decomposition of a volatile metal iodide.
- Leaching selectively dissolves the desired component of an ore in a suitable reagent. Alumina dissolves in concentrated sodium hydroxide owing to its amphoteric character.
- A flux reacts with gangue to produce a removable slag. Basic calcium oxide removes acidic silica gangue in a blast furnace.

Step 1: Name the refining method for zirconium Zirconium is refined by the van Arkel method, also called the iodide process. Impure zirconium reacts with iodine to form volatile zirconium tetraiodide. Its decomposition on a hot filament deposits pure zirconium:

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

The formation and decomposition are carried out under different temperature conditions.

Step 2: Identify the alumina purification process This process is leaching, specifically Bayerś process for purification of bauxite/alumina. Concentrated sodium hydroxide dissolves alumina as sodium aluminate, while insoluble impurities are separated by filtration. A conventional equation is

$$\mathrm{Al_2O_3} + 2\mathrm{NaOH} \longrightarrow 2\mathrm{NaAlO_2} + \mathrm{H_2O}.$$

In aqueous solution the aluminate may also be represented as a hydroxo complex.

Step 3: Explain the function of limestone Limestone supplies the basic flux calcium oxide on heating:

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

The calcium oxide then combines with silica gangue to give calcium silicate slag:

$$\mathrm{CaO} + \mathrm{SiO_2} \longrightarrow \mathrm{CaSiO_3}.$$

Thus limestone helps remove silica impurities; it is not the reducing agent for the iron oxide.

Step 4: Conclusion (i) Van Arkel (iodide) method. (ii) Leaching: Bayerś process. (iii) Limestone acts as a flux source, removing silica as calcium silicate slag.

Quick Tip to Solve: For limestone, write both reactions: formation of CaO first, followed by formation of calcium silicate slag.

20. (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:

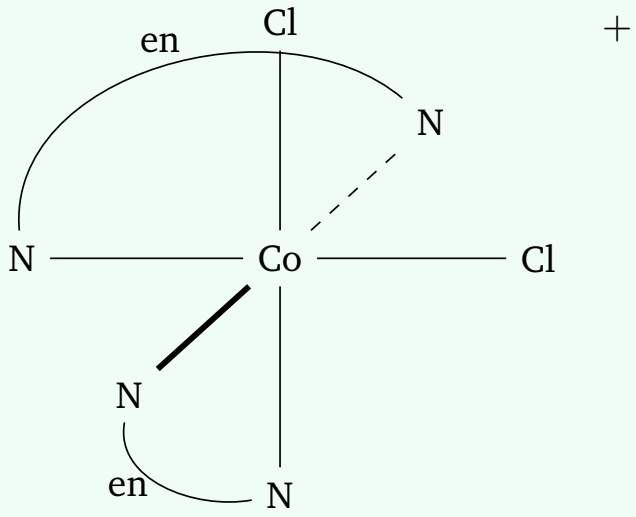
Concept:

- Fluoride has charge -1. The oxidation state of cobalt fixes its d-electron count before ligand strength is considered.
- In an octahedral weak-field complex, electrons occupy the upper e_g orbitals before pairing fully in t_{2g}, giving a high-spin arrangement.
- Ethylenediamine (en) is a neutral bidentate ligand. In $[Co(en)_2Cl_2]^+$, the cis geometrical isomer has nonsuperimposable mirror images and is optically active.

Step 1: Determine cobalt oxidation state and electron count Let the oxidation state of cobalt be x. Charge balance gives $x + 6(-1) = -3$, hence $x = +3$. Neutral cobalt has configuration $[Ar]3d^7 4s^2$, so Co^{3+} has configuration $[Ar]3d^6$. The coordination number is six, giving an octahedral complex.

Step 2: State hybridization, magnetic character and spin F^- is a weak-field ligand, so the octahedral d^6 configuration is $t_{2g}^4 e_g^2$. There are four unpaired electrons: two in t_{2g} and two in e_g. The complex is therefore paramagnetic and high spin, with total spin $S = 4(1/2) = 2$. In valence-bond terminology the outer orbitals $4s, 4p, 4d$ participate, giving sp^3d^2 hybridization.

