CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-5-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) **All questions** are compulsory.

(ii) 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 hcp while atoms of element B occupy two-third of the octahedral voids. What is the formula of the solid? [1 mark]

Solution:

Concept:

- In a close-packed structure, the number of octahedral voids equals the number of atoms forming the packing.
- The empirical formula gives the simplest whole-number ratio of the constituent atoms.

Step 1: Count the occupied voids Let the hcp arrangement contain N atoms of A. It therefore has N octahedral voids. Since B occupies only two-thirds of these voids, the number of B atoms is $\frac{2N}{3}$. The unoccupied voids do not contribute atoms to the formula.

Step 2: Reduce the atomic ratio The ratio of the two elements is

$$A : B = N : \frac{2N}{3} = 3 : 2.$$

Multiplying both entries by $3/N$ converts the fractional occupancy into the smallest whole-number ratio. The packing type does not change the equality between host atoms and octahedral voids.

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

Quick Tip to Solve: For octahedral occupancy, use one void per host atom; convert the occupancy fraction into a whole-number ratio.

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

Solution:

Concept:

- Ionisation isomerism occurs when a coordinated anionic ligand exchanges places with an anionic counter-ion.
- Ionisation isomers have the same overall composition but release different ions in aqueous solution.

Step 1: Identify the ligand and counter-ion In $[Co(NH_3)_5Cl]SO_4$, chloride lies inside the coordination sphere and is bonded to cobalt. Sulphate lies outside the square brackets and acts as the counter-ion. Ammonia is a neutral ligand, so it is not the ion exchanged here.

Step 2: Write the corresponding isomer Exchanging chloride and sulphate gives $[Co(NH_3)_5SO_4]Cl$. The original complex releases free sulphate ions, whereas this isomer releases free chloride ions. Both compounds contain the same cobalt, ammonia, chloride and sulphate constituents but differ in the ions formed on dissolution.

Step 3: Conclusion The complex shows $\boxed{\text{ionisation isomerism}}$.

Quick Tip to Solve: Look for an anion inside the brackets and another outside; exchanging them identifies ionisation isomerism.

OR

2(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 comparable octahedral complexes of the same metal ion, stronger-field ligands produce larger crystal field splitting energy Δ_o.
- The relevant spectrochemical order is $Cl^- < NH_3 < CN^-$.

Step 1: Check the metal ion and geometry Each complex contains six ligands and has the usual octahedral coordination. Chromium has oxidation state $+3$ in all three: six cyanide or chloride ions contribute -6 to a complex of charge -3, while ammonia is neutral in the complex of charge $+3$. Thus the metal and oxidation state are the same.

Step 2: Compare ligand field strengths Chloride is the weakest-field ligand of the three, ammonia has intermediate field strength, and cyanide is the strongest-field ligand. Consequently, the separation between the lower t_{2g} and upper e_g sets increases in that sequence. The charge of the whole complex alone does not determine this order.

Step 3: Conclusion The increasing order is

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

Quick Tip to Solve: First confirm the same metal oxidation state, then rank the ligands: chloride, ammonia, cyanide.

3. Oxidation of CH_3 - CHO is easier than CH_3 - $COCH_3$. Why? [1 mark]

Solution:

Concept:

- Aldehydes contain a hydrogen atom attached directly to the carbonyl carbon and oxidise readily to carboxylic acids.
- Ketones have two carbon groups attached to the carbonyl carbon; their oxidation generally requires carbon-carbon bond cleavage.

Step 1: Consider ethanal oxidation In CH_3CHO, the carbonyl carbon bears a hydrogen atom. Oxidation converts its aldehyde group into a carboxyl group without breaking the carbon skeleton:

$$CH_3CHO + [O] \longrightarrow CH_3COOH.$$

Hence even mild oxidising agents can oxidise ethanal.

Step 2: Compare propanone In CH_3COCH_3, the carbonyl carbon is bonded to two methyl groups and has no directly attached hydrogen. Oxidation cannot proceed by the same simple conversion. It

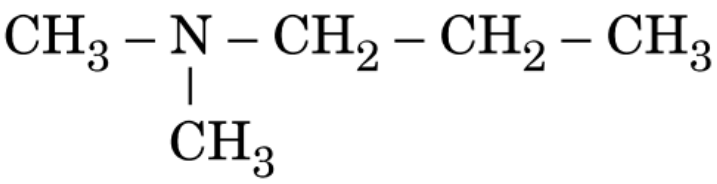
Quick Tip to Solve: Inspect the carbonyl carbon: an attached H allows easy aldehyde oxidation without breaking the carbon chain.

requires breaking a stronger carbon-carbon bond and therefore normally needs vigorous conditions and stronger oxidising agents.

Step 3: Conclusion Ethanal oxidises more easily because it has a carbonyl hydrogen; propanone oxidation requires carbon-carbon bond cleavage.

Quick Tip to Solve: Inspect the carbonyl carbon: an attached H allows easy aldehyde oxidation without breaking the carbon chain.

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



Solution:

Concept:

- Name an amine using the longest carbon chain bonded to nitrogen as the parent alkanamine.
- Additional alkyl groups attached directly to nitrogen receive the locant N, rather than a carbon-number locant.

Step 1: Select the parent chain The nitrogen is bonded to one propyl group, $-CH_2CH_2CH_3$, and two methyl groups, $-CH_3$. The longest chain directly attached to nitrogen has three carbon atoms. Numbering begins from the carbon bonded to nitrogen, so the parent name is propan-1-amine.

Step 2: Name the nitrogen substituents The two remaining methyl groups are both attached to nitrogen, not to carbon atoms of the propane chain. They are therefore described by N, N-dimethyl. Combine this prefix with the parent name, retaining the position 1 of the amino group. The structure is a tertiary amine because nitrogen is bonded to three carbon groups.

Step 3: Conclusion The IUPAC name is $\boxed{N, N\text{-dimethylpropan-1-amine}}$.

Quick Tip to Solve: Choose the propyl chain as the parent and label both methyl groups on nitrogen with N,N.

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

Solution:

Concept:

- Arsenic sulphide sol can be prepared by a chemical condensation method involving double decomposition.
- Passing hydrogen sulphide through a dilute solution of arsenious oxide produces colloidal As_2S_3.

Step 1: Prepare the dilute reactant solution Take a dilute aqueous solution of arsenious oxide, As_2O_3,

Quick Tip to Solve: Remember the preparation as oxide plus hydrogen sulphide: As2O3 produces the yellow As2S3 sol.

and pass hydrogen sulphide gas slowly through it. The dilute conditions allow the newly formed arsenic sulphide particles to remain dispersed in the liquid as colloidal particles rather than forming a coarse bulk precipitate.

Step 2: Write the sol-forming reaction The reaction is

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O.$$

The yellow arsenic sulphide formed constitutes the dispersed phase, and water is the dispersion medium. This is the standard laboratory preparation of arsenic sulphide sol by double decomposition.

Step 3: Conclusion Pass H_2S through dilute aqueous As_2O_3 to obtain a yellow As_2S_3 sol.

Quick Tip to Solve: Remember the preparation as oxide plus hydrogen sulphide: As2O3 produces the yellow As2S3 sol.

OR

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

Solution:

Concept:

- In heterogeneous catalysis, the catalyst and the reacting substances are in different phases.
- A solid catalyst can accelerate a reaction between gases by providing a surface for adsorption and reaction.

Step 1: Give a standard example The Haber process forms ammonia from nitrogen and hydrogen using finely divided solid iron as catalyst:

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

The iron speeds up the approach to equilibrium and is not consumed in the overall reaction.

Step 2: Identify the phase difference Both nitrogen and hydrogen are gaseous reactants, whereas iron is a solid. The reaction occurs at the catalyst surface after adsorption of the reactants. Since the reactants and catalyst occupy different phases, this reaction satisfies the definition of heterogeneous catalysis. The catalyst does not alter the equilibrium composition.

Step 3: Conclusion The Haber process, using solid iron to catalyse ammonia formation from gaseous N_2 and H_2, is an example.

Quick Tip to Solve: For a heterogeneous example, state both the reaction and phases: gaseous nitrogen/hydrogen with solid iron.

Section B (14 marks)

6. What happens when

(a) XeF_2 is hydrolysed?

(b) SO_2 is passed into aqueous solution of Fe^{3+} salt? [2 marks]

Solution:

Concept:

- Hydrolysis of xenon difluoride gives xenon, hydrofluoric acid and oxygen. Xenon in oxidation state $+2$ is reduced to the elemental state.
- Sulphur dioxide is a reducing agent in water: sulphur is oxidised from $+4$ to $+6$, while Fe^{3+} is reduced to Fe^{2+}.

Step 1: Hydrolyse xenon difluoride On reaction with water, xenon difluoride forms xenon gas, hydrofluoric acid and oxygen gas. The balanced equation is

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2.$$

The four fluorine atoms become four molecules of HF; the two oxygen atoms from water form one molecule of oxygen.

Step 2: Pass sulphur dioxide into ferric salt solution Sulphur dioxide reduces the ferric ions to ferrous ions, while it is itself oxidised to sulphate. The balanced ionic equation, valid independently of the spectator anion of the salt, is

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+.$$

One sulphur atom loses two electrons, which are accepted by two ferric ions; the total charge on each side is $+6$.

Step 3: Conclusion (a) XeF_2 gives Xe, HF and O_2 on hydrolysis. (b) SO_2 reduces Fe^{3+} to Fe^{2+} and forms sulphate.

Quick Tip to Solve: For the ferric-ion reaction, match the two electrons lost by one sulphur atom with two ferric ions.

7. Complete and balance the following equations:

(a) $MnO_4^- + I^- + H^+ \rightarrow$

(b) $Na_2Cr_2O_7 + KCl \rightarrow$ [2 marks]

Solution:

Concept:

- In acidic solution, permanganate is reduced from manganese oxidation state $+7$ to $+2$, and iodide is oxidised to iodine.
- Sodium dichromate reacts with potassium chloride by exchange of ions to give potassium dichro-

Quick Tip to Solve: Balance acidic permanganate by adding water and hydrogen ions first, then cancel electrons using the iodide half-reaction.

mate; crystallisation is favoured by its lower solubility.

