CBSE Class 12 Chemistry Question Paper 2016 with Solution PDF-Set 56/1 - Compartment

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) This question paper contains 26 questions. All questions are compulsory.

(ii) There is no overall choice. An internal choice is provided in 5 questions (Q10, Q16, Q24, Q25, Q26); attempt only one of the alternatives in such questions.

(iii) Marks for each question are indicated against it.

1. Define rate constant (k). [1 mark]

Solution:

Concept:

- For a reaction, the rate law relates rate to reactant concentrations: $r = k[A]^m[B]^n$. Here m, n are experimentally determined orders and k is the rate constant.
- At a fixed temperature, k is independent of the instantaneous reactant concentrations; its units depend on the overall reaction order.

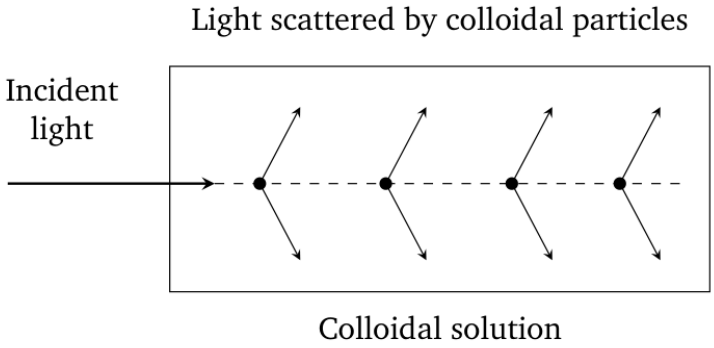
Step 1: Use the rate law Rearranging gives $k = r/([A]^m[B]^n)$. Thus the rate constant is the proportionality constant connecting the reaction rate with the concentration terms in the experimentally determined rate law.

Step 2: Give its usual interpretation If the concentration of each reactant is unity in the chosen concentration units, the concentration product is numerically one. The numerical value of the reaction rate then equals the numerical value of k at that temperature.

Step 3: Conclusion The rate constant k is the proportionality constant in the rate law; it is numerically equal to the reaction rate when each reactant concentration is unity.

Quick Tip to Solve: Define k using the rate law; do not confuse a changing rate with its constant k at fixed temperature.

2. Why is Tyndall effect shown by colloidal solutions? [1 mark]



Solution:

Concept:

- The Tyndall effect is the scattering of a beam of light by colloidal particles, which makes its path visible.
- Colloidal particles are large enough to scatter visible light appreciably; the dispersed phase and dispersion medium have different refractive indices.

Step 1: Consider the particle size Colloidal particles are much larger than the molecules or ions of a true solution. Their size permits appreciable scattering of the incident visible light, even though individual particles cannot usually be seen with the unaided eye.

Quick Tip to Solve: Link the visible beam to scattering by colloidal particles, rather than to absorption of the light.

Step 2: Explain the visible path As the incident beam passes through the colloid, light is scattered in different directions by the dispersed particles. Some scattered light reaches an observer looking from the side, making the beam path visible as a luminous cone.

Step 3: Conclusion Colloidal solutions show the Tyndall effect because their dispersed particles scatter incident light sufficiently to make the path of the beam visible.

Quick Tip to Solve: Link the visible beam to scattering by colloidal particles, rather than to absorption of the light.

3. Write the IUPAC name of the following coordination compound $[NiCl_4]^{2-}$. [1 mark]

Solution:

Concept:

- In $[NiCl_4]^{2-}$, each chlorido ligand has charge -1; the sum of ligand and metal charges equals the complex charge.
- For an anionic coordination entity, the metal name ends in -ate; the oxidation state is written in Roman numerals after the metal name.

Step 1: Find the nickel oxidation state Let the oxidation state of nickel be x. The charge balance is $x + 4(-1) = -2$, so $x = +2$. Thus the oxidation-state suffix is (II).

Step 2: Apply coordination nomenclature The four chloride ligands are named tetrachlorido. Since the entire complex ion has a negative charge, nickel becomes nickelate. Combining the ligand name, metal name and oxidation state gives the required systematic name.