Step 3: Draw the optically active geometrical isomer The required isomer is cis-$[Co(en)_2Cl_2]^+$. The two chloride ligands occupy adjacent octahedral positions, at $90°$. Each curved connection marked en joins the two nitrogen donors of one ethylenediamine ligand. The drawing shows one member of the optically active mirror-image pair. Its mirror image cannot be superimposed by rotation. The trans isomer, with opposite chloride ligands, is optically inactive.



cis-$[Co(en)_2Cl_2]^+$

One optically active cis form; paired N donors joined by en belong to the same ligand.

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

Quick Tip to Solve: Count the d electrons before applying ligand strength: Co(III) is d6, and weak-field fluoride gives four unpaired electrons.

21. Calculate E^o_{cell} for the following reaction at 298 K:

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

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

Solution:

Concept:

- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Pure solids have unit activity and are omitted from Q. Ionic concentrations enter with powers equal to their stoichiometric coefficients.

Step 1: Determine the electron transfer Chromium is oxidised and iron(II) ions are reduced. The balanced half-reactions are

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

Thus the reaction as written transfers $n = 6$ electrons. The coefficient 3 of iron is not itself the electron count, since each iron ion gains two electrons.

Step 2: Evaluate the reaction quotient Both chromium and iron are solids, so only the dissolved ions appear:

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

Although the two ionic concentrations are equal, their different stoichiometric powers mean that their contributions do not cancel.

Step 3: Calculate the standard cell potential Rearranging the Nernst equation and substituting the given measured cell potential,

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

Since $Q > 1$, the concentration correction lowers the measured potential relative to the standard potential, consistent with the positive correction used here.

Step 4: Conclusion The standard cell potential at 298 K is $\boxed{E^\circ_{\text{cell}} = 0.281\,\mathrm{V}}$, to three significant figures.

Quick Tip to Solve: Balance the half-reactions first: use six electrons and retain the unequal powers of the equal ionic concentrations.

22. 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:

- A face-centred cubic (f.c.c.) unit cell contains $Z = 4$ atoms: the eight corner atoms contribute $8 \times \frac{1}{8} = 1$, and the six face-centred atoms contribute $6 \times \frac{1}{2} = 3$.
- Density is $\rho = m/V$. A cubic unit cell of edge a has volume a^3, so its mass is ρa^3; dividing the sample mass by this gives the number of unit cells.

Step 1: Convert the edge length and find the cell volume Use centimetres because the given density is in g cm^{-3}. As $1\,\text{pm} = 10^{-10}$ cm,

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

Hence the volume of one unit cell is

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

The conversion factor must be cubed along with the numerical edge length.

Step 2: Find the number of unit cells in the sample The volume occupied by the 280 g sample is

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

Therefore the sample contains

$$N_{\text{cells}} = \frac{V_{\text{sample}}}{V_{\text{cell}}} = \frac{40}{6.40 \times 10^{-23}} = 6.25 \times 10^{23}\ \text{unit cells}.$$

The sample volume and cell volume are both in cubic centimetres, so their ratio is a pure count.

Step 3: Convert unit cells to atoms Each f.c.c. cell contributes four atoms after sharing the boundary atoms with neighbouring cells. Consequently,

$$N_{\text{atoms}} = Z N_{\text{cells}} = 4 \times 6.25 \times 10^{23} = 2.50 \times 10^{24}.$$

Counting all fourteen visible corner and face positions as complete atoms would overcount the shared atoms. The effective count four is essential here.

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

Quick Tip to Solve: Use $N = Zm/(\rho a^3)$ with $Z = 4$ for f.c.c.; convert picometres to centimetres before cubing the edge.

