CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-5-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) All questions are compulsory.

(ii) Section A : Questions number **1 to 5** are very short answer questions and carry **1 mark** each.

(iii) Section B : Questions number **6 to 12** are short answer questions and carry **2 marks** each.

(iv) Section C : Questions number **13 to 24** are also short answer questions and carry **3 marks** each.

(v) Section D : Questions number **25 to 27** are long answer questions and carry **5 marks** each.

(vi) There is no overall choice. However, an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.

(vii) Use of log tables, if necessary. **Use of calculators is not allowed.**

Section A (5 marks)

1. A cube solid is made up of two elements A and B. Element A forms ccp while atoms of element B occupy one-third of the tetrahedral voids. What is the formula of the solid? [1 mark]

Solution:

Concept:

- A cubic close-packed (ccp) arrangement has four atoms per unit cell.
- For N close-packed atoms, there are $2N$ tetrahedral voids; occupied voids count the atoms of the second element.

Step 1: Count the atoms of A Element A forms the ccp lattice, so a conventional unit cell contains $N_A = 4$ atoms. The number of tetrahedral voids is twice this number:

$$N_{\text{tet}} = 2 \times 4 = 8.$$

Step 2: Apply the occupied fraction Only one-third of these voids contain B. Hence

$$N_B = \frac{8}{3}, \qquad A : B = 4 : \frac{8}{3} = 12 : 8 = 3 : 2.$$

The fractional cell-average occupation is permissible; the chemical formula uses the simplest whole-number ratio.

Step 3: Conclusion The formula of the solid is $\boxed{\mathrm{A_3B_2}}$.

Quick Tip to Solve: First double the number of close-packed atoms to count tetrahedral voids, then apply the occupied fraction.

2(a). How will you prepare arsenic sulphide sol in the lab? [1 mark]

Solution:

Concept:

- Arsenic sulphide sol is prepared by a chemical condensation method, specifically double decomposition.
- In a colloidal sol, particles of the dispersed solid remain distributed through the liquid dispersion medium.

Step 1: Pass hydrogen sulphide through the solution Pass H_2S gas through a dilute aqueous solution of arsenious oxide, As_2O_3, with stirring. The reaction forms very small particles of arsenic sulphide rather than a bulk precipitate under the conditions used for sol preparation.

Step 2: Write the formation reaction The balanced double-decomposition reaction is

$$\mathrm{As_2O_3 + 3\,H_2S \longrightarrow As_2S_3 + 3\,H_2O}.$$

The yellow As_2S_3 particles constitute the dispersed phase and water is the dispersion medium.

Quick Tip to Solve: Remember the oxide-to-sulphide conversion: replace the three oxygen atoms by sulphur and form three water molecules.

Step 3: Conclusion Arsenic sulphide sol is obtained by passing H_2S through dilute aqueous As_2O_3.

Quick Tip to Solve: Remember the oxide-to-sulphide conversion: replace the three oxygen atoms by sulphur and form three water molecules.

OR

2(b). Give an example of heterogeneous catalysis. [1 mark]

Solution:

Concept:

- Heterogeneous catalysis occurs when the reactants and the catalyst are in different phases.
- A solid catalyst provides a surface on which gaseous reactants adsorb, react and then leave as products.

Step 1: Choose the Haber process In the manufacture of ammonia, nitrogen and hydrogen gases react in the presence of finely divided solid iron as the catalyst:

$$N_2(g) + 3\,H_2(g) \overset{Fe\,(s)}{\rightleftharpoons} 2\,NH_3(g).$$

Iron increases the reaction rate without being consumed in the net reaction.

Step 2: Compare the physical phases The reactants N_2 and H_2 are gases, whereas the iron catalyst is a solid. Thus the reaction takes place at a gas-solid interface, satisfying the defining condition for heterogeneous catalysis.

Step 3: Conclusion The Haber synthesis of ammonia using solid iron is an example of heterogeneous catalysis.

Quick Tip to Solve: For this example, explicitly identify gaseous nitrogen and hydrogen versus solid iron; the phase difference establishes the type.

3. CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. Why? [1 mark]

Solution:

Concept:

- Addition of HCN to a carbonyl compound begins with nucleophilic attack by CN^- on the electrophilic carbonyl carbon.
- Electron donation by alkyl groups and steric crowding around the carbonyl carbon both reduce the rate of nucleophilic addition.

Step 1: Compare the electronic effect CH_3CHO has one methyl group attached to the carbonyl carbon, whereas CH_3COCH_3 has two. The two methyl groups in acetone donate electron density through their $+I$ effect, decreasing the positive character of the carbonyl carbon more strongly.

Step 2: Compare access for the nucleophile The carbonyl carbon in ethanal is bonded to one methyl

Quick Tip to Solve: For aldehyde versus ketone addition, compare both the number of electron-donating alkyl groups and the crowding at the carbonyl carbon.

group and a small hydrogen atom. Acetone has two methyl groups, which provide greater steric hindrance to attack by CN^-. Both effects therefore favour nucleophilic addition to ethanal.

Step 3: Conclusion CH_3CHO is more reactive because its carbonyl carbon is more electrophilic and less sterically hindered than that of CH_3COCH_3.

Quick Tip to Solve: For aldehyde versus ketone addition, compare both the number of electron-donating alkyl groups and the crowding at the carbonyl carbon.

4. What are the products of exhaustive ammonolysis of an alkyl halide? [1 mark]

Solution:

Concept:

- Ammonolysis replaces the halogen of an alkyl halide by an amino group through reaction with ammonia.
- The initially formed amines also act as nucleophiles, so repeated alkylation can continue up to a quaternary ammonium salt.

Step 1: Identify successive amine products For an alkyl halide RX, the primary amine RNH_2 forms first. Further reaction with alkyl halide gives a secondary amine R_2NH and then a tertiary amine R_3N. These products arise because the nitrogen lone pair remains available for further alkylation.

Step 2: Identify the final alkylation product The tertiary amine can react once more with RX:

$$R_3N + RX \longrightarrow [R_4N]^+X^-.$$

The product is a quaternary ammonium salt. Its nitrogen bears four alkyl groups and a positive charge, so the sequence stops at this stage.

Step 3: Conclusion Exhaustive ammonolysis gives primary, secondary and tertiary amines and a quaternary ammonium salt: RNH_2, R_2NH, R_3N and $[R_4N]^+X^-$.

Quick Tip to Solve: Count the alkyl groups on nitrogen from one to four; the fourth product is an ammonium salt, not a neutral amine.

5(a). What type of isomerism is shown by complex $[Co(NH_3)_5Cl]SO_4$? [1 mark]

Solution:

Concept:

- Ionisation isomerism arises when a coordinated ligand and a counter-ion exchange positions while the overall composition remains the same.
- Ionisation isomers produce different ions on dissolution because the species outside the coordination sphere is different.

Step 1: Identify the coordinated and external anions In $[Co(NH_3)_5Cl]SO_4$, chloride is inside the

Quick Tip to Solve: Look across the square brackets: exchange coordinated chloride with external sulphate to recognise ionisation isomerism.

square brackets and is bonded to cobalt, while sulphate lies outside as the counter-ion. These two anions can exchange their roles without changing the overall composition.

Step 2: Write the corresponding isomer The ionisation isomer is $[Co(NH_3)_5SO_4]Cl$. The original compound releases SO_4^{2-} as its counter-ion in solution, whereas the isomer releases Cl^-. Their different ionisation behaviour establishes the isomerism.

Step 3: Conclusion $[Co(NH_3)_5Cl]SO_4$ shows $\boxed{\text{ionisation isomerism}}$, with $[Co(NH_3)_5SO_4]Cl$ as its isomer.

Quick Tip to Solve: Look across the square brackets: exchange coordinated chloride with external sulphate to recognise ionisation isomerism.

OR

5(b). Arrange the following in increasing order of crystal field splitting energy:
$[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$, $[CrCl_6]^{3-}$ [1 mark]

Solution:

Concept:

- For octahedral complexes with the same metal ion and oxidation state, crystal field splitting Δ_o increases with ligand field strength.
- The relevant spectrochemical-series order is $Cl^- < NH_3 < CN^-$.

Step 1: Check the common metal oxidation state In both anionic complexes the six monovalent ligands contribute charge -6, so chromium is in oxidation state $+3$. In $[Cr(NH_3)_6]^{3+}$, ammonia is neutral and chromium is again $+3$. Thus ligand strength is the basis of comparison.

Step 2: Rank the ligand fields Chloride is a weak-field ligand, ammonia produces a stronger field, and cyanide is the strongest of these three ligands. With chromium(III) and octahedral coordination common to all, the splitting increases in the same order as these ligand strengths.

Step 3: Conclusion The increasing order is

$$[CrCl_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}.$$

Quick Tip to Solve: Check that all three centres are chromium(III), then use the ligand order chloride, ammonia, cyanide; do not rank by complex charge.

Section B (14 marks)

6. Following reactions may occur at cathode and anode during electrolysis of aqueous sodium chloride. What products will be held at anode and cathode? Use given E° values to justify your answer.

Cathode: $Na^+(aq) + e^- \rightarrow Na(s)$; $E^\circ = -2.71$ V

$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$; $E^\circ = 0.00$ V

Anode: $Cl^-(aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$; $E^\circ = +1.36$ V

$2H_2O(aq) \rightarrow O_2(g) + 4H^+ + 4e^-$; $E^\circ = +1.23$ V [2 marks]

Solution:

Concept:

- Reduction occurs at the cathode; the species with the more positive reduction potential is more readily reduced.
- Anode products depend on both the electrode potential and overpotential, the extra potential needed for a reaction to proceed at an appreciable rate.

Step 1: Choose the cathode reaction The given reduction potentials are $E^\circ(\mathrm{Na^+/Na}) = -2.71\,\mathrm{V}$ and $E^\circ(\mathrm{H^+/H_2}) = 0.00\,\mathrm{V}$. Hydrogen formation is therefore preferred over sodium deposition. In aqueous solution, water supplies hydrogen and the cathode reaction can be written as

$$2\mathrm{H_2O} + 2e^- \longrightarrow \mathrm{H_2} + 2\mathrm{OH^-}.$$

Thus sodium ions remain in solution while hydrogen gas is liberated.

Step 2: Account for the anode overpotential From the given values alone, oxygen evolution at $1.23\,\mathrm{V}$ would be expected before chlorine evolution at $1.36\,\mathrm{V}$. However, oxygen evolution has a high overpotential. Hence, in electrolysis of aqueous sodium chloride, chloride ions are oxidised preferentially:

$$2\mathrm{Cl^-} \longrightarrow \mathrm{Cl_2} + 2e^-.$$

This explains why the actual anode product is chlorine despite the smaller listed potential for oxygen evolution.

Step 3: Conclusion Cathode: hydrogen gas; anode: chlorine gas. The cathode choice follows the reduction potentials; the anode choice requires the oxygen overpotential.

Quick Tip to Solve: Compare reduction potentials at the cathode, but include oxygen overpotential when selecting the anode product in aqueous NaCl.

7. Show that for a first order reaction, time required for completion of 99% of reaction is twice the time required for completion of 90% of reaction. [2 marks]

Solution:

Concept:

- For a first order reaction, $t = \dfrac{2.303}{k}\log_{10}\dfrac{a}{a-x}$, where a is the initial concentration, x is the concentration reacted and k is the rate constant.
- After 90% completion the fraction remaining is 0.10; after 99% completion it is 0.01.

Step 1: Calculate the time for 90 percent completion At 90% completion, the unreacted concentration is $a - x = 0.10a$. Substitution in the integrated rate law gives

$$t_{90\%} = \frac{2.303}{k}\log_{10}\frac{a}{0.10a} = \frac{2.303}{k}\log_{10} 10 = \frac{2.303}{k}.$$

The initial concentration cancels, as expected for the time required to consume a fixed fraction in a first order reaction.

Step 2: Calculate the time for 99 percent completion and compare At 99% completion, only 1% of the initial reactant remains, so $a - x = 0.01a$. Therefore,

$$t_{99\%} = \frac{2.303}{k}\log_{10}\frac{a}{0.01a} = \frac{2.303}{k}\log_{10} 100 = \frac{2(2.303)}{k}.$$

Taking the ratio gives $t_{99\%}/t_{90\%} = 2$. The same rate constant applies to both times because they refer to the same reaction under the same conditions.