Step 1: Balance the acidic permanganate reaction The two half-reactions are

$$\mathrm{MnO_4^- + 8H^+ + 5}e^- \longrightarrow \mathrm{Mn^{2+} + 4H_2O},$$
$$\mathrm{2I^- \longrightarrow I_2 + 2}e^-.$$

Multiply the first by two and the second by five to cancel ten electrons. Thus

$$\mathrm{2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O}.$$

Both sides contain two Mn, ten I, eight O and sixteen H atoms; each side has charge $+4$.

Step 2: Complete the dichromate reaction Two potassium ions replace the two sodium ions associated with the dichromate ion. The equation is

$$\mathrm{Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl}.$$

Chromium remains in oxidation state $+6$; this is not a redox reaction. The coefficient two on KCl supplies the two potassium ions required for potassium dichromate, and the two chloride ions form two NaCl units.

Step 3: Conclusion (a) $\mathrm{2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O}$. (b) $\mathrm{Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl}$.

Quick Tip to Solve: Balance acidic permanganate by adding water and hydrogen ions first, then cancel electrons using the iodide half-reaction.

8. 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: $\mathrm{Na^+(aq) + }e^- \rightarrow \mathrm{Na(s)};\quad E^\circ = -2.71\,\mathbf{V}$

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

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

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

Solution:

Concept:

- Reduction occurs at the cathode. Among competing reductions, a more positive reduction potential generally favours discharge.
- Actual gas evolution at an anode depends on overpotential as well as thermodynamic electrode potential; oxygen evolution has a substantial overpotential.

Step 1: Identify the cathode product The hydrogen reduction potential $0.00\,\mathrm{V}$ is more positive than the sodium reduction potential $-2.71\,\mathrm{V}$, so hydrogen is liberated in preference to sodium. The given hydrogen half-equation doubles to $\mathrm{2H^+ + 2}e^- \longrightarrow \mathrm{H_2}$. In aqueous sodium chloride the corresponding

Quick Tip to Solve: At the cathode compare reduction potentials; at the anode remember the oxygen overpotential in aqueous sodium chloride.

water reduction is

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

Thus sodium ions remain in solution and hydrogen gas forms at the cathode.

Step 2: Identify the anode product using overpotential The given values $1.23\,V$ for oxygen and $1.36\,V$ for chlorine suggest, on thermodynamic grounds alone, that water should oxidise before chloride. However, oxygen evolution requires a considerable additional potential (overpotential), so chloride oxidation is preferred in the usual electrolysis of aqueous sodium chloride:

$$2Cl^- \longrightarrow Cl_2 + 2e^-.$$

Therefore chlorine gas is collected at the anode. The listed positive values are the usual electrode-potential values used to compare the required oxidation thresholds; the practical preference cannot be inferred from those values alone without accounting for oxygen overpotential.

Step 3: Conclusion The products are H_2 at the cathode and Cl_2 at the anode. Hydrogen discharge is favoured over sodium; oxygen overpotential permits chlorine evolution.

Quick Tip to Solve: At the cathode compare reduction potentials; at the anode remember the oxygen overpotential in aqueous sodium chloride.

9. 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, $t = \dfrac{2.303}{k}\log_{10}\dfrac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0, [A]_t$ are initial and remaining concentrations.
- If a fraction f has reacted, the remaining concentration is $[A]_t = (1-f)[A]_0$. Use the amount remaining, not the amount consumed.

Step 1: Calculate the time for 90 percent completion Let the initial concentration be a. When 90% has reacted, only 10% remains, so $[A]_t = 0.10a$. Substitution into the integrated rate law gives

$$\begin{aligned} t_{90} &= \frac{2.303}{k}\log_{10}\frac{a}{0.10a} \\ &= \frac{2.303}{k}\log_{10} 10 = \frac{2.303}{k}. \end{aligned}$$

The initial concentration cancels because both concentrations refer to the same initial amount.

Step 2: Calculate the time for 99 percent completion and compare When 99% has reacted, 1%

Quick Tip to Solve: Convert completion percentages into remaining fractions: 90 percent leaves 0.10 and 99 percent leaves 0.01.

remains, so $[A]_t = 0.01a$. For the same reaction and temperature, k is unchanged. Hence

$$t_{99} = \frac{2.303}{k} \log_{10} \frac{a}{0.01a}$$
$$= \frac{2.303}{k} \log_{10} 100 = \frac{4.606}{k},$$
$$\frac{t_{99}}{t_{90}} = \frac{4.606/k}{2.303/k} = 2.$$

Each successive tenfold decrease in the amount remaining takes the same time in a first order reaction.

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

Quick Tip to Solve: Convert completion percentages into remaining fractions: 90 percent leaves 0.10 and 99 percent leaves 0.01.

10(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:

- Prolonged heating of D-glucose with excess HI reduces its oxygen-containing groups and gives the straight-chain hydrocarbon n-hexane.
- Nitric acid is a strong oxidising agent. It oxidises both the aldehyde group and the terminal primary alcohol group of glucose to carboxyl groups.

Step 1: Treat glucose with HI On prolonged heating with excess HI, D-glucose is converted to n-hexane. A balanced net equation is

$$\mathrm{CHO(CHOH)_4CH_2OH} + 14\mathrm{HI} \xrightarrow{\text{heat}} \mathrm{CH_3(CH_2)_4CH_3} + 6\mathrm{H_2O} + 7\mathrm{I_2}.$$

Removal of all six oxygen atoms and reduction of the functional groups leaves an unbranched six-carbon chain. This reaction supports the presence of six carbon atoms linked in a straight chain in glucose.

Step 2: Treat glucose with nitric acid On oxidation with nitric acid, both terminal groups are oxidised, giving the dicarboxylic acid saccharic acid (glucaric acid):

$$\mathrm{CHO(CHOH)_4CH_2OH} + 3[O] \xrightarrow{\mathrm{HNO_3}} \mathrm{HOOC(CHOH)_4COOH} + \mathrm{H_2O}.$$

Here $[O]$ denotes oxidising equivalents supplied by nitric acid. The four internal secondary alcohol groups are retained in the standard product; the aldehyde and primary alcohol ends become COOH groups.

Step 3: Conclusion (a) HI on prolonged heating gives n-hexane. (b) $\mathrm{HNO_3}$ gives saccharic acid,

Quick Tip to Solve: Distinguish reduction by HI from oxidation by nitric acid: HI gives hexane, while nitric acid oxidises both ends of glucose.

$HOOC(CHOH)_4COOH$.

Quick Tip to Solve: Distinguish reduction by HI from oxidation by nitric acid: HI gives hexane, while nitric acid oxidises both ends of glucose.

OR

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

Solution:

Concept:

- Protein molecules differ in the arrangement of their polypeptide chains and in their behaviour towards water.
- Globular proteins have compact folded chains; fibrous proteins have chains arranged in elongated fibres.

Step 1: Compare their shape and chain arrangement Globular proteins have polypeptide chains folded into compact, approximately spherical shapes. In fibrous proteins, polypeptide chains run parallel and are held together by hydrogen bonds and disulphide bonds, producing long, thread-like fibres. Thus compact folding distinguishes globular proteins from the elongated arrangement of fibrous proteins.

Step 2: Compare their solubility Globular proteins are generally soluble in water; insulin and albumin are examples. Fibrous proteins are generally insoluble in water; keratin in hair and wool, and myosin in muscles, are examples. The comparison concerns the usual properties of the two classes, rather than the solubility of every individual protein.

Step 3: Conclusion The two differences are: globular proteins are approximately spherical and generally water-soluble, whereas fibrous proteins are elongated and generally water-insoluble.

Quick Tip to Solve: Remember the paired contrasts: compact versus thread-like, and soluble versus insoluble.

11(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:

- Phenol undergoes the Reimer–Tiemann reaction with chloroform and aqueous alkali, followed by acidification, giving mainly ortho-hydroxybenzaldehyde and some para-hydroxybenzaldehyde.
- Zinc-dust distillation removes the oxygen-containing groups in the stated reaction sequence; an alkyl side chain on benzene can be oxidised to a carboxyl group.
- Soda-lime decarboxylation replaces the carboxylate group by hydrogen.

Quick Tip to Solve: Identify benzoic acid from its formula first, then use decarboxylation to check benzene.

Step 1: Identify A and trace the two aldehydes to B The aromatic compound is phenol, $A = C_6H_5OH$. Reimer–Tiemann reaction produces o- and p-hydroxybenzaldehyde, each containing one hydroxyl group and one aldehyde group on the ring. On distillation with zinc dust, both yield the same hydrocarbon, toluene, $B = C_6H_5CH_3$. The two substituent positions therefore cease to distinguish the products.

Step 2: Identify C and confirm D using both routes Oxidation of the methyl side chain of toluene gives benzoic acid, $C = C_6H_5COOH$, whose molecular formula is $C_7H_6O_2$, as required. Its sodium salt undergoes soda-lime decarboxylation:

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

Thus D is benzene. The second route confirms this identification:

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

Both routes give the same unsubstituted aromatic hydrocarbon.

Step 3: Conclusion A: phenol; B: toluene; C: benzoic acid; D: benzene.

Quick Tip to Solve: Identify benzoic acid from its formula first, then use decarboxylation to check benzene.

OR

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

(a) Phenol to Toluene

(b) Ethanol to Ethanal [2 marks]

Solution:

Concept:

- Zinc-dust distillation converts phenol into benzene by removing its oxygen as zinc oxide.
- Friedel–Crafts alkylation introduces a methyl group into benzene using methyl chloride and anhydrous aluminium chloride.
- Ethanol, a primary alcohol, undergoes dehydrogenation over heated copper at $573\,K$ to form ethanal.

Step 1: (a) Convert phenol into toluene First distil phenol with zinc dust to obtain benzene. Then treat benzene with methyl chloride in the presence of anhydrous aluminium chloride:

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

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

Benzene is the intermediate, and the second reaction is Friedel–Crafts methylation. It replaces a ring hydrogen with a methyl group to give toluene.