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, anxiety and mild or severe mental disease. They act on the central nervous system and produce a calming effect.
- Medicines must be taken in the prescribed dose under medical supervision. A drug that is useful at a suitable dose can cause harmful effects when used incorrectly.

Step 1: (i) Values displayed by Mr. Roy Mr. Roy shows concern and compassion for his friend's health: he notices the harmful practice and tries to help him. He also displays responsibility and scientific awareness by discouraging unsupervised use of medicines. His suggestion of Yoga, meditation and physical exercise reflects an awareness of a healthy lifestyle and a willingness to guide a friend constructively. Any two of concern for others, friendship, responsibility and health awareness answer this part.

Step 2: (ii) Reason for consulting a doctor Sleeping pills affect the central nervous system. Taking them without medical advice can lead to an unsuitable dose, excessive sedation and harmful side effects; repeated unsupervised use may also produce dependence or addiction. A doctor must assess the cause of the symptoms and decide the appropriate medicine, dose and duration. Thus, a person should not self-medicate with sleeping pills merely because they feel tense or unable to sleep.

Step 3: (iii) Meaning and examples of tranquilizers Tranquilizers are a class of drugs used for the treatment of stress and mild or even severe mental diseases. They reduce anxiety and bring about a feeling of well-being by acting on the central nervous system. Two examples are diazepam and chlordiazepoxide. Their therapeutic use requires medical supervision; the fact that such drugs can calm a patient does not justify taking them casually to cope with a busy schedule.

Step 4: Conclusion (i) Mr. Roy displays concern for his friend and responsible health awareness. (ii) Unsupervised sleeping-pill use can cause harmful side effects and dependence, so medical advice is necessary. (iii) Tranquilizers treat stress, anxiety and mental disease; examples are diazepam and chlordiazepoxide.

Quick Tip to Solve: Answer all three parts separately: state two values, explain the risk of self-medication, then give the drug class and two named examples.

24(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 a dilute solution, $\Delta T_b = iK_bm$, where i is the van't Hoff factor, K_b is the molal boiling-point elevation constant and m is the molality.
- Complete ionization of an electrolyte increases the number of dissolved particles. The factor i equals the number of ions produced per formula unit when ionization is complete.
- Molality is the number of moles of solute per kilogram of solvent. An ideal solution obeys Raoult's law for each component over its entire composition range.

Step 1: (a) Determine the particle factor Sodium sulphate dissociates completely according to

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

Complete dissociation gives two sodium cations and one sulphate anion per formula unit. Thus $i = 3$. The factor counts the ions, rather than the number of different kinds of ion: two sodium ions and one sulphate ion all contribute to the colligative effect.

Step 2: Calculate the molality and boiling-point elevation The amount of sodium sulphate and the mass of solvent in kilograms are

$$n = \frac{2}{142}\,\mathrm{mol}, \qquad w_{\text{water}} = \frac{50}{1000} = 0.050\,\mathrm{kg}.$$

Hence

$$m = \frac{2/142}{0.050} = 0.28169\,\mathrm{mol\ kg^{-1}}.$$

Applying the electrolyte form of the boiling-point elevation relation gives

$$\Delta T_b = 3 \times 0.52 \times 0.28169 = 0.4394\,\mathrm{K}.$$

This is an elevation, so it is added to the boiling point of pure water at normal atmospheric pressure:

$$T_b = 373.15 + 0.4394 = 373.5894\,\mathrm{K}.$$

Equivalently, the Celsius temperature is $100 + 0.4394 = 100.4394\,^\circ\mathrm{C}$. A temperature difference of one kelvin equals a temperature difference of one degree Celsius.

Step 3: (b)(i) Define colligative properties Colligative properties are the properties of dilute solutions that depend only on the number of solute particles present relative to the number of solvent particles, and not on the chemical nature of the solute. The solute is taken as non-volatile in the usual treatment. Relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure are examples. For an electrolyte, the dissolved ions must be counted as separate

particles.