Step 3: Conclusion $\boxed{t_{99\%} = 2t_{90\%}}$. Hence the time for 99 percent completion is twice that for 90 percent completion.

Quick Tip to Solve: Use the fraction left, not the fraction reacted: 90 percent and 99 percent completion leave 1/10 and 1/100 respectively.

8. Arrange the hydrides of group 16 in order of increasing boiling points, giving reason. Name the hydride which is most stable thermodynamically. [2 marks]

Solution:

Concept:

- The usual group 16 hydrides considered are H_2O, H_2S, H_2Se and H_2Te.
- London dispersion forces increase as molecular mass and polarisability increase; strong intermolecular hydrogen bonding gives water an exceptionally high boiling point.
- Thermodynamic stability of these hydrides decreases down the group as the element–hydrogen bond becomes weaker.

Step 1: Compare the boiling points of the heavier hydrides From H_2S to H_2Se to H_2Te, molecular size and polarisability increase. The resulting stronger dispersion forces require progressively more energy to separate the molecules into the gas phase. Their increasing boiling point order is therefore

Quick Tip to Solve: First order sulphur, selenium and tellurium hydrides by increasing size; then place water highest because of hydrogen bonding.

$H_2S < H_2Se < H_2Te$.

Step 2: Place water and identify the most stable hydride Oxygen is small and highly electronegative, so water molecules form strong intermolecular hydrogen bonds. These attractions make its boiling point higher than those of the other hydrides despite its lower molecular mass. Water must therefore be placed last in the increasing order. Water is also the most thermodynamically stable hydride: the strong $O-H$ bonds make it less prone to decomposition than the heavier group 16 hydrides.

Step 3: Conclusion Increasing boiling points: $\boxed{H_2S < H_2Se < H_2Te < H_2O}$. The most thermodynamically stable hydride is $\boxed{H_2O}$.

Quick Tip to Solve: First order sulphur, selenium and tellurium hydrides by increasing size; then place water highest because of hydrogen bonding.

9. How is $KMnO_4$ prepared from pyrolusite? Give steps involved with equations. [2 marks]

Solution:

Concept:

- Pyrolusite contains MnO_2, in which manganese has oxidation state $+4$.
- Preparation first oxidises manganese to green manganate, MnO_4^{2-}, and then to purple permanganate, MnO_4^-.

Step 1: Fuse pyrolusite with potassium hydroxide Finely powdered pyrolusite is fused with KOH in the presence of air or oxygen. The oxidation produces green potassium manganate:

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O.$$

Manganese changes from $+4$ in the ore to $+6$ in manganate. The fused mass is extracted with water to obtain an aqueous manganate solution.

Step 2: Oxidise manganate to permanganate The manganate solution is electrolytically oxidised. At the anode, manganate loses one electron:

$$MnO_4^{2-} \longrightarrow MnO_4^- + e^-.$$

Manganese thus changes from $+6$ to $+7$. Combining this with water reduction at the cathode gives

$$2K_2MnO_4 + 2H_2O \xrightarrow{\text{electrolysis}} 2KMnO_4 + 2KOH + H_2.$$

The purple solution is concentrated and cooled to crystallise potassium permanganate.

Step 3: Conclusion $\boxed{MnO_2 \xrightarrow[O_2]{KOH,\,\Delta} K_2MnO_4 \xrightarrow{\text{electrolytic oxidation}} KMnO_4}$.

Quick Tip to Solve: Track manganese through $+4$, $+6$ and $+7$: alkaline fusion makes green manganate; further oxidation makes purple permanganate.

10(a). An aromatic compound 'A' on treatment with $CHCl_3$ and KOH gives two compounds, both of which give same product 'B' when distilled with Zinc dust. Oxidation of 'B' gives 'C' with molecular formula $C_7H_6O_2$. Sodium salt of 'C' on heating with soda lime gives 'D' which may also be obtained by distilling 'A' with Zinc dust. Identify 'A', 'B', 'C' and 'D'. [2 marks]

Solution:

Concept:

- The Reimer–Tiemann reaction introduces a formyl group, $-CHO$, into phenol, mainly at the ortho position with a smaller para product.
- Distillation with zinc dust removes the phenolic oxygen, whereas oxidation of an aldehyde yields the corresponding carboxylic acid.
- Soda lime decarboxylates a sodium carboxylate: $RCOONa + NaOH \xrightarrow{CaO,\,\Delta} RH + Na_2CO_3$.

Step 1: Identify A and the common product B The compound A is phenol, C_6H_5OH. Treatment with $CHCl_3$ and KOH, followed by acidification, gives 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde. On distillation with zinc dust, the phenolic $-OH$ group in each product is replaced by hydrogen. Both isomers therefore yield the same compound, benzaldehyde:

$$HOC_6H_4CHO + Zn \xrightarrow{\Delta} C_6H_5CHO + ZnO.$$

Hence $B = C_6H_5CHO$.

Step 2: Identify C and verify D by both routes Oxidising benzaldehyde converts its aldehyde group into a carboxylic acid:

$$C_6H_5CHO + [O] \longrightarrow C_6H_5COOH.$$

Thus C is benzoic acid, whose molecular formula is $C_7H_6O_2$, as given. Its sodium salt gives benzene on heating with soda lime:

$$C_6H_5COONa + NaOH \xrightarrow{CaO,\,\Delta} C_6H_6 + Na_2CO_3.$$

Independently, phenol also gives benzene with zinc dust:

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

Both routes identify D consistently.

Step 3: Conclusion $\boxed{A = \text{phenol}, \quad B = \text{benzaldehyde},}$ $\boxed{C = \text{benzoic acid}, \quad D = \text{benzene}.}$

Quick Tip to Solve: Work backwards from C7H6O2 as benzoic acid: its aldehyde precursor is benzaldehyde and soda lime removes its carboxyl carbon.

OR

10(b). How do you convert the following:

(a) Phenol to Toluene

(b) Ethanol to Ethanal [2 marks]

Solution:

Concept:

- Distillation of phenol with zinc dust removes the oxygen of the hydroxyl group and gives benzene.
- Friedel–Crafts alkylation introduces a methyl group into benzene using methyl chloride and anhydrous aluminium chloride. A primary alcohol gives an aldehyde on controlled dehydrogenation.

Step 1: (a) Convert phenol into benzene, then methylate benzene First distil phenol with zinc dust. The oxygen is removed as zinc oxide:

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

Treat the benzene obtained with methyl chloride in the presence of anhydrous $AlCl_3$:

$$C_6H_6 + CH_3Cl \xrightarrow{\text{anhydrous } AlCl_3} C_6H_5CH_3 + HCl.$$

This introduces $-CH_3$ into the benzene ring. Direct alkylation of phenol would retain its hydroxyl group, so its removal is essential before preparing toluene.

Step 2: (b) Dehydrogenate ethanol to ethanal Pass ethanol vapour over heated copper at $573\,K$:

$$CH_3CH_2OH \xrightarrow{Cu,\ 573\,K} CH_3CHO + H_2.$$

One hydrogen is removed from the hydroxyl group and another from its carbon, forming the carbonyl group of ethanal while keeping the two-carbon skeleton unchanged.

Step 3: Conclusion (a) Phenol $\xrightarrow{Zn,\Delta}$ benzene $\xrightarrow{CH_3Cl/\text{anhydrous } AlCl_3}$ toluene. (b) Ethanol gives ethanal over copper at $573\,K$.

Quick Tip to Solve: For phenol to toluene, remove oxygen before adding the methyl group; use hot copper to stop ethanol at the aldehyde.

11(a). What happens when D-glucose is treated with the following? Give equations to support your answer.

(a) HI

(b) HNO_3 [2 marks]

Solution:

Concept:

- The open-chain structure of D-glucose is $CHO-(CHOH)_4-CH_2OH$, with six carbon atoms connected in one chain.
- Prolonged heating with HI reduces glucose to a hydrocarbon. Nitric acid oxidises both its aldehyde end and its primary alcohol end to carboxyl groups.

Step 1: (a) Heat D-glucose with HI On prolonged heating with excess hydriodic acid, the oxygen-containing groups are removed and glucose gives n-hexane. The balanced equation is

$$C_6H_{12}O_6 + 14HI \xrightarrow{\text{heat}} C_6H_{14} + 6H_2O + 7I_2.$$

Here C_6H_{14} is the straight-chain product $CH_3(CH_2)_4CH_3$. Its formation shows that the six carbon atoms of glucose are linked in a straight chain; the carbon skeleton is retained during reduction.

Step 2: (b) Oxidise D-glucose with nitric acid Nitric acid is a strong oxidising agent. It converts the terminal $-CHO$ and $-CH_2OH$ groups into $-COOH$, producing saccharic acid (glucaric acid):

$$CHO-(CHOH)_4-CH_2OH + 3[O]$$

$$\xrightarrow{HNO_3} HOOC-(CHOH)_4-COOH + H_2O.$$

The four internal secondary alcohol groups remain in the product. The symbol $[O]$ denotes oxygen supplied by the oxidising agent; both ends, rather than just the aldehyde end, are oxidised.

Step 3: Conclusion (a) D-glucose gives n-hexane on prolonged heating with HI. (b) It gives saccharic acid, $HOOC-(CHOH)_4-COOH$, on oxidation with HNO_3.

Quick Tip to Solve: HI removes oxygen groups to reveal the carbon chain; nitric acid changes both ends of glucose into carboxyl groups.

OR

11(b). Give any two points of difference between globular and fibrous proteins. [2 marks]

Solution:

Concept:

- The shape and folding of a protein determine its physical properties. Globular proteins have compact, roughly spherical shapes, whereas fibrous proteins have long, fibre-like shapes.
- Water solubility provides another standard distinction between these two protein classes; it is stated as a general property rather than an exception-free rule.

Quick Tip to Solve: Compare the same property in both classes: first shape, then water solubility; insulin and keratin help recall the contrast.

Step 1: First difference: shape and arrangement of chains In globular proteins, the polypeptide chains coil and fold into compact, approximately spherical structures. Insulin is an example. In fibrous proteins, the polypeptide chains form extended, thread-like or fibre-like structures, with chains commonly held together by hydrogen bonds and disulphide bonds. Keratin, found in hair and wool, is an example. Thus the structural comparison is compact and spherical versus elongated and fibrous.

Step 2: Second difference: solubility in water Globular proteins are generally soluble in water, whereas fibrous proteins are generally insoluble in water. Compact globular proteins often expose polar groups to water on their outer surfaces, which helps explain their solubility. Fibrous proteins form tough structures suited to structural roles; keratin does not dissolve in water. State this solubility distinction separately from shape so that the answer supplies two different points of comparison.

Step 3: Conclusion Globular proteins are compact and roughly spherical, and generally water-soluble. Fibrous proteins are long and fibre-like, and generally water-insoluble.

Quick Tip to Solve: Compare the same property in both classes: first shape, then water solubility; insulin and keratin help recall the contrast.

12. Write two differences between DNA and RNA. [2 marks]

Solution:

Concept:

- DNA is deoxyribonucleic acid and RNA is ribonucleic acid. Both are nucleic acids built from nucleotides containing a pentose sugar, a phosphate group and a nitrogenous base.
- Their sugar components and one of their pyrimidine bases differ. These chemical differences provide two direct comparisons independent of their biological functions.

Step 1: First difference: the pentose sugar DNA contains 2-deoxy-D-ribose, whereas RNA contains D-ribose. At the $2'$ carbon of the sugar, DNA has a hydrogen atom in place of the hydroxyl group present in RNA. Thus deoxyribose has one fewer oxygen atom than ribose. This difference accounts for the names deoxyribonucleic acid and ribonucleic acid; the phosphate component is common to both.

Step 2: Second difference: the nitrogenous bases The bases in DNA are adenine, guanine, cytosine and thymine, written A, G, C and T. RNA contains adenine, guanine, cytosine and uracil, written A, G, C and U. Adenine, guanine and cytosine are common to both, so the distinguishing base is thymine in DNA versus uracil in RNA. Comparing all four bases avoids suggesting that the two nucleic acids have entirely different sets of bases.

Step 3: Conclusion (i) DNA contains 2-deoxy-D-ribose; RNA contains D-ribose. (ii) DNA contains thymine, whereas RNA contains uracil in its place; A, G and C are common to both.

