CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-5-3

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

Solution:

Concept:

- Ionisation isomerism occurs when a coordinated anion and a counter-ion exchange positions, giving different ions in aqueous solution.
- A ligand inside square brackets is part of the coordination sphere; an ion outside them is a counter-ion.

Step 1: Identify the coordinated and free anions In $[Co(NH_3)_5Cl]SO_4$, chloride is coordinated to cobalt and sulphate is outside the coordination sphere. The sulphate ion is released when the salt dissolves in water.

Step 2: Exchange their positions The corresponding isomer is $[Co(NH_3)_5SO_4]Cl$. It releases chloride ions in water instead of sulphate ions. Thus the salts have the same overall composition but give different anions on ionisation.

Step 3: Conclusion The complex exhibits **ionisation isomerism**, with $[Co(NH_3)_5SO_4]Cl$ as its ionisation isomer.

Quick Tip to Solve: Look for two different anions: one inside and one outside the coordination brackets.

OR

1(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 the same metal ion and octahedral geometry, the crystal field splitting energy Δ_o increases with ligand field strength.
- The relevant spectrochemical order is $Cl^- < NH_3 < CN^-$.

Step 1: Compare the metal ions and geometry Each complex contains chromium in oxidation state $+3$ and six ligands in an octahedral arrangement. Hence differences in the metal oxidation state or coordination geometry do not affect this comparison.

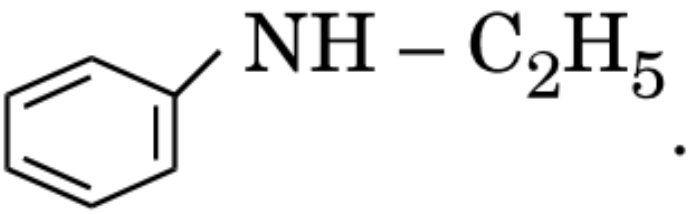
Step 2: Apply the ligand strength order Chloride is a weak-field ligand and produces the smallest separation between the t_{2g} and e_g levels. Ammonia gives a larger separation, while cyanide is the strongest-field ligand among the three and produces the largest splitting.

Step 3: Conclusion The increasing order is

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

Quick Tip to Solve: When the metal and its oxidation state are identical, compare the ligands directly using the spectrochemical series.

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



Solution:

Concept:

- A benzene ring bearing an amino group is named as aniline (benzenamine).
- An alkyl group bonded directly to the nitrogen is indicated by the locant N, rather than a numbered carbon locant.

Step 1: Identify the parent amine The displayed structure contains a benzene ring attached directly to an NH group. Thus the parent is aniline, also called benzenamine. There is only one amino group attached to the ring.

Step 2: Locate the ethyl substituent The same nitrogen is attached to an ethyl group, C_2H_5, and retains one hydrogen. It is therefore a secondary amine. Because ethyl is on nitrogen, its position is written as N-ethyl; no ring-carbon locant is required.

Step 3: Conclusion The IUPAC name is **N-ethylaniline** (also written N-ethylbenzenamine).

Quick Tip to Solve: Follow the bond from the ethyl group: if it ends at nitrogen, use the locant N.

3. p-nitrobenzoic acid has lower pK_a value than benzoic acid. Why? [1 mark]

Solution:

Concept:

- Acid strength increases when the conjugate base is stabilised; $pK_a = -\log_{10} K_a$, so a stronger acid has a lower pK_a.
- The nitro group withdraws electrons by both the inductive ($-I$) and resonance ($-R$) effects.

Step 1: Compare the conjugate bases Loss of H^+ produces benzoate from benzoic acid and p-nitrobenzoate from p-nitrobenzoic acid. Greater stabilisation of the negatively charged carboxylate ion favours this dissociation.

Step 2: Explain the effect of the para nitro group The electron-withdrawing NO_2 group at the para position stabilises the conjugate base through its $-I$ and $-R$ effects. Consequently p-nitrobenzoic acid dissociates more readily and has a larger K_a than benzoic acid.

Step 3: Conclusion The para nitro group stabilises the conjugate base by electron withdrawal; hence p-nitrobenzoic acid is stronger and has a lower pK_a.

Quick Tip to Solve: First compare conjugate-base stability, then remember that a larger Ka means a smaller pKa.

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

Solution:

Concept:

- A colloidal sol can be prepared by chemical condensation, in which small molecules react to form particles of colloidal size.
- Arsenic(III) sulphide is obtained by reacting arsenious oxide with hydrogen sulphide in dilute aqueous solution.

Step 1: Prepare the dilute reactant solution Prepare a dilute aqueous solution of arsenious oxide, As_2O_3, and pass hydrogen sulphide gas through it. The reactants must be dilute so that the product forms a colloidal dispersion rather than a coarse precipitate.

Step 2: Form the sulphide sol The reaction is

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

The newly formed arsenic(III) sulphide particles remain dispersed in water, producing a yellow sol. This is a chemical condensation method involving 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: For arsenic sulphide sol, pair arsenious oxide with hydrogen sulphide and balance three H2S molecules.

OR

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

Solution:

Concept:

- In heterogeneous catalysis the catalyst and reactants are in different physical phases.
- Reactant molecules adsorb on the catalyst surface, react, and the products desorb, leaving the catalyst available again.

Step 1: Choose a standard catalytic reaction In the Haber process, nitrogen and hydrogen combine to form ammonia in the presence of finely divided iron:

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

Iron provides a catalytic surface for the gaseous reactants.

Step 2: Compare the physical phases Both nitrogen and hydrogen are gases, whereas iron is a solid. Since the catalyst and reactants occupy different phases, the reaction is an example of heterogeneous catalysis. The iron increases the reaction rate without being consumed in the net reaction.

Step 3: Conclusion Ammonia synthesis from $N_2(g)$ and $H_2(g)$ using solid iron in the Haber process is heterogeneous catalysis.

Quick Tip to Solve: Always state the phases of both reactants and catalyst to justify a heterogeneous-catalysis example.

5. A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make ccp and those of the element X (as cations) occupy all octahedral voids. What is the formula of the compound? [1 mark]

Solution:

Concept:

- In a close-packed arrangement of N atoms or ions, the number of octahedral voids is also N.
- A cubic close-packed unit cell contains four lattice particles and four octahedral voids.

Step 1: Count the anions in the ccp unit cell The Y anions form a cubic close-packed lattice. The eight corners contribute $8 \times \frac{1}{8} = 1$ anion and the six faces contribute $6 \times \frac{1}{2} = 3$ anions, giving four Y anions per unit cell.

Step 2: Count the occupied octahedral voids The octahedral voids comprise one at the body centre and twelve at the edge centres, each edge void shared by four unit cells. Their number is $1 + 12 \times \frac{1}{4} = 4$. All are occupied by X cations, so the unit cell contains four X cations as well.

Step 3: Conclusion The ratio $X : Y = 4 : 4 = 1 : 1$; therefore the formula of the compound is $\boxed{XY}$.

Quick Tip to Solve: For all octahedral voids filled, the number of occupying ions equals the number of close-packed ions.

Section B (14 marks)

6. Differentiate between:

(a) Nucleotide and Nucleoside

(b) Amylose and Amylopectin [2 marks]

Solution:

Concept:

- A nucleoside contains a nitrogenous base joined to a pentose sugar; adding phosphate gives a nucleotide.
- Starch contains amylose and amylopectin, both polymers of α-D-glucose; the glycosidic linkages determine their chain structure.

Step 1: Compare nucleotide and nucleoside A nucleoside consists of a nitrogenous base (purine or pyrimidine) linked to ribose or deoxyribose by a glycosidic bond. A nucleotide contains these same two components plus a phosphate group, attached to the sugar through an ester linkage. Thus adenosine is a nucleoside, while adenosine monophosphate is a nucleotide. The distinguishing component is phosphate, not the nitrogenous base.

Step 2: Compare amylose and amylopectin Amylose is a straight-chain, unbranched polymer of α-D-glucose units linked through $\alpha(1 \rightarrow 4)$ glycosidic bonds; its chains adopt a helical form. Amylopectin is a branched polymer: the main chains have $\alpha(1 \rightarrow 4)$ linkages, whereas the branch points have $\alpha(1 \rightarrow 6)$ linkages. Amylose is water-soluble, while amylopectin is insoluble in water.

Quick Tip to Solve: Remember: a nucleotide has phosphate; amylopectin has extra 1-to-6 branch linkages.

Step 3: Conclusion (a) Nucleotide = base + pentose sugar + phosphate; nucleoside = base + pentose sugar. (b) Amylose is unbranched; amylopectin is branched through $\alpha(1 \to 6)$ linkages.

Quick Tip to Solve: Remember: a nucleotide has phosphate; amylopectin has extra 1-to-6 branch linkages.

7(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 with HI reduces all oxygen-containing groups of glucose while preserving its six-carbon skeleton.
- Nitric acid is a strong oxidising agent that oxidises both the aldehyde group and the terminal primary alcohol to carboxylic acid groups.

Step 1: Treat D-glucose with HI On prolonged heating with hydrogen iodide, D-glucose is reduced to n-hexane. All six carbon atoms therefore form an unbranched chain. The balanced overall equation is

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

The oxygen atoms leave as water and iodide is oxidised to iodine.

Step 2: Treat D-glucose with nitric acid Concentrated nitric acid oxidises the aldehyde end, $-\mathrm{CHO}$, and the primary alcohol end, $-\mathrm{CH_2OH}$, to $-\mathrm{COOH}$. The product is the dicarboxylic acid saccharic acid (glucaric acid):

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

Here $[O]$ denotes oxygen supplied by the oxidising agent. The four middle secondary alcohol groups remain in the product.