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

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

where x_A, x_B are liquid-phase mole fractions and p_A°, p_B° are the vapour pressures of the pure components. Such a solution has $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$, since interactions between unlike molecules are comparable with those between like molecules.

Step 5: Conclusion (a) The boiling point is approximately $\boxed{100.44\,^\circ\text{C}}$, or $\boxed{373.59\,\text{K}}$, at normal atmospheric pressure. (b) Colligative properties depend on the relative number of solute particles; an ideal solution obeys Raoult's law throughout the entire composition range.

Quick Tip to Solve: Write the dissociation equation first to obtain $i = 3$, and use the 50 g mass of water, not the mass of the whole solution, when calculating molality.

OR

24(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 when 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 number of moles of dissolved solute per kilogram of solvent and K_f is the molal freezing-point depression constant.
- For molecular sulphur, $M(S_x) = 32x$ g mol^{-1}. Its measured molar mass therefore gives the number of sulphur atoms in each molecule.
- Osmosis is the flow of solvent through a semipermeable membrane from a solution of lower solute concentration to one of higher solute concentration. A blood-cell membrane allows water to pass; isotonic solutions exert equal osmotic pressures at the same temperature.

Step 1: (a) Calculate the molality of the sulphur solution Here the lowering in freezing point is $\Delta T_f = 0.383\,\text{K}$ and $K_f = 3.83\,\text{K kg mol}^{-1}$. Thus

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

The mass of the solvent is $100\,\text{g} = 0.100\,\text{kg}$, so the number of moles of molecular sulphur dissolved is

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

Step 2: (a) Obtain the molar mass and molecular formula The given $2.56\,\text{g}$ of sulphur represents $0.0100\,\text{mol}$ of its molecules. Therefore,

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

Since one mole of sulphur atoms has a mass of $32\,\text{g}$, the number of atoms per molecule is

$$x = \frac{M(S_x)}{M(S)} = \frac{256}{32} = 8.$$

The colligative measurement counts dissolved sulphur molecules, so the atomic mass must be used only after determining this molecular molar mass.

Step 3: (b)(i) Place blood cells in 1.2 percent sodium chloride Blood cells are isotonic with 0.9% sodium chloride. The 1.2% sodium chloride solution is more concentrated and hence hypertonic relative to their contents. Water flows out of the cells by osmosis (exosmosis), toward the external solution of higher osmotic pressure. Consequently, the cells lose water and shrink, a process called crenation.

Step 4: (b)(ii) Place blood cells in 0.4 percent sodium chloride The 0.4% sodium chloride solution is less concentrated than the isotonic 0.9% solution, so it is hypotonic relative to the blood cells. Water enters the cells by osmosis (endosmosis). The cells swell and may burst; the rupture of red blood cells is called haemolysis. Thus the direction of water movement is reversed compared with the hypertonic solution.

Step 5: Conclusion (a) The molar mass of sulphur is $256\,\text{g mol}^{-1}$, so 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: Convert the solvent mass to kilograms before using molality; compare each NaCl concentration with 0.9 percent to decide which way water moves.

25(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:

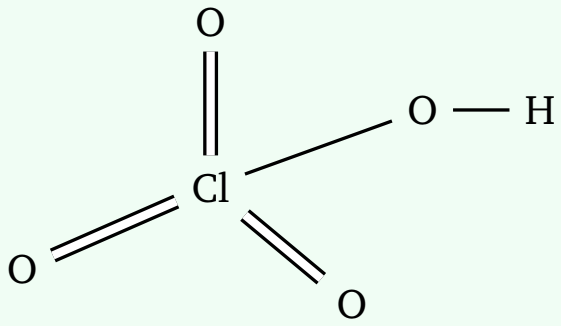
- The acidity of group 16 hydrides depends strongly on the strength of the hydrogen-element bond: a weaker bond releases a proton more readily.
- By Fajans' rule, greater charge and smaller size of a cation increase its polarising power and therefore the covalent character of a bond.
- Molecular polarity increases intermolecular attractions. VSEPR theory predicts molecular shape from the arrangement of bond pairs and lone pairs around the central atom.