Quick Tip to Solve: Link the D in DNA to deoxyribose, and remember the base replacement T in DNA becomes U in RNA.

Section C (36 marks)

13. (a) Following is the alignment of magnetic moments of a substance when placed in a magnetic field. Identify the type of magnetism exhibited by the substance.

(b) Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions? [3 marks]



Solution:

Concept:

- Ferromagnetism results from parallel alignment of magnetic moments, giving a large resultant magnetic moment in the direction of the applied field.
- Electrical neutrality requires the total positive charge on nickel ions to equal the magnitude of the negative charge on oxide ions. Each oxide ion is O^{2-}.

Step 1: (a) Identify the alignment All five arrows in the printed figure point in the same direction. Thus the magnetic moments reinforce one another rather than cancel. This parallel arrangement is characteristic of ferromagnetism. In an antiferromagnetic arrangement, equal neighbouring moments would point in opposite directions and cancel; that is not the arrangement shown here.

Step 2: (b) Determine the amounts of the two nickel ions Consider one formula unit of $Ni_{0.98}O_{1.00}$. Let the amount of Ni^{3+} be x, so the amount of Ni^{2+} is $0.98 - x$. The single oxide ion contributes charge -2. Therefore neutrality gives

$$2(0.98 - x) + 3x = 2 \quad \Rightarrow \quad 1.96 + x = 2 \quad \Rightarrow \quad x = 0.04.$$

Hence the amounts per formula unit are 0.04 of Ni^{3+} and 0.94 of Ni^{2+}. The extra positive charge from the trivalent ions compensates for the deficiency of nickel relative to stoichiometric NiO.

Step 3: Express the fractions among the nickel ions The total amount of nickel is 0.98, so the requested fractions must be normalised by this total:

$$f(Ni^{2+}) = \frac{0.94}{0.98} = \frac{47}{49} \approx 0.9592, \qquad f(Ni^{3+}) = \frac{0.04}{0.98} = \frac{2}{49} \approx 0.0408.$$

They add to unity, and the charge check is $2(0.94) + 3(0.04) = 2.00$, as required.

Step 4: Conclusion (a) The substance exhibits $\boxed{\text{ferromagnetism}}$. (b) The fractions of nickel ions are $\boxed{47/49 \text{ as } Ni^{2+}}$ and $\boxed{2/49 \text{ as } Ni^{3+}}$, approximately 95.92% and 4.08%, respectively.

Quick Tip to Solve: Find ionic amounts from charge neutrality first, then divide each amount by 0.98 to obtain fractions of the nickel ions.

14. Calculate the emf of the following cell at 25°C:

Al(s) | Al^{3+} (0.001 M) || (0.1 M) Ni^{2+} | Ni(s)

Given: $E^{\circ}_{(Ni^{2+}/Ni)}$ = -0.25 V; $E^{\circ}_{(Al^{3+}/Al)}$ = -1.66 V

[log 2 = 0.3010, log 3 = 0.4771] [3 marks]

Solution:

Concept:

- The standard cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$, using the standard reduction potentials at both electrodes.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred in the balanced cell reaction and Q is its reaction quotient. Pure solids have unit activity.

Step 1: Identify the electrodes and balance the cell reaction The aluminium electrode on the left undergoes oxidation and is the anode; the nickel electrode on the right undergoes reduction and is the cathode. The half-reactions are

$$\begin{aligned} \text{Al(s)} &\longrightarrow \text{Al}^{3+}(\text{aq}) + 3e^-, \\ \text{Ni}^{2+}(\text{aq}) + 2e^- &\longrightarrow \text{Ni(s)}. \end{aligned}$$

Multiplying the first by two and the second by three gives

$$2\text{Al(s)} + 3\text{Ni}^{2+}(\text{aq}) \longrightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Ni(s)}.$$

Thus $n = 6$. The electron count and the powers in Q must come from this balanced reaction.

Step 2: Calculate the standard potential and reaction quotient Using the supplied reduction potentials,

$$E^{\circ}_{\text{cell}} = (-0.25) - (-1.66) = 1.41\,\text{V}.$$

Potentials are not multiplied by the stoichiometric coefficients. Since the pure solid electrodes do not appear in Q,

$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \frac{(0.001)^2}{(0.1)^3} = \frac{10^{-6}}{10^{-3}} = 10^{-3}, \qquad \log Q = -3.$$

Step 3: Apply the Nernst equation Substituting at the stated temperature,

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6}(-3) \\ &= 1.41 + 0.02955 \\ &= 1.43955\,\text{V}. \end{aligned}$$

The small quotient $Q < 1$ makes the Nernst correction positive, so the calculated emf should exceed the standard emf, consistent with this result.

Step 4: Conclusion The emf of the given cell at 25°C is $\boxed{E_{\text{cell}} \approx 1.44\,\text{V}}$.

Quick Tip to Solve: Balance aluminium's three-electron oxidation with nickel's two-electron reduction before using n = 6 and the concentration powers 2 and 3.

15. The reaction between A and B is first order with respect to A and zero order with respect to B. For this reaction, fill in the blanks in the following table. [3 marks]

Experiment	[A] mol/L	[B] mol/L	Initial Rate Mol/L/min
I	0·1	0·1	$2{\cdot}0 \times 10^{-2}$
II	–	0·2	$4{\cdot}0 \times 10^{-2}$
III	0·4	0·4	–
IV	–	0·2	$2{\cdot}0 \times 10^{-2}$

Solution:

Concept:

- The order with respect to a reactant is its concentration exponent in the rate law. First order in A and zero order in B give $r = k[A]^1[B]^0 = k[A]$, where r is the initial rate and k is the rate constant.
- At fixed temperature, changing $[B]$ does not change this rate, while multiplying $[A]$ by a factor multiplies the rate by the same factor. The overall order is one, so k has units of reciprocal time.

Step 1: Determine the rate constant from experiment I Experiment I supplies both $[A] = 0.1\,\text{mol}\,\text{L}^{-1}$ and $r = 2.0 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}\,\text{min}^{-1}$. Substitution into the rate law gives

$$k = \frac{r}{[A]} = \frac{2.0 \times 10^{-2}}{0.1} = 0.20\,\text{min}^{-1}.$$

Use this rate constant in every experiment.

Step 2: Fill the missing A concentration in experiment II The rate in experiment II is twice the rate in experiment I. Since the rate is proportional to $[A]$, its A concentration must also double. Explicitly,

$$[A]_{\text{II}} = \frac{4.0 \times 10^{-2}}{0.20} = 0.20\,\text{mol}\,\text{L}^{-1}.$$

Step 3: Fill the missing rate in experiment III In experiment III, A has four times its concentration in experiment I, so the rate also quadruples:

$$r_{\text{III}} = 0.20(0.4) = 0.080 = 8.0 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}\,\text{min}^{-1}.$$

Step 4: Fill the missing A concentration in experiment IV Its rate equals that of experiment I, so its A concentration must equal that in experiment I, even though its B concentration differs:

$$[A]_{\text{IV}} = \frac{2.0 \times 10^{-2}}{0.20} = 0.10\,\text{mol}\,\text{L}^{-1}.$$

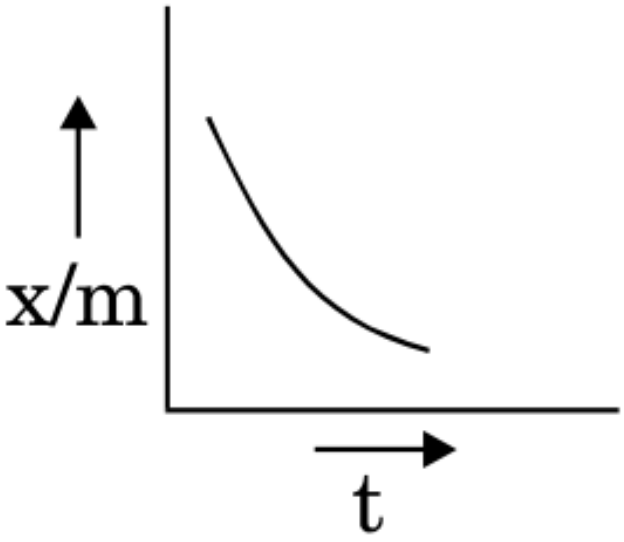
Step 5: Conclusion The blanks are $\boxed{[A]_{\text{II}} = 0.20\,\text{mol}\,\text{L}^{-1}}$, $\boxed{r_{\text{III}} = 8.0 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}\,\text{min}^{-1}}$, and $\boxed{[A]_{\text{IV}} = 0.10\,\text{mol}\,\text{L}^{-1}}$.

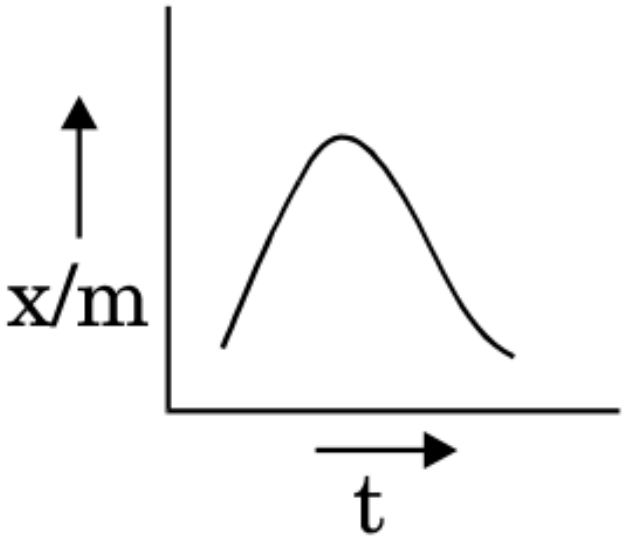
Quick Tip to Solve: Ignore changes in B for this zero-order dependence: compare each rate directly with experiment I using the ratio of A concentrations.

16. (a) A colloidal solution of AgI is prepared by adding $AgNO_3$ solution drop-by-drop to excess of KI solution. What will be the charge on the sol so formed? What is the cause of the charge?

(b) Which of the following adsorption isobars represents physisorption? Justify the answer. (x/m - Extent of adsorption; t - temperature)

(c) Two gases A and B have critical temperatures 430 K and 190 K respectively. Which gas will be readily adsorbed and why? [3 marks]





Solution:

Concept:

- A colloidal precipitate acquires charge by preferentially adsorbing the ion common to its lattice that is present in excess in the dispersion medium.
- Physisorption is exothermic and involves weak van der Waals forces; at constant pressure, its extent decreases as temperature increases.

Quick Tip to Solve: For an ionic sol, identify the excess lattice ion; for gas adsorption, compare critical temperatures and favour the gas that liquefies more easily.

- A higher critical temperature indicates easier liquefaction and stronger intermolecular attractions, favouring physical adsorption under comparable conditions.

Step 1: (a) Determine the charge on the AgI sol On adding silver nitrate to potassium iodide, the reaction is

$$\mathrm{AgNO_3 + KI \longrightarrow AgI + KNO_3}.$$

Since KI is in excess, iodide ions, $\mathrm{I^-}$, remain abundant in the solution. The AgI particles preferentially adsorb these common ions on their surfaces and consequently acquire a negative charge. Potassium ions act as counter-ions in the surrounding medium; they do not give the AgI particles a positive charge.

Step 2: (b) Identify the physisorption isobar The first (left-hand) isobar, in which x/m continuously decreases as t increases, represents physisorption. Here x is the amount of gas adsorbed and m the mass of adsorbent. Physical adsorption releases heat, so increasing temperature favours desorption and reduces the amount adsorbed at fixed pressure. The second curve initially rises with temperature; this initial increase is characteristic of chemisorption requiring activation energy, rather than the physisorption curve asked for here.

Step 3: (c) Compare the two gases Gas A has a critical temperature of $430\,\mathrm{K}$, higher than the $190\,\mathrm{K}$ of gas B. Thus A is more easily liquefied and has stronger intermolecular attractions. Under the same adsorption conditions, these stronger attractions favour its retention on the adsorbent surface, so A is more readily adsorbed.

Step 4: Conclusion (a) The AgI sol is negatively charged due to preferential adsorption of $\mathrm{I^-}$ from excess KI. (b) The first, decreasing isobar represents physisorption because it is exothermic. (c) Gas A is more readily adsorbed owing to its higher critical temperature and easier liquefaction.