Step 3: Conclusion (a) Prolonged heating with HI produces n-hexane. (b) HNO_3 produces saccharic acid, $\mathrm{HOOC(CHOH)_4COOH}$.

Quick Tip to Solve: For nitric acid, check both ends of glucose: CHO and CH2OH both become COOH.

OR

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

Solution:

Concept:

- Protein shape depends on the folding and association of its polypeptide chains.

Quick Tip to Solve: Use the same two comparison headings for both types: shape first, then water solubility.

- The two requested differences can be stated in terms of molecular shape and solubility in water.

Step 1: Compare the shapes In globular proteins, polypeptide chains fold into compact, approximately spherical structures. In fibrous proteins, polypeptide chains form elongated, fibre-like structures, often with chains arranged parallel to one another and held together by hydrogen bonds and other interactions. Thus globular proteins are compact, whereas fibrous proteins have a large length compared with their width.

Step 2: Compare solubility and give examples Globular proteins are generally soluble in water, whereas fibrous proteins are generally insoluble in water. Insulin and albumin are examples of globular proteins; keratin in hair and wool and myosin in muscles are examples of fibrous proteins. These examples illustrate the two categories without changing the required comparison: compact versus elongated shape, and generally soluble versus insoluble behaviour.

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

Quick Tip to Solve: Use the same two comparison headings for both types: shape first, then water solubility.

8. What happens when

(a) PCl_5 is heated?

(b) XeF_2 reacts with PF_5? [2 marks]

Solution:

Concept:

- Heating phosphorus pentachloride causes reversible dissociation into phosphorus trichloride and chlorine.
- PF_5 accepts a fluoride ion and acts as a Lewis acid; XeF_2 supplies the fluoride ion.

Step 1: Heat phosphorus pentachloride On heating, phosphorus pentachloride dissociates into phosphorus trichloride and chlorine:

$$PCl_5 \overset{\Delta}{\rightleftharpoons} PCl_3 + Cl_2.$$

The equation conserves one phosphorus atom and five chlorine atoms. Since the dissociation is reversible, cooling favours recombination of the products to form PCl_5. The observation required is thermal dissociation, not hydrolysis; no water is involved.

Step 2: React xenon difluoride with phosphorus pentafluoride Xenon difluoride transfers one fluoride ion to phosphorus pentafluoride, forming the ionic compound xenon fluorido hexafluoridophosphate:

$$XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-.$$

The cation is $[XeF]^+$ and the anion is $[PF_6]^-$. Their equal and opposite charges make the product neutral. There are seven fluorine atoms on each side; xenon and phosphorus each remain present once. This is fluoride-ion transfer, with PF_5 acting as the acceptor.

Quick Tip to Solve: When PF5 accepts F-minus, write PF6-minus and leave XeF-plus as the counterion.

Step 3: Conclusion (a) PCl_5 dissociates to $PCl_3 + Cl_2$. (b) $XeF_2 + PF_5$ gives $[XeF]^+[PF_6]^-$.

Quick Tip to Solve: When PF5 accepts F-minus, write PF6-minus and leave XeF-plus as the counterion.

9. Write the preparation of sodium dichromate from chromite ore. [2 marks]

Solution:

Concept:

- Chromite ore, $FeCr_2O_4$, is oxidised by air during roasting with sodium carbonate to form soluble sodium chromate.
- Acidification shifts chromate ions into dichromate ions: $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$.

Step 1: Roast chromite ore and extract sodium chromate Finely powdered chromite ore is fused with sodium carbonate in the presence of air. Chromium is oxidised from +3 in the ore to +6 in chromate:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\Delta} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

The roasted mass is extracted with water. Sodium chromate dissolves, while insoluble ferric oxide is removed by filtration.

Step 2: Acidify the chromate solution The filtered yellow sodium chromate solution is acidified with sulphuric acid to convert it into orange sodium dichromate:

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

The dichromate product can be obtained by concentrating and crystallising the solution. Acidification joins two chromate units into one dichromate unit; it does not change the +6 oxidation state of chromium.

Step 3: Conclusion Sodium dichromate is prepared by roasting chromite with Na_2CO_3 in air, extracting Na_2CrO_4 with water, and acidifying the extract with H_2SO_4.

Quick Tip to Solve: Remember the order: oxidising alkaline roast, water extraction, then acidification to dichromate.

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:

- Phenol undergoes the Reimer–Tiemann reaction with $CHCl_3$ and aqueous alkali, introducing a formyl group mainly at the ortho position and also at the para position.
- Hot zinc dust removes oxygen from the aromatic derivatives; oxidation of a methyl side chain gives benzoic acid. Soda-lime decarboxylation replaces $-COONa$ by hydrogen.

Step 1: Identify A and B from the two products The aromatic compound A is phenol, C_6H_5OH. With $CHCl_3/KOH$, followed by acidification, it gives ortho-hydroxybenzaldehyde (major) and para-hydroxybenzaldehyde (minor). On distillation with zinc dust, both oxygen-containing substituents are deoxygenated, giving the same hydrocarbon, toluene, $B = C_6H_5CH_3$. The two positional isomers converge because removal of the phenolic oxygen leaves just a methyl substituent on the ring.

Step 2: Identify C and verify D by both routes Oxidation of the methyl group of toluene gives benzoic acid:

$$C_6H_5CH_3 \xrightarrow{[O]} C_6H_5COOH.$$

Thus C has exactly the given formula $C_7H_6O_2$. Its sodium salt undergoes soda-lime decarboxylation:

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

Hence D is benzene. Independently, distillation of phenol with zinc dust gives

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO.$$

This confirms the same D.

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

Quick Tip to Solve: Work backward from soda-lime decarboxylation: benzoate gives benzene, which also identifies phenol through zinc-dust distillation.

OR

10(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 the phenolic oxygen. Friedel–Crafts alkylation introduces a methyl group into benzene.
- A primary alcohol gives an aldehyde by controlled oxidation or by dehydrogenation over heated copper; the latter prevents further oxidation to an acid.

Step 1: (a) Convert phenol into toluene First distil phenol with zinc dust to obtain benzene:

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

Then treat benzene with chloromethane in the presence of anhydrous aluminium chloride:

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

The second step is Friedel–Crafts methylation and gives the required toluene. Removing the hydroxyl group first is essential to this conversion sequence.

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

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

This is dehydrogenation: two hydrogen atoms are removed, one from the hydroxyl group and one from its attached carbon, forming the carbonyl group. The product is ethanal, an aldehyde. This route is preferable to uncontrolled oxidation with excess oxidant, which can carry the aldehyde onward to ethanoic acid.

Step 3: Conclusion Phenol $\xrightarrow{Zn,\Delta}$ benzene $\xrightarrow{CH_3Cl/AlCl_3}$ toluene; ethanol $\xrightarrow{Cu,573\,K}$ ethanal.

Quick Tip to Solve: For phenol to toluene, remove oxygen before adding methyl; for ethanol to ethanal, use heated copper at 573 K.

11. 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 the amount reacted, and k the rate constant.

Quick Tip to Solve: Convert completion to the remaining fraction first: 90 percent leaves 1/10, while 99 percent leaves 1/100.

- The logarithm uses the fraction of reactant remaining, not the percentage already consumed; the same reaction has the same k at the same temperature.

Step 1: Calculate the time for 90 percent completion At 90% completion, the fraction remaining is $10\% = 0.10$, so $a - x = 0.10a$. Substituting into the integrated first-order equation gives

$$t_{90} = \frac{2.303}{k} \log_{10}\left(\frac{a}{0.10a}\right) = \frac{2.303}{k} \log_{10} 10 = \frac{2.303}{k}.$$

The initial concentration cancels, as expected for the time to reach a specified fraction in a first-order reaction.

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

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

Dividing this result by the expression for t_{90} gives $t_{99}/t_{90} = 2$. Equivalently, each reduction of the remaining concentration by a factor of ten takes the same time, so reaching one hundredth requires two such intervals.

Step 3: Conclusion

$$\boxed{t_{99} = 2t_{90}}$$

Thus the required relation is proved.

Quick Tip to Solve: Convert completion to the remaining fraction first: 90 percent leaves 1/10, while 99 percent leaves 1/100.

12. 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° = -2.71 V

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

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

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

Solution:

Concept:

- At the cathode, reduction occurs: the species with the more positive reduction potential is discharged more readily.
- At the anode, competing oxidations depend on both thermodynamic potentials and the actual overpotential. Oxygen evolution has a substantial overpotential in aqueous sodium chloride.

Step 1: Choose the cathode product 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 favoured because its reduction potential is much more

Quick Tip to Solve: Use the more positive reduction potential at the cathode, but include oxygen overpotential when choosing the brine anode product.

positive. Thus hydrogen gas, rather than sodium metal, is liberated at the cathode. In the aqueous solution, this is conveniently written as

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

The hydroxide ions remain in solution with sodium ions.

Step 2: Choose the anode product, accounting for overpotential The printed values are $+1.36\,V$ for chlorine and $+1.23\,V$ for oxygen evolution. Comparing these values alone would suggest that water should oxidise more easily, yielding oxygen. However, oxygen evolution requires an additional potential, called overpotential. Consequently, in electrolysis of aqueous sodium chloride, chloride ions are discharged and chlorine gas is evolved:

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

The smaller nominal oxygen potential therefore does not establish the observed product; the oxygen overpotential makes chlorine evolution preferred under the stated electrolysis conditions.

Step 3: Conclusion Cathode: H_2 gas. Anode: Cl_2 gas; oxygen evolution is suppressed by its overpotential.