Step 1: (a)(i) Compare the hydride bond strengths Tellurium is larger than sulphur. Consequently, the H–Te bond is longer and weaker than the H–S bond. The bond dissociation enthalpy decreases down group 16, so H_2Te releases H^+ more readily than H_2S. Thus the dominant bond-strength effect makes the tellurium hydride more acidic, despite sulphur being more electronegative.

Step 2: (a)(ii) Apply the polarisation argument Phosphorus has oxidation state $+5$ in PCl_5 and $+3$ in PCl_3. In the usual Fajans' rule comparison, the higher positive charge associated with phosphorus in PCl_5 gives greater polarising power. It distorts the electron cloud of chlorine more strongly, increasing electron sharing and hence covalent character. This is the expected comparison for these molecular chlorides; it does not assert that isolated phosphorus cations exist in either molecule.

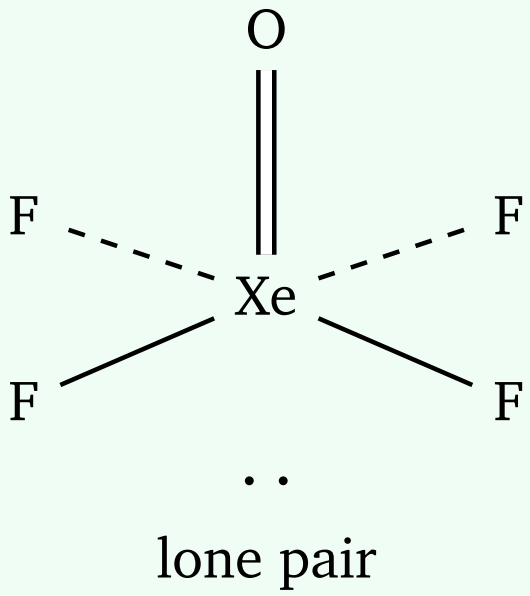
Step 3: (a)(iii) Compare intermolecular attractions An interhalogen molecule contains different halogen atoms, whose electronegativities differ, so its bonds are polar. In contrast, a pure diatomic halogen has a nonpolar bond because its two atoms have equal electronegativity. Interhalogens therefore have dipole-dipole attractions in addition to dispersion forces. For comparable molecules, the stronger intermolecular attractions require more energy to overcome, giving a slightly higher boiling point.

Step 4: (b)(i) Draw perchloric acid In $HClO_4$, chlorine is bonded to four oxygen atoms in an approximately tetrahedral arrangement. The conventional structural formula has three Cl=O bonds and one Cl–O–H group. The hydrogen belongs to an oxygen atom, not directly to chlorine. There is no lone pair on central chlorine in this conventional structure.



Conventional structure of perchloric acid; the four oxygen atoms surround chlorine tetrahedrally.

Step 5: (b)(ii) Draw xenon oxytetrafluoride In $XeOF_4$, xenon has six electron domains: four Xe–F bonds, one Xe=O bonding domain and one lone pair. A multiple bond counts as one domain. Their electron-domain arrangement is octahedral. The four fluorine atoms occupy the square base, oxygen occupies one axial position, and the lone pair occupies the opposite axial position. The molecular shape is therefore square pyramidal.



Square-pyramidal structure of xenon oxytetrafluoride, with the lone pair opposite oxygen.

Step 6: Conclusion H_2Te is more acidic because its hydrogen bond is weaker; the higher oxidation state of phosphorus accounts for the greater covalent character of PCl_5; polar interhalogens have stronger intermolecular attractions. $HClO_4$ has a tetrahedral oxygen arrangement, while $XeOF_4$ is square pyramidal with its lone pair opposite oxygen.

Quick Tip to Solve: Put H on O when drawing perchloric acid. For $XeOF_4$, count the double bond as one domain and place the lone pair opposite O before identifying the square pyramid.