Step 2: (b) Convert ethanol into ethanal Pass ethanol vapour over heated copper at $573\,K$. Dehydro-

Quick Tip to Solve: For phenol, remove oxygen before methylating the ring; for ethanol, use heated copper to stop at the aldehyde.

genation removes two hydrogen atoms as hydrogen gas while retaining the two-carbon skeleton:

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

The product CH_3CHO is ethanal. This route directly forms the aldehyde without requiring the strong oxidation conditions that can further oxidise it to ethanoic acid.

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

Quick Tip to Solve: For phenol, remove oxygen before methylating the ring; for ethanol, use heated copper to stop at the aldehyde.

12. Define the following terms:

(a) Polysaccharides

(b) Nucleotides [2 marks]

Solution:

Concept:

- Carbohydrates are classified by the number of monosaccharide units produced on hydrolysis.
- In nucleic acids, a nucleotide is the repeating unit made from a nitrogenous base, a pentose sugar and a phosphate group.

Step 1: (a) Define polysaccharides Polysaccharides are complex carbohydrates that yield a large number of monosaccharide units on hydrolysis. These units are joined by glycosidic linkages into long chains, which may be linear or branched. Starch, cellulose and glycogen are common examples; all yield glucose units on complete hydrolysis. The defining feature is the large number of monosaccharide units, rather than merely the presence of more than one sugar unit.

Step 2: (b) Define nucleotides A nucleotide is a compound consisting of a nitrogenous base linked to a pentose sugar, with a phosphate group attached to the sugar. The sugar is ribose in RNA nucleotides and deoxyribose in DNA nucleotides. The base and sugar together form a nucleoside; addition of the phosphate group gives a nucleotide. Nucleotides are the building blocks of nucleic acids and join through phosphodiester linkages.

Step 3: Conclusion (a) Polysaccharides yield many monosaccharide units on hydrolysis. (b) A nucleotide consists of a nitrogenous base, a pentose sugar and a phosphate group.

Quick Tip to Solve: Distinguish a nucleoside from a nucleotide by the presence of the phosphate group.

Section C (36 marks)

13. 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 electrode with the more positive standard reduction potential is the cathode. The standard cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$.
- 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 Since $-0.25\,\text{V}$ is more positive than $-1.66\,\text{V}$, nickel ions are reduced at the cathode and aluminium is oxidised at the anode:

$$\begin{aligned} 2\text{Al}(s) &\longrightarrow 2\text{Al}^{3+}(aq) + 6e^- \\ 3\text{Ni}^{2+}(aq) + 6e^- &\longrightarrow 3\text{Ni}(s). \end{aligned}$$

Thus the overall reaction is $2\text{Al}(s) + 3\text{Ni}^{2+}(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{Ni}(s)$, and $n = 6$. Multiplying an electrode reaction to balance electrons does not multiply its electrode potential.

Step 2: Calculate the standard potential and reaction quotient

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

Omitting the pure solids and using the given molar concentrations,

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

The powers two and three come from the balanced reaction, not from the charges on the ions.

Step 3: Apply the Nernst equation Since $\log(10^{-3}) = -3$,

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

The negative logarithm makes the concentration correction positive, consistent with $Q < 1$. The supplied logarithms of two and three are unnecessary because all concentrations here are powers of ten.

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

Quick Tip to Solve: Balance aluminium and nickel half-reactions first: use six electrons and square the aluminium concentration but cube the nickel concentration.

14. (a) What type of stoichiometric defect is shown by NaCl and why?

(b) Calculate the efficiency of packing in case of a metal crystal for face centred cubic unit cell.

[3 marks]

Solution:

Concept:

- A Schottky defect consists of equal numbers of cation and anion vacancies in a crystal, preserving electrical neutrality and the stoichiometric ratio.
- Packing efficiency is $100 \times$ volume occupied by atoms/unit-cell volume. In an FCC cell, $Z = 4$ atoms and the face diagonal gives $4r = \sqrt{2}a$, where r is the atomic radius and a is the edge length.

Step 1: (a) Explain the stoichiometric defect in sodium chloride NaCl shows a Schottky defect. Some Na^+ ions and an equal number of Cl^- ions are missing from their normal lattice sites. Removing both types in equal numbers maintains electrical neutrality and the $1:1$ ion ratio, so the defect is stoichiometric. Since mass is lost from the crystal while its volume is approximately unchanged, its density decreases. NaCl has a high coordination number and its cation and anion have comparable sizes, which favour Schottky vacancies. The sodium ion is not sufficiently small to readily occupy an interstitial site, as would be needed for a Frenkel defect.

Step 2: (b) Count atoms and relate radius to edge length An FCC unit cell has atoms at eight corners and six face centres. A corner atom contributes $1/8$ and a face-centred atom contributes $1/2$:

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

Atoms touch along a face diagonal. Its length is $\sqrt{2}a$, equal to four atomic radii, so $a = 2\sqrt{2}r$.

Step 3: Calculate the occupied-volume fraction Treating the atoms as touching spheres, their total volume within one cell is $4 \times (4\pi r^3/3)$. Therefore,

$$\text{Packing efficiency} = \frac{4(4\pi r^3/3)}{(2\sqrt{2}r)^3} \times 100$$
$$= \frac{\pi}{3\sqrt{2}} \times 100 \approx 74.05\%.$$

Thus about 74% of the unit-cell volume is occupied by atoms and about 26% is empty space.

Step 4: Conclusion (a) NaCl shows a $\boxed{\text{Schottky defect}}$ because equal cation and anion vacancies are favoured in its highly coordinated lattice. (b) The packing efficiency of an FCC metal crystal is $\boxed{74\%}$.

Quick Tip to Solve: For FCC, count four atoms per cell and use contact along the face diagonal; contact along the edge would give the wrong radius relation.

15. Write three differences between physisorption and chemisorption. [3 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance, the adsorbate, on the surface of another substance, the adsorbent. The nature of the attractive force distinguishes physisorption from chemisorption.
- Physisorption involves weak van der Waals forces, whereas chemisorption involves formation of chemical bonds between the adsorbate and the surface. This difference governs their heat of adsorption and specificity.

Step 1: Difference 1: Nature of the attractive force In physisorption, the adsorbate is held on the adsorbent by weak van der Waals forces. No chemical bond is formed, and the adsorbed molecules largely retain their chemical identity. In chemisorption, the adsorbate is attached to the surface through chemical bonds. These bonds are much stronger than the forces responsible for physical adsorption and may involve redistribution of electrons at the surface.

Step 2: Difference 2: Magnitude of the heat of adsorption Physisorption has a low heat of adsorption, typically about 20–$40\,\text{kJ mol}^{-1}$, because only weak intermolecular attractions are involved. Chemisorption has a much higher heat of adsorption, typically about 80–$240\,\text{kJ mol}^{-1}$, because chemical bonds form. Both processes are normally exothermic; the quoted positive values describe the magnitudes of the heat released, while the corresponding adsorption enthalpy changes are negative.

Step 3: Difference 3: Specificity of adsorption Physisorption is not highly specific: a given surface can physically adsorb several different gases because van der Waals attractions act between many substances. Chemisorption is highly specific: it occurs only when the adsorbate can form suitable chemical bonds with that particular surface. Thus the chemical nature of both the gas and the adsorbent determines whether chemisorption occurs.

Step 4: Conclusion The three differences are: physisorption involves weak van der Waals forces, a low heat of adsorption and low specificity; chemisorption involves chemical bonds, a high heat of adsorption and high specificity.

Quick Tip to Solve: Organise each difference as a matched pair under one heading: force, heat released, and specificity give three independent comparisons.

16. 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:

- For a reaction first order in A and zero order in B, the rate law is $r = k[A]^1[B]^0 = k[A]$. Here r is the initial rate and k is the rate constant.
- At the same temperature, k is constant. Doubling $[A]$ doubles the rate, whereas changing $[B]$ has no effect on the rate. The units of k are min^{-1} for the units used in the table.

Step 1: Determine the rate constant from experiment I The first row supplies both the initial concentration of A and the initial rate. Thus,

$$k = \frac{r_{\text{I}}}{[A]_{\text{I}}} = \frac{2.0 \times 10^{-2}\,\text{mol L}^{-1}\text{min}^{-1}}{0.1\,\text{mol L}^{-1}} = 0.20\,\text{min}^{-1}.$$

The concentration of B does not enter this calculation because its exponent in the rate law is zero.

Step 2: Fill the concentration in experiment II Using the supplied rate in experiment II,

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

The rate is twice that in experiment I, so the concentration of A must also be twice as large. The simultaneous doubling of B does not contribute to the increase.

Step 3: Fill the rate in experiment III and concentration in experiment IV For experiment III, the concentration of A is four times its value in experiment I. Therefore,

$$r_{\text{III}} = k[A]_{\text{III}} = 0.20 \times 0.40 = 8.0 \times 10^{-2}\,\text{mol L}^{-1}\text{min}^{-1}.$$

For experiment IV,

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

Experiments I and IV have equal rates and hence equal concentrations of A, despite their different concentrations of B.

Step 4: Conclusion The blanks are: experiment II, $[A] = 0.20\,\text{mol L}^{-1}$; experiment III, initial rate $= 8.0 \times 10^{-2}\,\text{mol L}^{-1}\text{min}^{-1}$; experiment IV, $[A] = 0.10\,\text{mol L}^{-1}$.

Quick Tip to Solve: Cross out the B column mentally: for this rate law, rate ratios are exactly the corresponding A concentration ratios.

17(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 stability of a transition-metal oxidation state depends on the electronic configuration obtained after removal of the outer electrons. A noble-gas configuration is particularly stable.
- Colour in many transition-metal complexes arises from absorption of visible light for a d-d transition between split d orbitals. Such a transition requires a d electron.
- For oxides of the same transition metal, basic character generally decreases and acidic character increases as the metal's oxidation state increases.