Step 3: Conclusion The IUPAC name is tetrachloridonickelate(II) ion.

Quick Tip to Solve: Find the metal oxidation state first, then use the -ate ending because the whole complex is an anion.

4. Out of CH_3OH and C_6H_5OH (phenol), which is more acidic? [1 mark]

Solution:

Concept:

- An acid loses a proton to form its conjugate base. A more stable conjugate base corresponds to a stronger acid.
- Phenoxide ion, $C_6H_5O^-$, is resonance stabilised; methoxide ion, CH_3O^-, has no comparable resonance delocalisation.

Step 1: Compare the conjugate bases Loss of H^+ from phenol gives phenoxide, whose negative charge is delocalised through resonance involving oxygen and the aromatic ring. This stabilises the product of deprotonation.

Step 2: Compare with methanol Methanol forms methoxide on loss of a proton. Its negative charge remains localised mainly on oxygen, and the electron-releasing methyl group increases electron

Quick Tip to Solve: For acidity comparisons, compare the stability of the conjugate bases formed after losing H+.

density there. Consequently methoxide is less stabilised, and methanol loses its proton less readily.

Step 3: Conclusion Phenol, C_6H_5OH, is more acidic than CH_3OH because its conjugate base is resonance stabilised.

Quick Tip to Solve: For acidity comparisons, compare the stability of the conjugate bases formed after losing H+.

5. What are Associated Colloids? Give an example. [1 mark]

Solution:

Concept:

- Associated colloids are substances whose molecules or ions associate to form colloidal-sized aggregates called micelles.
- Micelles form above the critical micelle concentration and, for soap solutions, above the appropriate micelle formation temperature (Krafft temperature).

Step 1: Explain association At low concentration, these substances behave as ordinary electrolytes. At sufficiently high concentration, many amphiphilic molecules or ions associate into aggregates. Their aggregates are large enough to behave as colloidal particles.

Step 2: Give a suitable example Soap such as sodium stearate, $C_{17}H_{35}COONa$, forms micelles in water. The hydrocarbon tails gather towards the micelle interior, while the ionic heads face water. Hence soap solutions above the critical micelle concentration are associated colloids.

Step 3: Conclusion Associated colloids form micelles by association of molecules or ions at suitable concentrations; a soap solution such as sodium stearate in water is an example.

Quick Tip to Solve: Name both the aggregate (micelle) and an actual example such as sodium stearate soap.

6. Explain the following terms with suitable examples :

(i) Frenkel defect

(ii) F-centres [2 marks]

Solution:

Concept:

- A Frenkel defect is a vacancy-interstitial pair caused when an ion leaves its normal lattice position and occupies an interstitial site.
- An F-centre is an anion vacancy occupied by an electron; the trapped electron can absorb visible light and produce colour in a crystal.

Step 1: Explain Frenkel defect with an example A small ion, generally a cation, is displaced from its regular lattice site to an interstitial position. This creates a vacancy at the original site and an interstitial defect at the new one. No ion leaves the crystal, so its stoichiometry, electrical neutrality and density remain unchanged. For example, $AgCl$ exhibits Frenkel defect because small Ag^+ ions

Quick Tip to Solve: Distinguish an ion displaced into an interstitial site from an electron trapped in an anion vacancy.

can occupy interstitial positions.

Step 2: Explain F-centres with an example In a metal-excess defect caused by anion vacancies, an electron can occupy a site normally occupied by an anion. Such an electron-containing anion vacancy is called an F-centre. For example, when NaCl is heated in sodium vapour, chloride vacancies containing trapped electrons form. Absorption of visible light by these electrons imparts a yellow colour to the salt; these vacancies are F-centres.

Step 3: Conclusion Frenkel defect: an ion shifts from its lattice site to an interstitial site, for example in AgCl. F-centres: anion vacancies containing electrons, for example in yellow NaCl heated in sodium vapour.

Quick Tip to Solve: Distinguish an ion displaced into an interstitial site from an electron trapped in an anion vacancy.