Quick Tip to Solve: Use the more positive reduction potential at the cathode, but include oxygen overpotential when choosing the brine anode product.

Section C (36 marks)

13. (a) What type of stoichiometric defect is shown by AgCl and why?

(b) Calculate the efficiency of packing in case of a metal crystal for simple cubic unit cell. [3 marks]

Solution:

Concept:

- A Frenkel defect is a vacancy-interstitial pair: an ion leaves its normal lattice site and occupies an interstitial site. The composition and electrical neutrality remain unchanged.
- Packing efficiency is the fraction of the unit-cell volume occupied by its atoms, multiplied by 100. For spheres of radius r, the volume of one atom is $4\pi r^3/3$.

Step 1: Identify the defect in silver chloride (a) AgCl exhibits a Frenkel defect. The small Ag^+ ion can leave its regular lattice site and enter an interstitial space, whereas the larger Cl^- ion remains at its lattice site. This creates a cation vacancy together with an interstitial cation. The appreciable difference between the sizes of the ions permits this displacement. Since no ion leaves the crystal, the ratio of cations to anions remains unchanged and the density is unaffected.

Step 2: Count the atoms and relate the edge to the radius (b) A simple cubic cell has an atom at each of its eight corners. Each corner atom is shared by eight neighbouring cells, so the effective number of atoms per cell is

$$N = 8 \times \frac{1}{8} = 1.$$

Quick Tip to Solve: For simple cubic packing, remember one effective atom per cell and contact along the edge: $a = 2r$. Do not use the face-diagonal contact relation for an fcc cell.

Neighbouring corner atoms touch along an edge. Hence the edge length is $a = 2r$, and the cell volume is $a^3 = 8r^3$.

Step 3: Calculate the occupied fraction The volume occupied by the one effective atom is $4\pi r^3/3$. Therefore,

$$\text{Packing efficiency} = \frac{N(4\pi r^3/3)}{a^3} \times 100$$
$$= \frac{4\pi r^3/3}{8r^3} \times 100 = \frac{\pi}{6} \times 100 \approx 52.36\%.$$

The radius cancels, so this efficiency depends on the simple cubic arrangement, rather than on the size of the metal atom. The remaining approximately 47.64% is empty space.

Step 4: Conclusion (a) AgCl shows a Frenkel defect because its relatively small Ag^+ ions can occupy interstitial sites. (b) The simple cubic packing efficiency is $\boxed{52.4\%}$ approximately.

Quick Tip to Solve: For simple cubic packing, remember one effective atom per cell and contact along the edge: $a = 2r$. Do not use the face-diagonal contact relation for an fcc cell.

14. Define the following terms:

(a) Coagulation

(b) Associated colloids

(c) Brownian movement [3 marks]

Solution:

Concept:

- A colloidal dispersion contains dispersed particles in a dispersion medium. Its stability depends on factors such as particle charge and interactions with the medium.
- Micelle formation is aggregation of amphiphilic molecules; Brownian movement is the irregular motion of colloidal particles caused by collisions with molecules of the dispersion medium.

Step 1: Define coagulation (a) Coagulation is the process in which colloidal particles aggregate into larger particles and separate from the dispersion medium as a precipitate. For example, adding an appropriate electrolyte to a charged sol can neutralise the charge that keeps the dispersed particles apart. Once repulsion is reduced, the particles come together and the colloidal dispersion loses stability. Coagulation is thus also called precipitation of the sol.

Step 2: Define associated colloids (b) Associated colloids are substances which behave as ordinary electrolytes at low concentrations but form aggregates of colloidal dimensions at higher concentrations. These aggregates are called micelles. Micelle formation occurs above the critical micelle concentration (CMC) and, for substances such as soaps, above the characteristic Krafft temperature. Soap and synthetic detergent solutions are examples: individual molecules or ions associate through their hydrophobic portions, while their hydrophilic portions interact with water.

Step 3: Define Brownian movement (c) Brownian movement is the continuous, random zigzag motion of colloidal particles in the dispersion medium. Molecules of the medium strike a dispersed particle from different directions. Their collisions are unequal at any instant, producing an unbalanced

Quick Tip to Solve: Keep the three mechanisms separate: coagulation joins particles into a precipitate, association creates micelles, and Brownian motion describes particle movement.

impulse and continually changing the particle's direction. This motion is a result of molecular thermal motion and helps oppose settling of colloidal particles under gravity.

Step 4: Conclusion Coagulation is aggregation and precipitation of colloidal particles; associated colloids form micelles at suitable concentration and temperature; Brownian movement is random zigzag motion caused by unequal molecular collisions.

Quick Tip to Solve: Keep the three mechanisms separate: coagulation joins particles into a precipitate, association creates micelles, and Brownian motion describes particle movement.

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 experimentally stated orders give the rate law $v = k[A]^1[B]^0 = k[A]$, where v is the initial rate and k is the rate constant.
- At the same temperature, the rate constant is the same in all experiments. Since the overall order is one, k has units of inverse time, here min^{-1}.

Step 1: Find the rate constant from experiment I Since the reaction is zero order in B, its concentration does not enter the rate calculation. Experiment I gives $[A] = 0.1\,\text{mol L}^{-1}$ and $v = 2.0 \times 10^{-2}\,\text{mol L}^{-1}\text{min}^{-1}$. Thus,

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

Step 2: Fill the concentration in experiment II Rearranging $v = k[A]$ gives $[A] = v/k$. Therefore,

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

The rate is twice the rate in experiment I, so the required concentration of A is also twice its original value.

Step 3: Fill the rate in experiment III Here $[A] = 0.4\,\text{mol L}^{-1}$, so

$$v_{\text{III}} = k[A] = (0.20)(0.4) = 8.0 \times 10^{-2}\,\text{mol L}^{-1}\text{min}^{-1}.$$

Quick Tip to Solve: Ignore changes in B when comparing these rates. Since $v/[A]$ is constant, obtain each missing entry directly from experiment I by proportionality.

This is four times the rate in experiment I because A has four times the concentration.

Step 4: Fill the concentration in experiment IV Experiment IV has the same rate as experiment I. Hence it must have the same concentration of A:

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

Experiments I and IV check the zero order in B: their rates agree although B differs.

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

Quick Tip to Solve: Ignore changes in B when comparing these rates. Since $v/[A]$ is constant, obtain each missing entry directly from experiment I by proportionality.

16. 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 higher standard reduction potential is the cathode. Cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log Q$, where n is the number of electrons transferred in the balanced cell reaction and Q is its reaction quotient.

Step 1: Identify the electrodes and balance the reaction Nickel has the less negative reduction potential, so nickel ions are reduced at the cathode and aluminium is oxidised at the anode. The balanced half-reactions are

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

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 $n = 6$.

Step 2: Calculate the standard cell potential and quotient Using the given reduction potentials,

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

Pure solids have unit activity and do not appear in the quotient. Using the given molar concentrations,

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

Quick Tip to Solve: Balance the electrons first: Al transfers three and Ni two, so use $n = 6$, with concentration powers 2 and 3.

Step 3: Apply the Nernst equation Substitute $n = 6$ and $\log Q = -3$:

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

Since $Q < 1$, the concentration correction increases the emf above its standard value, consistent with the calculation.

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

Quick Tip to Solve: Balance the electrons first: Al transfers three and Ni two, so use $n = 6$, with concentration powers 2 and 3.

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:

- Electronic configuration determines the accessible oxidation states and the availability of d-electrons for electronic transitions.
- Metal oxides in low oxidation states are generally ionic and basic; higher oxidation states increase covalent character and acidic behaviour.

Step 1: Explain the +3 oxidation state of scandium Scandium has atomic number 21 and configuration $[\text{Ar}]\,3d^1 4s^2$. Removal of the two $4s$ electrons and the one $3d$ electron gives Sc^{3+} with the stable noble-gas configuration $[\text{Ar}]$. Lower oxidation states do not attain this configuration; removal of a further electron would disrupt the closed argon core and needs a very large ionisation energy. Hence +3 is its characteristic oxidation state in compounds.

Step 2: Explain the colourless titanium complex Titanium has configuration $[\text{Ar}]\,3d^2 4s^2$. In $[Ti(H_2O)_6]^{4+}$, neutral water ligands imply titanium is in the +4 state, so Ti^{4+} has a $3d^0$ configuration. Although the ligand field splits the d-orbitals, there are no d-electrons to undergo a d-d transition by absorbing visible light. The complex is therefore colourless.

Step 3: Compare the two manganese oxides In MnO, manganese is in the +2 oxidation state. This low-state oxide is predominantly ionic and basic: it reacts with acids to form a salt and water, for example $MnO + 2HCl \longrightarrow MnCl_2 + H_2O$. In Mn_2O_7, manganese is in the high +7 state; the oxide is covalent and acidic. It is the acid anhydride of permanganic acid: $Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$.

Step 4: Conclusion Sc forms stable Sc^{3+} with an argon core; the titanium(IV) complex is d^0 and colourless; low-state MnO is basic, whereas high-state Mn_2O_7 is acidic.

Quick Tip to Solve: For colour, calculate the metal ion configuration first; for oxide character, calculate the metal oxidation state.

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 filling of the $4f$ subshell, whereas actinoids involve filling of the $5f$ subshell.
- An oxidation state is favoured when electron loss gives a stable configuration; closely spaced valence subshell energies allow different numbers of electrons to participate in bonding.

Step 1: Give the general lanthanoid configuration The general electronic configuration of lanthanoids is

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

Here $[\mathrm{Xe}]$ denotes the xenon core. Across the series, electrons progressively enter the inner $4f$ subshell, with occasional occupancy of $5d$. If lanthanum is included as the starting member, the range is written $[\mathrm{Xe}]\,4f^{0-14}5d^{0-1}6s^2$; lanthanum itself is $[\mathrm{Xe}]\,5d^16s^2$.