Quick Tip to Solve: For an ionic sol, identify the excess lattice ion; for gas adsorption, compare critical temperatures and favour the gas that liquefies more easily.

17(a). State the principle involved in the following metallurgical processes:

(a) Froth Floatation

(b) Zone Refining

(c) Vapour Phase Refining [3 marks]

Solution:

Concept:

- Metallurgical separation exploits a difference in physical properties or chemical behaviour between the desired material and impurities.
- Froth flotation uses selective wetting; zone refining uses different solubilities in liquid and solid metal; vapour phase refining uses selective formation and decomposition of a volatile compound.

Step 1: (a) Principle of froth flotation Froth flotation is based on the difference in the wetting properties of sulphide ore particles and gangue. The sulphide particles are preferentially wetted by oil, whereas the gangue particles are wetted by water. On passing air through the agitated mixture,

Quick Tip to Solve: Remember the distinctive property for each process: flotation uses wetting, zone refining uses melt solubility, and vapour refining uses volatility plus decomposition.

the oil-coated ore particles attach to air bubbles and rise with the froth; the water-wetted gangue remains behind. The froth can then be skimmed off to recover the concentrated ore.

Step 2: (b) Principle of zone refining Zone refining is based on impurities being more soluble in the molten metal than in the solid metal. A narrow molten zone is moved slowly along a metal rod. As the melt solidifies behind the moving heater, relatively pure metal crystallises while impurities preferentially remain in the liquid zone. Repeated passes carry and concentrate the impurities at one end, which is removed. This method can provide very high purity for materials such as silicon and germanium.

Step 3: (c) Principle of vapour phase refining The impure metal is converted selectively into a volatile compound, which is separated from the non-volatile impurities. The purified vapour is then decomposed under suitable conditions to deposit pure metal. Therefore, the metal must form a volatile compound with an appropriate reagent, and that compound must decompose readily to regenerate the metal. For example, nickel forms volatile $\mathrm{Ni(CO)_4}$, which decomposes on heating to give pure nickel and carbon monoxide.

Step 4: Conclusion Froth flotation depends on preferential wetting by oil and water; zone refining depends on greater impurity solubility in the molten metal; vapour phase refining depends on forming a volatile metal compound and subsequently decomposing it to obtain pure metal.

Quick Tip to Solve: Remember the distinctive property for each process: flotation uses wetting, zone refining uses melt solubility, and vapour refining uses volatility plus decomposition.

OR

17(b). Give one point of difference between the following:

(a) Cast Iron and Pig Iron

(b) Hydraulic Washing and Liquation

(c) Leaching and Roasting [3 marks]

Solution:

Concept:

- Carbon content distinguishes the iron products: pig iron obtained from the blast furnace contains more carbon than cast iron prepared from it.
- Hydraulic washing exploits a density difference, whereas liquation exploits a melting-point difference.
- Leaching selectively dissolves an ore constituent in a suitable reagent; roasting heats an ore strongly in excess air to cause chemical conversion.

Step 1: (a) Cast iron and pig iron The distinguishing point is their carbon content. Pig iron contains about 4% carbon, whereas cast iron contains about 3% carbon and therefore has a lower carbon content. Pig iron is the iron obtained from the blast furnace; cast iron is prepared by melting pig iron with scrap iron and coke using a hot-air blast. The percentage comparison is the requested difference, and the preparation explains the relation between the two products.

Quick Tip to Solve: State the same comparison property for both members of each pair: carbon content, separating physical property, or the treatment applied to the ore.

Step 2: (b) Hydraulic washing and liquation Hydraulic washing separates ore from lighter gangue on the basis of a difference in density. A stream of water removes the lighter particles while the heavier ore particles remain. Liquation, in contrast, separates a low-melting metal from higher-melting impurities on the basis of a difference in melting points: the metal melts and flows away, while the solid impurities remain behind. Thus the distinguishing physical property is density for hydraulic washing and melting point for liquation.

Step 3: (c) Leaching and roasting Leaching involves treating the ore with a suitable chemical reagent so that the desired constituent dissolves selectively while insoluble impurities are left behind. Roasting involves strong heating of the ore in an excess supply of air, commonly converting a sulphide into its oxide and releasing sulphur dioxide. Thus leaching separates through selective dissolution in a reagent, whereas roasting changes the ore chemically by heating in air.

Step 4: Conclusion (a) Cast iron has about 3% carbon, while pig iron has about 4%. (b) Hydraulic washing uses a density difference; liquation uses a melting-point difference. (c) Leaching uses selective chemical dissolution; roasting uses strong heating in excess air.

Quick Tip to Solve: State the same comparison property for both members of each pair: carbon content, separating physical property, or the treatment applied to the ore.

18(a). Give reasons for the following:

(a) The only oxidation state shown by Scandium is +3.

(b) $[Ti(H_2O)_6]^{4+}$ **is colourless.**

(c) MnO **is basic while** Mn_2O_7 **is acidic.** [3 marks]

Solution:

Concept:

- The oxidation states of a metal depend on the electrons available for removal and the stability of the resulting configuration. Scandium has configuration $[Ar]3d^1 4s^2$.
- A d-d transition requires an occupied d orbital and an empty d orbital at a suitable higher energy. A d^0 ion cannot undergo such a transition.
- Lower oxidation state metal oxides are generally ionic and basic; higher oxidation state oxides become more covalent and acidic.

Step 1: (a) Explain the +3 state of scandium Scandium loses its two $4s$ electrons and its one $3d$ electron to form Sc^{3+}:

$$Sc : [Ar]3d^1 4s^2 \quad \longrightarrow \quad Sc^{3+} : [Ar].$$

The resulting noble-gas configuration is particularly stable. The $+1$ and $+2$ states do not give this configuration, while removal of a fourth electron would require breaking into the stable argon core and therefore demands a very high ionisation energy. Thus $+3$ is the characteristic oxidation state of scandium in its compounds.

Step 2: (b) Explain the colourless titanium complex Water is a neutral ligand, so the oxidation state of titanium in $[Ti(H_2O)_6]^{4+}$ is $+4$. Neutral titanium is $[Ar]3d^2 4s^2$; loss of four electrons gives

Quick Tip to Solve: First find the metal's oxidation state; then check its d-electron count for colour and the oxidation state trend for oxide acidity.

Ti^{4+} : $[Ar]3d^0$. Although the ligands split the energies of the d orbitals, there is no d electron to excite between them. Hence no visible-light d-d absorption occurs and the complex is colourless.

Step 3: (c) Compare the manganese oxides Manganese has oxidation state $+2$ in MnO and $+7$ in Mn_2O_7. The low oxidation state makes MnO predominantly ionic and basic; it neutralises acids:

$$MnO + 2HCl \longrightarrow MnCl_2 + H_2O.$$

The high oxidation state makes Mn_2O_7 covalent and acidic. It is the acid anhydride of permanganic acid:

$$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4.$$

Step 4: Conclusion Scandium forms stable Sc^{3+} with an argon core; Ti^{4+} is d^0 and cannot undergo d-d transitions; and the rise from Mn(+2) to Mn(+7) changes the oxide from basic MnO to acidic Mn_2O_7.

Quick Tip to Solve: First find the metal's oxidation state; then check its d-electron count for colour and the oxidation state trend for oxide acidity.

OR

18(b). Answer the following:

(a) What is the general electronic configuration of lanthanoids?

(b) What are the common oxidation states of Cerium (At. no. 58)?

(c) Why do actinoids show a wide range of oxidation states? [3 marks]

Solution:

Concept:

- Lanthanoids show progressive filling of the $4f$ subshell after the xenon core, whereas actinoids involve the $5f$ subshell after the radon core.
- Removal of outer electrons produces oxidation states; a noble-gas core or an empty, half-filled or filled subshell can favour a particular state.
- Electrons in subshells of comparable energy can participate in bonding, giving a greater variety of oxidation states.

Step 1: (a) State the lanthanoid configuration The general electronic configuration is

$$\boxed{[Xe]4f^{1-14}5d^{0-1}6s^2}.$$

Here $[Xe]$ denotes the xenon noble-gas core. The superscripts indicate the ranges of possible occupancies, not subtraction. As atomic number increases through the lanthanoid series, the added electrons enter mainly the $4f$ subshell. The $5d$ occupancy can be zero or one because the $4f$ and $5d$ levels are close in energy. If lanthanum is included with this family, the range is often written $4f^{0-14}$, since La is $[Xe]5d^16s^2$.

Quick Tip to Solve: Associate lanthanoids with 4f filling, Ce(IV) with the xenon core, and actinoid variability with the close energies of 5f, 6d and 7s.

Step 2: (b) Find the common oxidation states of cerium Cerium, with atomic number 58, has ground-state configuration

$$\mathrm{Ce} : [\mathrm{Xe}]4f^1 5d^1 6s^2.$$

Its common oxidation states are $+3$ and $+4$. Removal of the two $6s$ electrons and the $5d$ electron gives $\mathrm{Ce}^{3+} : [\mathrm{Xe}]4f^1$, the usual trivalent state of a lanthanoid. Loss of the remaining $4f$ electron gives $\mathrm{Ce}^{4+} : [\mathrm{Xe}]$. The stable xenon configuration accounts for the occurrence of the +4 state as well as +3.

Step 3: (c) Explain the wide range for actinoids In actinoids, the $5f$, $6d$ and $7s$ subshells have comparable energies. Therefore electrons from all three subshells, rather than only the outer $7s$ electrons, can participate in bonding. Different numbers of these electrons can be involved in different compounds, producing several oxidation states. The $5f$ electrons are less deeply buried than the $4f$ electrons of lanthanoids, especially in the early actinoids, so they are more readily available for bonding. This accounts for the broader oxidation-state range of actinoids compared with the predominantly +3 lanthanoids.

Step 4: Conclusion The lanthanoid configuration is $[\mathrm{Xe}]4f^{1-14}5d^{0-1}6s^2$; cerium commonly shows +3 and +4; and actinoids show many oxidation states because their $5f$, $6d$ and $7s$ electrons have similar energies and can participate in bonding.

Quick Tip to Solve: Associate lanthanoids with 4f filling, Ce(IV) with the xenon core, and actinoid variability with the close energies of 5f, 6d and 7s.

19. Using valence bond theory, predict the hybridization and magnetic character of the following:
(a) $[Co(NH_3)_6]^{3+}$
(b) $[Ni(CO)_4]$
[At. no.: Co = 27, Ni = 28] [3 marks]

Solution:

Concept:

- In valence bond theory, the metal provides vacant hybrid orbitals that accept lone pairs donated by ligands. The number and type of hybrid orbitals determine coordination geometry.
- An octahedral inner-orbital complex uses d^2sp^3 hybridisation; a tetrahedral complex uses sp^3 hybridisation.
- Unpaired electrons cause paramagnetism; a complex with all electrons paired is diamagnetic. The metal oxidation state must be found before counting its d electrons.

Step 1: (a) Determine the cobalt configuration and pairing Ammonia is a neutral ligand, so cobalt has oxidation state +3 in $[\mathrm{Co}(\mathrm{NH_3})_6]^{3+}$. Using atomic number 27,

$$\mathrm{Co} : [\mathrm{Ar}]3d^7 4s^2, \qquad \mathrm{Co}^{3+} : [\mathrm{Ar}]3d^6.$$

The two $4s$ electrons are removed before a $3d$ electron. In this Co(III) complex, the ligand field due to ammonia causes the six $3d$ electrons to pair in three of the five $3d$ orbitals. Two inner $3d$ orbitals are consequently vacant. Thus the metal has no unpaired electrons after pairing.

Quick Tip to Solve: Count d electrons after finding oxidation state: Co(III) is d6 with pairing, whereas Ni(0) in the carbonyl becomes fully paired d10.

Step 2: Assign cobalt hybridisation and magnetic character The two vacant $3d$ orbitals, one vacant $4s$ orbital and three vacant $4p$ orbitals mix to form six equivalent d^2sp^3 hybrid orbitals. Each accepts a lone pair from one ammonia molecule. The six metal-ligand bonds point towards the vertices of an octahedron. Therefore $[Co(NH_3)_6]^{3+}$ is an inner-orbital octahedral complex with d^2sp^3 hybridisation. All six d electrons are paired, so it is diamagnetic.

