CBSE Class 12 Chemistry Question Paper 2018 with Solution PDF-Set 56-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) **All questions** are compulsory.
(ii) Questions number **1 to 5** are very short answer questions and carry **1** mark each.
(iii) Questions number **6 to 10** are short answer questions and carry **2** marks each.
(iv) Questions number **11 to 22** are also short answer questions and carry **3** marks each.
(v) Question number **23** is a value based question and carries **4** marks.
(vi) Questions number **24 to 26** are long answer questions and carry **5** marks each.
(vii) Use log tables, if necessary. Use of calculators is not allowed.

1. Analysis shows that FeO has a non-stoichiometric composition with formula $Fe_{0.95}O$. Give reason.

[1 mark]

Solution:

Concept:

- FeO exhibits a metal-deficiency defect: some iron-ion sites are vacant while oxygen-ion sites remain occupied.
- Electrical neutrality is maintained when some Fe^{2+} ions are replaced by Fe^{3+} ions.

Step 1: Identify the missing ions The formula $Fe_{0.95}O$ contains fewer iron ions than the ideal $1:1$ ratio in FeO. Thus, the non-stoichiometry is caused by vacancies at iron-ion sites, rather than by a change in the oxygen charge.

Step 2: Explain charge compensation For each missing Fe^{2+} ion, two other Fe^{2+} ions become Fe^{3+}. Their extra positive charges compensate for the vacancy. Per oxygen ion, 0.85 divalent and 0.10 trivalent iron ions give $2(0.85) + 3(0.10) = 2$.

Step 3: Conclusion FeO has a metal-deficiency defect, with iron vacancies compensated by the presence of some Fe^{3+} ions; hence its composition is $Fe_{0.95}O$.

Quick Tip to Solve: For a metal-deficiency oxide, explain both the cation vacancies and the higher oxidation state that maintains neutrality.

2. CO (g) and H_2 (g) react to give different products in the presence of different catalysts. Which ability of the catalyst is shown by these reactions?

[1 mark]

Solution:

Concept:

- Selectivity is the ability of a catalyst to direct a reaction towards a particular product.
- Different catalysts can favour different reaction pathways for the same starting reactants.

Step 1: Compare the reactants In the stated reactions, the starting substances are the same: carbon monoxide and hydrogen. Therefore, the difference in products is linked to the choice of catalyst, rather than to a different pair of reactants.

Step 2: Identify the ability demonstrated A catalyst can promote a particular pathway among several possible transformations of these reactants. Changing the catalyst changes the favoured pathway and hence the product obtained. This product-directing property is called selectivity; catalytic activity instead describes how effectively a catalyst accelerates a reaction.

Step 3: Conclusion The reactions demonstrate the **selectivity** of catalysts.

Quick Tip to Solve: When the same reactants give different products with different catalysts, identify selectivity from the product choice.

3. Write the coordination number and oxidation state of Platinum in the complex $[Pt(en)_2Cl_2]$.

[1 mark]

Solution:

Concept:

- Coordination number counts the donor atoms directly bonded to the central metal.
- Ethylenediamine, en, is a neutral bidentate ligand; each coordinated chloride has charge -1.

Step 1: Count donor atoms Each en ligand coordinates through its two nitrogen atoms. The two en ligands therefore supply four donor atoms. The two chloride ligands supply one donor atom each, giving a total of $2 \times 2 + 2 = 6$. Counting ligand molecules alone would miss the bidentate nature of en.

Step 2: Use the charge balance The printed complex $[\mathrm{Pt(en)_2Cl_2}]$ carries no overall charge. If the oxidation state of platinum is x, the neutral en ligands contribute zero and the chloride ligands contribute -2, so $x + 2(0) + 2(-1) = 0$, which gives $x = +2$.

Step 3: Conclusion The coordination number of platinum is 6, and its oxidation state is $+2$.

Quick Tip to Solve: Count donor atoms for coordination number, but use ligand charges and the overall complex charge for oxidation state.

4. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why?

[1 mark]

Solution:

Concept:

- Hydrolysis by aqueous NaOH replaces chlorine with an $-\mathrm{OH}$ group through nucleophilic substitution.
- In chlorobenzene, resonance gives the aryl carbon-chlorine bond partial double-bond character.

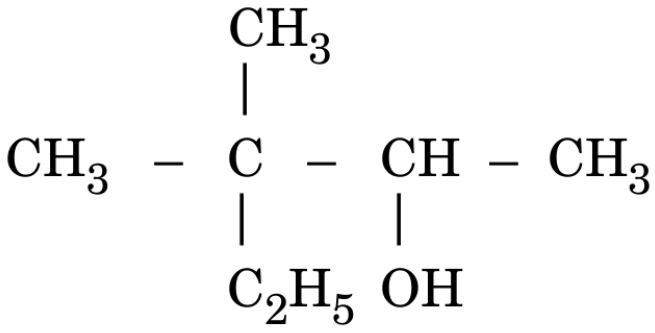
Step 1: Examine benzyl chloride In benzyl chloride, $\mathrm{C_6H_5CH_2Cl}$, chlorine is attached to the benzylic sp^3 carbon. Its carbon-chlorine bond is a normal single bond and substitution at this position is facilitated by the neighbouring aromatic ring, which stabilises the developing charge in the substitution process.

Step 2: Compare chlorobenzene In chlorobenzene, chlorine is bonded directly to an sp^2 ring carbon. Delocalisation of a chlorine lone pair into the ring gives the carbon-chlorine bond partial double-bond character, making it shorter and stronger. This bond is consequently much harder to cleave during hydrolysis under ordinary conditions.

Step 3: Conclusion Benzyl chloride is hydrolysed more easily by aqueous NaOH; chlorobenzene resists hydrolysis because its carbon-chlorine bond has partial double-bond character.

Quick Tip to Solve: First locate chlorine: on the ring means an aryl halide, while on the adjacent carbon means a benzyl halide.

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



Solution:

Concept:

- The parent chain must contain the carbon bonded to $-\mathrm{OH}$, the principal functional group.
- Number the parent chain from the end that gives the hydroxyl group its lowest locant.

Step 1: Select and number the parent chain The longest continuous chain containing the hydroxyl-bearing carbon has five carbons. Trace it from the right-hand methyl group through $\mathrm{CH(OH)}$, the central carbon, and the ethyl branch: $\mathrm{CH_3-CH(OH)-C-CH_2-CH_3}$. Numbering from the right places the hydroxyl group at carbon 2.

Step 2: Locate the substituents The central carbon is carbon 3 of this parent chain. Its two remaining branches, the methyl group drawn above it and the methyl group drawn to its left, are both methyl substituents. Their combined prefix is therefore $3,3$-dimethyl, and the parent alcohol name is pentan-2-ol.

Step 3: Conclusion The IUPAC name is 3,3-dimethylpentan-2-ol.

Quick Tip to Solve: Include the ethyl branch in the longest chain; the two methyl branches then both lie at carbon 3.

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6. Calculate the freezing point of a solution containing 60 g of glucose (Molar mass = 180 g mol^{-1}) in 250 g of water.

(K_f of water = 1.86 K kg mol^{-1}) [2 marks]

Solution:

Concept:

- For a dilute solution, $\Delta T_f = iK_f m$, where m is the solute molality and K_f is the cryoscopic constant.
- Glucose neither dissociates nor associates in water, so its van't Hoff factor is $i = 1$. Molality uses the mass of solvent in kilograms.

Quick Tip to Solve: Convert only the solvent mass to kilograms, take i = 1 for glucose, and subtract the depression from water's freezing point.

Step 1: Calculate molality The amount of glucose and mass of water are

$$n = \frac{60\,\text{g}}{180\,\text{g mol}^{-1}} = \frac{1}{3}\,\text{mol}, \qquad w = 250\,\text{g} = 0.250\,\text{kg}.$$

Hence the molality is

$$m = \frac{n}{w} = \frac{1/3}{0.250} = \frac{4}{3}\,\text{mol kg}^{-1}.$$

The denominator is the water mass, not the combined mass of water and glucose.

Step 2: Calculate depression and freezing point Substituting the given cryoscopic constant,

$$\Delta T_f = 1 \times 1.86 \times \frac{4}{3} = 2.48\,\text{K}.$$

Pure water freezes at $0\,^\circ$C, and adding a non-volatile solute lowers this temperature. Thus

$$T_f = 0 - 2.48 = -2.48\,^\circ\text{C}.$$

Equivalently, on the Kelvin scale, $T_f = 273.15 - 2.48 = 270.67\,\text{K}$. A temperature interval of $2.48\,\text{K}$ is also an interval of $2.48\,^\circ$C.

Step 3: Conclusion The freezing point of the solution is $\boxed{-2.48\,^\circ\text{C}}$, or $270.67\,\text{K}$.

Quick Tip to Solve: Convert only the solvent mass to kilograms, take i = 1 for glucose, and subtract the depression from water's freezing point.

7. For the reaction

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$,

the rate of formation of NO_2 (g) is 2.8×10^{-3} M s^{-1}. Calculate the rate of disappearance of N_2O_5 (g). [2 marks]

Solution:

Concept:

- The rate of a reaction is divided by the stoichiometric coefficient of each species: reactant disappearance and product formation then give the same reaction rate.
- For concentration in molarity, rates are expressed in M s^{-1}. A disappearance rate is reported as a positive quantity, $-d[\text{reactant}]/dt$.

Step 1: Relate the rates using the balanced equation In $2N_2O_5 \longrightarrow 4NO_2 + O_2$, every two moles of N_2O_5 consumed produce four moles of NO_2. Thus

$$r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}.$$

The disappearance rate of the reactant is therefore half the formation rate of nitrogen dioxide.