Step 2: State the common cerium oxidation states Cerium, atomic number 58, has the configuration $[\mathrm{Xe}]\,4f^15d^16s^2$. Its common oxidation states are $\boxed{+3 \text{ and } +4}$. Loss of the two $6s$ electrons and the $5d$ electron gives Ce^{3+}, with configuration $[\mathrm{Xe}]\,4f^1$. Loss of the additional $4f$ electron gives Ce^{4+}, with the stable xenon-core configuration $[\mathrm{Xe}]$. This explains why cerium also shows +4 in addition to the usual lanthanoid +3 state.

Step 3: Explain the wide range of actinoid oxidation states The energies of the $5f$, $6d$ and $7s$ subshells in actinoids are comparable. Consequently, electrons from all three subshells can participate in bonding, and different numbers can be used in different compounds. This produces a wider range of oxidation states than in lanthanoids, whose $4f$ electrons are generally more deeply buried and less available for bonding. The effect is especially prominent among the early actinoids.

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

Quick Tip to Solve: Remember the three active actinoid subshells as $5f, 6d, 7s$; Ce(+4) is favoured by its xenon-core configuration.

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:

- Separation exploits differences in the physical or chemical properties of an ore or metal and its impurities.
- The three processes respectively use preferential wetting, unequal impurity solubility and formation of a volatile metal compound.

Step 1: (a) Froth floatation Froth floatation is based on the different wetting behaviour of sulphide ore and gangue. Sulphide ore particles are preferentially wetted by oil, while gangue particles are wetted by water. Air is blown through the agitated suspension. The oil-wetted ore particles attach to the air bubbles and rise to the surface with the froth, which is skimmed off. The water-wetted gangue remains in the water. Thus the difference in wetting allows the ore to be concentrated.

Step 2: (b) Zone refining Impurities are more soluble in molten metal than in solid metal. A moving heater creates a narrow molten zone in a rod of impure metal. As the zone advances, relatively pure metal crystallises behind it, while impurities remain preferentially in the melt and travel with the molten zone. Repeated passes concentrate impurities at one end of the rod, which is cut off. The method is used for highly pure silicon and germanium required in semiconductor manufacture.

Step 3: (c) Vapour phase refining The impure metal is first converted into a volatile compound using a suitable reagent. This compound is separated from the nonvolatile impurities and then decomposed to obtain pure metal. The essential requirements are that the metal should form a volatile compound readily and that this compound should decompose readily to regenerate the metal. For example, in Mond refining nickel forms volatile nickel tetracarbonyl, which is subsequently decomposed by heating to deposit pure nickel.

Step 4: Conclusion Froth floatation uses preferential wetting; zone refining uses greater impurity solubility in molten metal; vapour phase refining uses formation and subsequent decomposition of a volatile metal compound.

Quick Tip to Solve: Associate each process with its key property: wetting, solubility in the melt, or volatility of a metal 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:

- The properties of iron depend strongly on its carbon content and other impurities.
- Concentration processes exploit density, melting point or chemical solubility; roasting is a chemical treatment with air at high temperature.

Step 1: (a) Cast iron and pig iron The point of difference is carbon content: cast iron contains about 3% carbon, whereas pig iron contains about 4% carbon. Pig iron is the impure iron obtained from the blast furnace and contains other impurities such as silicon, phosphorus and manganese. Cast iron is obtained by melting pig iron with scrap iron and coke using a hot-air blast. Its lower carbon content distinguishes it from the original pig iron. The comparison refers to the usual textbook compositions; these are approximate percentages rather than exact fixed compositions of every sample.

Step 2: (b) Hydraulic washing and liquation Hydraulic washing is based on a difference in density between ore and gangue, whereas liquation is based on a difference in melting point. In hydraulic washing, a stream of water carries away lighter gangue particles while the heavier ore particles remain. In liquation, the material is heated sufficiently to melt the low-melting metal, which flows away from higher-melting impurities left behind. Thus hydraulic washing separates using water and relative densities, while liquation separates by selective melting.

Step 3: (c) Leaching and roasting Leaching involves selectively dissolving the desired ore constituent in a suitable chemical reagent, whereas roasting involves heating the ore strongly in excess air, below its melting point. In leaching, insoluble gangue is removed by filtration and the useful constituent is subsequently recovered from the solution. Roasting commonly converts a sulphide ore into its oxide, releasing sulphur dioxide. Hence leaching uses selective chemical solubility in a liquid medium, while roasting uses chemical reaction with oxygen at high temperature.

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

Quick Tip to Solve: Compare each pair on one common basis: carbon content, the physical property used, and the chemical treatment applied.

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

(a) $[NiCl_4]^{2-}$

(b) $[Co(C_2O_4)_3]^{3-}$

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

Solution:

Concept:

- Find the metal oxidation state from the complex charge and ligand charges, then determine the metal-ion d-electron configuration.
- In valence bond theory, four-coordinate tetrahedral complexes use sp^3 hybridisation; inner-orbital octahedral complexes use d^2sp^3 hybridisation. Unpaired electrons cause paramagnetism; complete pairing gives diamagnetism.

Step 1: (a) Oxidation state and electronic configuration of nickel Each chloride ligand has charge -1. If the oxidation state of nickel is x, then

$$x + 4(-1) = -2 \quad \Rightarrow \quad x = +2.$$

Neutral nickel has configuration $[\mathrm{Ar}]3d^8 4s^2$; removal of the two $4s$ electrons gives Ni^{2+} : $[\mathrm{Ar}]3d^8$. Chloride is a weak-field ligand and does not induce further pairing of the $3d$ electrons. There are two unpaired electrons in the $3d$ subshell.

Step 2: (a) Hybridisation and magnetism of the nickel complex The metal uses one $4s$ and three $4p$ orbitals to form four equivalent sp^3 hybrid orbitals. Each accepts a lone pair from one chloride ligand, giving a tetrahedral complex. Since two $3d$ electrons remain unpaired, $[\mathrm{NiCl_4}]^{2-}$ is paramagnetic. The absence of an available vacant inner $3d$ orbital without extra pairing is consistent with this tetrahedral, outer-orbital arrangement.

Step 3: (b) Oxidation state and electronic configuration of cobalt Each oxalate ligand, $\mathrm{C_2O_4^{2-}}$, has charge -2 and is bidentate. For cobalt,

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

Neutral cobalt is $[\mathrm{Ar}]3d^7 4s^2$, so Co^{3+} is $[\mathrm{Ar}]3d^6$. Three bidentate oxalate ligands supply six donor atoms, giving coordination number six.

Step 4: (b) Hybridisation and magnetism of the cobalt complex In this cobalt(III) complex, the $3d$ electrons pair to leave two vacant inner $3d$ orbitals. These combine with one $4s$ and three $4p$ orbitals to produce six d^2sp^3 hybrid orbitals, directed octahedrally. Each donor atom supplies a lone pair to one hybrid orbital. All six d electrons are paired, so the complex is diamagnetic. It is therefore an inner-orbital, low-spin octahedral complex.

Step 5: Conclusion (a) $[\mathrm{NiCl_4}]^{2-}$: sp^3, tetrahedral and paramagnetic with two unpaired electrons. (b) $[\mathrm{Co(C_2O_4)_3}]^{3-}$: d^2sp^3, octahedral and diamagnetic with no unpaired electrons.

Quick Tip to Solve: Count donor atoms, not just ligand molecules: three bidentate oxalate ligands give six coordination positions around cobalt.

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; their spatial arrangement differs while their connectivity is identical.
- Optical rotations add algebraically. Resonance and carbon hybridisation determine the strength of an aryl carbon–chlorine bond.

Step 1: (a)(i) Enantiomers Enantiomers are a pair of stereoisomers which are non-superimposable mirror images of each other. In an achiral medium they have identical ordinary physical properties, but rotate plane-polarised light through equal angles in opposite directions. Thus one is dextrorotatory and the other is laevorotatory.

Step 2: (a)(ii) Racemic mixture A racemic mixture contains equal amounts of the two enantiomers, the dextrorotatory and laevorotatory forms. Their equal and opposite optical rotations cancel, so the mixture is optically inactive by external compensation. It is represented by $(\pm)$ or dl.

Step 3: (b) Resistance of chlorobenzene A lone pair on chlorine is conjugated with the benzene ring. Resonance therefore gives the $\mathrm{C-Cl}$ bond partial double-bond character, making it shorter and stronger than the corresponding bond in a haloalkane. Also, chlorine is attached to an sp^2-hybridised carbon, whose greater s-character further strengthens this bond. Bond cleavage is consequently difficult. An S_N1 route would require an unstable phenyl cation, and the aromatic ring obstructs the usual backside displacement of an S_N2 route.

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

Quick Tip to Solve: For an aryl halide, first identify conjugation of the halogen lone pair with the ring; then relate partial double-bond character to difficult bond cleavage.

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21. Answer the following with reason:

(a) Is $(\mathrm{NH\text{-}CHR\text{-}CO})_n$, 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 a single monomer species; a copolymer incorporates two or more distinct monomer species.

Quick Tip to Solve: Count monomer species for homo/copolymer, check small-molecule loss for addition/condensation, and check permanent cross-links for thermal classification.

- Addition polymerisation joins unsaturated monomers without eliminating a small molecule. Thermosetting polymers have permanent cross-linked networks.