7. Define osmotic pressure. How is osmotic pressure related to the concentration of a solute in a solution? [2 marks]

Solution:

Concept:

- Osmosis is the net movement of solvent through a semipermeable membrane from pure solvent (or a dilute solution) towards a more concentrated solution.
- For a dilute ideal solution, the van't Hoff equation is $\pi V = nRT$, where π is osmotic pressure, V is solution volume, n is moles of solute, R is the gas constant and T is absolute temperature.

Step 1: Define osmotic pressure Osmotic pressure is the minimum excess external pressure that must be applied to the solution side of a semipermeable membrane to stop the net entry of solvent into the solution. At this pressure the tendency of solvent to enter is balanced, so there is no net osmosis.

Step 2: Express the concentration dependence If the molar concentration of solute is $C = n/V$, rearranging the dilute-solution equation gives

$$\pi = \frac{n}{V}RT = CRT.$$

Thus, at a fixed temperature, osmotic pressure is directly proportional to the molar concentration of solute particles. Doubling this concentration doubles π, within the dilute ideal-solution approximation. For a solute that dissociates or associates, the particle-number correction is included as $\pi = iCRT$, with i the van't Hoff factor.

Step 3: Conclusion Osmotic pressure is the excess pressure required on a solution to prevent osmosis; for a dilute ideal solution, $\boxed{\pi = CRT}$, so $\pi \propto C$ at constant temperature.

Quick Tip to Solve: Specify that pressure is applied to the solution side, and keep temperature fixed when stating $\pi \propto C$.

8. What happens when :

(i) Concentrated H_2SO_4 is added to calcium fluoride?

(ii) SO_3 is passed through water? [2 marks]

Solution:

Concept:

- Concentrated sulphuric acid reacts with fluoride salts to liberate hydrogen fluoride; the calcium ion forms calcium sulphate.
- Sulphur trioxide is the acidic oxide (acid anhydride) of sulphuric acid, so its reaction with water forms the corresponding oxoacid.

Step 1: React calcium fluoride with concentrated sulphuric acid (i) Hydrogen fluoride gas is liberated when concentrated H_2SO_4 is added to calcium fluoride. Calcium sulphate is the other product. The balanced reaction is

$$CaF_2 + H_2SO_4(\text{conc}) \longrightarrow CaSO_4 + 2\,HF\uparrow.$$

The two fluoride ions in each formula unit of calcium fluoride receive the two acidic hydrogen atoms, accounting for the coefficient 2 before hydrogen fluoride. Sulphur remains in the +6 oxidation state, so this is not an oxidation-reduction reaction.

Step 2: Pass sulphur trioxide through water (ii) Sulphur trioxide combines vigorously with water to give sulphuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

The reaction is highly exothermic and can form a fine mist of sulphuric acid. Sulphur is in the +6 oxidation state in both the oxide and the acid. No sulphurous acid is formed; that acid corresponds instead to the lower oxide, sulphur dioxide.

Step 3: Conclusion (i) HF is liberated and $CaSO_4$ is formed. (ii) SO_3 reacts exothermically with water to form H_2SO_4.

Quick Tip to Solve: For the first reaction balance both fluoride ions as 2 HF; for the second remember that SO_3 is the anhydride of H_2SO_4.

9. Give reasons :

(i) Zn is not regarded as a transition element.

(ii) Cr^{2+} is a strong reducing agent. [2 marks]

Solution:

Concept:

- A transition element has a partially filled d subshell in its atom or in at least one of its common oxidation states; merely belonging to the d block is insufficient.
- A reducing agent donates electrons and is itself oxidised. Relative stability of the resulting oxidation state helps explain the tendency to donate an electron.