Quick Tip to Solve: Multiply the given species rate by requested coefficient/given coefficient; do not confuse it with the normalized reaction rate.

Step 2: Substitute the given formation rate Using $d[NO_2]/dt = 2.8 \times 10^{-3}\,\mathrm{M\,s^{-1}}$,

$$-\frac{d[N_2O_5]}{dt} = \frac{2}{4}\left(2.8 \times 10^{-3}\right) = 1.4 \times 10^{-3}\,\mathrm{M\,s^{-1}}.$$

The negative sign in the concentration derivative indicates consumption; the magnitude is the requested rate.

Step 3: Conclusion The rate of disappearance of N_2O_5 is $\boxed{1.4 \times 10^{-3}\,\mathrm{M\,s^{-1}}}$.

Quick Tip to Solve: Multiply the given species rate by requested coefficient/given coefficient; do not confuse it with the normalized reaction rate.

8. Among the hydrides of Group-15 elements, which have the

(a) lowest boiling point?

(b) maximum basic character?

(c) highest bond angle?

(d) maximum reducing character? [2 marks]

Solution:

Concept:

- Group-15 hydrides are NH_3, PH_3, AsH_3, SbH_3 and BiH_3. Their properties reflect intermolecular forces, lone-pair availability and E–H bond strength.
- Ammonia has hydrogen bonding; down the group, basicity and bond angle generally decrease while reducing character increases.

Step 1: Identify the lowest boiling point and strongest base (a) PH_3 has the lowest boiling point. Ammonia has an anomalously high boiling point because its molecules form hydrogen bonds. Below phosphine, increasing molecular size and polarizability strengthen dispersion forces and raise boiling points.

(b) NH_3 has maximum basic character. Its compact nitrogen lone pair is most readily donated to a proton; the tendency to donate this pair decreases down the group.

Step 2: Identify the largest bond angle and strongest reducing agent (c) NH_3 has the highest bond angle, about $107°$. The other hydrides have angles closer to $90°$; their bonding involves progressively less hybridization.

(d) BiH_3 has maximum reducing character. The E–H bonds weaken down the group, so the heavier hydrides decompose and release hydrogen more readily; reducing power consequently increases.

Step 3: Conclusion (a) $\boxed{PH_3}$; (b) $\boxed{NH_3}$; (c) $\boxed{NH_3}$; (d) $\boxed{BiH_3}$.

Quick Tip to Solve: Remember the boiling-point exception: hydrogen bonding pushes ammonia above phosphine, so the lowest boiling point is not ammonia.

9(a). How do you convert the following?

(a) Ethanal to Propanone

(b) Toluene to Benzoic acid [2 marks]

Solution:

Concept:

- A methyl Grignard reagent adds one carbon to ethanal and forms a secondary alcohol after hydrolysis; oxidation of that alcohol gives a ketone.
- Hot alkaline permanganate oxidizes a benzylic side chain to a carboxylate; acidification then produces the carboxylic acid.

Step 1: Convert ethanal into propanone Treat ethanal with methylmagnesium bromide in dry ether, then hydrolyse the addition product to obtain propan-2-ol. Oxidize this secondary alcohol with acidified potassium dichromate:

$$\begin{aligned} CH_3CHO &\xrightarrow[\text{dry ether}]{CH_3MgBr} CH_3CH(OMgBr)CH_3 \\ &\xrightarrow{H_3O^+} CH_3CH(OH)CH_3 \\ &\xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3COCH_3. \end{aligned}$$

Dry ether is essential for the Grignard addition because water destroys the reagent. The oxidation retains all three carbon atoms.

Step 2: Convert toluene into benzoic acid Heat toluene with alkaline potassium permanganate. Its methyl side chain is oxidized to potassium benzoate. Acidify the resulting salt with dilute hydrochloric acid:

$$C_6H_5CH_3 \xrightarrow[\Delta]{KMnO_4/KOH} C_6H_5COOK \xrightarrow{HCl} C_6H_5COOH.$$

The benzene ring remains intact; the carbon of the methyl group becomes the carboxyl carbon.

Step 3: Conclusion Ethanal gives propanone by methyl Grignard addition, hydrolysis and oxidation; toluene gives benzoic acid by alkaline $KMnO_4$ oxidation followed by acidification.

Quick Tip to Solve: Count carbons first: ethanal needs one added carbon before oxidation, whereas toluene needs oxidation of its existing side-chain carbon.

OR

9(b). Account for the following:

(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. [2 marks]

Solution:

Concept:

- Friedel–Crafts reactions are electrophilic aromatic substitutions and require an aromatic ring sufficiently reactive towards the electrophile.
- Acid strength depends on conjugate-base stability: $pK_a = -\log_{10} K_a$, so a larger K_a corresponds to a smaller pK_a.

Step 1: Explain the absence of Friedel–Crafts reaction (a) The $-COOH$ group withdraws electron density from the aromatic ring through both its negative inductive and negative resonance effects. This strongly deactivates the ring towards electrophilic substitution, so it does not undergo Friedel–Crafts alkylation or acylation. In addition, the carboxyl group interacts with the Lewis-acid catalyst, $AlCl_3$, further hindering the reaction. The ordinary Friedel–Crafts conditions cannot overcome this strong deactivation.

Step 2: Compare the acidity of the two acids (b) The para $-NO_2$ group is strongly electron withdrawing through its $-I$ and $-R$ effects. It stabilizes the conjugate base, 4-nitrobenzoate, relative to benzoate and favours loss of H^+. Thus 4-nitrobenzoic acid has a larger acid-dissociation constant, K_a. Since $pK_a = -\log_{10} K_a$, its pK_a is lower than that of benzoic acid.

Step 3: Conclusion (a) $-COOH$ strongly deactivates the ring and interacts with $AlCl_3$. (b) Para $-NO_2$ stabilizes the conjugate base, increasing acidity and lowering pK_a.

Quick Tip to Solve: For acidity comparisons, stabilize the conjugate base first; then reverse the acidity order when writing the pKa order.

10. Complete and balance the following chemical equations:

(a) $Fe^{2+} + MnO_4^- + H^+ \longrightarrow$

(b) $MnO_4^- + H_2O + I^- \longrightarrow$ [2 marks]

Solution:

Concept:

- Redox balancing conserves atoms and total charge by equating the electrons lost and gained.
- Acidic permanganate is reduced to Mn^{2+}; in neutral or weakly alkaline medium it gives MnO_2.

Step 1: (a) Balance in acidic medium Iron loses one electron, whereas manganese changes from $+7$ to $+2$, gaining five electrons:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O.$$

Quick Tip to Solve: Identify the medium first: acid gives Mn^{2+}, whereas water here gives MnO_2; match electron changes and then check charge.

Multiply the iron half-reaction by five and add. The electrons cancel; four oxygen atoms and eight hydrogen atoms are conserved. The total charge on each side is $+17$.

Step 2: (b) Balance the reaction with water Without added acid, permanganate gives manganese dioxide and oxidises iodide to iodate. The half-reactions are

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$
$$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-.$$

Multiply the first half-reaction by two and add. Cancel six electrons, three water molecules and six hydroxide ions. The final equation conserves seven oxygen atoms and two hydrogen atoms, and has total charge -3 on both sides.

Step 3: Conclusion The completed equations are

$$\text{(a)} \quad 5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O,$$
$$\text{(b)} \quad 2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + IO_3^- + 2OH^-.$$

Quick Tip to Solve: Identify the medium first: acid gives Mn^{2+}, whereas water here gives MnO_2; match electron changes and then check charge.

11. Give reasons for the following:

(a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.

(b) Aquatic animals are more comfortable in cold water than in warm water.

(c) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution.

[3 marks]

Solution:

Concept:

- Osmotic pressure of a dilute solution is $\pi = CRT = wRT/(MV)$, where C is molar concentration, w is solute mass, M is molar mass and V is solution volume.
- Gas solubility generally decreases as temperature rises. Boiling-point elevation is a colligative property: $\Delta T_b = iK_b m$, where i counts effective solute particles and m is molality.

Step 1: (a) Why osmotic pressure is preferred Proteins and polymers have very large molar masses, so a given small mass produces a low number of dissolved molecules. Their freezing-point depression and boiling-point elevation are consequently extremely small and difficult to measure accurately. Osmotic pressure is appreciable even for very dilute solutions and can be measured at ordinary temperature, avoiding heating that could denature proteins or decompose sensitive macromolecules. The measured pressure gives the molar mass from $M = wRT/(\pi V)$.

Step 2: (b) Why cold water is more comfortable The dissolution of oxygen in water is favoured at lower temperature. Cold water therefore contains more dissolved oxygen than warm water at the same oxygen pressure. Aquatic animals obtain oxygen for respiration from the water, so the greater

Quick Tip to Solve: For these reasons, link osmotic pressure to dilute solutions, cold water to dissolved oxygen, and KCl to its two dissociated ions.

oxygen availability in cold water makes breathing easier and supports their survival.

Step 3: (c) Compare KCl and sugar solutions Sugar remains as molecules in water, so its van't Hoff factor is $i = 1$. Potassium chloride dissociates into two ions:

$$KCl \longrightarrow K^+ + Cl^-.$$

Hence its van't Hoff factor is nearly two. For the comparison in the question, the solvent and solute concentration are comparable, and $\Delta T_b = iK_b m$ means that twice as many dissolved particles produce nearly twice the boiling-point elevation. The value is described as nearly double because ionic interactions can make the effective factor slightly less than two; strictly, the elevation formula uses molality rather than molarity.

Step 4: Conclusion (a) Osmotic pressure is measurable in very dilute macromolecular solutions at ordinary temperature. (b) Cold water contains more dissolved oxygen. (c) KCl produces nearly two particles per formula unit, whereas sugar produces one, giving nearly twice the boiling-point elevation.