Step 1: (a) Classify the polyamide The polymer $[-\mathrm{NH}-\mathrm{CH(R)}-\mathrm{CO}-]_n$ is a homopolymer. Its repeating units arise from one type of amino acid, $\mathrm{H_2N}-\mathrm{CH(R)}-\mathrm{COOH}$, by condensation between amino and carboxyl groups with loss of water. Both functional groups occur in the same monomer molecule; two different functional groups do not imply two different monomers. For the fixed R represented in the question, only one monomer species is involved.

Step 2: (b) Classify PVC by its formation PVC is an addition polymer of vinyl chloride (chloroethene). Its carbon–carbon double bonds open and the monomers join into a chain:

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

No water, hydrogen chloride or other small molecule is eliminated during this polymerisation. Chlorine remains as a substituent on the polymer backbone.

Step 3: (c) Classify Bakelite by its thermal behaviour Bakelite is a thermosetting plastic. Phenol reacts with formaldehyde to form a highly cross-linked, three-dimensional network containing methylene bridges between phenolic units. Once cured, these covalent links prevent the chains from sliding past one another on heating. It therefore cannot be softened and remoulded repeatedly; strong heating causes degradation instead of reversible melting.

Step 4: Conclusion (a) Homopolymer: one amino-acid monomer species. (b) Addition polymer: vinyl chloride adds without eliminating a small molecule. (c) Thermosetting plastic: Bakelite has a permanent cross-linked network.

Quick Tip to Solve: Count monomer species for homo/copolymer, check small-molecule loss for addition/condensation, and check permanent cross-links for thermal classification.

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 delocalisation stabilises aromatic diazonium ions. Loss of nitrogen is particularly favourable when an unstable aliphatic diazonium ion decomposes.
- Methylamine is a weak proton-accepting base: it accepts a proton from water, producing hydroxide ions. Ferric ions precipitate with hydroxide ions.

Step 1: (a) Compare diazonium-ion stability In an aromatic diazonium ion such as $\mathrm{C_6H_5}-\mathrm{N_2^+}$, the diazonium group is conjugated with the benzene ring. Resonance delocalises the positive charge through the conjugated system, stabilising the ion. Aromatic diazonium salts can therefore be retained in cold solution, typically at 273–278 K. Aliphatic diazonium ions lack this resonance stabilisation and

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

readily decompose even at low temperature, losing very stable nitrogen gas:

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

The resulting carbocation undergoes further reactions. Thus aromatic diazonium salts are more stable than aliphatic ones.

Step 2: (b) Formation of hydroxide in methylamine solution The lone pair on nitrogen enables methylamine to accept a proton from water. Its aqueous solution is consequently basic:

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

The hydroxide ions so produced react with ferric ions supplied by ferric chloride.

Step 3: (b) Precipitation of hydrated ferric oxide Ferric hydroxide is sparingly soluble and forms a reddish-brown precipitate:

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

This precipitate is commonly described as hydrated ferric oxide. A corresponding overall equation is

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

Removal of hydroxide ions by precipitation drives further ionisation of methylamine in water.

Step 4: Conclusion (a) Aromatic diazonium salts have resonance stabilisation absent in aliphatic salts. (b) Methylamine generates $\mathrm{OH^-}$ in water, which precipitates $\mathrm{Fe^{3+}}$ as reddish-brown hydrated ferric oxide, $\mathrm{Fe(OH)_3}$.

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

- Basicity measures the readiness of a nitrogen lone pair to accept a proton. Electron-donating groups increase its availability; electron-withdrawing groups reduce it.
- $pK_b = -\log K_b$: greater basic strength corresponds to a larger K_b and hence a smaller pK_b. Therefore, decreasing pK_b means increasing basic strength.
- In the gaseous state, alkylamines are compared by their intrinsic proton affinity; aqueous solvation effects do not determine the stated order.

Quick Tip to Solve: First arrange basic strength using substituent effects, then reverse that order for pK_b; the gaseous-state condition excludes hydration effects.

Step 1: (a) Compare the substituent effects in aromatic amines In aniline, the nitrogen lone pair is partly delocalised into the benzene ring and is less available for protonation. The para nitro group in p-nitroaniline strongly withdraws electrons through both its inductive and resonance effects. It further decreases electron density and lone-pair availability at nitrogen, making this the weakest base of the three. The para methyl group in p-toluidine donates electron density by its positive inductive effect and hyperconjugation, so this compound is more basic than aniline. Thus basicity increases as p-nitroaniline, aniline, p-toluidine. Reverse the basicity order to obtain the requested decreasing pK_b order.

Step 2: (b) Compare the gaseous ethylamines Each ethyl group has an electron-releasing $+I$ effect. Increasing the number of ethyl groups attached to nitrogen increases its electron density and favours proton acceptance. In the gaseous state there is no hydration of the amine or its conjugate acid to alter this trend. The basicity therefore increases from ethylamine to diethylamine to triethylamine. Since pK_b varies inversely with basic strength, the requested order follows by reversing this trend; do not use the different order applicable to aqueous ethylamines.

Step 3: Conclusion The decreasing orders of pK_b are:

$$\text{(a)} \quad p\text{-nitroaniline} > \text{aniline} > p\text{-toluidine},$$
$$\text{(b)} \quad C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N.$$

Quick Tip to Solve: First arrange basic strength using substituent effects, then reverse that order for pK_b; the gaseous-state condition excludes hydration effects.

23(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 chemical test must give a different observable result for the two substances under the same stated conditions.
- Phenols form coloured complexes with neutral ferric chloride, whereas ordinary aliphatic alcohols do not. Alcohols possess an $O-H$ bond and release hydrogen on reaction with sodium; ethers lack this bond.
- Lucas reagent is concentrated HCl with anhydrous $ZnCl_2$. The insoluble alkyl chloride formed gives turbidity; tertiary alcohols react rapidly at room temperature, while primary alcohols do not.

Step 1: (a) Phenol and 1-propanol: neutral ferric chloride test Add a few drops of neutral aqueous $FeCl_3$ to separate samples. Phenol produces a violet colour owing to formation of a ferric phenolate complex. 1-Propanol does not give this violet colour. The characteristic colour therefore identifies phenol; the absence of this colour distinguishes the aliphatic alcohol.

Quick Tip to Solve: Link each test to a visible observation: violet colour for phenol, hydrogen bubbles for ethanol, and immediate Lucas turbidity for the tertiary alcohol.

Step 2: (b) Ethanol and dimethyl ether: sodium metal test Add a small piece of sodium to each dry sample. Ethanol shows effervescence as hydrogen gas is evolved, forming sodium ethoxide:

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

Dimethyl ether gives no corresponding hydrogen evolution because it has no hydroxyl hydrogen. Dry samples are essential so that water does not itself react with sodium and confuse the observation.

Step 3: (c) 1-Propanol and 2-methyl-2-propanol: Lucas test Add Lucas reagent to separate samples at room temperature. Tertiary 2-methyl-2-propanol gives immediate turbidity because it forms insoluble 2-chloro-2-methylpropane readily:

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

Primary 1-propanol gives no turbidity at room temperature in this test. The rapid formation of a stable tertiary carbocation accounts for the immediate reaction of the tertiary alcohol.

Step 4: Conclusion Use neutral $FeCl_3$ for (a): phenol gives violet colour; dry sodium for (b): ethanol liberates hydrogen; and Lucas reagent at room temperature for (c): 2-methyl-2-propanol gives immediate turbidity. The other member of each pair does not give the stated response.

Quick Tip to Solve: Link each test to a visible observation: violet colour for phenol, hydrogen bubbles for ethanol, and immediate Lucas turbidity for the tertiary alcohol.

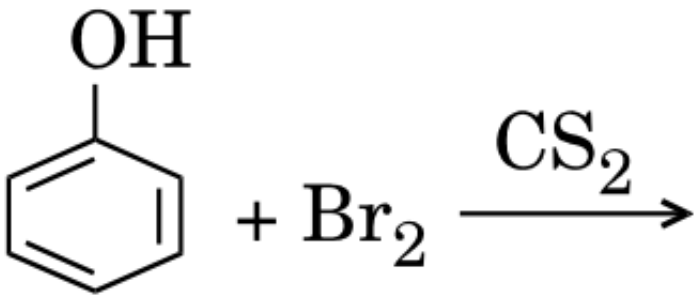
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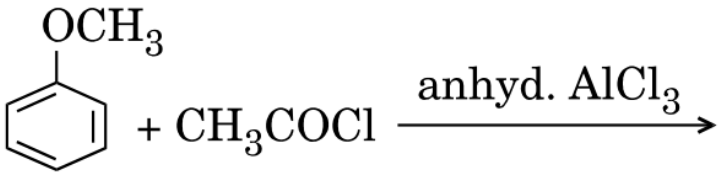
23(b). Write the products of the following reactions:

(i) CH_3 - CH_2 - O - CH_3 + HI →

(ii) Phenol + Br_2 in CS_2 →

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





Solution:

Concept:

- After protonation of an ether oxygen by HI, iodide attacks the less hindered alkyl group by an S_N2 reaction when both groups are primary or methyl.
- The hydroxyl and methoxy groups activate the benzene ring and direct electrophilic substitution to ortho and para positions. The reagent and solvent determine the extent of substitution.
- In Friedel–Crafts acylation, CH_3COCl with anhydrous $AlCl_3$ introduces an acetyl group, $-COCH_3$, into the aromatic ring.

Step 1: (i) Cleave ethyl methyl ether with HI Protonation of the oxygen makes ether cleavage possible. The methyl carbon is less hindered than the ethyl carbon, so iodide attacks the methyl group and breaks its bond to oxygen. The products are methyl iodide and ethanol:

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

This is the cleavage reaction specified by the printed equation. Conversion of the resulting alcohol into an additional alkyl iodide would require further reaction with excess HI, which is not the condition stated here.