Step 1: (a) Explain the oxidation state of scandium Scandium has atomic number 21 and electronic configuration $[\mathrm{Ar}]\,3d^1 4s^2$. Loss of its two $4s$ electrons and one $3d$ electron gives

$$\mathrm{Sc}^{3+} : [\mathrm{Ar}].$$

Thus the +3 ion has a stable noble-gas configuration. A lower oxidation state retains outer-shell electrons, while removal of another electron after formation of Sc^{3+} would require breaking into the closed argon core and needs very high energy. Hence +3 is the usual stable oxidation state shown by scandium.

Step 2: (b) Explain why the titanium complex is colourless Water is a neutral ligand, so titanium has oxidation state +4 in $[\mathrm{Ti}(\mathrm{H_2O})_6]^{4+}$. Neutral Ti has configuration $[\mathrm{Ar}]\,3d^2 4s^2$; removal of four electrons gives $\mathrm{Ti}^{4+} : [\mathrm{Ar}]$, a d^0 configuration. Although the ligands split the energies of the d orbitals, there is no d electron available for a d-d transition. Consequently the complex is colourless.

Step 3: (c) Compare the acid-base character of the manganese oxides In MnO, manganese is in the low oxidation state +2 and the oxide is predominantly ionic. It behaves as a basic oxide and reacts with acids, for example,

$$\mathrm{MnO} + 2\mathrm{HCl} \longrightarrow \mathrm{MnCl_2} + \mathrm{H_2O}.$$

In $\mathrm{Mn_2O_7}$, manganese is in the high oxidation state +7. This oxide is covalent and acidic; it is the acid anhydride of permanganic acid:

$$\mathrm{Mn_2O_7} + \mathrm{H_2O} \longrightarrow 2\mathrm{HMnO_4}.$$

Step 4: Conclusion (a) Sc^{3+} attains the stable $[\mathrm{Ar}]$ configuration. (b) Ti^{4+} is d^0, so no d-d transition occurs. (c) The low-oxidation-state oxide MnO is basic, whereas the high-oxidation-state oxide $\mathrm{Mn_2O_7}$ is acidic.

Quick Tip to Solve: Write the metal ion's configuration first; for the oxide comparison, calculate Mn's oxidation state before deciding acidic or basic character.

OR

17(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 involve the progressive filling of the $4f$ subshell. Their outer electronic configuration includes $6s^2$, with occasional occupancy of a $5d$ orbital.
- The common $+3$ state results from removal of the outer electrons. Additional stable states can occur when removal of another electron produces an empty, half-filled or completely filled f subshell.
- Several oxidation states are possible when the energies of the available valence subshells are close enough that different numbers of electrons can participate in bonding.

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

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

Here $[\mathrm{Xe}]$ denotes the xenon core. The $4f$ subshell fills progressively and a $5d$ electron is sometimes present. Lanthanum itself is $[\mathrm{Xe}]\, 4f^0 5d^1 6s^2$.

Step 2: (b) Give the common oxidation states of cerium Cerium, with atomic number 58, has electronic configuration $[\mathrm{Xe}]\, 4f^1 5d^1 6s^2$. Its common oxidation states are $+3$ and $+4$. Removal of the two $6s$ electrons and the $5d$ electron gives

$$\mathrm{Ce}^{3+} : [\mathrm{Xe}]\, 4f^1.$$

Removal of the additional $4f$ electron gives

$$\mathrm{Ce}^{4+} : [\mathrm{Xe}],$$

which has an empty $4f$ subshell and a noble-gas configuration. This explains why $+4$ is accessible in addition to the usual lanthanoid $+3$ state.

Step 3: (c) Explain the range of actinoid oxidation states In actinoids, the $5f$, $6d$ and $7s$ subshells have comparable energies. Consequently, electrons from all three subshells can participate in bonding or be removed during compound formation. Depending on the element and the chemical environment, different numbers of these electrons are involved, producing a wide range of oxidation states. This participation of $5f$ electrons is particularly significant among the earlier actinoids and gives more varied oxidation states than the predominant $+3$ state of the lanthanoids.

Step 4: Conclusion (a) The general configuration is $[\mathrm{Xe}]\, 4f^{1-14}5d^{0-1}6s^2$. (b) Cerium commonly shows $+3$ and $+4$ oxidation states. (c) Actinoids show varied oxidation states because the $5f$, $6d$ and $7s$ subshells have comparable energies and their electrons can participate in bonding.

Quick Tip to Solve: Link Ce(IV) to the empty 4f subshell, and name all three comparable-energy actinoid subshells: 5f, 6d and 7s.

18(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 a physical or chemical property of the desired material and the impurities.
- Froth floatation uses selective wetting; zone refining uses unequal solubility in liquid and solid metal; vapour phase refining uses formation and decomposition of a volatile compound.

Step 1: (a) Froth floatation Sulphide ore particles are preferentially wetted by oil, whereas gangue particles are wetted by water. When air is blown through the aqueous suspension, the oil-wetted ore adheres to air bubbles and rises as froth. The water-wetted gangue remains in the water. Separation therefore depends on the different wetting behaviour of ore and gangue; the ore-rich froth is skimmed off.

Step 2: (b) Zone refining Impurities are more soluble in the molten metal than in the solid metal. A narrow molten zone is moved along an impure metal rod. As metal behind the zone solidifies, relatively pure metal crystallises while impurities remain in the melt and travel with the moving zone. Repeated passage concentrates impurities at one end, which is cut off.

Step 3: (c) Vapour phase refining The impure metal is converted selectively into a volatile compound with a suitable reagent. The volatile compound is separated from nonvolatile impurities and then decomposed to give pure metal. The compound must form readily and must decompose under suitable conditions; for example, nickel forms volatile nickel tetracarbonyl, which yields pure nickel on heating.

Step 4: Conclusion The principles are: (a) differential wetting of ore and gangue, (b) greater solubility of impurities in molten metal, and (c) formation followed by decomposition of a volatile metal compound.

Quick Tip to Solve: Associate froth with wetting, a moving molten zone with solubility, and vapour refining with a volatile compound.

OR

18(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:

- Pig iron and cast iron are iron-carbon materials distinguished here by their carbon content.
- Hydraulic washing exploits density, liquation exploits melting point, leaching exploits selective dissolution, and roasting involves heating in air.

Step 1: (a) Cast iron and pig iron: carbon content Cast iron contains about 3% carbon, whereas pig iron contains about 4% carbon. Thus cast iron has a lower carbon content than pig iron. Pig iron is the crude iron obtained from the blast furnace; cast iron is prepared by melting pig iron with scrap iron and coke using a hot-air blast. Carbon content is the requested distinguishing point.

Step 2: (b) Hydraulic washing and liquation: basis of separation Hydraulic washing separates ore from gangue using their difference in density: a stream of water carries away lighter gangue while the heavier ore remains. Liquation separates a low-melting metal from higher-melting impurities using their difference in melting point: on heating, the metal melts and flows away while the impurities remain solid. The distinguishing property is therefore density versus melting point.

Step 3: (c) Leaching and roasting: nature of the operation Leaching is treatment with a suitable chemical solution that selectively dissolves the ore or its desired constituent, leaving insoluble impurities behind. Roasting is strong heating of the ore, generally a sulphide ore, in excess air below its melting point, usually converting it into an oxide. Thus leaching uses selective dissolution in a reagent, whereas roasting uses heating in air to cause chemical conversion.

Step 4: Conclusion The differences are: (a) cast iron has about 3% carbon and pig iron about 4%; (b) hydraulic washing uses density difference and liquation uses melting-point difference; (c) leaching uses selective dissolution and roasting uses heating in excess air.

Quick Tip to Solve: Name one precise comparison property for each pair: carbon content, separation property, and treatment medium.

19. Using valence bond theory, predict the hybridization and magnetic character of the following:

(a) $[CoF_6]^{3-}$

(b) $[Ni(CN)_4]^{2-}$

[At. no.: Co = 27, Ni = 28] [3 marks]

Solution:

Concept:

- In valence bond theory, ligand electron pairs occupy vacant hybrid orbitals of the central metal ion. The ligand strength determines whether the metal's d electrons pair before bonding.
- An unpaired electron gives paramagnetism; a complex with all electrons paired is diamagnetic. Six-coordinate outer-orbital complexes use sp^3d^2, while four-coordinate square-planar complexes use dsp^2.

Step 1: (a) Determine the cobalt ion configuration In $[CoF_6]^{3-}$, each fluoride has charge -1. If the cobalt oxidation state is x, then $x - 6 = -3$, so $x = +3$. Cobalt has configuration $[Ar]3d^7 4s^2$; removing the two $4s$ electrons and one $3d$ electron gives Co^{3+} : $[Ar]3d^6$.

Step 2: Predict bonding and magnetism of the fluoride complex Fluoride is a weak-field ligand and does not cause pairing of the $3d$ electrons. The high-spin $3d^6$ arrangement has one doubly occupied d orbital and four singly occupied d orbitals, hence four unpaired electrons. Two vacant inner $3d$ orbitals are unavailable. The metal uses one $4s$, three $4p$, and two $4d$ orbitals to form six sp^3d^2 hybrid orbitals. The complex is an outer-orbital octahedral complex and is paramagnetic.

Step 3: (b) Determine the nickel ion configuration In $[Ni(CN)_4]^{2-}$, each cyanide has charge -1. Thus $x - 4 = -2$, giving nickel oxidation state $+2$. Nickel has configuration $[Ar]3d^8 4s^2$, so Ni^{2+} has configuration $[Ar]3d^8$.

Step 4: Predict bonding and magnetism of the cyanide complex Cyanide is a strong-field ligand and causes pairing of the $3d$ electrons. The eight d electrons occupy four orbitals as pairs, leaving one $3d$ orbital vacant. This vacant $3d$ orbital, one $4s$, and two $4p$ orbitals form four dsp^2 hybrid orbitals. The resulting complex is square planar. All electrons are paired, so it is diamagnetic.

Step 5: Conclusion $[CoF_6]^{3-}$: sp^3d^2, octahedral and paramagnetic with four unpaired electrons. $[Ni(CN)_4]^{2-}$: dsp^2, square planar and diamagnetic.