OR

25(i). Arrange the following in the increasing order of their reducing character:

H_3PO_3, H_3PO_4, H_3PO_2 [1 mark]

Solution:

Concept:

- Reducing action of phosphorus oxoacids is associated with hydrogen atoms directly bonded to phosphorus, rather than those in hydroxyl groups.
- Count the P-H bonds from the structures before comparing reducing strength.

Step 1: Count the reducing bonds H_3PO_4 has no $P-H$ bond, H_3PO_3 has one, and H_3PO_2 has two. The hydrogens in $P-OH$ groups do not produce the reducing character being compared.

Step 2: Compare the acids Phosphoric acid is non-reducing in this comparison. Phosphorous acid can be oxidised and is reducing, while hypophosphorous acid, with two directly bonded hydrogens, has the strongest reducing character.

Step 3: Conclusion Increasing reducing character: $\boxed{H_3PO_4 < H_3PO_3 < H_3PO_2}$.

Quick Tip to Solve: Draw or recall the structures and count P-H bonds, not the total number of hydrogens.

25(ii). Out of He and Xe, which one can easily form compound and why? [1 mark]

Solution:

Concept:

- Noble gases have closed valence shells; forming compounds requires overcoming their resistance to electron removal or sharing.
- Ionisation enthalpy decreases down Group 18 as atomic size and shielding increase.

Step 1: Compare atomic size and ionisation enthalpy Xenon has many more occupied electron shells than helium. Its outer electrons are farther from the nucleus and more strongly shielded, so its first ionisation enthalpy is much lower than that of helium.

Step 2: Relate the comparison to compound formation The electrons of xenon can therefore participate in bonding with strongly electronegative elements such as fluorine and oxygen more readily. Helium has a very small, tightly held $1s^2$ shell and exceptionally high ionisation enthalpy.

Step 3: Conclusion $\boxed{Xe}$ forms compounds more easily because its ionisation enthalpy is lower than that of He.

Quick Tip to Solve: For noble gas compound formation, compare how tightly the outer electrons are held.

25(iii). Write the conditions to maximize the yield of ammonia in Haber's process. [1 mark]

Solution:

Concept:

- For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the forward reaction is exothermic and reduces the number of gas molecules.
- Le Chatelier's principle predicts how pressure, temperature and removal of product affect equilibrium yield.

Step 1: Choose equilibrium conditions High pressure favours ammonia because four moles of reactant gases form two moles of product gas. Low temperature favours the exothermic forward reaction. Continuous removal of ammonia also shifts equilibrium towards further ammonia formation.

Step 2: State practical operating conditions A very low temperature gives a slow reaction, so industry uses a compromise temperature of about $700\,K$ and a pressure near 200 atm, with an iron catalyst. The catalyst speeds attainment of equilibrium but does not change the equilibrium yield.

Step 3: Conclusion Use high pressure and low temperature to favour the equilibrium yield, with continuous ammonia removal; practically about $700\,K$, 200 atm and an iron catalyst.

Quick Tip to Solve: Count gas molecules and note the heat change before choosing pressure and temperature.

25(iv). Write two uses of Chlorine gas. [1 mark]

Solution:

Concept:

- Chlorine is an oxidising agent and reacts with water to produce species with disinfecting and bleaching action.
- Its applications include treatment of water and bleaching suitable materials.

Step 1: Use in water treatment Chlorine gas is used to disinfect drinking water and swimming-pool water. In controlled quantities it destroys disease-causing microorganisms and helps make the water suitable for use.

Step 2: Use in bleaching Chlorine gas is used as a bleaching agent for wood pulp and suitable textiles. Its bleaching action requires moisture; oxidising species produced on reaction with water destroy the coloured substances.

Step 3: Conclusion Two uses are disinfection of drinking water and bleaching of wood pulp or textiles.

Quick Tip to Solve: State two distinct applications, such as water disinfection and pulp bleaching.