Quick Tip to Solve: For these reasons, link osmotic pressure to dilute solutions, cold water to dissolved oxygen, and KCl to its two dissociated ions.

12. An element 'X' (At. mass = 40 g mol^{-1}) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of X and the number of unit cells in 4 g of X. (N_A = 6.022×10^{23} mol^{-1}) [3 marks]

Solution:

Concept:

- An f.c.c. unit cell contains $Z = 8(1/8) + 6(1/2) = 4$ atoms: each corner is shared by eight cells and each face centre by two.
- Unit-cell density is $\rho = ZM/(N_A a^3)$, where M is molar mass, N_A is Avogadro's constant and a is edge length. The number of cells is the number of atoms divided by Z.

Step 1: Convert the edge length and obtain the cell volume Use centimetres so that density is obtained in g cm^{-3}. Since $1\,\text{pm} = 10^{-10}\,\text{cm}$,

$$a = 400 \times 10^{-10} = 4.00 \times 10^{-8}\,\text{cm},$$
$$a^3 = (4.00 \times 10^{-8})^3 = 6.40 \times 10^{-23}\,\text{cm}^3.$$

The f.c.c. cell's four atoms have total mass $4M/N_A$; the edge length determines the volume of the entire cubic unit cell.

Step 2: Calculate the density Substitute $Z = 4$, $M = 40\,\text{g mol}^{-1}$ and the cell volume:

$$\rho = \frac{4 \times 40}{(6.022 \times 10^{23})(6.40 \times 10^{-23})}$$
$$= \frac{160}{38.5408} = 4.151\,\text{g cm}^{-3}.$$

Quick Tip to Solve: For an f.c.c. solid use four atoms per cell, convert pm to cm before cubing, and divide the sample's atom count by four.

Avogadro's constant converts molar mass to mass per atom; multiplying by four accounts for the atoms in one cell.

Step 3: Calculate the number of unit cells in the sample The $4\,\text{g}$ sample contains $4/40 = 0.100\,\text{mol}$ of atoms. Divide its number of atoms by four atoms per cell:

$$N_{\text{cells}} = \frac{(4/40)(6.022 \times 10^{23})}{4} = 1.5055 \times 10^{22}.$$

This also follows from dividing the sample mass by the mass of one unit cell, $160/(6.022 \times 10^{23})\,\text{g}$.

Step 4: Conclusion The density of X is $\boxed{4.15\,\text{g cm}^{-3}}$, and $4\,\text{g}$ of X contains $\boxed{1.5055 \times 10^{22}}$ unit cells (approximately 1.51×10^{22}).

Quick Tip to Solve: For an f.c.c. solid use four atoms per cell, convert pm to cm before cubing, and divide the sample's atom count by four.

13. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction.

(Given: log 2 = 0.3010, log 4 = 0.6021, R = 8.314 J K^{-1} mol^{-1}) [3 marks]

Solution:

Concept:

- For a first order reaction, the time for 50% completion is the half-life, $t_{1/2} = 0.693/k$, where k is the rate constant. Thus, the rate constant is inversely proportional to the half-life.
- The two-temperature Arrhenius relation is $\log(k_2/k_1) = \dfrac{E_a}{2.303R}(1/T_1 - 1/T_2)$, where E_a is activation energy, R is the gas constant and temperatures are in kelvin.

Step 1: Identify the half-lives and rate-constant ratio Since the reaction is 50% completed at each stated time, $t_{1/2,1} = 40\,\text{min}$ at $T_1 = 300\,\text{K}$, and $t_{1/2,2} = 20\,\text{min}$ at $T_2 = 320\,\text{K}$. Therefore,

$$k_1 = \frac{0.693}{40}\,\text{min}^{-1}, \qquad k_2 = \frac{0.693}{20}\,\text{min}^{-1}, \qquad \frac{k_2}{k_1} = \frac{40}{20} = 2.$$

Both rate constants use the same time unit, so minutes cancel in their ratio; conversion to seconds is unnecessary.

Step 2: Substitute in the Arrhenius equation Using the given $\log 2 = 0.3010$ and $R = 8.314\,\text{J K}^{-1}\text{mol}^{-1}$,

$$0.3010 = \frac{E_a}{2.303(8.314)}\left(\frac{1}{300} - \frac{1}{320}\right),$$

$$E_a = \frac{2.303(8.314)(0.3010)(300)(320)}{320 - 300} \approx 2.766 \times 10^4\,\text{J mol}^{-1}.$$

The temperature difference is positive in this form, giving a positive activation energy. The doubling

Quick Tip to Solve: At 50% completion, use the inverse half-life ratio directly: halving the half-life doubles the rate constant.

of the rate constant on heating also agrees with the Arrhenius temperature dependence.

Step 3: Conclusion The activation energy of the reaction is $\boxed{E_a \approx 27.66\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: At 50% completion, use the inverse half-life ratio directly: halving the half-life doubles the rate constant.

14. What happens when

(a) a freshly prepared precipitate of $Fe(OH)_3$ is shaken with a small amount of $FeCl_3$ solution?

(b) persistent dialysis of a colloidal solution is carried out?

(c) an emulsion is centrifuged? [3 marks]

Solution:

Concept:

- Peptization converts a freshly prepared precipitate into a colloidal sol by adding a small quantity of a suitable electrolyte, called the peptizing agent. Adsorption of an ion gives the particles a common charge.
- Dialysis removes dissolved ions through a semipermeable membrane. A small amount of electrolyte helps maintain the stability of a lyophobic sol; excessive removal can destabilize it.
- An emulsion consists of droplets of one liquid dispersed in another immiscible liquid. Centrifugation promotes separation of its liquid phases.

Step 1: (a) Fresh ferric hydroxide with ferric chloride The freshly prepared Fe(OH)_3 precipitate is peptized to form a reddish-brown, positively charged ferric hydroxide sol. FeCl_3 supplies Fe^{3+} ions, which are preferentially adsorbed on the precipitate particles. The particles acquire the same positive charge and repel one another, enabling the precipitate to disperse into colloidal-sized particles. Thus, the small quantity of ferric chloride acts as the peptizing agent.

Step 2: (b) Persistent dialysis of a colloidal solution Initially, dialysis removes excess dissolved electrolyte and other small dissolved impurities through the membrane. If it is continued persistently, even the small amount of electrolyte needed for colloidal stability is removed. The sol then loses its stability and the colloidal particles coagulate, producing a precipitate. Hence, dialysis should not be prolonged beyond removal of the unwanted excess electrolyte.

Step 3: (c) Centrifuging an emulsion Centrifugation breaks the emulsion and separates it into its constituent immiscible liquid layers. Under rapid rotation, the phases separate according to their densities, and the dispersed droplets collect into a separate liquid phase. This process is called demulsification.

Step 4: Conclusion (a) A positively charged Fe(OH)_3 sol forms by peptization; (b) persistent dialysis causes coagulation; (c) centrifugation breaks the emulsion into its constituent liquid phases.

Quick Tip to Solve: Associate a small amount of ferric chloride with peptization, prolonged dialysis with loss of stability, and centrifugation with demulsification.

15. Write the chemical reactions involved in the process of extraction of Gold. Explain the role of dilute NaCN and Zn in this process. [3 marks]

Solution:

Concept:

- In the cyanide process, gold is leached from its ore by dilute aqueous sodium cyanide in the presence of oxygen from air. Gold forms the soluble dicyanidoaurate(I) complex, $[Au(CN)_2]^-$.
- Zinc is more electropositive than gold. It reduces the dissolved gold complex to metallic gold while itself forming the soluble tetracyanidozincate(II) complex, $[Zn(CN)_4]^{2-}$.

Step 1: Leach gold with dilute sodium cyanide The crushed gold-bearing ore is treated with dilute $NaCN$ solution while air supplies oxygen. The reaction is

$$4Au + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Au(CN)_2] + 4NaOH.$$

Cyanide ions complex gold, bringing it into solution as sodium dicyanidoaurate(I); oxygen acts as the oxidizing agent. Gold changes from oxidation state zero to $+1$. The soluble gold-containing solution is separated from the insoluble residue. Thus, dilute sodium cyanide acts as the leaching and complex-forming reagent, allowing gold to be extracted from the ore.

Step 2: Recover gold by displacement with zinc Zinc is added to the gold-containing solution. The displacement reaction is

$$2Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Au.$$

Zinc is oxidized from zero to $+2$, and the two gold(I) ions are reduced to metallic gold. The cyanide ligands bind the resulting zinc ion, leaving a soluble zinc complex while gold precipitates. Zinc therefore acts as the reducing agent used to recover metallic gold from its cyanide complex. The deposited gold is collected for further purification.

Step 3: Conclusion Dilute $NaCN$, with oxygen from air, leaches gold as soluble $Na[Au(CN)_2]$. Zinc then reduces this complex and precipitates metallic gold, forming $Na_2[Zn(CN)_4]$.

Quick Tip to Solve: Remember the two stages: oxygen-assisted cyanide leaching gives the gold complex, and zinc displacement recovers the metal.

16. Give reasons:

(a) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(b) Iron has higher enthalpy of atomization than that of copper.

(c) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. [3 marks]

Solution:

Concept:

- A standard reduction potential measures the tendency of the oxidised species to accept electrons; greater stability of the reduced state favours reduction.
- A half-filled d^5 configuration is especially stable. Metallic bond strength depends on the number of

Quick Tip to Solve: Write the ionic d-electron configurations first: remove 4s electrons before 3d electrons.

electrons available for bonding.

- Colour in aqueous transition-metal ions commonly arises from absorption of visible light during transitions between split d orbitals.