Quick Tip to Solve: Find the oxidation state first, then count d electrons and use ligand strength before selecting hybridization.

20. (a) Define the following terms:

(i) Enantiomers

(ii) Racemic mixture

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

Solution:

Concept:

- Stereoisomers have the same connectivity but differ in the spatial arrangement of atoms. Enantiomers are related as non-superimposable mirror images.
- Optical rotation depends on the relative amounts of the two enantiomers; equal amounts give external compensation.
- Nucleophilic substitution requires cleavage of the carbon-halogen bond. Resonance and the hybridisation of the bonded carbon affect its strength.

Step 1: (a)(i) Define enantiomers Enantiomers are stereoisomers that are non-superimposable mirror images of each other. A pair has opposite configurations at its chiral centre(s). Under identical conditions, the two members rotate plane-polarised light through equal angles in opposite directions: one is dextrorotatory and the other is laevorotatory.

Step 2: (a)(ii) Define a racemic mixture A racemic mixture contains equal amounts of the two enantiomers of an optically active substance. It is optically inactive because the clockwise rotation caused by one enantiomer is exactly cancelled by the anticlockwise rotation caused by the other. This cancellation is called external compensation; it does not mean that the individual molecules are achiral.

Step 3: (b) Explain resistance of chlorobenzene to substitution In chlorobenzene, a lone pair on chlorine is delocalised into the benzene ring. Consequently, the $\mathrm{C-Cl}$ bond acquires partial double-bond character through resonance and becomes shorter and stronger than the corresponding bond in an alkyl chloride. Also, chlorine is bonded to an sp^2-hybridised carbon, whose greater s-character holds the bonding electrons more tightly than an sp^3 carbon does. Cleavage of this bond is therefore difficult. An S_N1 pathway would require an unstable phenyl carbocation, while the aromatic ring makes the usual S_N2 backside attack difficult. Thus ordinary nucleophilic substitution conditions are ineffective.

Step 4: Conclusion Enantiomers are non-superimposable mirror-image stereoisomers; a racemic mixture is their optically inactive equimolar mixture. Chlorobenzene resists nucleophilic substitution chiefly because its resonance-strengthened $\mathrm{C-Cl}$ bond is difficult to break.

Quick Tip to Solve: For chlorobenzene, connect chlorine lone-pair resonance to partial double-bond character before discussing the difficult substitution pathways.

21(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 delocalisation stabilises aromatic diazonium ions, whereas aliphatic diazonium ions readily lose nitrogen gas.
- Amines are weak bases: their nitrogen lone pair accepts a proton from water, producing hydroxide ions.
- Ferric ions form an insoluble hydrated ferric oxide precipitate with hydroxide ions, conventionally represented as $Fe(OH)_3$.

Step 1: (a) Compare aromatic and aliphatic diazonium salts In an aromatic diazonium ion, $Ar - N_2^+$, the diazonium group is directly attached to the aromatic ring. Conjugation permits resonance delocalisation involving the ring and the diazonium group, stabilising the ion. Aliphatic diazonium ions, $R - N_2^+$, have no corresponding aromatic resonance stabilisation and readily decompose with evolution of nitrogen:

$$R - N_2^+ \longrightarrow R^+ + N_2 \uparrow.$$

Loss of nitrogen from an aryl diazonium ion would generate a very unstable aryl carbocation. Hence aromatic diazonium salts are comparatively more stable and can be maintained in cold solution at 273–278 K; this comparison does not imply stability on strong heating.

Step 2: (b) Show how methylamine supplies hydroxide ions The nitrogen lone pair of methylamine accepts a proton from water. Methylamine therefore makes the solution alkaline:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-.$$

Ferric chloride supplies Fe^{3+} ions, which react with these hydroxide ions to give a reddish-brown precipitate:

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

The precipitate is hydrated ferric oxide, commonly represented by ferric hydroxide. Combining the base equilibrium with precipitation gives the overall equation

$$FeCl_3 + 3CH_3NH_2 + 3H_2O \longrightarrow Fe(OH)_3 \downarrow + 3CH_3NH_3Cl.$$

Removal of hydroxide ions by precipitation drives further reaction of methylamine with water.

Step 3: Conclusion Aromatic diazonium salts are more stable because of resonance stabilisation. Aqueous methylamine produces OH^- ions, which precipitate ferric ions as reddish-brown hydrated ferric oxide.

Quick Tip to Solve: For an amine reacting with a metal salt, first write its equilibrium with water and then the metal-ion precipitation equation.

OR

21(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:

- The basicity constant K_b measures the tendency of a base to accept a proton; $pK_b = -\log_{10} K_b$. Thus stronger bases have smaller pK_b values.
- Electron-withdrawing substituents decrease the availability of the nitrogen lone pair, whereas electron-releasing substituents increase it.
- For gaseous alkylamines, the electron-releasing inductive effect of alkyl groups governs the usual basicity order; aqueous solvation effects do not apply.

Step 1: (a) Compare the substituted anilines In aniline, the nitrogen lone pair is delocalised into the benzene ring and is less readily available for protonation than in an aliphatic amine. The para nitro group in p-nitroaniline withdraws electron density through both its inductive and resonance effects. This further reduces the availability of the amino nitrogen lone pair and makes p-nitroaniline the weakest base of the three. In p-toluidine, the para methyl group releases electron density by its positive inductive effect and hyperconjugation, making it more basic than aniline. Therefore the basicity order is

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

Since pK_b varies inversely with basic strength, the requested decreasing order is

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

Step 2: (b) Compare ethylamines in the gaseous state An ethyl group has a positive inductive effect and supplies electron density towards nitrogen. Increasing the number of ethyl groups increases the tendency of the nitrogen lone pair to accept a proton and stabilises the resulting conjugate acid. In the gaseous state there is no hydration of the amine or its conjugate acid, so the aqueous solvation-based order must not be used. The basicity order is

$$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2.$$

Reversing this gives the decreasing order of pK_b:

$$\boxed{C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N}.$$

Step 3: Conclusion The decreasing pK_b orders are

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

(b) $C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$ (gas).

Quick Tip to Solve: First arrange the bases by lone-pair availability, then reverse the entire order for decreasing pKb; check whether the medium is gaseous or aqueous.

22(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 distinguishing test must give different visible observations for the two substances under the same conditions.
- Phenols form coloured complexes with neutral ferric chloride; an alcohol's O–H group reacts with sodium, while an ether has no O–H bond.
- Lucas reagent is concentrated HCl with anhydrous $ZnCl_2$. At room temperature, tertiary alcohols form insoluble alkyl chlorides immediately, while primary alcohols do not give immediate turbidity.

Step 1: (a) Phenol and 1-propanol: neutral ferric chloride test Add a few drops of neutral aqueous $FeCl_3$ solution to each sample. Phenol gives a violet colour due to formation of a ferric phenolate complex. 1-Propanol gives no violet colour. Thus the coloured sample is phenol; the ordinary aliphatic alcohol does not respond to this phenol test.

Step 2: (b) Ethanol and dimethyl ether: sodium metal test Add a small piece of sodium to each dry sample. Ethanol gives effervescence of hydrogen and forms sodium ethoxide:

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

Dry dimethyl ether gives no such hydrogen evolution because it has no hydroxyl hydrogen. Dry conditions are essential, since water would itself react with sodium and obscure the distinction.

Step 3: (c) 1-Propanol and 2-methyl-2-propanol: Lucas test Shake each sample with Lucas reagent at room temperature. 2-Methyl-2-propanol, a tertiary alcohol, gives immediate turbidity as insoluble tert-butyl chloride forms:

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

1-Propanol is a primary alcohol and gives no turbidity at room temperature during the test. The rapid tertiary-alcohol reaction is favoured by the stability of its tertiary carbocation.

Step 4: Conclusion Use neutral $FeCl_3$ for (a), sodium metal for (b), and Lucas reagent at room temperature for (c). The positive observations are violet colour for phenol, hydrogen evolution for ethanol, and immediate turbidity for 2-methyl-2-propanol.

Quick Tip to Solve: Match the test to the difference: phenolic OH gives the ferric chloride colour, alcoholic OH liberates hydrogen with sodium, and tertiary alcohol gives immediate Lucas turbidity.

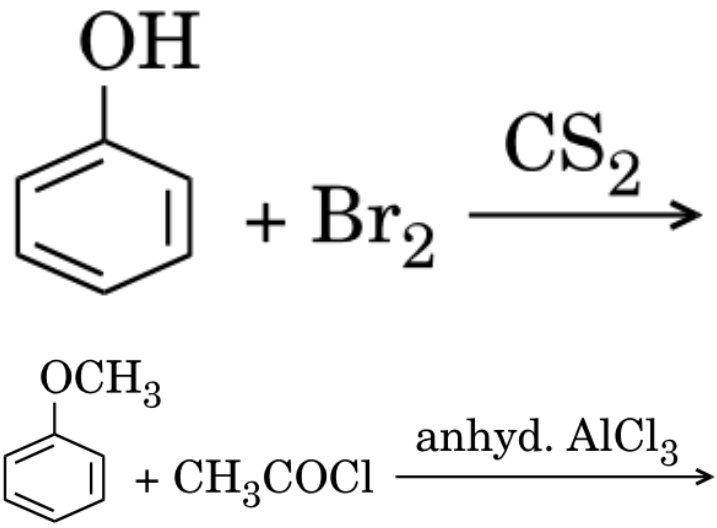
OR

22(b). Write the products of the following reactions:

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

(ii) Phenol + Br_2 in CS_2 $\rightarrow$

(iii) Anisole + CH_3COCl in presence of anhydrous $AlCl_3$ $\rightarrow$ [3 marks]



Solution:

Concept:

- HI protonates an ether oxygen; iodide then attacks the less hindered alkyl group when both groups are primary or methyl.
- The $-OH$ and $-OCH_3$ groups activate a benzene ring and direct electrophilic substitution to the ortho and para positions.
- Bromination of phenol in a non-polar solvent gives monobrominated products. Friedel–Crafts acylation introduces $-COCH_3$ using acetyl chloride and anhydrous $AlCl_3$.