25(v). How can you detect the presence of SO_2 gas? [1 mark]

Solution:

Concept:

- Sulphur dioxide is a reducing agent and reduces orange dichromate(VI) ions to green chromium(III) ions in acidic solution.
- A characteristic colour change provides a chemical test for the gas.

Step 1: Perform the test Pass the gas through a small quantity of acidified potassium dichromate solution, or bring it into contact with paper moistened with that solution. The orange colour changes to green.

Step 2: Explain the observation The gas is oxidised to sulphate while dichromate is reduced:

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O.$$

The formation of green chromium(III) accounts for the observed change.

Step 3: Conclusion Sulphur dioxide turns acidified potassium dichromate solution from orange to green.

Quick Tip to Solve: Remember the complete test observation: acidified dichromate changes orange to green.

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

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

(ii) $C_6H_5OH \xrightarrow{\textbf{Zn dust}} ?$

(iii) $C_6H_5OCH_3 + CH_3COCl \xrightarrow{\textbf{anhyd. } AlCl_3} ?$

(b) Write the mechanism of the following reaction:

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

Solution:

Concept:

- Pyridinium chlorochromate (PCC) oxidises a primary alcohol to an aldehyde without oxidising an isolated carbon-carbon double bond under the usual conditions.
- Zinc dust reduces phenol to benzene. The methoxy group in anisole activates its ring and directs electrophilic substitution to the ortho and para positions.
- At $413\,K$, concentrated sulphuric acid catalyses intermolecular dehydration of ethanol. Protonation converts its poor leaving group $-OH$ into water; a second ethanol molecule acts as the nucleophile.

Step 1: (a)(i) Oxidation of the allylic alcohol The primary alcohol group is oxidised while the double

bond remains intact:

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

The product is prop-2-enal (acrolein). PCC stops at the aldehyde, so the product is not acrylic acid; it also does not saturate the alkene.

Step 2: (a)(ii) Reduction of phenol with zinc dust On heating with zinc dust, the phenolic oxygen is removed as zinc oxide:

$$\mathrm{C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO}.$$

Thus the organic product is benzene. The hydrogen count is conserved: the hydrogen of the hydroxyl group replaces the hydroxyl group on the ring.

Step 3: (a)(iii) Friedel-Crafts acylation of anisole Anhydrous $\mathrm{AlCl_3}$ activates acetyl chloride to generate the electrophile $\mathrm{CH_3CO^+}$. Donation of an oxygen lone pair into the aromatic ring makes the methoxy group ortho/para directing. Consequently,

$$\begin{aligned}\mathrm{C_6H_5OCH_3 + CH_3COCl} &\xrightarrow{\text{anhyd. } \mathrm{AlCl_3}} o\text{-}\mathrm{CH_3OC_6H_4COCH_3} \\ &\quad + p\text{-}\mathrm{CH_3OC_6H_4COCH_3}.\end{aligned}$$

This notation denotes the two alternative organic products of substitution, each formed with elimination of HCl, rather than a balanced equation summing both products. They are 2-methoxyacetophenone and 4-methoxyacetophenone. The para isomer predominates because it experiences less steric crowding between the methoxy and acetyl groups.

Step 4: (b) Protonate ethanol Write $\mathrm{Et} = \mathrm{C_2H_5}$. An oxygen lone pair accepts a proton from the acid:

$$\mathrm{EtOH + H^+ \rightleftharpoons EtOH_2^+}.$$

The resulting ethyloxonium ion has water as a good leaving group. This activation is necessary because direct loss of hydroxide from neutral ethanol is unfavourable.

Step 5: Attack by a second ethanol molecule The oxygen lone pair of another ethanol molecule attacks the primary carbon bonded to water. Carbon-oxygen bond formation and departure of water occur together in an $S_\mathrm{N}2$ step:

$$\mathrm{EtOH + EtOH_2^+ \longrightarrow [Et{-}O(H){-}Et]^+ + H_2O}.$$

The product of this step is protonated diethyl ether. A free primary ethyl carbocation is not required by this mechanism.