Step 3: (b) Determine the nickel configuration in nickel carbonyl Carbon monoxide is neutral and the complex is uncharged, so nickel has oxidation state zero in $[Ni(CO)_4]$. Neutral nickel, atomic number 28, is initially $[Ar]3d^84s^2$. In the valence-bond description of complex formation with the strong-field CO ligands, the two $4s$ electrons become paired in the $3d$ subshell, giving an effective $3d^{10}$ arrangement and making the $4s$ orbital vacant. Every $3d$ orbital then contains a pair of electrons.

Step 4: Assign nickel hybridisation and magnetic character One vacant $4s$ orbital and three vacant $4p$ orbitals form four sp^3 hybrid orbitals. They accept the four lone pairs donated by the four CO ligands and give tetrahedral geometry. The filled $3d^{10}$ subshell has no unpaired electrons, so $[Ni(CO)_4]$ is diamagnetic. Coordination number four alone does not imply square-planar geometry; the available orbitals here give sp^3, not dsp^2.

Step 5: Conclusion (a) $[Co(NH_3)_6]^{3+}$: d^2sp^3 hybridisation, octahedral geometry, diamagnetic.
(b) $[Ni(CO)_4]$: sp^3 hybridisation, tetrahedral geometry, diamagnetic.

Quick Tip to Solve: Count d electrons after finding oxidation state: Co(III) is d6 with pairing, whereas Ni(0) in the carbonyl becomes fully paired d10.

20. (a) Define the following terms:

(i) Enantiomers

(ii) Racemic mixture

(b) Why is chlorobenzene resistant to nucleophilic substitution reaction? [3 marks]

Solution:

Concept:

- Enantiomers are stereoisomers related as non-superimposable mirror images; they have opposite configurations at corresponding stereogenic centres.
- A racemic mixture contains equal amounts of two enantiomers. Their equal and opposite optical rotations cancel, giving external compensation.
- The ease of nucleophilic substitution depends on carbon-halogen bond strength and on whether backside attack or carbocation formation is possible.

Step 1: Define enantiomers (a)(i) Enantiomers are a pair of stereoisomers which are non-superimposable mirror images of each other. For example, the two enantiomers of 2-butanol have the same connectivity but opposite configurations at the asymmetric carbon. In an achiral medium they have the same ordinary physical properties, but rotate plane-polarised light by equal amounts in opposite directions under identical conditions.

Step 2: Define a racemic mixture (a)(ii) A racemic mixture is an equimolar mixture of the dextro-

Quick Tip to Solve: For aryl halides, begin with resonance strengthening of the carbon-halogen bond, then check carbocation stability and backside attack separately.

rotatory and laevorotatory enantiomers of a compound. It is optically inactive because the rotation produced by one enantiomer is cancelled by that of the other. This cancellation is called external compensation; it does not mean that each individual enantiomer is optically inactive.

Step 3: Explain the resistance of chlorobenzene (b) A lone pair on chlorine is conjugated with the benzene ring. Resonance therefore gives the carbon-chlorine bond partial double-bond character, making it shorter and stronger than the corresponding bond in an alkyl chloride. The chlorine is also bonded to an sp^2-hybridised carbon, whose greater s-character strengthens the bond relative to an sp^3 carbon-chlorine bond.

An S_N1 reaction would require an unstable phenyl carbocation, so cleavage of the bond to form that intermediate is difficult. In an S_N2 reaction, backside attack at the aryl carbon is obstructed by the aromatic ring and its electron cloud. These factors make chlorobenzene resistant to ordinary nucleophilic substitution.

Step 4: Conclusion Enantiomers are non-superimposable mirror-image stereoisomers; a racemic mixture contains them in equal proportions and is optically inactive. Chlorobenzene resists nucleophilic substitution because of its strong, partially double carbon-chlorine bond and unfavourable S_N1 and S_N2 pathways.

Quick Tip to Solve: For aryl halides, begin with resonance strengthening of the carbon-halogen bond, then check carbocation stability and backside attack separately.

21(a). Give one chemical test to distinguish between the following:

(a) Phenol and 1-propanol

(b) Ethanol and dimethyl ether

(c) 1-propanol and 2-Methyl-2-propanol [3 marks]

Solution:

Concept:

- A useful distinguishing test gives a visible observation for one compound and a different observation for the other under the same conditions.
- Phenols give a coloured complex with neutral ferric chloride. Alcohols contain an O-H bond and can liberate hydrogen on reaction with sodium; ethers lack this bond.
- Lucas reagent is concentrated hydrochloric acid with anhydrous zinc chloride. Tertiary alcohols rapidly form insoluble alkyl chlorides at room temperature, producing turbidity.

Step 1: Test phenol and 1-propanol with ferric chloride (a) Add a few drops of neutral aqueous $FeCl_3$ solution to separate samples. Phenol produces a violet colour due to formation of a coloured iron(III)-phenolate complex. Under the same conditions, 1-propanol does not give the characteristic violet colour. Thus the coloured sample contains phenol. Neutral ferric chloride is used because strongly acidic conditions interfere with this phenol test.

Step 2: Test ethanol and dimethyl ether with sodium (b) Add a small piece of sodium metal to

Quick Tip to Solve: Use ferric chloride for a phenolic O-H group, sodium for an alcohol versus an ether, and Lucas reagent at room temperature for tertiary versus primary alcohols.

separate dry samples. Ethanol gives effervescence of hydrogen and forms sodium ethoxide:

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

Dimethyl ether gives no hydrogen in this test because it has no hydroxyl hydrogen. The samples must be dry: water also reacts with sodium and would produce misleading effervescence.

Step 3: Test the two propanols with Lucas reagent (c) Shake separate samples with Lucas reagent at room temperature. 2-Methyl-2-propanol is tertiary and produces immediate turbidity as insoluble tert-butyl chloride forms:

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

1-Propanol is primary and gives no turbidity at room temperature during the test. Tertiary substitution is rapid because the corresponding carbocation is stabilised by three alkyl groups; a primary alcohol does not ionise readily under these conditions.

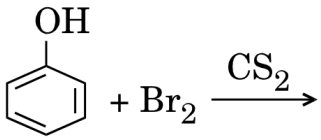
Step 4: Conclusion (a) Neutral ferric chloride: violet colour with phenol, no violet colour with 1-propanol. (b) Sodium in dry samples: hydrogen with ethanol, no hydrogen with dimethyl ether. (c) Lucas reagent at room temperature: immediate turbidity with 2-methyl-2-propanol, no turbidity with 1-propanol.

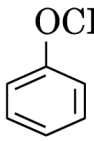
Quick Tip to Solve: Use ferric chloride for a phenolic O-H group, sodium for an alcohol versus an ether, and Lucas reagent at room temperature for tertiary versus primary alcohols.

OR

21(b). Write the products of the following reactions: [3 marks]

(i) $CH_3 - CH_2 - O - CH_3 + HI \longrightarrow$

(ii)  $+ Br_2 \xrightarrow{CS_2}$

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

Solution:

Concept:

- Hydrogen iodide protonates an ether; iodide then attacks the less hindered carbon by the S_N2 pathway.
- Hydroxyl and methoxy groups activate the benzene ring and direct electrophilic substitution to ortho and para positions. The less crowded para isomer is major.

Quick Tip to Solve: For ether cleavage select the less hindered carbon; for phenol and anisole use ortho/para direction, checking the solvent and catalyst first.

Step 1: Cleave the ether (i) After protonation of the ether oxygen, iodide attacks the methyl group rather than the more hindered ethyl group. The products are iodomethane and ethanol:

$$CH_3CH_2OCH_3 + HI \longrightarrow CH_3I + CH_3CH_2OH$$

Further conversion of the alcohol to an iodide would require additional hydrogen iodide under suitable conditions.

Step 2: Brominate phenol (ii) Bromination in nonpolar CS_2 gives 2-bromophenol and 4-bromophenol, with the para isomer major. The hydroxyl group directs substitution to these positions:

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

The product formula represents both positional isomers. This differs from bromine water, which gives 2,4,6-tribromophenol.

Step 3: Acylate anisole (iii) Anhydrous $AlCl_3$ activates acetyl chloride. Friedel-Crafts acylation gives 2-methoxyacetophenone and 4-methoxyacetophenone (para major):

$$C_6H_5OCH_3 + CH_3COCl \xrightarrow{\text{anhyd. } AlCl_3} CH_3OC_6H_4COCH_3 + HCl$$

The acetyl group attaches to a ring carbon at an ortho or para position; the original methoxy group remains intact. Steric crowding is lower at the para position.

Step 4: Conclusion (i) CH_3I and C_2H_5OH. (ii) 2-Bromophenol and 4-bromophenol (para major). (iii) 2-Methoxyacetophenone and 4-methoxyacetophenone (para major).

Quick Tip to Solve: For ether cleavage select the less hindered carbon; for phenol and anisole use ortho/para direction, checking the solvent and catalyst first.

22(a). Account for the following, supporting your answer with diagrams or equations wherever possible:

(a) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(b) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. [3 marks]

Solution:

Concept:

- Resonance stabilises a species by delocalising electrons over a conjugated system; an aromatic diazonium group is conjugated with the benzene ring.
- An amine acts as a base in water by accepting a proton, thereby producing hydroxide ions. Ferric ions precipitate with hydroxide ions as hydrated ferric oxide.

Step 1: Explain the stability of aromatic diazonium salts In an aromatic diazonium ion, such as $C_6H_5N_2^+$, the diazonium group is attached directly to the benzene ring. Conjugation between the ring and the nitrogen-containing group allows resonance delocalisation of the positive charge. This lowers the energy of the ion and gives it greater stability. Aromatic diazonium salts can therefore be

Quick Tip to Solve: For an amine-induced precipitate, first write the amine-water equilibrium and then the metal-ion hydroxide equation.

maintained in cold solution, usually at 273–278 K.

An aliphatic diazonium ion has no aromatic ring to provide this resonance stabilisation. It readily decomposes by losing very stable nitrogen gas, producing a carbocation that undergoes further reactions:

$$\mathrm{R{-}N_2^+ \longrightarrow R^+ + N_2 \uparrow}.$$

Thus the comparison concerns relative stability; aromatic diazonium salts also decompose on warming.

Step 2: Explain the ferric oxide precipitate The nitrogen lone pair enables methylamine to accept a proton from water:

$$\mathrm{CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-}.$$

Ferric chloride supplies $\mathrm{Fe^{3+}}$ ions. These combine with the hydroxide ions generated by methylamine to form a reddish-brown precipitate of ferric hydroxide, conventionally representing hydrated ferric oxide:

$$\mathrm{Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3 \downarrow}.$$

Removal of hydroxide as the precipitate drives further ionisation of methylamine. The overall equation is

$$\mathrm{FeCl_3 + 3CH_3NH_2 + 3H_2O \longrightarrow}$$

$$\mathrm{Fe(OH)_3 \downarrow + 3CH_3NH_3Cl}.$$

Step 3: Conclusion (a) Aromatic diazonium ions are resonance-stabilised by conjugation with the benzene ring, unlike aliphatic diazonium ions. (b) Methylamine produces $\mathrm{OH^-}$ in water, which precipitates ferric ions as $\mathrm{Fe(OH)_3}$, hydrated ferric oxide.

Quick Tip to Solve: For an amine-induced precipitate, first write the amine-water equilibrium and then the metal-ion hydroxide equation.

OR

22(b). Arrange the following in decreasing order of pK_b, giving reason:

(a) Aniline, p-nitroaniline and p-toluidine

(b) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ in gaseous state [3 marks]

Solution:

Concept:

- $\mathrm{p}K_b = -\log_{10} K_b$, where K_b is the base dissociation constant. A stronger base has a larger K_b and a smaller $\mathrm{p}K_b$.
- Electron-withdrawing groups reduce the availability of the nitrogen lone pair, whereas electron-releasing groups increase it. In the gaseous state, the electron-releasing inductive effect of alkyl groups governs the usual basicity order.

Step 1: Compare the substituted anilines In aniline, the nitrogen lone pair is delocalised into the benzene ring and is consequently less available for protonation. The para nitro group in p-nitroaniline

Quick Tip to Solve: Write the basicity order first, then reverse it for decreasing pKb; check whether the question specifies gas or water.

withdraws electrons through both its inductive and resonance effects. This further decreases electron density associated with the amino group and makes p-nitroaniline the weakest base of the three.