Step 1: (i) Cleavage of ethyl methyl ether by HI After protonation of the oxygen, iodide attacks the less hindered methyl group by an S_N2 displacement. The products of the stated cleavage are methyl iodide and ethanol:

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

The ether bond broken is the methyl–oxygen bond, so the oxygen remains with the ethyl group. Conversion of the resulting ethanol to ethyl iodide would require further reaction with additional HI; excess HI is not specified here.

Step 2: (ii) Bromination of phenol in carbon disulphide In the non-polar solvent CS_2, phenol forms a mixture of 2-bromophenol and 4-bromophenol, with the para product predominant:

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

Here bromine occupies position 2 or 4 relative to the hydroxyl group at position 1. The hydroxyl group directs substitution to both positions; the para position is less sterically hindered. Do not use

Quick Tip to Solve: For HI cleavage select the methyl side; for phenol check whether the reagent is bromine water or bromine in CS2; for anisole place the acetyl group ortho and para to methoxy.

the 2,4,6-tribromophenol product of bromine water for these solvent conditions.

Step 3: (iii) Friedel–Crafts acylation of anisole Acetyl chloride with anhydrous $AlCl_3$ gives an acetyl electrophile. Substitution on anisole yields 2-methoxyacetophenone and 4-methoxyacetophenone, the para isomer being the major product:

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

The $-COCH_3$ group is attached directly to the ring at an ortho or para position relative to $-OCH_3$. Acylation occurs on the aromatic ring rather than replacing the methoxy group.

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

Quick Tip to Solve: For HI cleavage select the methyl side; for phenol check whether the reagent is bromine water or bromine in CS2; for anisole place the acetyl group ortho and para to methoxy.

23. Differentiate between the following:

(a) Antiseptics and Disinfectants

(b) Antacids and Antihistamines

(c) Soaps and Detergents [3 marks]

Solution:

Concept:

- Antimicrobial agents are distinguished by where they can safely be applied; drugs are distinguished by their physiological action.
- A cleansing agent must retain its activity in the water used. Calcium and magnesium ions in hard water precipitate soap but do not form insoluble scum with ordinary synthetic detergents.

Step 1: (a) Antiseptics and disinfectants Antiseptics kill or inhibit microorganisms and can be applied to living tissues such as skin, wounds and cuts in suitable concentrations. Examples are tincture of iodine and dilute Dettol. Disinfectants kill microorganisms on non-living objects such as floors, drains and instruments; they are generally unsuitable for application to living tissues at their disinfecting concentrations. For example, a 1 percent phenol solution acts as a disinfectant, whereas a 0.2 percent phenol solution can act as an antiseptic. Thus the site of application and concentration, rather than just the chemical name, determine the use.

Step 2: (b) Antacids and antihistamines Antacids neutralise excess hydrochloric acid in the stomach and relieve acidity. Magnesium hydroxide and sodium hydrogencarbonate are examples. For instance,

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O.$$

Antihistamines used against allergies block the action of histamine at its receptors, reducing allergic responses such as sneezing and itching. Brompheniramine is an example. Their usual anti-allergy action is receptor blocking, whereas antacids act by acid–base neutralisation.

Quick Tip to Solve: Compare each pair on a single useful basis: tissue versus surface, acid neutralisation versus histamine blocking, and scum formation versus effective cleaning in hard water.

Step 3: (c) Soaps and detergents Soaps are sodium or potassium salts of long-chain fatty acids, for example sodium stearate, $C_{17}H_{35}COONa$. Common synthetic detergents are salts of long-chain alkyl sulphates or alkylbenzene sulphonates, for example sodium lauryl sulphate, $C_{12}H_{25}OSO_3Na$. Soaps form insoluble calcium and magnesium salts in hard water, producing scum and reducing cleansing action. Detergents remain effective in hard water because their corresponding salts do not precipitate as soap scum. Thus soaps and detergents differ both in the chemical nature of their ionic heads and in their behaviour in hard water.

Step 4: Conclusion Antiseptics are used on living tissues and disinfectants on non-living objects. Antacids neutralise excess stomach acid, while anti-allergy antihistamines block histamine action. Soaps are fatty-acid salts that form scum in hard water; common synthetic detergents are sulphate or sulphonate salts that clean effectively in hard water.

Quick Tip to Solve: Compare each pair on a single useful basis: tissue versus surface, acid neutralisation versus histamine blocking, and scum formation versus effective cleaning in hard water.

24. Answer the following with reason:

(a) Is $(NH\text{-}CHR\text{-}CO)_n$, 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; a copolymer is formed from two or more different kinds of monomer.
- Addition polymerisation joins unsaturated monomers without eliminating small molecules. Condensation polymerisation eliminates a small molecule such as water.
- Thermosetting plastics acquire a permanent cross-linked network on heating, whereas thermoplastics soften repeatedly on heating.

Step 1: (a) Identify the monomer of the polyamide The repeating unit $(-NH-CHR-CO-)_n$ is obtained by condensation of a single kind of amino acid, $H_2N-CHR-COOH$. Each amino acid has both an amino group and a carboxyl group, so molecules of the same monomer join by peptide (amide) linkages with elimination of water. Thus it is a homopolymer. Having two different functional groups within one monomer does not make the polymer a copolymer.

Step 2: (b) Classify PVC by its polymerisation reaction PVC is formed by addition polymerisation of vinyl chloride (chloroethene):

$$n\,CH_2=CHCl \longrightarrow (-CH_2-CHCl-)_n\,.$$

The carbon-carbon double bond opens and monomers join without loss of water, hydrogen chloride or any other small molecule. PVC is therefore an addition polymer.

Step 3: (c) Relate Bakelite to its structure Bakelite is a thermosetting plastic. Phenol and formaldehyde

Quick Tip to Solve: Count the kinds of monomer for homopolymer versus copolymer; check loss of small molecules for addition versus condensation, and cross-links for thermosetting behaviour.

form a highly cross-linked, three-dimensional network during curing. These covalent cross-links restrict movement of the polymer chains, making the cured material hard and infusible. On reheating it cannot soften and be remoulded like a thermoplastic; strong heating causes decomposition instead.

Step 4: Conclusion (a) Homopolymer, because one kind of amino acid forms it; (b) addition polymer, because vinyl chloride adds without elimination of a small molecule; (c) thermosetting plastic, because Bakelite has a permanent cross-linked network.

Quick Tip to Solve: Count the kinds of monomer for homopolymer versus copolymer; check loss of small molecules for addition versus condensation, and cross-links for thermosetting behaviour.

Section D (15 marks)

25(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, number the longest chain containing $-\mathrm{CHO}$ from the aldehyde carbon, which is carbon 1.
- Tollens' reagent oxidises an aldehyde to a carboxylate ion while silver ions are reduced to metallic silver; an ordinary alcohol does not give this test.
- Grignard reagents add an alkyl group to a carbonyl compound. Acidic hydrolysis of the resulting magnesium alkoxide yields an alcohol.
- The Hell-Volhard-Zelinsky reaction brominates the alpha carbon of a carboxylic acid containing an alpha hydrogen; aqueous alkali can then replace bromine by hydroxyl.

Step 1: (a) Number the unsaturated aldehyde Write the chain from the aldehyde end as $\mathrm{CHO-CH=CH-CH_3}$. It contains four carbons, so the parent is butanal. The double bond is between carbons 2 and 3. Combining the double-bond locant and the aldehyde suffix gives but-2-enal. The aldehyde group has priority in numbering, so the aldehyde carbon must receive locant 1. The double-bond locant happens to be 2 from either end, but the aldehyde group determines the numbering direction.

Step 2: (b) Apply Tollens' test Warm separate samples gently with freshly prepared Tollens' reagent. Ethanal gives a silver mirror (or a grey deposit of metallic silver), whereas ethanol gives no silver mirror under the test conditions. The reaction for ethanal is

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

Quick Tip to Solve: Check the carbon count before choosing a conversion: ethanol needs one added carbon, while propanal needs an alpha-hydroxyl group on its existing three-carbon chain.

Ethanal has an oxidisable aldehyde group; ethanol lacks this group. This difference, rather than smell alone, provides the chemical distinction.

Step 3: (c)(i) Oxidise the side chain of toluene Heat toluene with alkaline potassium permanganate to oxidise its methyl side chain to potassium benzoate, then acidify to obtain benzoic acid:

$$C_6H_5CH_3 \xrightarrow[\Delta]{KMnO_4/OH^-} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH.$$

The benzene ring remains intact; oxidation occurs at the benzylic side chain.

Step 4: (c)(ii) Add one carbon to ethanol through ethanal First oxidise ethanol to ethanal with PCC (pyridinium chlorochromate), avoiding further oxidation to the acid. Treat ethanal with methylmagnesium bromide in dry ether, then hydrolyse the alkoxide with dilute acid:

$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO,$$

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

The methyl group adds to the aldehyde carbon, increasing the chain from two to three carbons and giving the required secondary alcohol, propan-2-ol.

Step 5: (c)(iii) Oxidise, alpha-brominate and hydrolyse propanal Oxidise propanal to propanoic acid using acidified potassium dichromate. Brominate the alpha carbon by the Hell-Volhard-Zelinsky reaction, using bromine and red phosphorus followed by water. Hydrolyse the resulting 2-bromopropanoic acid with aqueous alkali, then acidify:

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

$$CH_3CH_2COOH \xrightarrow[\text{then } H_2O]{Br_2/\text{red P}} CH_3CHBrCOOH,$$

$$CH_3CHBrCOOH \xrightarrow[\text{then } H^+]{\text{aq. NaOH}} CH_3CH(OH)COOH.$$

Substitution of bromine by hydroxyl places the hydroxyl group on carbon 2 without changing the three-carbon skeleton. The product is 2-hydroxypropanoic acid (lactic acid).

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

Quick Tip to Solve: Check the carbon count before choosing a conversion: ethanol needs one added carbon, while propanal needs an alpha-hydroxyl group on its existing three-carbon chain.