Step 2: (ii) Brominate phenol in carbon disulphide In the nonpolar solvent CS_2, phenol undergoes monobromination at its activated ortho and para positions. The products are 2-bromophenol and 4-bromophenol, with the para product predominating because it is less sterically hindered. For either positional isomer the balanced substitution is

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

The bromine and hydroxyl groups in the product are either adjacent (ortho) or opposite (para). The aqueous bromine-water condition giving 2,4,6-tribromophenol is not the solvent printed in this question.

Step 3: (iii) Acylate anisole with acetyl chloride Anhydrous $AlCl_3$ activates acetyl chloride to produce the acyl electrophile. The methoxy group directs its attack to the ortho and para positions. The products are 2-methoxyacetophenone and 4-methoxyacetophenone, the para isomer being major:

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

In the two product isomers, $-OCH_3$ and $-COCH_3$ occupy respectively the 1,2 and 1,4 ring positions. The acetyl group attaches through its carbonyl carbon.

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

Quick Tip to Solve: For HI cleavage attack the methyl group; for phenol in CS_2 and anisole acylation list both ortho and para products, marking para as major.

24. (a) Which one of the following drugs is an antibiotic:

Equanil, Ofloxacin, Aspirin, Luminal

(b) Why is use of aspartame limited to cold food and drinks?

(c) Why do we require artificial sweetening agents? [3 marks]

Solution:

Concept:

- Antibiotics are drugs that kill microorganisms or inhibit their growth; a drug's therapeutic class determines its use.
- Artificial sweeteners provide sweetness in small amounts and allow the intake of ordinary sugar to be reduced.

Step 1: (a) Identify the antibiotic Ofloxacin is the antibiotic among the four drugs. It is a broad-spectrum antibacterial drug used against bacterial infections. Equanil is a tranquilliser; aspirin is an analgesic and antipyretic; Luminal is a barbiturate used as a sedative and anticonvulsant. These three are not antibiotics, so their therapeutic effects do not make them substitutes for ofloxacin in this classification.

Step 2: (b) Explain the restriction on aspartame Aspartame is the methyl ester of the dipeptide formed from aspartic acid and phenylalanine. It is unstable at cooking temperatures and decomposes on heating, losing its sweetening effectiveness. It is therefore used mainly in cold foods and drinks rather than in foods that must be cooked or baked. Its high sweetness alone does not make it suitable for heating; thermal stability is the deciding property.

Step 3: (c) Explain the need for artificial sweeteners Ordinary sugar, such as sucrose, supplies calories, and its intake must be restricted by people who need to control blood glucose or calorie consumption. Artificial sweetening agents provide a sweet taste with little or negligible caloric contribution at the small quantities used. They are thus useful for diabetic people and for people controlling body weight: sweetness can be retained while reducing the amount of sugar consumed. Their function is to sweeten food, rather than to supply the nutritional energy of sugar.

Step 4: Conclusion (a) Ofloxacin is an antibiotic. (b) Aspartame decomposes on heating, so its use is limited to cold foods and drinks. (c) Artificial sweeteners supply sweetness while helping to restrict sugar and calorie intake.

Quick Tip to Solve: Match each drug to its therapeutic class, and distinguish a sweetener's sweetness from its stability at cooking temperatures.

Section D (15 marks)

25(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 an unpaired electron can stabilise an odd-electron molecule; intermolecular attractions determine the boiling behaviour of molecular substances.
- Electron gain enthalpy depends on the repulsion experienced by an added electron as well as the nuclear attraction; a very compact orbital can resist electron addition.
- Chlorine bleaches by oxidation in the presence of water, while fluorine's very high electronegativity restricts the oxidation states it can exhibit.

Step 1: (a) Explain the dimerisation of nitrogen dioxide A molecule of NO_2 contains an odd number of valence electrons and hence an unpaired electron. Two such molecules combine through formation of an $N - N$ bond, pairing these electrons to give the more stable, diamagnetic dimer N_2O_4:

$$2NO_2 \rightleftharpoons N_2O_4.$$

The tendency to attain an electron-paired arrangement accounts for ready dimerisation.

Step 2: (b) Explain chlorine's bleaching action Chlorine reacts with water to form hydrochloric acid and hypochlorous acid. The latter acts as an oxidising agent; the conventional textbook representation is

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl,$$
$$HOCl \longrightarrow HCl + [O].$$

Here $[O]$ represents oxidising oxygen in this simplified account. Oxidation converts the coloured substance into a colourless product, so chlorine bleaches permanently. Moisture is essential: dry chlorine does not bleach dry material.

Step 3: (c) Compare electron gain enthalpies of oxygen and sulphur In oxygen, the incoming electron must enter a small, compact $2p$ orbital, where it experiences strong repulsion from electrons already present. In sulphur it enters the larger $3p$ orbital, where electron-electron repulsion is smaller. Consequently, adding an electron to sulphur releases more energy. Oxygen's electron gain enthalpy is therefore less negative than sulphur's, despite oxygen's smaller atomic size.

Step 4: (d) Explain why fluorine forms only HOF Fluorine is the most electronegative element and does not exhibit positive oxidation states in its compounds. Thus it cannot form the series of oxoacids requiring positive halogen oxidation states that chlorine forms. Its small size and absence of vacant d orbitals also prevent the expanded valence arrangements conventionally used to describe the higher

Quick Tip to Solve: For these five reasons, identify the decisive factor in order: unpaired electron, oxidation, compact orbital repulsion, fluorine's oxidation state, and weak dispersion forces.

oxoacids of chlorine. In HOF, fluorine remains in oxidation state -1; with hydrogen at $+1$, oxygen is at 0. Hence HOF is the sole oxoacid of fluorine.

Step 5: (e) Explain the low boiling points of noble gases Noble gases exist as separate monatomic particles with complete valence shells. The atoms are held together only by weak London dispersion forces, rather than by strong chemical bonds between atoms. Very little energy is required to overcome these weak attractions and separate the atoms into the gaseous state, so their boiling points are very low. Dispersion forces increase down the group as atomic size and polarizability increase, but the boiling points remain low.

Step 6: Conclusion NO_2 dimerises by pairing its unpaired electrons; chlorine bleaches by oxidation in moist conditions; compact $2p$ orbitals make oxygen's electron gain enthalpy less negative than sulphur's; fluorine cannot attain the positive oxidation states required for higher oxoacids; and weak dispersion forces give noble gases very low boiling points.

Quick Tip to Solve: For these five reasons, identify the decisive factor in order: unpaired electron, oxidation, compact orbital repulsion, fluorine's oxidation state, and weak dispersion forces.

OR

25(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:

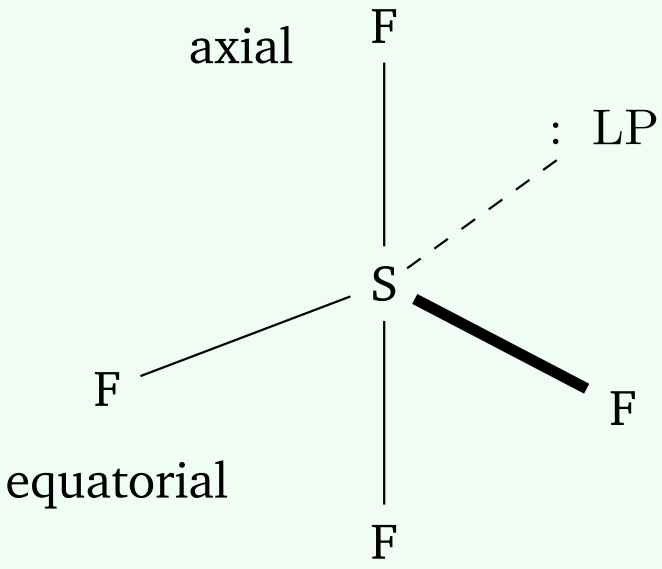
- VSEPR theory predicts molecular shape from repulsions between electron pairs around the central atom. A lone pair repels more strongly than a bonding pair, so it occupies an equatorial site in a trigonal-bipyramidal electron-pair arrangement.
- Chlorine undergoes disproportionation in hot, concentrated alkali: the same element is both reduced to chloride and oxidised to chlorate.
- Complete hydrolysis replaces all xenon–fluorine bonds by xenon–oxygen bonds. Concentrated sulphuric acid is a strong dehydrating agent and removes water from carbohydrates.

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. Thus there are five electron-pair domains: four bonding pairs and one lone pair, represented as AX_4E. Their electron-pair arrangement is trigonal bipyramidal (conventionally described by sp^3d hybridisation).

The lone pair occupies an equatorial position, where it has fewer 90° interactions than in an axial

Quick Tip to Solve: Count five electron-pair domains in both molecules, then place lone pairs equatorially. For the reactions, link hot alkali with chlorate, complete xenon hydrolysis with trioxide, and sugar dehydration with carbon.

position. Two fluorine atoms remain axial and two equatorial. Ignoring the lone pair when naming the molecular shape, the structure is **see-saw**. Lone-pair repulsion distorts the bond angles from the ideal trigonal-bipyramidal values.