Step 1: Examine the configurations of zinc and its ion (i) Zinc has atomic number 30, and its

Quick Tip to Solve: For transition character check the atom and common ion; for a reducing agent write its electron-loss half-equation first.

electronic configuration is

$$\mathrm{Zn} : [\mathrm{Ar}]\, 3d^{10}4s^{2}.$$

Its common ion is Zn^{2+}, obtained by removal of the two 4s electrons:

$$\mathrm{Zn}^{2+} : [\mathrm{Ar}]\, 3d^{10}.$$

The d subshell is completely filled in both the atom and the common ion. Zinc therefore fails the partially-filled-d-subshell criterion and is not regarded as a transition element.

Step 2: Explain oxidation of the chromium(II) ion (ii) Cr^{2+} has the configuration $[\mathrm{Ar}]3d^{4}$. It readily loses an electron to form Cr^{3+}, with configuration $[\mathrm{Ar}]3d^{3}$:

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

In the usual aqueous octahedral environment, the d^3 ion has the particularly stable t_{2g}^{3} arrangement. The tendency of Cr^{2+} to attain this more stable $+3$ state makes it an effective electron donor, and hence a strong reducing agent.

Step 3: Conclusion (i) Zinc and its common $+2$ ion have filled $3d^{10}$ subshells. (ii) Cr^{2+} is readily oxidised from d^4 to the more stable d^3 Cr^{3+} ion, so it acts as a strong reducing agent.

Quick Tip to Solve: For transition character check the atom and common ion; for a reducing agent write its electron-loss half-equation first.

10(a). Write the equations for the preparation of 1-bromobutane from :

(i) 1-butanol

(ii) but-1-ene [2 marks]

Solution:

Concept:

- A primary alcohol gives an alkyl bromide by substitution of its hydroxyl group with bromine using hydrogen bromide.
- Hydrogen bromide adds to an unsymmetrical alkene in the presence of an organic peroxide by a radical mechanism, giving the anti-Markovnikov product.

Step 1: Replace the hydroxyl group of 1-butanol (i) Heat 1-butanol with concentrated hydrobromic acid. The hydroxyl group is replaced by bromine, while the straight four-carbon skeleton is retained:

$$\mathrm{CH_3CH_2CH_2CH_2OH} + \mathrm{HBr} \xrightarrow{\text{heat}} \mathrm{CH_3CH_2CH_2CH_2Br} + \mathrm{H_2O}.$$

This is a substitution reaction. The bromine atom occupies the same terminal carbon that originally carried the hydroxyl group, so the organic product is 1-bromobutane.

Step 2: Add hydrogen bromide to but-1-ene in peroxide (ii) Treat but-1-ene with hydrogen bromide

Quick Tip to Solve: To obtain a terminal bromide from but-1-ene, write peroxide over the HBr addition arrow to select anti-Markovnikov addition.

in the presence of an organic peroxide, ROOR:

$$CH_2{=}CHCH_2CH_3 + HBr \xrightarrow{ROOR} CH_2BrCH_2CH_2CH_3.$$

Under these radical conditions bromine attaches to the terminal, less substituted carbon of the double bond and hydrogen to the other carbon. This anti-Markovnikov orientation gives 1-bromobutane. The peroxide condition is essential: ordinary addition of HBr without peroxide mainly gives 2-bromobutane instead.

Step 3: Conclusion Use HBr with heat for 1-butanol, and HBr in the presence of an organic peroxide for but-1-ene; both routes give $CH_3CH_2CH_2CH_2Br$.

Quick Tip to Solve: To obtain a terminal bromide from but-1-ene, write peroxide over the HBr addition arrow to select anti-Markovnikov addition.

OR

10(b). Which compound in each of the following pairs will react faster in S_N2 reaction with $-OH$?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ and CH_3Cl [2 marks]

Solution:

Concept:

- An S_N2 reaction proceeds in one concerted step: the nucleophile attacks the carbon from the side opposite the leaving group while the carbon–halogen bond breaks.
- The reaction is faster with a better leaving group and with less steric hindrance at the carbon being attacked. For halides, leaving-group ability increases in the order $Cl^- < Br^- < I^-$.