OR

25(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:

- In naming a hydroxybenzoic acid, the ring carbon bearing the carboxyl group is numbered 1; the hydroxy substituent receives the lowest possible locant.
- Acidity depends on the stability of the conjugate base. An electron-withdrawing group stabilises a carboxylate ion through its negative inductive effect.
- Clemmensen reduction converts an aldehyde group $-CHO$ into $-CH_3$. An aldehyde without an alpha hydrogen undergoes Cannizzaro disproportionation in concentrated alkali.
- Semicarbazide, $H_2N-NH-C(=O)-NH_2$, condenses with the carbonyl group through its terminal amino group to form a semicarbazone with elimination of water.

Step 1: (a) Name salicylic acid Salicylic acid has a carboxyl group and a hydroxy group on adjacent carbon atoms of a benzene ring. The parent is benzoic acid because the carboxyl group is the principal functional group. Numbering from the ring carbon attached to $-COOH$ places $-OH$ at position 2. Its IUPAC name is therefore 2-hydroxybenzoic acid.

Step 2: (b) Compare the conjugate bases The relevant acid dissociation equilibria are

$$ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+,$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+.$$

Chlorine is electronegative and withdraws electron density through sigma bonds by its $-I$ effect. This disperses and stabilises the negative charge of the chloroacetate ion. In contrast, the methyl group of acetate has a $+I$ effect, which increases electron density and destabilises the negatively charged carboxylate group. Hence chloroacetic acid loses a proton more readily and is more acidic than acetic acid.

Step 3: (c)(i) Reduce the aldehyde with zinc amalgam Zinc amalgam and dilute hydrochloric acid carry out Clemmensen reduction. The aldehyde carbon is retained, but its carbonyl oxygen is removed and the $-CHO$ group becomes $-CH_3$:

$$(CH_3)_3C-CHO \xrightarrow{Zn(Hg),\ \text{dil. } HCl} (CH_3)_3C-CH_3.$$

The product is 2,2-dimethylpropane (neopentane). The tert-butyl carbon skeleton remains intact.

Step 4: (c)(ii) Treat with concentrated sodium hydroxide The carbon adjacent to the aldehyde group is bonded to three methyl groups and the aldehyde carbon, so it has no alpha hydrogen. The aldehyde therefore undergoes Cannizzaro reaction rather than aldol condensation. One molecule is reduced to

Quick Tip to Solve: First check the carbon next to -CHO for an alpha hydrogen: its absence identifies Cannizzaro reaction with concentrated NaOH.

an alcohol while another is oxidised to a carboxylate salt:

$$2(CH_3)_3C - CHO + NaOH \longrightarrow (CH_3)_3C - CH_2OH + (CH_3)_3C - COONa.$$

The products in the alkaline reaction mixture are 2,2-dimethylpropan-1-ol and sodium 2,2-dimethylpropanoate. The salt, rather than the free carboxylic acid, is written because no acidification is specified.

Step 5: (c)(iii) Form the semicarbazone In the presence of a weak acid, the terminal $-NH_2$ group of semicarbazide attacks the aldehyde carbonyl group. Subsequent elimination of water forms a carbon-nitrogen double bond:

$$(CH_3)_3C - CHO + H_2N - NH - C(=O) - NH_2 \longrightarrow (CH_3)_3C - CH = N - NH - C(=O) - NH_2 + H_2O.$$

This product is the semicarbazone of 2,2-dimethylpropanal. The amino group directly attached to the carbonyl group of semicarbazide is resonance-deactivated, so condensation takes place at the terminal amino group.

Step 6: Conclusion (a) 2-Hydroxybenzoic acid. (b) The $-I$ effect of chlorine stabilises chloroacetate and increases acidity. (c) The products are (i) $(CH_3)_3CCH_3$, (ii) $(CH_3)_3CCH_2OH$ and $(CH_3)_3CCOONa$, and (iii) $(CH_3)_3CCH = N - NH - C(=O) - NH_2$.

Quick Tip to Solve: First check the carbon next to -CHO for an alpha hydrogen: its absence identifies Cannizzaro reaction with concentrated NaOH.

26(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:

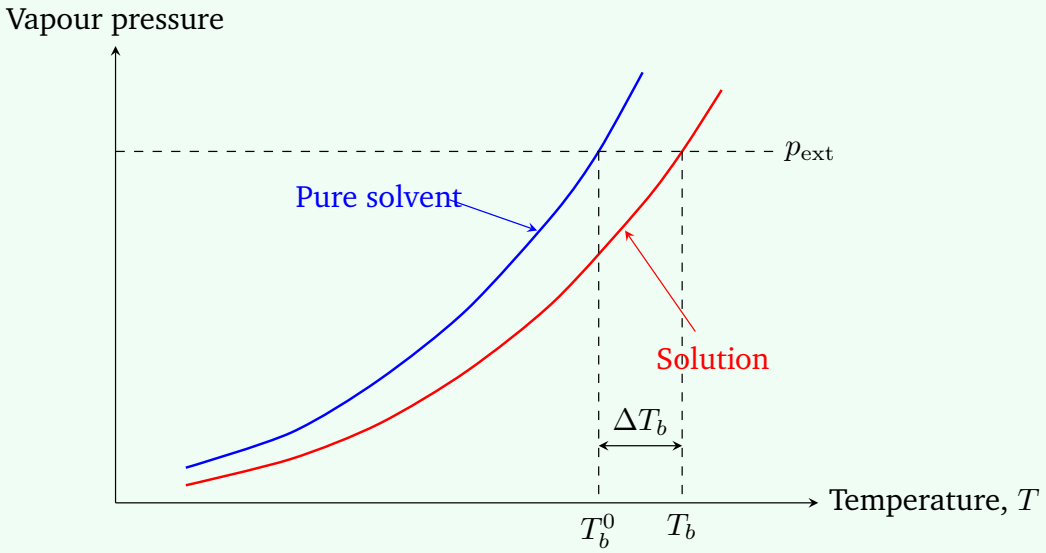
Concept:

- A non-volatile solute lowers the vapour pressure of its solvent. For an ideal solution, Raoult's law gives $p = x_{\text{solvent}}p^0$, where p^0 is the vapour pressure of the pure solvent at the same temperature.
- A liquid boils when its vapour pressure equals the external pressure. The elevation in boiling point is $\Delta T_b = T_b - T_b^0$, with T_b^0 and T_b the boiling temperatures of the pure solvent and solution, respectively.
- Osmotic pressure is $\pi = iCRT = i(n/V)RT$. Here i is the van't Hoff factor, C the formula-unit molarity, R the gas constant and T the absolute temperature.

Step 1: (a) Compare the vapour-pressure curves Plot vapour pressure on the vertical axis and temperature on the horizontal axis. Both vapour pressures rise with temperature, but the curve for a

Quick Tip to Solve: Convert 25 mg to 0.025 g first, then count all three ions from complete dissociation of one formula unit of potassium sulphate.

solution containing a non-volatile solute lies below that for the pure solvent. At a given temperature, fewer solvent molecules are available at the liquid surface, and the solvent's escaping tendency is reduced. In Raoult's-law terms, $x_{\text{solvent}} < 1$, so $p < p^0$. Draw a horizontal line for the external pressure p_{ext}. It intersects the pure-solvent curve at T_b^0 and the solution curve at the higher temperature T_b, as shown in the schematic graph.



Vapour-pressure curves showing elevation in boiling point at fixed external pressure.

Step 2: (a) Explain the elevation in boiling point At T_b^0, the pure solvent has reached the external pressure and boils, whereas the solution still has a lower vapour pressure. The solution must therefore be heated further before its vapour pressure becomes equal to the same external pressure. Consequently,

$$T_b > T_b^0, \qquad \Delta T_b = T_b - T_b^0 > 0.$$

This increase is called elevation in boiling point. For a dilute solution it is proportional to the solute molality: $\Delta T_b = K_b m$ for a non-electrolyte, where K_b is the molal elevation constant of the solvent.

Step 3: (b) Obtain the molar mass and particle factor The molar mass of potassium sulphate is

$$M(\mathrm{K_2SO_4}) = 2(39) + 32 + 4(16) = 174\,\mathrm{g\ mol^{-1}}.$$

Complete dissociation gives

$$\mathrm{K_2SO_4} \longrightarrow 2\mathrm{K^+} + \mathrm{SO_4^{2-}}.$$

Each formula unit produces three ions, so $i = 3$. Convert the solute mass before finding the amount:

$$w = 25\,\mathrm{mg} = 0.025\,\mathrm{g}, \qquad n = \frac{0.025}{174} = 1.437 \times 10^{-4}\,\mathrm{mol}.$$

Step 4: (b) Calculate the osmotic pressure For this very dilute solution, take the solution volume as $V = 2\,\mathrm{L}$. Its formula-unit concentration and absolute temperature are

$$C = \frac{0.025}{174 \times 2} = 7.184 \times 10^{-5}\,\mathrm{mol\ L^{-1}}, \qquad T = 25 + 273 = 298\,\mathrm{K}.$$

Quick Tip to Solve: Convert 25 mg to 0.025 g first, then count all three ions from complete dissociation of one formula unit of potassium sulphate.

Using $R = 0.0821\,\text{L atm mol}^{-1}\text{K}^{-1}$,

$$\begin{aligned}\pi &= iCRT \\ &= 3 \times \frac{0.025}{174 \times 2} \times 0.0821 \times 298 \\ &= 5.27 \times 10^{-3}\,\text{atm}.\end{aligned}$$

The factor three multiplies the pressure because osmotic pressure counts all independently moving solute particles. Using the mass in milligrams as though it were grams would overestimate the pressure by a factor of one thousand.

Step 5: Conclusion (a) The solution curve lies below the pure-solvent curve and reaches the external pressure at a higher temperature; hence $\Delta T_b = T_b - T_b^0 > 0$. (b) The osmotic pressure is $\boxed{\pi = 5.27 \times 10^{-3}\,\text{atm}}$, approximately $5.34 \times 10^2\,\text{Pa}$.

Quick Tip to Solve: Convert 25 mg to 0.025 g first, then count all three ions from complete dissociation of one formula unit of potassium sulphate.