Step 1: (a) Compare the electron configurations Mn^{3+} is $3d^4$, whereas Mn^{2+} is $3d^5$. Reduction of Mn^{3+} therefore produces the particularly stable half-filled d subshell. In contrast, Fe^{3+} already has the stable $3d^5$ configuration, and its reduction produces Fe^{2+}, with $3d^6$. Thus manganese(III) has a much greater tendency to be reduced than iron(III), making its reduction potential more positive.

Step 2: (b) Relate atomisation to metallic bonding Iron has configuration $[Ar]3d^6 4s^2$, with several unpaired d electrons available for metallic bonding. Copper has $[Ar]3d^{10}4s^1$, with a filled d subshell and fewer unpaired electrons. Stronger metallic bonding in iron requires more energy to separate the solid into isolated gaseous atoms, so its enthalpy of atomisation is higher.

Step 3: (c) Explain the difference in colour Sc^{3+} has configuration $[Ar]3d^0$: there is no d electron to undergo a d-d transition. Its aqueous solution is therefore colourless. Ti^{3+} is $[Ar]3d^1$. In its hydrated complex, the d orbitals split into different energy levels, and its electron can absorb visible light to move to a higher level. The transmitted light consequently gives the solution a colour.

Step 4: Conclusion The reasons are the stability gained on forming Mn^{2+} with d^5, stronger metallic bonding in iron, and the availability of a d-d transition in Ti^{3+} but not in Sc^{3+}.

Quick Tip to Solve: Write the ionic d-electron configurations first: remove 4s electrons before 3d electrons.

17. (a) Identify the chiral molecule in the following pair:

(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH. [3 marks]



(i) (ii)

Solution:

Concept:

- A tetrahedral carbon bonded to four different groups is a stereogenic centre; its molecule can be chiral.
- Wurtz–Fittig coupling joins an aryl halide and an alkyl halide using sodium in dry ether.
- Alcoholic KOH promotes elimination of a beta hydrogen and halide. Saytzeff's rule favours the more substituted alkene.

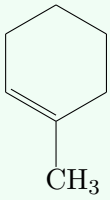
Quick Tip to Solve: Compare all four groups at the OH carbon, then choose the more substituted double bond for alcoholic-KOH elimination.

Step 1: (a) Inspect the carbon bearing OH Molecule (i) is $CH_3CH(OH)CH(CH_3)CH_3$, 3-methylbutan-2-ol. Its OH-bearing carbon is attached to four different groups: $-OH$, $-H$, $-CH_3$, and $-CH(CH_3)_2$. It is therefore a chiral molecule. In molecule (ii), the OH-bearing carbon has two identical $-CH(CH_3)_2$ groups, along with H and OH. It is not a stereogenic centre, and molecule (ii) is achiral.

Step 2: (b) Couple chlorobenzene with methyl chloride Sodium in dry ether brings about Wurtz–Fittig coupling. The chlorine on the phenyl group is replaced by a methyl group, giving methylbenzene (toluene), with structure $C_6H_5 - CH_3$:

$$C_6H_5Cl + CH_3Cl + 2Na \xrightarrow{\text{dry ether}} C_6H_5CH_3 + 2NaCl.$$

Step 3: (c) Eliminate HBr from the cyclic halide The carbon bearing Br and methyl is carbon 1. Removing Br from it and a beta hydrogen from the adjacent ring carbon forms a double bond within the ring. This gives the more substituted, trisubstituted alkene, 1-methylcyclohex-1-ene, as the major product. Its structure is



Elimination from the methyl group would give the less substituted exocyclic alkene and is not the major Saytzeff product.

Step 4: Conclusion (a) Molecule (i) is chiral. (b) The product is toluene, $C_6H_5CH_3$. (c) The major alkene is 1-methylcyclohex-1-ene.

Quick Tip to Solve: Compare all four groups at the OH carbon, then choose the more substituted double bond for alcoholic-KOH elimination.

18. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollens' test whereas isomer (B) does not give Tollens' test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/conc. HCl give the same product (D).

(a) Write the structures of (A), (B), (C) and (D).

(b) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN? [3 marks]

Solution:

Concept:

- Aldehydes reduce Tollens' reagent to metallic silver; ordinary ketones do not give this test.
- A methyl ketone containing CH_3CO- gives the iodoform test. Clemmensen reduction replaces $C = O$ by CH_2 without changing the carbon skeleton.
- HCN adds by nucleophilic attack at the carbonyl carbon. Alkyl groups reduce its electrophilicity and also increase steric hindrance.

Quick Tip to Solve: Use the shared Clemmensen product to distinguish straight-chain butanal from branched 2-methylpropanal.

Step 1: Identify ketone (B) using both tests Since (B) does not give Tollens' test, it is a ketone. The positive iodoform test requires the methyl-ketone group CH_3CO-. For molecular formula C_4H_8O, the non-cyclic ketone is butan-2-one:

$$(B) = CH_3 - C(=O) - CH_2 - CH_3.$$

Clemmensen reduction converts this carbonyl group into a methylene group, giving

$$(D) = CH_3 - CH_2 - CH_2 - CH_3,$$

which is butane.

Step 2: Assign aldehydes (A) and (C) Both (A) and (C) give Tollens' test and are aldehydes. The two acyclic aldehydes of this formula are butanal and 2-methylpropanal. Since (A) gives the same straight-chain butane as (B) on Clemmensen reduction, (A) must be butanal:

$$(A) = CH_3 - CH_2 - CH_2 - C(=O)H.$$

The remaining isomer is

$$(C) = (CH_3)_2CH - C(=O)H,$$

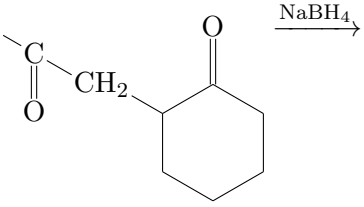
namely 2-methylpropanal. Its reduction would retain the branched skeleton and produce 2-methylpropane, confirming that it cannot be (A).

Step 3: Compare addition of HCN Butan-2-one (B) has two alkyl groups attached to its carbonyl carbon, while each aldehyde has one alkyl group and one hydrogen. The two alkyl groups donate electron density by the positive inductive effect, reducing the positive character of the carbonyl carbon. They also hinder approach of the attacking cyanide ion more than hydrogen does. Hence (B) is least reactive towards nucleophilic addition of HCN.

Step 4: Conclusion (A) is butanal, (B) is butan-2-one, (C) is 2-methylpropanal, and (D) is butane. The least reactive isomer towards HCN addition is (B), butan-2-one.

Quick Tip to Solve: Use the shared Clemmensen product to distinguish straight-chain butanal from branched 2-methylpropanal.

19. Write the structures of the main products in the following reactions:

(i) 

(ii) $C_6H_5 - CH = CH_2 + H_2O \xrightarrow{H^+}$

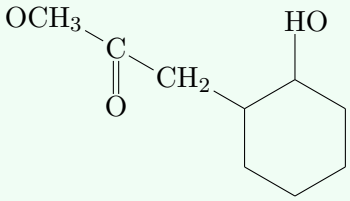
(iii) $C_6H_5 - O - C_2H_5 + HI \longrightarrow$ [3 marks]

Solution:

Concept:

- Sodium borohydride, $NaBH_4$, reduces an aldehyde or ketone to an alcohol under ordinary conditions, while leaving an ester group unchanged.
- Acid-catalysed hydration adds H and OH across an alkene through the more stable carbocation intermediate.
- In an aryl alkyl ether, HI cleaves the alkyl–oxygen bond; the aryl–oxygen bond remains intact.

Step 1: (i) Reduce the ring ketone selectively The substrate contains both a cyclic ketone and the side chain $-CH_2 - C(=O) - OCH_3$. Hydride from $NaBH_4$ attacks the ketone carbonyl carbon; protonation of the resulting alkoxide gives a secondary alcohol. The ester is not reduced by this reagent under the usual conditions. Thus the carbonyl at ring position 1 becomes $-CH(OH)-$, while the side chain at the adjacent ring carbon stays unchanged. The product structure is



It is methyl 2-(2-hydroxycyclohexyl)acetate. No particular stereochemical configuration is specified by the question.

Step 2: (ii) Hydrate styrene Protonation of the terminal CH_2 carbon produces a resonance-stabilised benzylic carbocation, $C_6H_5 - CH^+ - CH_3$. Water attacks this carbon, and loss of a proton produces the alcohol. Therefore the hydroxyl group attaches to the carbon next to the benzene ring:

$$C_6H_5 - CH = CH_2 + H_2O \xrightarrow{H^+} C_6H_5 - CH(OH) - CH_3.$$

The main product is 1-phenylethanol, as expected from Markovnikov addition.

Step 3: (iii) Cleave phenetole with HI The printed ether has an ethyl group, $-OC_2H_5$. After protonation of oxygen, iodide attacks the primary ethyl carbon and breaks its bond to oxygen. Substitution does not take place at the aromatic carbon because the aryl–oxygen bond has partial double-bond character. The reaction is

$$C_6H_5 - O - CH_2CH_3 + HI \longrightarrow C_6H_5 - OH + CH_3CH_2 - I.$$

Quick Tip to Solve: Identify the reagent first: NaBH4 leaves the ester intact, hydration favours the benzylic carbon, and HI attacks the ethyl side of phenetole.

Hence the products are phenol and iodoethane.

Step 4: Conclusion The main products are (i) the ring alcohol with its $-CH_2COOCH_3$ group unchanged, (ii) $C_6H_5CH(OH)CH_3$, and (iii) C_6H_5OH and CH_3CH_2I.

Quick Tip to Solve: Identify the reagent first: NaBH4 leaves the ester intact, hydration favours the benzylic carbon, and HI attacks the ethyl side of phenetole.

20. (a) Why is bithional added to soap?