Step 1: Compare methyl bromide and methyl iodide Both CH_3Br and CH_3I have the same methyl group, so their steric hindrance is the same. The $C-I$ bond is weaker than the $C-Br$ bond, and I^- is a better leaving group than Br^-. Thus hydroxide displaces iodide more readily, and CH_3I reacts faster.

Step 2: Compare tert-butyl chloride and methyl chloride Both compounds have chloride as the leaving group. In $(CH_3)_3CCl$, three methyl groups crowd the carbon bonded to chlorine and strongly obstruct the backside approach of OH^-. In CH_3Cl, the corresponding carbon is attached only to hydrogen atoms and is readily accessible. Therefore methyl chloride reacts much faster by the S_N2 mechanism; tertiary halides are practically unreactive by this pathway.

Step 3: Conclusion The faster compounds are (i) $\boxed{CH_3I}$, owing to better leaving-group ability, and (ii) $\boxed{CH_3Cl}$, owing to minimum steric hindrance.

Quick Tip to Solve: For each pair, first hold the common factor fixed: compare leaving groups for the two methyl halides, but compare crowding for the two chlorides.

11. Silver crystallises in f.c.c. lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver. [3 marks]

Solution:

Concept:

- For a cubic unit cell, $\rho = \dfrac{ZM}{N_A a^3}$, where ρ is density, Z is the number of atoms per cell, M is molar mass, N_A is Avogadro's constant and a is the cell edge.
- In a face-centred cubic lattice, the eight corner atoms contribute $8 \times \frac{1}{8} = 1$ atom and the six face-centred atoms contribute $6 \times \frac{1}{2} = 3$ atoms. Hence $Z = 4$.

Step 1: Calculate the volume of one unit cell Use centimetres for the edge because the density is in g cm^{-3}. The given edge is $a = 4.07 \times 10^{-8}$ cm, so

$$V_{\text{cell}} = a^3 = (4.07 \times 10^{-8})^3 = 6.7419143 \times 10^{-23}\ \text{cm}^3.$$

Cubing the power of ten gives 10^{-24}, which combines with 4.07^3 to give the volume above.

Step 2: Relate the cell mass to the molar mass The cell contains four silver atoms. Since one mole contains $N_A = 6.022 \times 10^{23}$ atoms, its mass is $4M/N_A$. Equating this with ρa^3 gives

$$M = \frac{\rho a^3 N_A}{4} = \frac{10.5 \times 6.7419143 \times 10^{-23} \times 6.022 \times 10^{23}}{4} = 106.5745\ \text{g mol}^{-1}.$$

The powers 10^{-23} and 10^{23} cancel. The product of density, volume and Avogadro's constant has units g mol^{-1}, as required.

Step 3: Conclusion The atomic mass of silver calculated from the supplied data is $\boxed{106.6\ \text{u}}$, corresponding to a molar mass of approximately 106.6 g mol^{-1}.

Quick Tip to Solve: For an f.c.c. density calculation use four atoms per cell, and cube both the numerical edge and its power of ten before substituting.

12. An aqueous solution of 2 percent non-volatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute? [Vapour pressure of water = 1.013 bar] [3 marks]

Solution:

Concept:

- Raoult's law for a solution containing a non-volatile solute is $p = x_1 p^\circ$, where p and p° are the solution and pure-solvent vapour pressures at the same temperature and x_1 is the solvent mole fraction.

Quick Tip to Solve: In a 2 percent mass solution take 2 g solute and 98 g water; use the pressure difference 0.009 bar and keep both pressures at the same temperature.

- The relative lowering of vapour pressure is $\dfrac{p^\circ - p}{p^\circ} = x_2 = \dfrac{n_2}{n_1 + n_2}$. For a dilute solution, $n_2 \ll n_1$, so $x_2 \simeq n_2/n_1$. Subscripts 1 and 2 denote water and solute respectively.

Step 1: Choose a mass basis and calculate the pressure lowering A 2 percent solution by mass contains $2\,\text{g}$ of solute and $98\,\text{g}$ of water in $100\,\text{g}$ of solution. Taking the molar mass of water as $18\,\text{g mol}^{-1}$,

$$n_1 = \frac{98}{18}\,\text{mol}, \qquad \Delta p = 1.013 - 1.004 = 0.009\,\text{bar}.$$

Both pressures refer to the same temperature, so Raoult's law applies directly; no boiling-point elevation constant is needed.