Step 6: Regenerate the acid catalyst Loss of a proton from the oxonium ion gives the neutral ether:

$$[\mathrm{Et{-}O(H){-}Et}]^{+} \rightleftharpoons \mathrm{Et{-}O{-}Et} + \mathrm{H}^{+}.$$

Thus the acid is regenerated. Adding the elementary steps gives

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

The specified temperature favours intermolecular 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) Ethanol forms diethyl ether through protonation, nucleophilic substitution by a second ethanol molecule, and deprotonation.

Quick Tip to Solve: At 413 K, join two ethanol molecules through oxygen after removing water; write the protonated ether intermediate to show regeneration of the acid.

OR

26(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 phenol ring and directs electrophilic substitution to the ortho and para positions. In a nonpolar solvent such as $\mathrm{CS_2}$, controlled bromination gives monobromophenols.
- Phenol undergoes Reimer-Tiemann formylation with chloroform and aqueous alkali. Hydrogen iodide cleaves anisole at its methyl-oxygen bond.
- Alcohols contain an acidic hydroxyl hydrogen and react with sodium. The Lucas test distinguishes primary and tertiary alcohols by the rate of formation of an insoluble alkyl chloride.

Step 1: (a)(i) Bromination of phenol in carbon disulphide At low temperature, bromine in $\mathrm{CS_2}$ gives a mixture of ortho- and para-bromophenol, with the para product predominating because it is less sterically hindered:

$$\mathrm{C_6H_5OH} + \mathrm{Br_2} \xrightarrow[\text{low temperature}]{\mathrm{CS_2}} \mathrm{BrC_6H_4OH} + \mathrm{HBr}.$$

Here $\mathrm{BrC_6H_4OH}$ denotes the two positional isomers, 2-bromophenol and 4-bromophenol (major). These are monobromination products under the stated conditions.

Step 2: (a)(ii) Reimer-Tiemann reaction On heating phenol with chloroform and aqueous sodium hydroxide, followed by acidification, 2-hydroxybenzaldehyde (salicylaldehyde) is the major product. A small amount of 4-hydroxybenzaldehyde is also formed. The overall equation, with the neutral organic product shown after work-up, is

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow[\text{then } H^+]{\Delta} \text{o-}HOC_6H_4CHO + 3NaCl + 2H_2O.$$

The formyl group $-CHO$ is introduced mainly adjacent to the hydroxyl group; acidification converts the phenoxide salt into the free phenolic product.

Step 3: (a)(iii) Cleavage of anisole by hydrogen iodide

$$C_6H_5OCH_3 + HI \xrightarrow{\text{heat}} C_6H_5OH + CH_3I.$$

Protonation of the ether oxygen is followed by attack of iodide on the methyl carbon. The methyl-oxygen bond breaks to give phenol and iodomethane. The aryl-oxygen bond has partial double-bond character and is not cleaved by the usual substitution pathway.

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

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

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

Step 5: (b)(ii) Distinguish propanol from tert-butyl alcohol Add Lucas reagent, concentrated hydrochloric acid with anhydrous $ZnCl_2$, to each sample at room temperature. Tert-butyl alcohol produces immediate turbidity from insoluble tert-butyl chloride:

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

Propan-1-ol gives no turbidity at room temperature on the same short time scale, since it is a primary alcohol. If propanol is taken as propan-2-ol, it gives turbidity only after several minutes; either is readily distinguished from the immediate response of the tertiary alcohol. The rapid tertiary reaction follows easy formation of the stable tertiary carbocation.

Step 6: Conclusion The reaction products are ortho- and para-bromophenol (para major), salicylaldehyde (major), and phenol with methyl iodide, respectively. Sodium distinguishes ethanol by hydrogen evolution; Lucas reagent distinguishes tert-butyl alcohol by immediate turbidity.

Quick Tip to Solve: Check the bromination solvent first: bromine in carbon disulphide gives monobromophenols, whereas bromine water gives 2,4,6-tribromophenol.