(b) What is tincture of iodine? Write its one use.

(c) Among the following, which one acts as a food preservative?

Aspartame, Aspirin, Sodium Benzoate, Paracetamol [3 marks]

Solution:

Concept:

- Antiseptics destroy or inhibit microorganisms and can be used on living tissues in suitable concentrations.
- Food preservatives protect stored food by inhibiting microbial growth and reducing spoilage.

Step 1: (a) Purpose of bithional in soap Bithional is added to soap to impart antiseptic properties. It controls microorganisms, including bacteria associated with unpleasant body odour, on the skin. Thus it improves the soap's germicidal action in addition to its ordinary cleansing action. The required property is antiseptic activity; it is not added as a food preservative or artificial sweetener.

Step 2: (b) Composition and use of tincture of iodine Tincture of iodine is a 2–3% solution of iodine in an alcohol–water mixture. It is used as an antiseptic on minor cuts and wounds, where it helps destroy microorganisms and prevent infection. The dilute preparation is suitable for this local application; the term tincture refers to the alcoholic preparation rather than solid iodine itself.

Step 3: (c) Identify the food preservative Sodium benzoate, C_6H_5COONa, is the food preservative in the list. It inhibits microbial growth and is commonly used to preserve acidic food products. Aspartame is an artificial sweetener. Aspirin and paracetamol are medicines used for pain relief and fever reduction, so neither is the required food preservative.

Step 4: Conclusion (a) Bithional imparts antiseptic properties to soap. (b) Tincture of iodine is a 2–3% iodine solution in alcohol–water, used on minor wounds as an antiseptic. (c) Sodium benzoate is the food preservative.

Quick Tip to Solve: Match each substance to its function: bithional and dilute iodine are antiseptics; sodium benzoate prevents food spoilage.

21(a). Define the following with an example of each:

(a) Polysaccharides

(b) Denatured protein

(c) Essential amino acids [3 marks]

Solution:

Concept:

- Biomolecules are classified using their composition, structure and biological role. A definition should identify the distinguishing feature before giving an example.
- Denaturation changes a protein's higher-order structure; essentiality of an amino acid concerns the body's ability to synthesise it.

Step 1: (a) Polysaccharides Polysaccharides are high-molecular-mass carbohydrates composed of a large number of monosaccharide units joined by glycosidic linkages. On hydrolysis they yield many monosaccharide molecules. For example, starch is a polysaccharide made of glucose units and serves as a storage carbohydrate in plants. It contains amylose and amylopectin. The word polysaccharide therefore describes a carbohydrate polymer rather than a single sugar molecule or a disaccharide.

Step 2: (b) Denatured protein A denatured protein is a protein whose native secondary and tertiary structures have been disrupted by heat, a change in pH or another denaturing agent, causing loss of its characteristic biological activity. Its primary structure, the amino-acid sequence joined by peptide bonds, remains intact in ordinary denaturation. For example, the albumin in egg white becomes denatured and coagulates when an egg is boiled. This visible change results from loss of the original folded structure rather than hydrolysis into amino acids.

Step 3: (c) Essential amino acids Essential amino acids are amino acids that the human body cannot synthesise in sufficient amounts to meet its needs and must therefore obtain from the diet. For example, valine is an essential amino acid. Such amino acids are needed for protein synthesis just like the other amino acids, but their dietary supply is necessary. The term essential does not mean that the remaining amino acids are unimportant; those can be synthesised adequately by the body.

Step 4: Conclusion Examples are starch for a polysaccharide, coagulated egg-white albumin for a denatured protein, and valine for an essential amino acid.

Quick Tip to Solve: Keep the three definitions distinct: many sugar units, loss of protein folding, and compulsory dietary supply of an amino acid.

OR

21(b). (a) Write the product when D-glucose reacts with conc. HNO_3.

(b) Amino acids show amphoteric behaviour. Why?

(c) Write one difference between α-helix and β-pleated structures of proteins. [3 marks]

Solution:

Concept:

- Strong oxidation converts both the aldehyde group and terminal primary alcohol group of open-chain glucose into carboxyl groups.
- An amino acid contains a basic amino group and an acidic carboxyl group; its zwitterion can accept or donate a proton.
- Secondary protein structures are stabilised by hydrogen bonds between peptide carbonyl and peptide N–H groups.

Step 1: (a) Oxidise both ends of glucose Concentrated nitric acid oxidises the aldehyde end, $-CHO$, as well as the primary alcohol end, $-CH_2OH$, of D-glucose. The four intervening $CHOH$ groups remain in the carbon skeleton. The product is the dicarboxylic acid saccharic acid (D-glucaric acid):

$$CHO - (CHOH)_4 - CH_2OH \xrightarrow{\text{conc. } HNO_3} HOOC - (CHOH)_4 - COOH.$$

Step 2: (b) Explain amphoteric behaviour Amino acids have both $-NH_2$ and $-COOH$ groups. In aqueous solution they exist predominantly as zwitterions, $^+H_3N - CH(R) - COO^-$. Their carboxylate group accepts a proton from an acid, while their ammonium group gives a proton to a base. Thus they react with both acids and bases:

$$^+H_3N - CH(R) - COO^- + H^+ \longrightarrow {}^+H_3N - CH(R) - COOH,$$
$$^+H_3N - CH(R) - COO^- + OH^- \longrightarrow H_2N - CH(R) - COO^- + H_2O.$$

Step 3: (c) Compare the secondary structures In an α-helix, a polypeptide chain coils into a helix and hydrogen bonds form within that coiled chain. In a β-pleated sheet, extended polypeptide strands lie side by side and hydrogen bonds form between neighbouring strands. This distinguishes a coiled structure from a sheet-like structure; both are secondary structures of proteins.

Step 4: Conclusion (a) Saccharic acid, $HOOC - (CHOH)_4 - COOH$, is formed. (b) Amino acids can accept and donate protons because they contain acidic and basic groups. (c) An α-helix is coiled with intrachain hydrogen bonds, whereas a β-pleated sheet has extended strands linked by hydrogen bonds.

Quick Tip to Solve: For nitric-acid oxidation of glucose, change both terminal groups to COOH; mild oxidation changes only CHO.

22. (a) Write the formula of the following coordination compound:

Iron(III) hexacyanoferrate(II)

(b) What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$?

(c) Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic No. of Co = 27) [3 marks]

Solution:

Concept:

- A coordination salt must be electrically neutral. The charge of a complex equals the metal oxidation state plus the total ligand charge.
- Ionisation isomers exchange a coordinated ligand with a counter-ion and therefore release different ions in solution.
- Fluoride is a weak-field ligand. A six-coordinate cobalt(III) fluoride complex is high spin and uses outer-orbital sp^3d^2 hybridisation.

Step 1: (a) Balance the charges of the coordination salt Iron(III) supplies Fe^{3+} cations. In hexacyanoferrate(II), the central iron has oxidation state $+2$ and each of the six cyanide ligands has charge -1. Thus the complex-ion charge is

$$+2 + 6(-1) = -4,$$

giving $[Fe(CN)_6]^{4-}$. Four iron(III) cations balance three complex anions, since $4(+3) + 3(-4) = 0$. Therefore the formula is $Fe_4[Fe(CN)_6]_3$.

Step 2: (b) Identify the isomerism The complex $[Co(NH_3)_5Cl]SO_4$ exhibits ionisation isomerism. Its coordinated chloride can exchange with the sulfate counter-ion to give $[Co(NH_3)_5SO_4]Cl$. The first compound releases sulfate ions in aqueous solution, whereas the second releases chloride ions. Their different free ions distinguish the two ionisation isomers.

Step 3: (c) Find the electron configuration and hybridisation For $[CoF_6]^{3-}$, let the oxidation state of cobalt be x. Then $x + 6(-1) = -3$, so $x = +3$. Neutral cobalt has configuration $[Ar]3d^74s^2$, hence Co^{3+} is $3d^6$. Fluoride is a weak-field ligand and does not cause pairing of the d electrons to produce an inner-orbital complex. The octahedral high-spin arrangement is $t_{2g}^4e_g^2$: the three lower orbitals contain one pair and two single electrons, and each upper orbital contains one single electron. Therefore there are four unpaired electrons. The complex uses the outer $4d$ orbitals, giving sp^3d^2 hybridisation and octahedral geometry.

Step 4: Conclusion (a) $Fe_4[Fe(CN)_6]_3$. (b) Ionisation isomerism. (c) sp^3d^2 hybridisation with four unpaired electrons.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons; then use the ligand field strength to decide pairing.

23. Shyam went to a grocery shop to purchase some food items. The shopkeeper packed all the items in polythene bags and gave them to Shyam. But Shyam refused to accept the polythene bags and asked the shopkeeper to pack the items in paper bags. He informed the shopkeeper about the heavy penalty imposed by the government for using polythene bags. The shopkeeper promised that he would use paper bags in future in place of polythene bags.

Answer the following:

(a) Write the values (at least two) shown by Shyam.

(b) Write one structural difference between low-density polythene and high-density polythene.

(c) Why did Shyam refuse to accept the items in polythene bags?

(d) What is a biodegradable polymer? Give an example. [4 marks]

Solution:

Concept:

- Chain branching prevents close packing; nearly linear chains pack closely and give higher density.
- Polythene is resistant to ordinary microbial decomposition and therefore persists as solid waste in the environment.
- Biodegradable polymers undergo decomposition through microorganisms or their enzymes.

Step 1: (a) Identify the values shown by Shyam Shyam shows environmental awareness and concern for protecting nature by refusing a material that produces persistent waste. He also shows social responsibility: he explains the problem to the shopkeeper and encourages a change that benefits the community.