In p-toluidine, the para methyl group releases electron density through its positive inductive effect and hyperconjugation. It therefore increases the basicity relative to aniline. The increasing basicity order is

$$\text{p-nitroaniline} < \text{aniline} < \text{p-toluidine}.$$

Because $\mathrm{p}K_b$ decreases as basicity increases, reverse this order to obtain the requested decreasing $\mathrm{p}K_b$ order:

$$\boxed{\text{p-nitroaniline} > \text{aniline} > \text{p-toluidine}}.$$

Step 2: Compare the ethylamines in the gaseous state Each ethyl group has a positive inductive effect and supplies electron density towards nitrogen. With three ethyl groups, triethylamine has the greatest electron-releasing effect; diethylamine has two such groups and ethylamine has only one. The nitrogen lone pair is therefore most available for proton acceptance in triethylamine.

In the gaseous state, aqueous solvation of the protonated amine does not enter this comparison. Hence basicity increases as

$$\mathrm{C_2H_5NH_2} < (\mathrm{C_2H_5})_2\mathrm{NH} < (\mathrm{C_2H_5})_3\mathrm{N}.$$

Reversing the basicity order gives decreasing $\mathrm{p}K_b$:

$$\boxed{\mathrm{C_2H_5NH_2} > (\mathrm{C_2H_5})_2\mathrm{NH} > (\mathrm{C_2H_5})_3\mathrm{N}}.$$

Step 3: Conclusion Decreasing $\mathrm{p}K_b$:

(a) p-nitroaniline $>$ aniline $>$ p-toluidine.

(b) In the gaseous state:

$$\mathrm{C_2H_5NH_2} > (\mathrm{C_2H_5})_2\mathrm{NH} > (\mathrm{C_2H_5})_3\mathrm{N}.$$

Quick Tip to Solve: Write the basicity order first, then reverse it for decreasing pKb; check whether the question specifies gas or water.

23. Answer the following with reason:

(a) Is $(\text{NH-CHR-CO})_n$, a homopolymer or copolymer?

(b) Is PVC a condensation or addition polymer?

(c) Is Bakelite a thermoplastic or a thermosetting plastic? [3 marks]

Solution:

Concept:

- A homopolymer is formed from one kind of monomer, whereas a copolymer is formed from two or more different kinds of monomers.
- Addition polymerisation joins unsaturated monomers without eliminating small molecules. Con-

Quick Tip to Solve: Count monomer types for homopolymer classification, check small-molecule loss for addition, and check cross-links for thermosetting behaviour.

densation polymerisation joins functional groups, usually with loss of molecules such as water.

- Thermosetting plastics have a permanently cross-linked network after curing; thermoplastics can soften on heating and be reshaped.

Step 1: Identify the polymer of an amino acid The repeat unit $-\mathrm{NH}-\mathrm{CHR}-\mathrm{CO}-$ can be obtained from the single amino acid monomer $\mathrm{H_2N}-\mathrm{CHR}-\mathrm{COOH}$. The amino group of one molecule reacts with the carboxyl group of another, forming an amide linkage with elimination of water. Repetition joins identical monomers into the chain:

$$n\,\mathrm{H_2N}-\mathrm{CHR}-\mathrm{COOH} \longrightarrow \mathrm{H}[-\mathrm{NH}-\mathrm{CHR}-\mathrm{CO}-]_{\mathrm{n}}\mathrm{OH} + (n-1)\mathrm{H_2O}.$$

Since one kind of monomer supplies the repeated unit, it is a homopolymer. The presence of two functional groups in the same monomer does not make it a copolymer; the classification depends on the kinds of monomers used.

Step 2: Classify the polymerisation of PVC Polyvinyl chloride (PVC) is formed from vinyl chloride, $\mathrm{CH_2}=\mathrm{CHCl}$. The carbon-carbon double bond opens and the monomers join to form a saturated carbon backbone:

$$n\,\mathrm{CH_2}=\mathrm{CHCl} \longrightarrow [-\mathrm{CH_2}-\mathrm{CHCl}-]_{\mathrm{n}}.$$

No water, hydrogen chloride or other small molecule is eliminated in this process. PVC is therefore an addition polymer, even though its monomer contains chlorine.

Step 3: Classify Bakelite by its behaviour on heating Bakelite is formed from phenol and formaldehyde. On curing, methylene bridges connect the phenolic units to produce a rigid, three-dimensional cross-linked network. The covalent links prevent the chains from moving freely when heated.

Consequently, cured Bakelite does not soften and melt for remoulding. Strong heating eventually causes decomposition instead of reversible softening. This permanent network makes Bakelite a thermosetting plastic.

Step 4: Conclusion (a) $(\mathrm{NH}-\mathrm{CHR}-\mathrm{CO})_{\mathrm{n}}$ is a homopolymer of a single amino acid. (b) PVC is an addition polymer of vinyl chloride. (c) Bakelite is a thermosetting plastic because it has a permanent cross-linked network.

Quick Tip to Solve: Count monomer types for homopolymer classification, check small-molecule loss for addition, and check cross-links for thermosetting behaviour.

24. Answer the following:

(a) What is tincture of iodine? What is its use?

(b) What are the main constituents of dettol?

(c) Label the hydrophilic and hydrophobic parts of the given compound:

$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$ [3 marks]

Solution:

Concept:

- Antiseptics are chemicals applied to living tissues to prevent microbial growth and infection.

Quick Tip to Solve: Identify the long hydrocarbon tail first; the oxygen-rich chain ending in OH is the water-attracting part.

- A detergent molecule has a non-polar hydrophobic part that associates with grease and a polar hydrophilic part that interacts with water.

Step 1: (a) Identify tincture of iodine and its use Tincture of iodine is a 2–3% solution of iodine in an alcohol–water mixture. Iodine is the active antiseptic ingredient; the alcohol–water mixture acts as its solvent. It is applied to cuts and wounds as an antiseptic to prevent infection by inhibiting or destroying microorganisms. Thus, its use is on living tissue, with the iodine present in a dilute solution.

Step 2: (b) State the main constituents of Dettol The main constituents of Dettol are chloroxylenol and terpineol. Chloroxylenol provides antiseptic action. These constituents should be distinguished from iodine: tincture of iodine and Dettol are different antiseptic preparations.

Step 3: (c) Label the water-repelling and water-attracting parts The long hydrocarbon chain $CH_3(CH_2)_{16}$ is the hydrophobic part. It is non-polar, so it has affinity for oily dirt and grease rather than for water. The oxygen-containing portion $COO(CH_2CH_2O)_nCH_2CH_2OH$ is the hydrophilic part. Its ester, ether and terminal hydroxyl groups interact with water; the ether oxygen atoms and the hydroxyl group can participate in hydrogen bonding with water. The labelling is therefore

$$\underbrace{CH_3(CH_2)_{16}}_{\text{hydrophobic}}\underbrace{COO(CH_2CH_2O)_nCH_2CH_2OH}_{\text{hydrophilic}}.$$

The molecule is a non-ionic detergent: its water-attracting region contains polar oxygen groups without requiring an ionic head.

Step 4: Conclusion Tincture of iodine is iodine in alcohol–water, used as an antiseptic; Dettol mainly contains chloroxylenol and terpineol. The hydrocarbon tail is hydrophobic and the oxygen-containing region is hydrophilic.

Quick Tip to Solve: Identify the long hydrocarbon tail first; the oxygen-rich chain ending in OH is the water-attracting part.

Section D (15 marks)

25(a). Draw the graph between vapour pressure and temperature and explain the elevation in boiling point of a solvent in solution.

(b) Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litres of water at 25°C assuming it to be completely dissociated. (Atomic masses K = 39 u, S = 32 u, O = 16 u) [5 marks]

Solution:

Concept:

- A liquid boils when its vapour pressure equals the external pressure. At a fixed temperature a non-volatile solute lowers the solvent's vapour pressure: $p = x_1 p^0$, where x_1 is the solvent mole fraction and p^0 is the pure solvent's vapour pressure.
- For a dilute solution, elevation in boiling point is $\Delta T_b = T_b - T_b^0 = iK_b m$, where K_b is the molal

Quick Tip to Solve: Convert mg to g, count all three ions from K2SO4, and use kelvin in the osmotic-pressure equation.

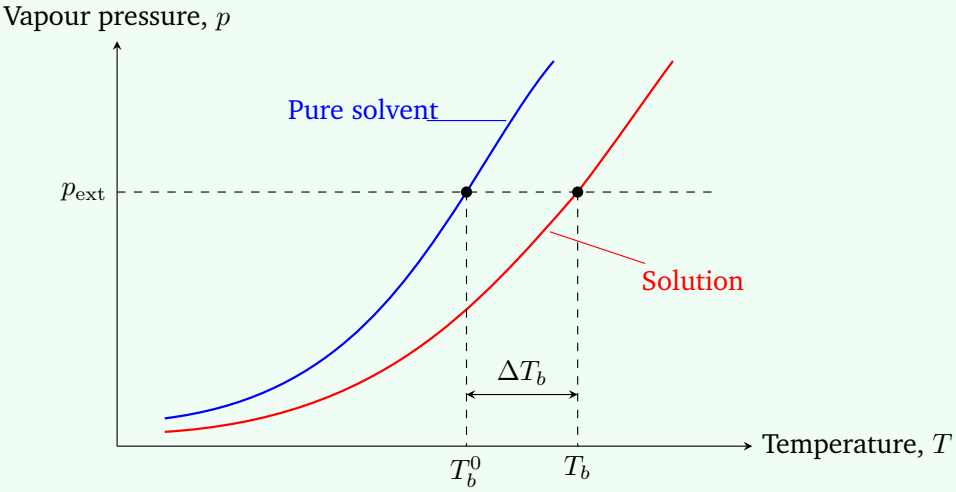
elevation constant, m is molality and i is the van't Hoff factor.

- Osmotic pressure is $\pi = iCRT = i(n/V)RT$, where C is formula-unit molarity, T is absolute temperature and R is the gas constant.

Step 1: (a) Draw and interpret the vapour-pressure curves Consider a solution containing a non-volatile solute. Its solvent mole fraction is less than unity, so at any given temperature the solution has a lower vapour pressure than the pure solvent. Both vapour pressures increase with temperature. In the graph the horizontal line represents a fixed external pressure, p_{ext}. It cuts the pure solvent curve at T_b^0 and the solution curve at the higher temperature T_b. The curves are schematic; their intersections show the boiling temperatures.

$$p^0(T_b^0) = p_{\text{ext}}, \qquad p_{\text{solution}}(T_b) = p_{\text{ext}}.$$

At T_b^0 the solution's vapour pressure is still below the external pressure. Consequently the solution must be heated further before it boils. Thus $\Delta T_b = T_b - T_b^0 > 0$, which is the elevation in boiling point. For a dilute solution of a non-dissociating solute, $\Delta T_b = K_b m$.



Vapour pressure versus temperature: boiling-point elevation at fixed external pressure.

Step 2: (b) Find the number of dissolved formula units and the particle factor The molar mass of potassium sulphate is

$$M(\text{K}_2\text{SO}_4) = 2(39) + 32 + 4(16) = 174\,\text{g mol}^{-1}.$$

Convert the solute mass before calculating its amount:

$$25\,\text{mg} = 0.025\,\text{g}, \qquad n = \frac{0.025}{174} = 1.4368 \times 10^{-4}\,\text{mol}.$$

Complete dissociation gives

$$\text{K}_2\text{SO}_4 \longrightarrow 2\text{K}^+ + \text{SO}_4^{2-}, \qquad i = 3.$$

Each formula unit produces three ions. Therefore the effective particle concentration is three times the formula-unit concentration. For this very dilute solution, take the solution volume as the given 2 L

Quick Tip to Solve: Convert mg to g, count all three ions from K2SO4, and use kelvin in the osmotic-pressure equation.

of water:

$$C = \frac{n}{V} = \frac{1.4368 \times 10^{-4}}{2} = 7.1839 \times 10^{-5}\,\text{mol L}^{-1}.$$

Step 3: Calculate the osmotic pressure at the stated temperature Use absolute temperature, $T = 25 + 273 = 298\,\text{K}$, and $R = 0.0821\,\text{L atm mol}^{-1}\text{K}^{-1}$, consistent with a volume in litres. Substitution gives

$$\begin{aligned}\pi &= iCRT \\ &= 3(7.1839 \times 10^{-5})(0.0821)(298) \\ &= 5.27 \times 10^{-3}\,\text{atm}.\end{aligned}$$

Equivalently, using $1\,\text{atm} = 1.01325 \times 10^5\,\text{Pa}$, the pressure is about $5.34 \times 10^2\,\text{Pa}$. The small value is consistent with the very small dissolved mass distributed through two litres.