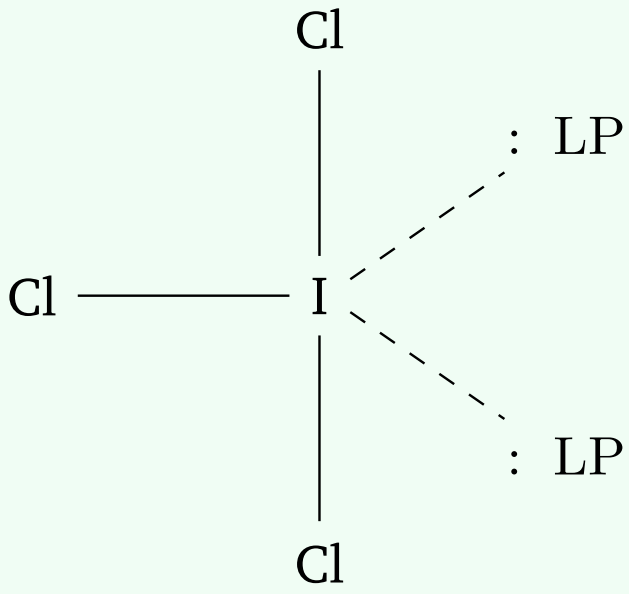


See-saw structure of SF_4; LP denotes the equatorial lone pair.

Step 2: (a)(ii) Structure and shape of iodine trichloride Iodine has seven valence electrons. Three I–Cl bonds leave four electrons, or two lone pairs, on iodine. Hence ICl_3 has five electron-pair domains, AX_3E_2, with a trigonal-bipyramidal electron-pair arrangement (sp^3d hybridisation).

Both lone pairs occupy equatorial positions to minimise repulsion. Two chlorine atoms are axial and the third is equatorial, giving a **T-shaped** molecule. The diagram shows the two equatorial lone pairs explicitly; they are counted in the electron-pair arrangement but not as atoms in the molecular shape.

Quick Tip to Solve: Count five electron-pair domains in both molecules, then place lone pairs equatorially. For the reactions, link hot alkali with chlorate, complete xenon hydrolysis with trioxide, and sugar dehydration with carbon.



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

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

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

Chlorine changes from oxidation state 0 to -1 in chloride and to $+5$ in chlorate. This is disproportionation: five chlorine atoms are reduced while one is oxidised. The stated hot, concentrated conditions favour chlorate formation.

Step 4: (b)(ii) Complete hydrolysis of xenon hexafluoride On complete hydrolysis, xenon hexafluoride forms xenon trioxide and hydrogen fluoride:

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

All six fluorine atoms are removed as HF; the three oxygen atoms from water become bonded to xenon. Xenon remains in oxidation state $+6$, so this hydrolysis is not a redox reaction. Complete hydrolysis is essential here: oxyfluorides correspond to partial hydrolysis.

Step 5: (b)(iii) Concentrated sulphuric acid poured over cane sugar Cane sugar (sucrose), $C_{12}H_{22}O_{11}$, is dehydrated by concentrated sulphuric acid. A black, porous mass of carbon forms and swells as heat and water vapour are produced:

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

The acid removes the hydrogen and oxygen of the sugar in the proportion present in water. It is shown over the arrow because its role in this equation is that of a dehydrating agent; the visible blackening is due to the carbon residue.

Quick Tip to Solve: Count five electron-pair domains in both molecules, then place lone pairs equatorially. For the reactions, link hot alkali with chlorate, complete xenon hydrolysis with trioxide, and sugar dehydration with carbon.

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: Count five electron-pair domains in both molecules, then place lone pairs equatorially. For the reactions, link hot alkali with chlorate, complete xenon hydrolysis with trioxide, and sugar dehydration with carbon.

26(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 an aldehyde, the carbon of the $-CHO$ group is carbon 1. The parent name records the chain length and the position of the carbon-carbon double bond.
- Aldehydes reduce Tollens' reagent, whereas ordinary alcohols do not. Oxidation, Grignard addition and alpha-halogenation provide the required conversions.

Step 1: (a) Name the unsaturated aldehyde Numbering from the aldehyde carbon gives $CHO(1) - CH(2) = CH(3) - CH_3(4)$. The longest chain contains four carbons and the double bond begins at carbon 2. Hence the IUPAC name is but-2-enal. The displayed formula does not specify a geometrical configuration, so no stereochemical prefix is required.

Step 2: (b) Distinguish ethanol from ethanal Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Ethanal gives a silver mirror on the inner wall of the test tube; ethanol gives no silver mirror under these test conditions. Ethanal is oxidised to ethanoate while the silver(I) complex is reduced to metallic silver:

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

Thus the positive silver-mirror test identifies ethanal. The iodoform test is unsuitable here because both ethanol and ethanal can give a positive result.

Step 3: (c)(i) Convert toluene to benzoic acid Heat toluene with alkaline potassium permanganate, then acidify the resulting benzoate salt. Strong oxidation converts the entire methyl side chain into a carboxyl group without changing the benzene ring:

$$C_6H_5CH_3 \xrightarrow[\text{heat}]{\text{alkaline } KMnO_4} C_6H_5COO^-K^+ \xrightarrow{H^+} C_6H_5COOH.$$

Acidification is necessary to obtain the free carboxylic acid from its salt.

Quick Tip to Solve: For propanal to lactic acid, oxidise first and then replace an alpha hydrogen through HVZ bromination and hydrolysis; HCN addition would increase the carbon count.

Step 4: (c)(ii) Convert ethanol to propan-2-ol First oxidise ethanol in a controlled manner to ethanal, for example using PCC. Add methylmagnesium bromide to ethanal in dry ether, followed by acidic hydrolysis:

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

$$CH_3CHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH(OMgBr)CH_3,$$

$$CH_3CH(OMgBr)CH_3 \xrightarrow{H_3O^+} CH_3CH(OH)CH_3.$$

The methyl group adds to the carbonyl carbon and increases the chain from two carbons to three. Hydrolysis protonates the alkoxide, giving the required secondary alcohol. Dry conditions during Grignard addition prevent destruction of the reagent by water.

Step 5: (c)(iii) Convert propanal to 2-hydroxypropanoic acid Oxidise propanal to propanoic acid. Carry out the Hell-Volhard-Zelinsky reaction using bromine and red phosphorus, followed by hydrolysis, to obtain the alpha-bromo acid. Replace bromine with hydroxyl using aqueous alkali, then acidify:

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

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

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

Bromination occurs at the carbon adjacent to the carboxyl group, which is carbon 2. Its subsequent substitution gives 2-hydroxypropanoic acid while retaining the original three-carbon skeleton.

Step 6: Conclusion (a) But-2-enal. (b) Ethanal gives a silver mirror with Tollens' reagent; ethanol does not. (c) The conversions give benzoic acid, propan-2-ol and 2-hydroxypropanoic acid, respectively, by the sequences shown above.

Quick Tip to Solve: For propanal to lactic acid, oxidise first and then replace an alpha hydrogen through HVZ bromination and hydrolysis; HCN addition would increase the carbon count.

OR

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

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

(c) Write the products formed when $(CH_3)_3$C-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:

- Substituted benzoic acids are numbered with the ring carbon bearing $-COOH$ as carbon 1. Electron-withdrawing groups stabilise the carboxylate ion and increase acidity.

Quick Tip to Solve: Inspect the carbon immediately next to CHO: in this aldehyde it has no hydrogen, so concentrated NaOH gives Cannizzaro alcohol plus carboxylate salt.

- Clemmensen reduction converts $-CHO$ into $-CH_3$. Aldehydes without alpha hydrogen undergo Cannizzaro disproportionation. Semicarbazide condenses with the carbonyl group to form a semicarbazone.

Step 1: (a) Give the IUPAC name of salicylic acid Salicylic acid contains a hydroxyl group adjacent to the carboxyl group on a benzene ring. Taking benzoic acid as the parent and numbering the ring from the carbon bearing $-COOH$, the hydroxyl group lies at carbon 2. Its IUPAC name is therefore 2-hydroxybenzoic acid. The carboxyl group has priority over the phenolic hydroxyl group, so the latter is expressed by the prefix hydroxy.

Step 2: (b) Explain the greater acidity of chloroacetic acid The chlorine atom in $ClCH_2COOH$ exerts a negative inductive, or $-I$, effect through sigma bonds. It withdraws electron density and stabilises the negative charge of the conjugate base $ClCH_2COO^-$. Consequently, loss of a proton from chloroacetic acid is more favourable:

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

In acetic acid, the methyl group exerts a positive inductive, or $+I$, effect and increases electron density in the carboxylate group. It therefore destabilises the negatively charged conjugate base relative to the chlorine-substituted case. Chloroacetic acid is thus more acidic than acetic acid; the comparison concerns the stability of their conjugate bases.

Step 3: (c)(i) Reaction with zinc amalgam and dilute hydrochloric acid The starting aldehyde is $(CH_3)_3CCHO$, or 2,2-dimethylpropanal. Zinc amalgam with hydrochloric acid performs Clemmensen reduction: the carbonyl oxygen is removed and the aldehyde group becomes a methyl group.

$$(CH_3)_3CCHO \xrightarrow{Zn(Hg),\ HCl} (CH_3)_3CCH_3.$$

The product is 2,2-dimethylpropane (neopentane). The carbon skeleton remains unchanged, and the carbonyl carbon is retained as the new terminal methyl carbon.

Step 4: (c)(ii) Reaction with concentrated sodium hydroxide The alpha carbon, the carbon directly adjoining $-CHO$, is bonded to three methyl groups and the aldehyde carbon. It has no hydrogen. Therefore this aldehyde undergoes the Cannizzaro reaction rather than aldol condensation. One molecule is reduced to a primary alcohol and another is oxidised to the sodium salt of a carboxylic acid:

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

The products are 2,2-dimethylpropan-1-ol and sodium 2,2-dimethylpropanoate. In the stated alkaline medium the oxidised product is the carboxylate salt; the free acid would require a subsequent acidification step.