Step 2: (b) Compare the structures of the two polythenes Low-density polythene (LDPE) has highly branched polymer chains. Its branches obstruct close packing of neighbouring chains, resulting in lower density. High-density polythene (HDPE) consists of essentially linear chains with very little branching; these chains can pack closely and therefore have a higher density.

Step 3: (c) Explain the refusal of polythene bags Shyam refused the bags because polythene is non-biodegradable: microorganisms do not readily break it down under ordinary environmental conditions. Discarded bags accumulate and cause pollution; they can also block drains and harm animals that ingest them. Choosing paper bags reduces the use of such persistent plastic waste, since paper can undergo biodegradation.

Step 4: (d) Define a biodegradable polymer and give an example A biodegradable polymer is a polymer that can be decomposed by microorganisms, or by the enzymes they produce, into simpler products that can be assimilated in natural processes. A standard example is PHBV, poly(β-hydroxybutyrate-co-β-hydroxyvalerate). It is a biodegradable polyester whose ester linkages can undergo biological degradation.

Step 5: Conclusion (a) Shyam shows environmental awareness and social responsibility. (b) LDPE has branched chains, while HDPE has essentially linear chains. (c) Polythene is non-biodegradable and polluting. (d) Biodegradable polymers undergo microbial decomposition; PHBV is an example.

Quick Tip to Solve: For the density comparison, connect branching to poor packing: LDPE is branched, HDPE is nearly linear. For biodegradability, state microbial decomposition and give PHBV as a standard example.

24(a). Give reasons:

(i) H_3PO_3 undergoes disproportionation reaction but H_3PO_4 does not.

(ii) When Cl_2 reacts with excess of F_2, ClF_3 is formed and not FCl_3.

(iii) Dioxygen is a gas while Sulphur is a solid at room temperature.

(b) Draw the structures of the following:

(i) XeF_4

(ii) $HClO_3$ [5 marks]

Solution:

Concept:

- Disproportionation is simultaneous oxidation and reduction of the same element. An intermediate oxidation state can show both changes; the highest oxidation state cannot be oxidised further under these conditions.
- Fluorine is the most electronegative element and has oxidation state -1 in its compounds. Chlorine can have positive oxidation states when bonded to fluorine.
- Molecular size and polarisability control London dispersion forces. VSEPR predicts molecular shape from bonding domains and lone pairs around the central atom; a multiple bond counts as one domain.

Step 1: (a)(i) Compare the oxidation states of phosphorus In H_3PO_3, let the oxidation state of phosphorus be x. Then $3(+1) + x + 3(-2) = 0$, giving $x = +3$. This intermediate state can increase to $+5$ or decrease to -3. On heating, phosphorous acid therefore disproportionates:

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3.$$

Three phosphorus atoms are oxidised to $+5$ and one is reduced to -3. In H_3PO_4, phosphorus is already at its highest oxidation state, $+5$, and cannot undergo the oxidation half of disproportionation.

Step 2: (a)(ii) Explain the interhalogen formed In ClF_3, three fluorine atoms each have oxidation state -1, so chlorine has oxidation state $+3$. This is possible because chlorine is less electronegative and larger than fluorine, allowing it to be the central atom bonded to three smaller fluorine atoms:

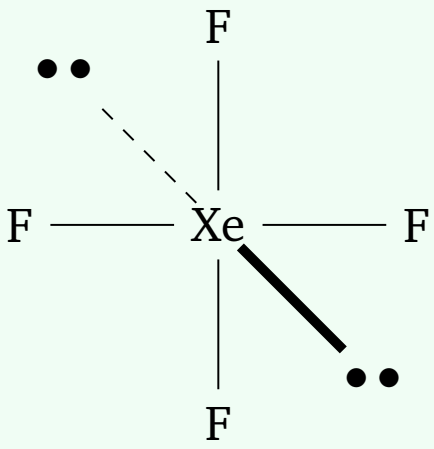
$$Cl_2 + 3F_2 \longrightarrow 2ClF_3.$$

The reversed formula FCl_3 would require a central fluorine atom bonded to three chlorine atoms and, with chlorine assigned -1, fluorine at $+3$. Fluorine cannot have a positive oxidation state in such a compound and cannot expand its octet; thus this reversed arrangement is not formed.

Step 3: (a)(iii) Compare the molecular forms and intermolecular attractions Oxygen exists as small diatomic O_2 molecules, whereas sulphur commonly exists as much larger cyclic S_8 molecules. The larger electron cloud of S_8 is more polarisable and gives much stronger London dispersion attractions between molecules. Consequently, sulphur has a much higher melting and boiling temperature and is solid at room temperature. The weak attractions between small O_2 molecules allow dioxygen to remain gaseous under the same conditions. This comparison concerns intermolecular attractions, rather than the strength of the covalent bonds within each molecule.

Quick Tip to Solve: Count bond domains and lone pairs before drawing: XeF4 has four bonds plus two opposite lone pairs; HClO3 has three oxygen domains plus one lone pair on Cl.

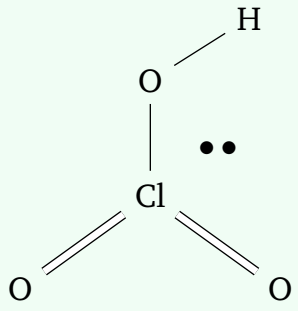
Step 4: (b)(i) Draw xenon tetrafluoride Xenon has eight valence electrons. Four Xe–F bonds and two lone pairs give six electron-pair domains around Xe, with an octahedral electron-pair arrangement. The two lone pairs occupy opposite positions to minimise repulsion, leaving the four fluorine atoms in one plane. Thus XeF_4 is square planar, with adjacent F–Xe–F angles of 90°. The lone pairs in the drawing lie above and below the fluorine plane.



Two opposite axial lone pairs

Square-planar XeF4; axial lone pairs are shown by perspective bonds.

Step 5: (b)(ii) Draw chloric acid The conventional structure of chloric acid is $HO-Cl(=O)_2$. Hydrogen is attached to oxygen, not directly to chlorine. Chlorine has two double bonds to terminal oxygen atoms, one single bond to the hydroxyl oxygen and one lone pair. These are four electron-pair domains around Cl, giving a tetrahedral electron-pair arrangement and a trigonal-pyramidal arrangement of the three oxygen atoms. The lone pair is shown explicitly in the structural drawing.



Trigonal-pyramidal oxygen arrangement

Chloric acid: two terminal Cl=O bonds, one Cl–OH bond and a lone pair on Cl.

Step 6: Conclusion H_3PO_3 disproportionates because P is at $+3$, while H_3PO_4 has P at its maximum $+5$. Fluorine's electronegativity and restricted valency favour ClF_3. Stronger dispersion forces in S_8 make sulphur solid. The structures are square-planar XeF_4 and trigonal-pyramidal $HO-Cl(=O)_2$, each with the lone pairs shown.

Quick Tip to Solve: Count bond domains and lone pairs before drawing: XeF4 has four bonds plus two opposite lone pairs; HClO3 has three oxygen domains plus one lone pair on Cl.

OR

24(b). (a) When concentrated sulphuric acid was added to an unknown salt present in a test tube a brown gas (A) was evolved. This gas intensified when copper turnings were added to this test tube. On cooling, the gas (A) changed into a colourless solid (B).

(i) Identify (A) and (B).

(ii) Write the structures of (A) and (B).

(iii) Why does gas (A) change to solid on cooling?

(b) Arrange the following in the decreasing order of their reducing character:

HF, HCl, HBr, HI

(c) Complete the following reaction:

$XeF_4 + SbF_5 \longrightarrow$ [5 marks]

Solution:

Concept:

- Nitrogen dioxide, NO_2, is a brown odd-electron molecule. Two molecules combine through an $N-N$ bond to form colourless dinitrogen tetroxide, N_2O_4.
- For the exothermic equilibrium $2NO_2(g) \rightleftharpoons N_2O_4(g)$, lowering the temperature favours dimer formation; sufficiently strong cooling gives solid N_2O_4.
- The reducing character of hydrogen halides increases as the $H-X$ bond becomes weaker down the group. A fluoride-ion acceptor acts as a Lewis acid.

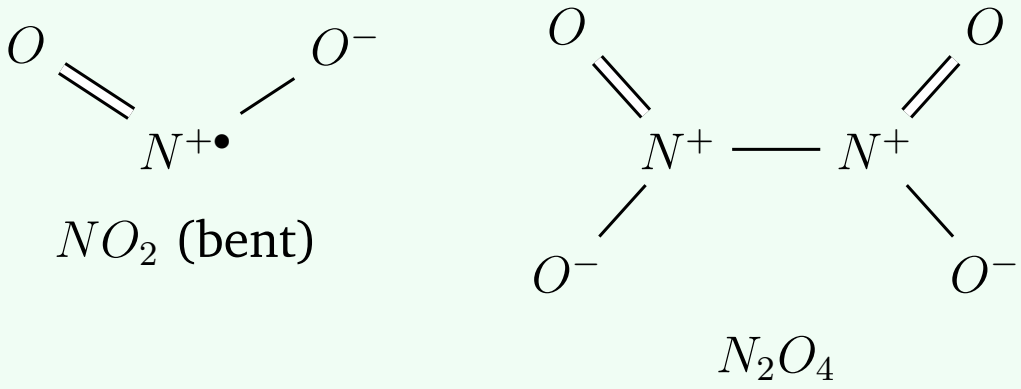
Step 1: (a)(i) Identify the brown gas and the colourless solid The unknown salt contains nitrate ions. Concentrated sulphuric acid liberates nitric acid from the nitrate salt, and decomposition produces brown nitrogen dioxide. Copper reacts with concentrated nitric acid to produce still more of the same brown gas:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O.$$

Thus the intensified brown fumes identify A as NO_2. On cooling, these molecules associate to give colourless dinitrogen tetroxide; hence B is N_2O_4. The change in colour reflects formation of a different molecular species, rather than merely compression of the brown gas.