Step 4: Conclusion The solution boils at a higher temperature because its vapour pressure reaches the external pressure only at $T_b > T_b^0$. The osmotic pressure of the completely dissociated potassium sulphate solution is $\boxed{\pi = 5.27 \times 10^{-3}\,\text{atm}}$, approximately $5.34 \times 10^2\,\text{Pa}$.

Quick Tip to Solve: Convert mg to g, count all three ions from K2SO4, and use kelvin in the osmotic-pressure equation.

OR

25(b). (a) Write two characteristics of non-ideal solution.

(b) 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution? [5 marks]

Solution:

Concept:

- Non-ideal solutions do not obey Raoult's law over the entire composition range because unlike intermolecular interactions differ from those between like molecules.
- Freezing-point depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the molal depression constant and m the analytical molality of the solute.
- For dimerisation $2\text{A} \rightleftharpoons \text{A}_2$, the fraction associated, α, is related to the particle-number factor by $i = 1 - \alpha/2$.

Step 1: (a) State two characteristics of non-ideal solutions First, the partial vapour pressures depart from Raoult's law: $p_A \neq x_A p_A^\circ$ and $p_B \neq x_B p_B^\circ$. The solution therefore shows positive or negative deviation depending on the relative strengths of intermolecular attractions. Second, mixing involves a non-zero enthalpy change, $\Delta H_{\text{mix}} \neq 0$, because replacing like interactions by unlike interactions either absorbs or releases heat. Non-ideal solutions also generally have $\Delta V_{\text{mix}} \neq 0$; mixing volumes need not be additive.

Quick Tip to Solve: For dimers use $\alpha = 2(1-i)$; calculate i from observed depression divided by the depression predicted without association.

Step 2: (b) Calculate the analytical molality Benzoic acid has formula $C_7H_6O_2$, so its molar mass is

$$M = 7(12) + 6(1) + 2(16) = 122\,\text{g mol}^{-1}.$$

The solvent is benzene, whose mass is $25\,\text{g} = 0.025\,\text{kg}$. Thus the molality calculated before allowing for association is

$$m = \frac{2/122}{0.025} = 0.65574\,\text{mol kg}^{-1}.$$

Use the solvent mass in this expression, not the total solution mass.

Step 3: Obtain the van't Hoff factor from the observed depression Without association the calculated depression would be

$$(\Delta T_f)_{\text{normal}} = K_f m = 4.9 \times 0.65574 = 3.2131\,\text{K}.$$

The observed depression is smaller because association reduces the number of independently moving solute particles. Therefore

$$i = \frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{normal}}} = \frac{1.62}{3.2131} = 0.50418.$$

Step 4: Relate particle numbers to the fraction forming dimers Starting with one mole of acid molecules, association of a fraction α leaves $1-\alpha$ mole of monomers and creates $\alpha/2$ mole of dimers. The total particle amount is consequently $1-\alpha/2$ mole. Hence

$$i = 1 - \frac{\alpha}{2},$$

$$\alpha = 2(1-i) = 2(1-0.50418) = 0.99164,$$

$$\text{Percentage association} = 100\alpha = 99.164\%.$$

As a check, complete dimerisation would give $i = 0.5$; the calculated value slightly above this indicates nearly complete association.

Step 5: Conclusion (a) Non-ideal solutions deviate from Raoult's law and have $\Delta H_{\text{mix}} \neq 0$. (b) The percentage association of benzoic acid into dimers is approximately $\boxed{99.2\%}$.

Quick Tip to Solve: For dimers use $\alpha = 2(1-i)$; calculate i from observed depression divided by the depression predicted without association.

26(a). Give reasons for the following:

(a) NO_2 dimerises readily.

(b) Chlorine acts as a bleaching agent.

(c) In spite of small size, electron gain enthalpy of oxygen is less negative as compared to sulphur.

(d) Unlike chlorine, fluorine forms only one oxoacid, HOF.

(e) Noble gases have very low boiling points. [5 marks]

Solution:

Concept:

- Pairing of unpaired electrons can stabilise an odd-electron molecule through formation of a covalent bond.
- Oxidative bleaching destroys the coloured form of a substance; electron gain enthalpy depends on both nuclear attraction and electron-electron repulsion.
- Fluorine's exceptional electronegativity restricts its oxidation-state chemistry, whereas the boiling points of noble gases depend on weak London dispersion forces.

Step 1: (a) Explain ready dimerisation of nitrogen dioxide NO_2 is an odd-electron molecule containing one unpaired electron. Two such molecules combine so that these electrons pair to form an $N-N$ covalent bond:

$$2NO_2 \rightleftharpoons N_2O_4.$$

The resulting N_2O_4 molecule has paired electrons and is diamagnetic. Electron pairing and bond formation stabilise the dimer, accounting for the ready association of NO_2; cooling favours dimer formation.

Step 2: (b) Explain the bleaching action of chlorine In the presence of moisture chlorine produces hypochlorous acid:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

Hypochlorous acid acts as an oxidising agent. In the conventional school representation,

$$HOCl \longrightarrow HCl + [O].$$

Here $[O]$ represents available oxidising oxygen. Oxidation converts the coloured substance into a colourless product, so chlorine bleaching is permanent. Moisture is needed for this action; dry chlorine does not bleach dry litmus paper.

Step 3: (c) Compare the electron gain enthalpies of oxygen and sulphur The added electron enters oxygen's compact $2p$ subshell, where the existing electron density is high. Strong repulsion between the incoming electron and the electrons already present opposes its addition. In sulphur the electron enters the larger, more diffuse $3p$ subshell, and this repulsion is smaller. Thus less energy is released when oxygen accepts an electron: its electron gain enthalpy is less negative than sulphur's despite oxygen's smaller atomic size.

Step 4: (d) Explain why fluorine has only the oxoacid HOF Fluorine is the most electronegative element and does not exhibit positive oxidation states in its compounds. In chlorine oxoacids, chlorine can occur in positive oxidation states, allowing a series such as $HOCl$, $HClO_2$, $HClO_3$ and $HClO_4$.

Quick Tip to Solve: Link each reason to its controlling factor: electron pairing, oxidation, orbital crowding, fluorine's electronegativity, and weak interatomic forces.

Fluorine cannot form the analogous series. Its only oxoacid is HOF, with connectivity $H - O - F$. Even in this compound fluorine remains in oxidation state -1; hydrogen is $+1$ and oxygen is 0.

Step 5: (e) Explain the low boiling points of noble gases Noble gases have completely filled valence shells and exist as individual, non-polar atoms. They therefore attract one another only through weak instantaneous dipole-induced dipole, or London dispersion, forces. Very little energy is needed to overcome these attractions and separate the atoms into the gaseous state, resulting in very low boiling points. Down the group, increasing atomic size and polarisability strengthen these forces, so boiling points rise, while remaining low.

Step 6: Conclusion NO_2 dimerises by pairing its unpaired electrons; moist chlorine bleaches by oxidation; compact oxygen $2p$ orbitals cause greater electron repulsion than sulphur $3p$ orbitals; fluorine cannot form the positive-oxidation-state oxoacid series of chlorine; and noble gases have only weak dispersion attractions between their atoms.

Quick Tip to Solve: Link each reason to its controlling factor: electron pairing, oxidation, orbital crowding, fluorine's electronegativity, and weak interatomic forces.

OR

26(b). (a) Draw structure and name the shape of the following:

(i) SF_4

(ii) ICl_3

(b) What happens when (Support your answer with equation):

(i) Chlorine gas is passed through hot and concentrated sodium hydroxide solution?

(ii) Xenon hexafluoride is subjected to complete hydrolysis?

(iii) Concentrated sulphuric acid is poured over cane sugar? [5 marks]

Solution:

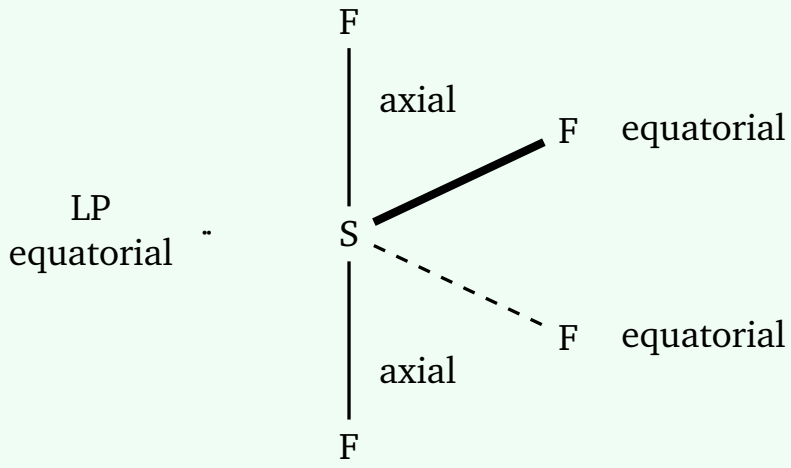
Concept:

- VSEPR theory places electron pairs around the central atom to minimise repulsion. A lone pair repels more strongly than a bond pair, and occupies an equatorial site in a trigonal-bipyramidal arrangement to reduce 90° interactions.
- Molecular shape describes the positions of bonded atoms, whereas electron-pair geometry includes lone pairs. Both SF_4 and ICl_3 have five electron-pair domains at the central atom.
- Chlorine disproportionates in hot concentrated alkali; complete hydrolysis replaces all Xe–F bonds; concentrated sulphuric acid acts as a dehydrating agent towards cane sugar.

Step 1: (a)(i) Structure and shape of sulphur tetrafluoride Sulphur has six valence electrons. In SF_4, it forms four S–F bonds and retains one lone pair, giving the VSEPR type AX_4E. Its five electron-pair domains have a trigonal-bipyramidal arrangement (conventional hybridisation sp^3d). The lone pair occupies one equatorial position. The four fluorine atoms therefore occupy two axial and two equatorial positions, producing a **see-saw shape**. Lone-pair repulsion distorts the ideal bond angles.

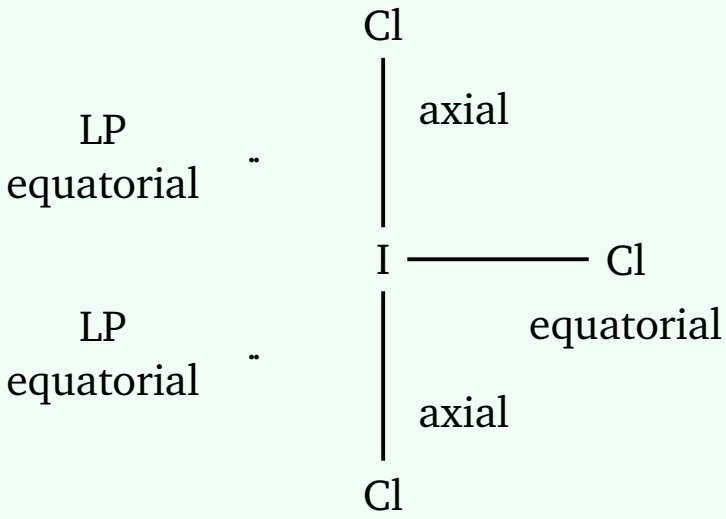
Quick Tip to Solve: For the shapes, count central-atom lone pairs and put them equatorial first. For the reactions, distinguish hot alkali (chlorate) from cold alkali, and complete xenon fluoride hydrolysis (trioxide) from partial hydrolysis.

The labelled drawing shows the axial and equatorial bonds and the equatorial lone pair.



See-saw structure of SF_4; LP denotes the equatorial lone pair. Solid and dashed bonds indicate spatial directions.