Step 5: (c)(iii) Reaction with semicarbazide and a weak acid Semicarbazide is $H_2N-NH-C(=O)-NH_2$. Its terminal hydrazino amino group reacts with the aldehyde carbonyl group in a weakly acidic medium. Addition followed by loss of water gives the semicarbazone:

$$(CH_3)_3CCHO + H_2NNHC(=O)NH_2 \xrightarrow{\text{weak acid}} (CH_3)_3CCH=NNHC(=O)NH_2 + H_2O.$$

Quick Tip to Solve: Inspect the carbon immediately next to CHO: in this aldehyde it has no hydrogen, so concentrated NaOH gives Cannizzaro alcohol plus carboxylate salt.

The original aldehyde oxygen is replaced by the $= NNHC(= O)NH_2$ group. The weak acid catalyses condensation, and the carbonyl group within the semicarbazide residue remains intact.

Step 6: Conclusion (a) 2-Hydroxybenzoic acid. (b) Chlorine stabilises the chloroacetate ion through its $-I$ effect. (c) The products are (i) 2,2-dimethylpropane, (ii) 2,2-dimethylpropan-1-ol and sodium 2,2-dimethylpropanoate, and (iii) $(CH_3)_3CCH = NNHC(= O)NH_2$, the semicarbazone.

Quick Tip to Solve: Inspect the carbon immediately next to CHO: in this aldehyde it has no hydrogen, so concentrated NaOH gives Cannizzaro alcohol plus carboxylate salt.

27(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]

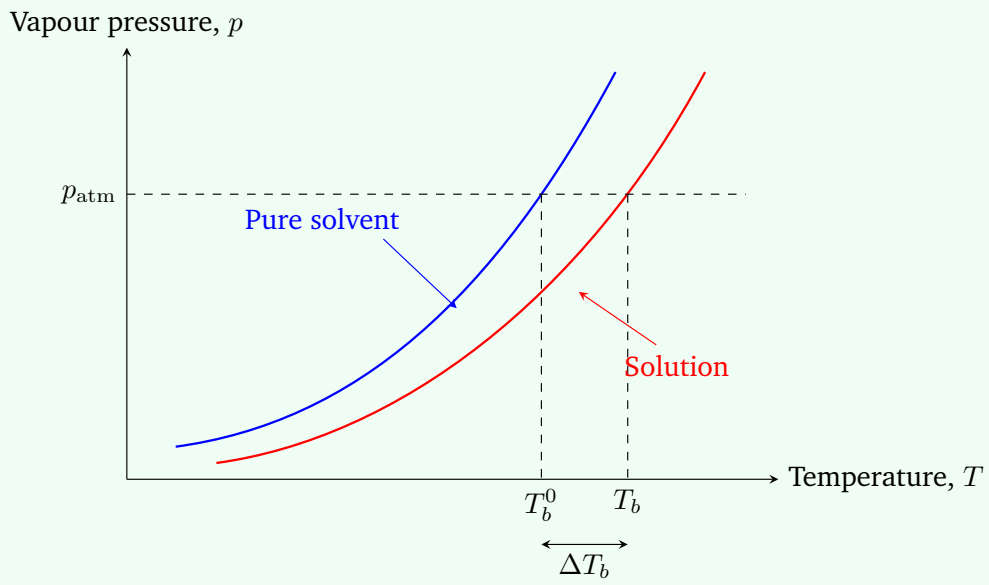
Solution:

Concept:

- For a solution containing a non-volatile solute, Raoult's law gives $p = x_1 p^0$, where p^0 is the vapour pressure of the pure solvent and $x_1 < 1$ is its mole fraction. Thus the solution has lower vapour pressure at the same temperature.
- A liquid boils when its vapour pressure equals the external pressure. The boiling point elevation is $\Delta T_b = T_b - T_b^0$, where T_b^0 and T_b refer to the pure solvent and solution respectively.
- Osmotic pressure is $\pi = iCRT = i(n/V)RT$. Here i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature. Complete dissociation determines the number of solute particles.

Step 1: (a) Compare the vapour pressure curves Plot vapour pressure vertically and temperature horizontally. Both vapour pressures rise with temperature, but the solution curve lies below the pure-solvent curve because the non-volatile solute lowers the solvent's escaping tendency. Draw a horizontal line at atmospheric pressure p_{atm}. Its intersections with the two curves give the respective boiling points, as shown below.

Quick Tip to Solve: For fully dissociated K2SO4 use i = 3, and convert 25 mg to 0.025 g before finding molarity.



Vapour pressure curves showing elevation in boiling point

Step 2: (a) Explain the rise in boiling point At T_b^0, the pure solvent reaches atmospheric pressure and boils. At this same temperature, the solution's vapour pressure is still less than atmospheric pressure. It must therefore be heated further, to T_b, before its vapour pressure reaches p_{atm}. Consequently $T_b > T_b^0$, and the positive temperature difference $\Delta T_b = T_b - T_b^0$ is the elevation in boiling point.

Step 3: (b) Find the concentration and dissociation factor The molar mass is

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

Convert the mass before calculating moles: $25\,\text{mg} = 0.025\,\text{g}$. Hence

$$n = \frac{0.025}{174} = 1.437 \times 10^{-4}\,\text{mol}, \qquad C = \frac{1.437 \times 10^{-4}}{2} = 7.184 \times 10^{-5}\,\text{mol L}^{-1}.$$

For this dilute solution, take its volume as $2\,\text{L}$. Complete dissociation gives

$$\text{K}_2\text{SO}_4 \longrightarrow 2\text{K}^+ + \text{SO}_4^{2-},$$

so one formula unit produces three ions and $i = 3$.

Step 4: (b) Calculate the osmotic pressure With $T = 25{+}273 = 298\,\text{K}$ and $R = 0.0821\,\text{L atm mol}^{-1}\text{K}^{-1}$,

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

The dissociation factor multiplies the pressure because osmosis depends on the total number of dissolved particles, rather than just the number of salt formula units.

Step 5: Conclusion (a) The lower vapour pressure of the solution makes its boiling point higher:

Quick Tip to Solve: For fully dissociated K2SO4 use i = 3, and convert 25 mg to 0.025 g before finding molarity.

$\Delta T_b = T_b - T_b^0 > 0$. (b) The osmotic pressure is $\boxed{5.27 \times 10^{-3}\,\text{atm}}$.

Quick Tip to Solve: For fully dissociated K2SO4 use i = 3, and convert 25 mg to 0.025 g before finding molarity.

OR

27(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 the entire range of composition because interactions between unlike molecules 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 is the molal depression constant and m is the molality calculated from the formula mass of the solute.
- The van't Hoff factor is the ratio of the actual number of solute particles to the number expected without association. For dimerisation, $i = 1 - \alpha/2$, where α is the fraction of original molecules that associate.

Step 1: (a) State two characteristics of a non-ideal solution First, its components do not obey Raoult's law throughout the composition range: the partial vapour pressure p_A differs from $x_A p_A^0$, and similarly for component B. Depending on the relative strengths of unlike and like molecular interactions, the solution shows a positive or negative deviation from the ideal vapour pressure.

Second, mixing is accompanied by a heat change, so $\Delta H_{\text{mix}} \neq 0$. Weaker unlike interactions give endothermic mixing and positive deviation; stronger unlike interactions give exothermic mixing and negative deviation. This contrasts with an ideal solution, for which the enthalpy of mixing is zero.

Step 2: (b) Calculate the molality before association The molar mass of benzoic acid, C_6H_5COOH, is

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

Use the mass of benzene, the solvent, in kilograms. The analytical molality, calculated before allowing for association, is

$$m = \frac{2/122}{25/1000} = \frac{40}{61}\,\text{mol kg}^{-1} = 0.65574\,\text{mol kg}^{-1}.$$

If all acid molecules remained separate, the predicted freezing-point depression would be

$$K_f m = 4.9 \times 0.65574 = 3.21311\,\text{K}.$$

The observed depression, $1.62\,\text{K}$, is smaller, indicating a reduced number of solute particles due to association.

Quick Tip to Solve: Use the solvent mass in kilograms to find molality, then compute i from the observed depression. For dimers, percentage association is $200(1 - i)$; a value of i close to 0.5 means nearly complete association.

Step 3: Determine the van't Hoff factor Divide the observed depression by the value calculated without association:

$$i = \frac{\Delta T_f}{K_f m} = \frac{1.62}{3.21311} = 0.50418.$$

The result is below unity, as expected when molecules combine. For complete dimerisation it would be 0.5, so this value indicates nearly complete association.

Step 4: Relate the particle count to the fraction associated The association is represented by

$$2\,C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2.$$

Suppose the initial amount of acid is n mol and a fraction α of its molecules forms dimers. Unassociated acid contributes $n(1-\alpha)$ mol of particles, while the dimers contribute $n\alpha/2$ mol. Thus,

$$i = \frac{n(1-\alpha) + n\alpha/2}{n} = 1 - \frac{\alpha}{2}.$$

Therefore,

$$\alpha = 2(1-i) = 2(1-0.50418) = 0.99163, \qquad 100\alpha = 99.163\%.$$

The percentage refers to the original acid molecules that participate in dimer formation, not the percentage of particles that are dimers.

Step 5: Conclusion (a) A non-ideal solution deviates from Raoult's law and has a nonzero enthalpy of mixing. (b) The percentage association of benzoic acid is approximately $\boxed{99.2\%}$.

Quick Tip to Solve: Use the solvent mass in kilograms to find molality, then compute i from the observed depression. For dimers, percentage association is $200(1-i)$; a value of i close to 0.5 means nearly complete association.