Step 2: (a)(ii) Write the molecular structures NO_2 has a bent structure and an unpaired electron on nitrogen. One resonance contributor is $O=N^{+\bullet}-O^-$; interchanging the single and double $N-O$ bonds gives the other equivalent contributor. The real molecule has equivalent $N-O$ bonds. In N_2O_4, two nitrogen atoms are joined by a single bond, and each is bonded to two oxygen atoms. One contributor is $^-O-N^+(=O)-N^+(=O)-O^-$. Resonance operates within each NO_2 group; pairing of the two odd electrons in the $N-N$ bond leaves the dimer without an unpaired electron. The structures below show these contributors.

Quick Tip to Solve: For a fluoride-transfer product, remove one F from the donor and give it a positive charge; add that F to the acceptor and give it a negative charge.



One resonance contributor for each molecule; the dot in nitrogen dioxide denotes its unpaired electron.

Step 3: (a)(iii) Explain the effect of cooling The association is exothermic:

$$2NO_2(g) \rightleftharpoons N_2O_4(g), \qquad \Delta H < 0.$$

By Le Chatelier's principle, cooling favours the heat-producing forward reaction, so the proportion of colourless N_2O_4 increases. At sufficiently low temperature the dimer condenses and solidifies, producing the colourless solid stated in the question. Dimerisation also pairs the unpaired electrons and forms an $N - N$ bond.

Step 4: (b) Compare the reducing character of the hydrogen halides Down the group, increasing halogen size weakens the $H - X$ bond. Consequently, hydrogen iodide is most readily oxidised and hydrogen fluoride is least readily oxidised. Equivalently, the ease of oxidation of halide ions follows $I^- > Br^- > Cl^- > F^-$. The decreasing order of reducing character is therefore $HI > HBr > HCl > HF$.

Step 5: (c) Complete the fluoride-transfer reaction SbF_5 is a strong Lewis acid and accepts one fluoride ion from XeF_4. Removing F^- from neutral XeF_4 leaves the cation $[XeF_3]^+$, while adding it to neutral SbF_5 forms $[SbF_6]^-$. The balanced reaction is

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-.$$

There are nine fluorine atoms on each side and the ionic product is electrically neutral overall. This is fluoride transfer, not a change in the oxidation states of xenon or antimony.

Step 6: Conclusion (a) $A = NO_2$, a bent odd-electron molecule; $B = N_2O_4$, with an $N - N$ single bond. Cooling favours exothermic dimerisation and eventual solidification. (b) $HI > HBr > HCl > HF$. (c) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$.

Quick Tip to Solve: For a fluoride-transfer product, remove one F from the donor and give it a positive charge; add that F to the acceptor and give it a negative charge.

25(a). Write the cell reaction and calculate the e.m.f. of the following cell at 298 K:

Sn (s) | Sn^{2+} (0.004 M) || H^+ (0.020 M) | H_2 (g) (1 bar) | Pt (s)

(Given: $E^\circ_{Sn^{2+}/Sn} = -0.14$ V)

(b) Give reasons:

(i) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(ii) Conductivity of CH_3COOH decreases on dilution. [5 marks]

Solution:

Concept:

- The left electrode is the anode (oxidation) and the right electrode is the cathode (reduction). Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- Actual electrode products depend on kinetic overpotential as well as standard electrode potentials. Conductivity κ measures conduction by ions per unit volume; molar conductivity Λ_m measures conduction per mole of electrolyte.

Step 1: (a) Write the half-reactions and cell reaction Tin undergoes oxidation at the left electrode, while hydrogen ions undergo reduction at the platinum electrode on the right:

$$\begin{aligned} \text{Anode:} \quad & \mathrm{Sn(s)} \longrightarrow \mathrm{Sn^{2+}(aq)} + 2\mathrm{e^-}, \\ \text{Cathode:} \quad & 2\mathrm{H^+(aq)} + 2\mathrm{e^-} \longrightarrow \mathrm{H_2(g)}. \end{aligned}$$

Adding these cancels the two electrons and gives the cell reaction

$$\mathrm{Sn(s)} + 2\mathrm{H^+(aq)} \longrightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}.$$

Thus $n = 2$. Platinum provides an inert conducting surface for the hydrogen electrode and does not appear in the net reaction.

Step 2: (a) Calculate the standard potential and reaction quotient The standard reduction potential of the hydrogen electrode is zero. Therefore

$$E^\circ_{\text{cell}} = 0 - (-0.14) = 0.14\,\text{V}.$$

Using the numerical concentration ratios relative to 1 M, and the hydrogen pressure relative to 1 bar, the dimensionless reaction quotient is

$$Q = \frac{[\mathrm{Sn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.004 \times 1}{(0.020)^2} = 10.$$

The hydrogen-ion concentration is squared because its stoichiometric coefficient in the balanced reaction is two.

Quick Tip to Solve: Balance the cell reaction before writing Q: two hydrogen ions require the square of their concentration. For dilution questions, distinguish conductivity per unit volume from molar conductivity per mole.

Step 3: (a) Apply the Nernst equation Substituting $n = 2$ and $\log 10 = 1$,

$$E_{\text{cell}} = 0.14 - \frac{0.0591}{2} \log 10$$
$$= 0.14 - 0.02955 = 0.11045\,\text{V}.$$

The correction is negative because the reaction quotient exceeds unity; these conditions lower the potential below its standard value.

Step 4: (b)(i) Explain liberation of chlorine at the anode Standard electrode potentials suggest that oxidation of water to oxygen should occur preferentially. However, oxygen evolution has a high overpotential: an additional potential is needed to overcome the slow electrode kinetics. Consequently, under the conditions of aqueous sodium chloride electrolysis, oxidation of chloride ions becomes more favourable in practice and chlorine is liberated:

$$2\text{Cl}^-(\text{aq}) \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-.$$

Thus the observed product is explained by the overpotential for oxygen evolution, which is not accounted for by standard potential values alone.

Step 5: (b)(ii) Explain the decrease in conductivity on dilution Acetic acid is a weak electrolyte:

$$\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq}).$$

Dilution increases its degree of ionisation, but also increases the volume of solution. The number of conducting ions per unit volume decreases overall, so the conductivity κ decreases. This does not imply a decrease in molar conductivity: Λ_m increases on dilution because ionisation per mole increases and interionic effects diminish.

Step 6: Conclusion (a) The cell reaction is $\text{Sn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$, and its e.m.f. at $298\,\text{K}$ is $\boxed{0.11045\,\text{V} \approx 0.110\,\text{V}}$. (b)(i) Chlorine evolves because oxygen evolution has a high overpotential. (b)(ii) Acetic-acid conductivity decreases on dilution because the concentration of conducting ions per unit volume decreases.

Quick Tip to Solve: Balance the cell reaction before writing Q: two hydrogen ions require the square of their concentration. For dilution questions, distinguish conductivity per unit volume from molar conductivity per mole.

OR

25(b). (a) For the reaction

$2AgCl(s) + H_2(g)\,(1\,atm) \longrightarrow 2Ag(s) + 2H^+(0.1\,M) + 2Cl^-(0.1\,M)$,

$\Delta G^\circ = -43600$ **J at** 25°**C.**

Calculate the e.m.f. of the cell.

[$\log 10^{-n} = -n$**]**

(b) Define fuel cell and write its two advantages. [5 marks]

Solution:

Concept:

- The standard Gibbs energy change and standard cell potential are related by $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and $F = 96500\,\text{C mol}^{-1}$ is the Faraday constant.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$. Pure solids have unit activity; gas pressure is measured relative to its standard pressure and dilute solute activities are approximated by their molar concentrations relative to 1 M.
- A fuel cell converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy through electrochemical reactions.

Step 1: (a) Identify the electron transfer and calculate the standard potential Hydrogen is oxidised and silver chloride is reduced. The half-reactions are

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-,$$
$$2AgCl(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-(aq).$$

Adding these gives the reaction in the question, so $n = 2$. The given Gibbs energy change is for this complete reaction; it must not be divided by two independently of the electron count. Thus

$$E^\circ_{\text{cell}} = -\frac{\Delta G^\circ}{nF} = \frac{43600}{2 \times 96500} = 0.2259\,\text{V}.$$

The negative standard Gibbs energy therefore corresponds to a positive standard cell potential.

Step 2: (a) Evaluate the reaction quotient and use the Nernst equation The solid $AgCl$ and Ag do not appear in the reaction quotient. Both ionic concentrations are raised to the power two because their stoichiometric coefficients are two. With hydrogen at the specified standard pressure,

$$Q = \frac{[H^+]^2[Cl^-]^2}{p_{H_2}/p^\circ} = \frac{(0.1)^2(0.1)^2}{1} = 10^{-4}.$$

Using the printed logarithm relation gives $\log Q = -4$. Consequently,

$$E_{\text{cell}} = 0.2259 - \frac{0.0591}{2}(-4)$$
$$= 0.2259 + 0.1182 = 0.3441\,\text{V}.$$

Since the product ion concentrations are below their standard values, $Q < 1$, so the actual cell potential exceeds the standard potential, consistent with this calculation.

Quick Tip to Solve: Count the electrons first, then square both ionic concentrations in Q: here $Q = 10^{-4}$, so the Nernst correction increases the e.m.f.

Step 3: (b) Define a fuel cell and explain its advantages A fuel cell is a galvanic cell in which the fuel and oxidising agent are supplied continuously, and their chemical energy is converted directly into electrical energy. For example, a hydrogen–oxygen fuel cell consumes hydrogen and oxygen while producing water:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l).$$

Two advantages are: (i) high energy-conversion efficiency, because electricity is obtained directly by electrochemical reaction instead of first producing heat to drive an engine; and (ii) low pollution, particularly for the hydrogen–oxygen fuel cell, whose reaction product is water. Continuous reactant supply enables operation as long as fuel and oxidant remain available.