Step 2: (a)(ii) Structure and shape of iodine trichloride Iodine has seven valence electrons. It forms three I–Cl bonds and has two lone pairs, so its VSEPR type is AX_3E_2. The five electron-pair domains again have a trigonal-bipyramidal arrangement (conventional hybridisation sp^3d). Both lone pairs occupy equatorial sites, leaving two axial chlorine atoms and one equatorial chlorine atom. Hence ICl_3 has a **T-shaped structure**, with bond angles close to $90°$ and $180°$, slightly distorted by the lone pairs.



T-shaped structure of ICl_3; both lone pairs occupy equatorial positions.

Step 3: (b)(i) Chlorine with hot concentrated sodium hydroxide Chlorine undergoes disproportionation to form sodium chloride and sodium chlorate, together with water:

$$3Cl_2 + 6NaOH \xrightarrow{\text{hot, concentrated}} 5NaCl + NaClO_3 + 3H_2O.$$

Chlorine starts at oxidation state zero; part is reduced to -1 in chloride and part is oxidised to $+5$ in

Quick Tip to Solve: For the shapes, count central-atom lone pairs and put them equatorial first. For the reactions, distinguish hot alkali (chlorate) from cold alkali, and complete xenon fluoride hydrolysis (trioxide) from partial hydrolysis.

chlorate. The hot, concentrated conditions are essential: chlorate is the oxidised product under the stated conditions.

Step 4: (b)(ii) Complete hydrolysis of xenon hexafluoride Complete hydrolysis of XeF_6 gives xenon trioxide and hydrogen fluoride. All six fluorine atoms are replaced by three oxygen atoms:

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

This is hydrolysis rather than a redox reaction: xenon remains in oxidation state $+6$. The word "complete" distinguishes this product from the oxyfluorides formed during partial hydrolysis.

Step 5: (b)(iii) Concentrated sulphuric acid with cane sugar Cane sugar is sucrose, $C_{12}H_{22}O_{11}$. Concentrated sulphuric acid removes the elements of water from it, causing charring. A black, porous mass of carbon is formed, with heat and water vapour released:

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O.$$

The acid is written above the arrow because its role here is to act as a strong dehydrating agent. The 12 carbon atoms remain as carbon, and the 22 hydrogen and 11 oxygen atoms account for 11 water molecules.

Step 6: Conclusion SF_4 is see-saw shaped and ICl_3 is T-shaped. Hot concentrated NaOH converts chlorine into chloride and chlorate; complete XeF_6 hydrolysis produces XeO_3 and HF; concentrated H_2SO_4 chars sucrose to carbon by dehydration, as shown in the balanced equations.

Quick Tip to Solve: For the shapes, count central-atom lone pairs and put them equatorial first. For the reactions, distinguish hot alkali (chlorate) from cold alkali, and complete xenon fluoride hydrolysis (trioxide) from partial hydrolysis.

27(a). Give IUPAC name of CH_3 - CH = CH - CHO.

(b) How can you distinguish between ethanol and ethanal?

(c) How will you convert the following:

(i) Toluene to benzoic acid

(ii) Ethanol to propan-2-ol

(iii) Propanal to 2-hydroxypropanoic acid [5 marks]

Solution:

Concept:

- In naming an aldehyde, the carbon of the $-CHO$ group is carbon 1. The longest chain containing this carbon determines the parent name and the double-bond locant.
- Aldehydes reduce Tollens' reagent to metallic silver, whereas ordinary alcohols do not give this test. Grignard reagents add a carbon group to the carbonyl carbon and give an alcohol after hydrolysis.
- Strong oxidation converts an alkylbenzene side chain with a benzylic hydrogen into $-COOH$. The Hell–Volhard–Zelinsky reaction substitutes an alpha hydrogen of a carboxylic acid by bromine.

Quick Tip to Solve: Count carbons before choosing reagents: ethanol needs one added carbon, but propanal to lactic acid must retain three, so use alpha bromination rather than HCN addition.

Step 1: (a) Name the unsaturated aldehyde Number the four-carbon chain from the aldehyde end: $CHO - CH = CH - CH_3$. The double bond joins carbons 2 and 3. The parent is butane, the unsaturation is indicated by $-2-en-$, and the aldehyde suffix is $-al$. Hence its IUPAC name is but-2-enal. No cis/trans or E/Z descriptor is assigned because the printed formula does not specify the geometry.

Step 2: (b) Distinguish ethanol and ethanal using Tollens' reagent Warm separate samples gently with freshly prepared Tollens' reagent (ammoniacal silver nitrate). Ethanal produces a silver mirror on the inner wall of the test tube; ethanol does not. Ethanal is oxidised to ethanoate while silver(I) is reduced:

$$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Thus the positive silver-mirror test identifies ethanal. The iodoform test is unsuitable for distinguishing this pair because both ethanol and ethanal give it.

Step 3: (c)(i) Oxidise toluene to benzoic acid Heat toluene with alkaline potassium permanganate, then acidify the benzoate formed. The benzylic methyl group is oxidised completely to a carboxyl group, while the aromatic ring is retained:

$$C_6H_5CH_3 + 3[O] \xrightarrow{\text{hot alkaline } KMnO_4;H^+} C_6H_5COOH + H_2O.$$

Acidification is necessary to obtain benzoic acid rather than its salt.

Step 4: (c)(ii) Convert ethanol to propan-2-ol First dehydrogenate ethanol over heated copper at 573 K, producing ethanal. Add methylmagnesium bromide in dry ether, then hydrolyse with dilute acid:

$$CH_3CH_2OH \xrightarrow{Cu,573\,K} CH_3CHO + H_2,$$

$$CH_3CHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH(OMgBr)CH_3 \xrightarrow{H_3O^+} CH_3CH(OH)CH_3.$$

The methyl group adds to the aldehyde carbon, increasing the chain from two carbons to three. Hydrolysis converts the magnesium alkoxide into the required secondary alcohol.

Step 5: (c)(iii) Convert propanal to 2-hydroxypropanoic acid Oxidise propanal to propanoic acid with acidified potassium dichromate. Brominate at the alpha carbon using bromine and red phosphorus, followed by water (the Hell–Volhard–Zelinsky reaction). Finally replace bromine by hydroxyl using aqueous alkali and acidify:

$$CH_3CH_2CHO + [O] \xrightarrow{K_2Cr_2O_7/H^+} CH_3CH_2COOH,$$

$$CH_3CH_2COOH \xrightarrow{Br_2/\text{red P};H_2O} CH_3CHBrCOOH,$$

$$CH_3CHBrCOOH + 2NaOH \xrightarrow{\text{aqueous}} CH_3CH(OH)COONa + NaBr + H_2O,$$

$$CH_3CH(OH)COONa + HCl \longrightarrow CH_3CH(OH)COOH + NaCl.$$

The product is 2-hydroxypropanoic acid (lactic acid). This route preserves the three-carbon skeleton and places hydroxyl on carbon 2.

Quick Tip to Solve: Count carbons before choosing reagents: ethanol needs one added carbon, but propanal to lactic acid must retain three, so use alpha bromination rather than HCN addition.

Step 6: Conclusion (a) But-2-enal. (b) Ethanal gives a silver mirror with Tollens' reagent; ethanol does not. (c) Use side-chain oxidation for toluene; ethanal followed by methylmagnesium bromide and hydrolysis for ethanol; and oxidation, alpha bromination, then aqueous-alkali hydrolysis and acidification for propanal.

Quick Tip to Solve: Count carbons before choosing reagents: ethanol needs one added carbon, but propanal to lactic acid must retain three, so use alpha bromination rather than HCN addition.

OR

27(b). (a) Give IUPAC name of Salicylic acid.

(b) Chloroacetic acid is more acidic than acetic acid. Why?

(c) Write the products formed when $(CH_3)_3C$-CHO reacts with the following:

(i) Zinc amalgam and dilute hydrochloric acid

(ii) Concentrated sodium hydroxide solution

(iii) Semicarbazide and a weak acid [5 marks]

Solution:

Concept:

- Carboxylic acids are named using the $-COOH$ group as the principal functional group. Electron-withdrawing substituents increase acidity by stabilising the carboxylate conjugate base through their inductive effect.
- Clemmensen reduction, using zinc amalgam and hydrochloric acid, converts an aldehyde group $-CHO$ into $-CH_3$.
- An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction in concentrated alkali: one molecule is oxidised to a carboxylate and another is reduced to an alcohol.
- Semicarbazide condenses with a carbonyl group through its terminal $-NH_2$ group, forming a semicarbazone with elimination of water.

Step 1: (a) Give the IUPAC name of salicylic acid Salicylic acid has a hydroxyl group adjacent to the carboxyl group on a benzene ring. Take benzoic acid as the parent and number the ring carbon bonded to $-COOH$ as carbon 1. The hydroxyl substituent is then at carbon 2. Its IUPAC name is 2-hydroxybenzoic acid, with condensed formula $o\text{-}HO-C_6H_4-COOH$. The hydroxyl group is named as a prefix because the carboxyl group has higher nomenclature priority.

Step 2: (b) Explain the greater acidity of chloroacetic acid The electronegative chlorine atom in $ClCH_2COOH$ withdraws electron density through sigma bonds by its negative inductive ($-I$) effect. This stabilises the negative charge of the chloroacetate conjugate base, $ClCH_2COO^-$. Therefore loss of H^+ is more favourable:

$$ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+.$$

In contrast, the methyl group in acetic acid has a positive inductive ($+I$) effect, which tends to destabilise the acetate ion by donating electron density. Both conjugate bases have carboxylate

Quick Tip to Solve: Check hydrogens on the carbon immediately next to CHO: here that carbon has none, so concentrated NaOH gives Cannizzaro products even though methyl hydrogens are present.

resonance stabilisation, but chlorine supplies additional inductive stabilisation. Hence chloroacetic acid is more acidic than acetic acid.

Step 3: (c)(i) Reaction with zinc amalgam and dilute hydrochloric acid The reactant $(CH_3)_3CCHO$ is 2,2-dimethylpropanal. Clemmensen reduction replaces its aldehyde oxygen by hydrogen without changing the carbon skeleton:

$$(CH_3)_3CCHO + 4[H] \xrightarrow{Zn(Hg)/HCl} (CH_3)_3CCH_3 + H_2O.$$

The organic product is 2,2-dimethylpropane (neopentane). In this aldehyde the carbonyl carbon becomes a terminal methyl carbon.

Step 4: (c)(ii) Reaction with concentrated sodium hydroxide The alpha carbon is the quaternary carbon $C(CH_3)_3$ directly adjacent to $-CHO$. It has no hydrogen, even though the methyl groups have hydrogens farther away. Therefore this aldehyde undergoes Cannizzaro disproportionation rather than aldol condensation:

$$2(CH_3)_3CCHO + NaOH \longrightarrow (CH_3)_3CCOONa + (CH_3)_3CCH_2OH.$$

The products are sodium 2,2-dimethylpropanoate and 2,2-dimethylpropan-1-ol. Under the stated alkaline conditions the oxidised product is a sodium carboxylate, not the free acid; no acidification is specified.

Step 5: (c)(iii) Reaction with semicarbazide and a weak acid Semicarbazide is $H_2N - NH - C(=O) - NH_2$. Its terminal amino nitrogen attacks the aldehyde carbonyl carbon. Weak acid catalyses the subsequent dehydration, producing the semicarbazone:

$$(CH_3)_3CCHO + H_2N - NH - C(=O) - NH_2$$
$$\xrightarrow{\text{weak acid}} (CH_3)_3CCH = N - NH - C(=O) - NH_2 + H_2O.$$

The product is the semicarbazone of 2,2-dimethylpropanal. The aldehyde oxygen is replaced by $= N - NH - C(=O) - NH_2$; the semicarbazide carbonyl group remains intact. The terminal amino group reacts because its lone pair is available, whereas the amino group directly attached to the semicarbazide carbonyl is resonance-deactivated.

Step 6: Conclusion (a) Salicylic acid is 2-hydroxybenzoic acid. (b) Chlorine's $-I$ effect stabilises chloroacetate, making chloroacetic acid more acidic. (c) The products are (i) 2,2-dimethylpropane, (ii) sodium 2,2-dimethylpropanoate and 2,2-dimethylpropan-1-ol, and (iii) $(CH_3)_3CCH = N - NH - C(=O) - NH_2$.

Quick Tip to Solve: Check hydrogens on the carbon immediately next to CHO: here that carbon has none, so concentrated NaOH gives Cannizzaro products even though methyl hydrogens are present.