OR

26(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:

- A non-ideal solution does not obey Raoult's law over its entire composition range because unlike-molecule interactions differ from like-molecule interactions.
- 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.
- For dimerisation, if a fraction α of the initial molecules associates, $i = 1 - \alpha/2$.

Step 1: (a) State two characteristics of a non-ideal solution First, its component vapour pressures deviate from Raoult's law: in general $p_A \neq x_A p_A^\circ$ and $p_B \neq x_B p_B^\circ$. The deviation may be positive or negative depending on the relative strengths of intermolecular attractions. Second, mixing is accompanied by a non-zero enthalpy change, $\Delta H_{\text{mix}} \neq 0$; the volume change on mixing is also generally non-zero. Stronger unlike-molecule attractions favour negative deviation and heat evolution, whereas weaker unlike-molecule attractions favour positive deviation and heat absorption.

Step 2: (b) Calculate the molality before association Benzoic acid has formula $C_7H_6O_2$, so its molar mass is $7(12) + 6(1) + 2(16) = 122\,\text{g mol}^{-1}$. The solvent mass is $25\,\text{g} = 0.025\,\text{kg}$. Hence the molality based on the mass of acid added is

$$m = \frac{2/122}{0.025} = 0.6557\,\text{mol kg}^{-1}.$$

Quick Tip to Solve: For dimer formation use $\alpha = 2(1 - i)$, and convert the solvent mass to kilograms before finding molality.

This analytical molality counts benzoic acid units before they combine into dimers; the factor i corrects the actual number of solute particles.

Step 3: Determine the van't Hoff factor and degree of association Without association, the predicted depression is $K_f m = 4.9(0.6557) = 3.213\,\text{K}$. Therefore

$$i = \frac{1.62}{3.213} = 0.5042.$$

The association is $2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$. Starting with one mole of monomer units, $1-\alpha$ mole remains monomeric and $\alpha/2$ mole of dimers forms. The total particle amount is $1-\alpha/2$, giving

$$\alpha = 2(1-i) = 2(1-0.5042) = 0.9916.$$

The factor lies just above the complete-dimerisation limit of 0.5, consistently showing nearly complete association.

Step 4: Conclusion (a) Non-ideal solutions deviate from Raoult's law and have $\Delta H_{\text{mix}} \neq 0$ (generally also $\Delta V_{\text{mix}} \neq 0$). (b) The percentage association of benzoic acid is $100\alpha \approx \boxed{99.2\%}$.

Quick Tip to Solve: For dimer formation use $\alpha = 2(1-i)$, and convert the solvent mass to kilograms before finding molality.

27(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:

- Electron pairing stabilises an odd-electron molecule; intermolecular attractions determine the energy needed to boil a substance.
- Electron gain enthalpy depends on both nuclear attraction and repulsion within the orbital receiving the added electron.
- Chlorine bleaches through oxidation in moist conditions. Fluorine's very high electronegativity restricts its oxoacid chemistry.

Step 1: (a) Explain the ready dimerisation of nitrogen dioxide NO_2 is an odd-electron molecule, containing an unpaired electron. Two such molecules combine so that their unpaired electrons form an N–N covalent bond. The product N_2O_4 has paired electrons and is more stable under conditions favouring association:

$$2NO_2 \rightleftharpoons N_2O_4.$$

Thus the tendency to pair the odd electrons explains why nitrogen dioxide dimerises readily.

Quick Tip to Solve: For electron gain enthalpy exceptions, compare the size of the receiving orbital and its electron repulsion, not atomic size alone.

Step 2: (b) Explain the bleaching action of chlorine Chlorine reacts with moisture to form hypochlorous acid:

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

Hypochlorous acid oxidises coloured substances into colourless products. In the conventional school representation, $HOCl \rightarrow HCl + [O]$, where $[O]$ denotes available oxygen for oxidation. The colour-bearing substance undergoes chemical change, so the bleaching is permanent. Moisture is necessary for this bleaching action.

Step 3: (c) Compare the electron gain enthalpies of oxygen and sulphur The added electron enters the compact $2p$ subshell of oxygen, where electron density is high. It therefore experiences strong repulsion from electrons already present. In sulphur it enters the larger, more diffuse $3p$ subshell, where interelectronic repulsion is smaller. The repulsion in oxygen offsets more of the attractive energy released on adding an electron. Consequently oxygen has a less negative electron gain enthalpy than sulphur despite its smaller atomic size.

Step 4: (d) Explain why fluorine forms only HOF among oxoacids Fluorine is the most electronegative element and does not exhibit the positive oxidation states that chlorine exhibits in its series of oxoacids. It also has no vacant valence-shell d orbitals in the conventional school description. It therefore cannot form an analogous series of higher oxoacids. In HOF, fluorine still has oxidation state -1; hydrogen is $+1$, so oxygen has oxidation state 0. Thus the existence of HOF does not require fluorine to acquire a positive oxidation state.

Step 5: (e) Explain the very low boiling points of noble gases Noble gases occur as monatomic species with closed electron shells. Their atoms interact mainly through weak London dispersion forces, arising from temporary and induced dipoles. Very little thermal energy is required to overcome these weak interatomic attractions and separate the atoms into the gaseous state, so their boiling points are very low. Dispersion forces increase with atomic size and polarisability down the group, explaining the general increase in boiling point from lighter to heavier noble gases.

Step 6: Conclusion (a) NO_2 dimerises by pairing its odd electrons. (b) Moist chlorine bleaches by oxidation through HOCl. (c) Compact oxygen 2p orbitals cause greater electron repulsion than sulphur 3p orbitals. (d) Fluorine cannot show the positive oxidation states needed for a chlorine-like oxoacid series. (e) Noble gases have only weak interatomic dispersion attractions.

Quick Tip to Solve: For electron gain enthalpy exceptions, compare the size of the receiving orbital and its electron repulsion, not atomic size alone.

OR

27(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:

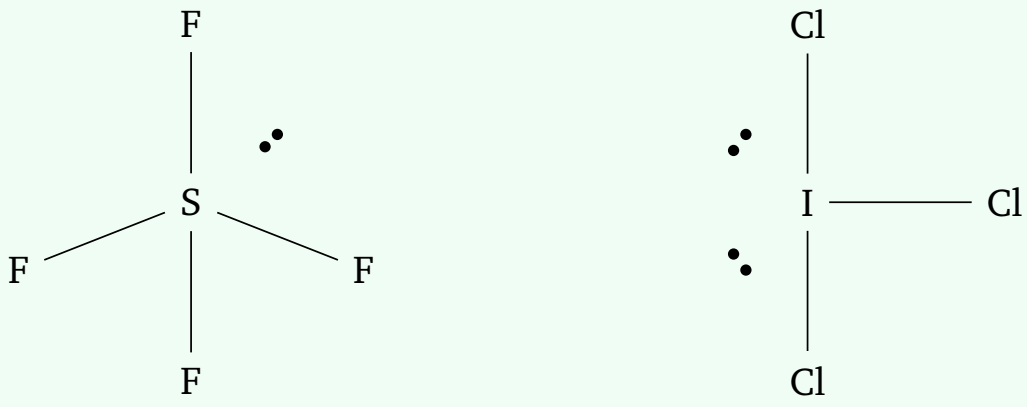
Concept:

- VSEPR theory predicts molecular shape from repulsions between electron pairs around the central atom. Lone pairs repel more strongly than bond pairs; in a trigonal-bipyramidal electron-pair arrangement, they preferentially occupy equatorial positions.
- Disproportionation is the simultaneous oxidation and reduction of the same element. Hydrolysis replaces fluorine in xenon fluorides by oxygen, while concentrated sulphuric acid acts as a dehydrating agent for 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 five electron-pair domains: AX_4E. The electron-pair arrangement is trigonal bipyramidal. The lone pair occupies an equatorial position, where it has fewer repulsions at approximately 90° than in an axial position. Two fluorine atoms are axial and two are equatorial. Thus the molecular shape, determined by the positions of the atoms, is **see-saw**.

Step 2: (a)(ii) Structure and shape of iodine trichloride Iodine has seven valence electrons. Three I–Cl bonds leave two lone pairs on iodine, giving five electron-pair domains: AX_3E_2. Both lone pairs occupy equatorial positions in a trigonal-bipyramidal electron-pair arrangement. The chlorine atoms therefore occupy two axial positions and the remaining equatorial position. The molecular shape is **T-shaped**. The dots in the structures denote lone pairs on the central atoms.

Quick Tip to Solve: For five electron-pair domains, put lone pairs equatorially first: one lone pair gives see-saw and two give T-shaped geometry.



SF_4: see-saw $\qquad$ ICl_3: T-shaped

Structures of SF4 and ICl3, with central-atom lone pairs shown as dots.

Step 3: (b)(i) Chlorine with hot, concentrated sodium hydroxide Chlorine disproportionates to sodium chloride and sodium chlorate in hot, concentrated sodium hydroxide solution:

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

Chlorine changes from oxidation state 0 to -1 in chloride and to $+5$ in chlorate. Formation of chlorate is characteristic of the stated hot, concentrated conditions.

Step 4: (b)(ii) Complete hydrolysis of xenon hexafluoride On complete hydrolysis, all six fluorine atoms are replaced and xenon trioxide and hydrogen fluoride are formed:

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

The three water molecules supply the three oxygen atoms of xenon trioxide and six hydrogen atoms for hydrogen fluoride. Xenon's oxidation state remains $+6$, so this is hydrolysis rather than a redox reaction.

Step 5: (b)(iii) Concentrated sulphuric acid with cane sugar Concentrated sulphuric acid removes the elements of water from cane sugar (sucrose), leaving a black mass of carbon. Heat is released and the carbon mass swells into a porous column as steam escapes. The dehydration is represented by

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

Here sulphuric acid acts as the dehydrating agent; its role is indicated above the reaction arrow.

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 hydrolysis of XeF_6 gives XeO_3 and HF; concentrated H_2SO_4 dehydrates cane sugar to black carbon.

Quick Tip to Solve: For five electron-pair domains, put lone pairs equatorially first: one lone pair gives see-saw and two give T-shaped geometry.