Step 4: Conclusion (a) The cell e.m.f. at 25°C is $\boxed{E_{\text{cell}} \approx 0.344\,\text{V}}$. (b) A fuel cell continuously converts supplied fuel and oxidant into electricity; two advantages are high efficiency and low pollution.

Quick Tip to Solve: Count the electrons first, then square both ionic concentrations in Q: here $Q = 10^{-4}$, so the Nernst correction increases the e.m.f.

26(a). Write the reactions involved in the following:

(i) Hofmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalimide synthesis

(b) Give reasons:

(i) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts. [5 marks]

Solution:

Concept:

- Hofmann degradation converts a primary amide into a primary amine containing one carbon atom fewer; diazotisation converts a primary aromatic amine into an aromatic diazonium salt.
- Gabriel synthesis uses the nucleophilic nitrogen of potassium phthalimide to prepare primary aliphatic amines by alkylation followed by hydrolysis.
- Aqueous basicity depends on both electron donation to nitrogen and solvation of the conjugate acid. Aromatic diazonium ions gain resonance stabilisation through conjugation with the benzene ring.

Step 1: (a)(i) Hofmann bromamide degradation Heat a primary amide with bromine and aqueous sodium hydroxide:

$$\text{RCONH}_2 + \text{Br}_2 + 4\text{NaOH} \longrightarrow \text{RNH}_2 + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}.$$

Here R is an alkyl or aryl group. The carbonyl carbon of the amide is removed, so the amine has one carbon fewer than its parent amide. For example, ethanamide gives methanamine:

$$\text{CH}_3\text{CONH}_2 + \text{Br}_2 + 4\text{NaOH} \longrightarrow \text{CH}_3\text{NH}_2 + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}.$$

Quick Tip to Solve: For Hofmann degradation count the lost carbonyl carbon; for aqueous amine basicity compare hydration as well as the alkyl groups' electron donation.

Step 2: (a)(ii) Diazotisation Treat aniline with nitrous acid generated in situ from sodium nitrite and hydrochloric acid at 273–278 K:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{–}278\,K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

The product is benzenediazonium chloride. The low temperature is essential because the diazonium salt decomposes readily on warming. This conversion of a primary aromatic amino group into a diazonium group is called diazotisation.

Step 3: (a)(iii) Gabriel phthalimide synthesis Phthalimide reacts with alcoholic potassium hydroxide to form potassium phthalimide. This salt reacts with a primary alkyl halide $R{-}X$, and hydrolysis of the resulting N-alkylphthalimide releases the primary amine:

$$C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK + H_2O,$$
$$C_6H_4(CO)_2NK + R{-}X \longrightarrow C_6H_4(CO)_2NR + KX,$$
$$C_6H_4(CO)_2NR + 2NaOH \xrightarrow{heat} C_6H_4(COONa)_2 + RNH_2.$$

In these formulae the two adjacent carbonyl groups belong to the cyclic phthalimide unit. Alkylation replaces the imide hydrogen with R; alkaline hydrolysis opens the imide and forms disodium phthalate and the primary amine. Aryl halides do not undergo this nucleophilic substitution readily, so the method is unsuitable for preparing aniline.

Step 4: (b)(i) Compare basicity in aqueous solution An amine accepts a proton in water:

$$B + H_2O \rightleftharpoons BH^+ + OH^-.$$

Although three methyl groups donate electron density to nitrogen more strongly than two, aqueous basicity also depends on hydration of the protonated amine. The dimethylammonium ion, $(CH_3)_2NH_2^+$, has two N–H bonds and less steric crowding than $(CH_3)_3NH^+$, which has only one N–H bond. It therefore undergoes more effective hydration and hydrogen bonding with water. The greater stabilisation of the secondary ammonium ion outweighs the extra electron-donating effect in trimethylamine, making dimethylamine more basic in water.

Step 5: (b)(ii) Compare diazonium-salt stability In an aromatic diazonium ion, $Ar{-}N_2^+$, the diazonium group is conjugated with the aromatic ring. Resonance delocalises the positive charge and stabilises the ion. An aliphatic diazonium ion has no aromatic ring to provide this resonance stabilisation and readily loses nitrogen gas to form a carbocation:

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

Hence aromatic diazonium salts are relatively more stable, although they too are generally prepared and kept at low temperature.

Step 6: Conclusion Hofmann degradation gives a primary amine with one fewer carbon; diazotisation gives a diazonium salt at 273–278 K; Gabriel synthesis gives a primary aliphatic amine. In water, better hydration makes $(CH_3)_2NH$ more basic than $(CH_3)_3N$, while resonance makes aromatic diazonium salts more stable than aliphatic ones.

Quick Tip to Solve: For Hofmann degradation count the lost carbonyl carbon; for aqueous amine basicity compare hydration as well as the alkyl groups' electron donation.

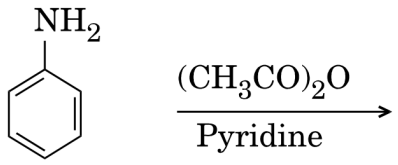
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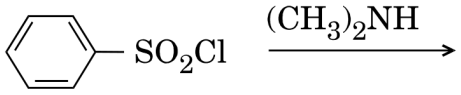
26(b). **(a) Write the structures of the main products of the following reactions:**

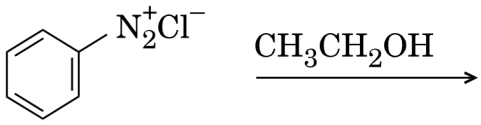
(b) Give a simple chemical test to distinguish between Aniline and N,N-dimethylaniline.

(c) Arrange the following in the increasing order of their pK_b values:

$C_6H_5NH_2,\ C_2H_5NH_2,\ C_6H_5NHCH_3$ [5 marks]

(i) 

(ii) 

(iii) 

Solution:

Concept:

- Primary amines undergo acylation with acid anhydrides. Aniline forms an amide by replacing one hydrogen on nitrogen with an acetyl group, CH_3CO-.
- A secondary amine reacts with benzenesulphonyl chloride to give an N,N-disubstituted sulphonamide. Its nitrogen has no hydrogen after substitution.
- Ethanol reduces an aryl diazonium group to hydrogen, releasing nitrogen gas and itself being oxidised to ethanal.
- The carbylamine test is given only by primary amines. Also, $pK_b = -\log K_b$, so a stronger base has a smaller pK_b.

Step 1: (a)(i) Acylation of aniline The lone pair on aniline nitrogen attacks acetic anhydride. Acetylation produces acetanilide (N-phenylethanamide); pyridine acts as a base during the reaction. The main product has the condensed structure $C_6H_5-NH-C(=O)-CH_3$:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

The phenyl ring remains attached to nitrogen; the acetyl group is introduced on nitrogen, rather than on the aromatic ring.

Step 2: (a)(ii) Reaction with benzenesulphonyl chloride Dimethylamine is a secondary amine. Its

Quick Tip to Solve: First rank the amines by availability of the nitrogen lone pair, then reverse that ranking for pKb; remember that ethanol replaces an aryl diazonium group by hydrogen.

N-H hydrogen is replaced by a benzenesulphonyl group to form N,N-dimethylbenzenesulphonamide:

$$C_6H_5SO_2Cl + HN(CH_3)_2 \longrightarrow C_6H_5SO_2N(CH_3)_2 + HCl.$$

The product structure is $C_6H_5{-}S(=O)_2{-}N(CH_3)_2$. Nitrogen is bonded to sulphur and to both methyl groups, so this sulphonamide has no N-H bond.

Step 3: (a)(iii) Reduction of benzenediazonium chloride Ethanol replaces the diazonium group by hydrogen. The aromatic product is benzene, C_6H_6, while ethanol is oxidised to ethanal:

$$C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

Nitrogen gas is liberated. The main organic product derived from the diazonium salt is benzene, not phenol; the stated reagent is ethanol.

Step 4: (b) Distinguish the amines by the carbylamine test Heat separate small samples with chloroform and alcoholic potassium hydroxide. Aniline, a primary aromatic amine, forms foul-smelling phenyl isocyanide:

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O.$$

N,N-dimethylaniline, $C_6H_5N(CH_3)_2$, is a tertiary amine and does not give the carbylamine reaction. Thus formation of the characteristic offensive-smelling isocyanide identifies aniline; its absence identifies N,N-dimethylaniline.

Step 5: (c) Compare basicity and reverse the order for pKb In ethylamine the nitrogen lone pair is localised and the ethyl group increases electron density through its positive inductive effect. It is therefore more readily available for protonation than in either aromatic amine. In aniline the nitrogen lone pair is delocalised into the benzene ring by resonance, reducing its availability for bonding to a proton. N-methylaniline also shows this resonance effect, but its methyl group donates electron density and makes it more basic than aniline. Hence the basicity order is

$$C_2H_5NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2.$$

Since greater basicity means larger K_b, taking the negative logarithm reverses this order for pK_b.

Step 6: Conclusion (a) The products are (i) $C_6H_5NHCOCH_3$, acetanilide; (ii) $C_6H_5SO_2N(CH_3)_2$, N,N-dimethylbenzenesulphonamide; and (iii) C_6H_6, benzene. (b) Aniline gives the carbylamine test; N,N-dimethylaniline does not. (c) Increasing pK_b: $C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$.

Quick Tip to Solve: First rank the amines by availability of the nitrogen lone pair, then reverse that ranking for pKb; remember that ethanol replaces an aryl diazonium group by hydrogen.