Step 2: Apply the standard dilute-solution expression Let the solute molar mass be M_2. Then $n_2 = 2/M_2$, and

$$\frac{0.009}{1.013} \simeq \frac{2/M_2}{98/18},$$
$$M_2 \simeq \frac{2 \times 18 \times 1.013}{98 \times 0.009}$$
$$\simeq 41.35\,\text{g mol}^{-1}.$$

This is the usual dilute-solution calculation. The approximation neglects the small solute contribution to the total number of moles.

Step 3: Check using the exact mole fraction Retaining that contribution, $n_2/n_1 = (p^\circ - p)/p$, and hence

$$M_2 = \frac{2 \times 18 \times 1.004}{98 \times 0.009} = 40.98\,\text{g mol}^{-1}.$$

This differs from the dilute result by less than one percent, consistent with the small solute mole fraction $0.009/1.013$.

Step 4: Conclusion The standard dilute-solution answer is $\boxed{M_2 \simeq 41.4\,\text{g mol}^{-1}}$. Exact Raoult's law gives $40.98\,\text{g mol}^{-1}$; both give a molecular mass of about $41\,\text{u}$.

Quick Tip to Solve: In a 2 percent mass solution take 2 g solute and 98 g water; use the pressure difference 0.009 bar and keep both pressures at the same temperature.

13. The rates of most reactions double when their temperature is raised from 298 K to 308 K. Calculate their activation energy. [R = 8.314 JK^{-1} mol^{-1}] [3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A is the frequency factor, E_a is activation energy and T is absolute temperature.
- For unchanged reactant concentrations, the rate ratio equals the rate-constant ratio. Taking the ratio at two temperatures eliminates A, treated as constant over this small temperature interval.

Step 1: Identify the temperatures and rate ratio The temperature rises from $T_1 = 298\,\text{K}$ to $T_2 = 308\,\text{K}$. Since the rate doubles under otherwise identical conditions, $k_2/k_1 = 2$. Use $R = 8.314\,\text{J mol}^{-1}\text{K}^{-1}$;

Quick Tip to Solve: Use $k_2/k_1 = 2$ and $T_1T_2/(T_2 - T_1) = 298 \times 308/10$; pair $\ln 2$ with R, or $\log 2$ with $2.303R$.

temperatures must be inserted in kelvin, not degrees Celsius.

Step 2: Apply the two-temperature Arrhenius equation Taking natural logarithms and subtracting the two Arrhenius equations gives

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

Consequently,

$$E_a = \frac{R \ln 2\, T_1 T_2}{T_2 - T_1} = \frac{8.314 \times 0.6931 \times 298 \times 308}{10}\ \text{J mol}^{-1}.$$

The reciprocal-temperature difference is positive because $T_2 > T_1$, giving a positive activation energy.

Step 3: Evaluate and convert the energy unit The substitution yields

$$E_a = 5.289 \times 10^4\ \text{J mol}^{-1} = 52.89\ \text{kJ mol}^{-1}.$$

The factor of $10\,\text{K}$ in the denominator is the actual temperature increase. The use of R in joule units first gives the energy in joules per mole; divide by 1000 to express it in kilojoules per mole.

Step 4: Conclusion The activation energy is $\boxed{E_a \approx 52.9\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Use $k_2/k_1 = 2$ and $T_1T_2/(T_2 - T_1) = 298 \times 308/10$; pair $\ln 2$ with R, or $\log 2$ with $2.303R$.

14. Explain the following terms :

(i) Peptization

(ii) Lyophobic colloids

(iii) Dialysis [3 marks]

Solution:

Concept:

- Colloidal particles are larger than ordinary solute ions or molecules. Their surface properties govern colloidal stability and methods of preparation.
- A suitable semipermeable membrane allows small dissolved ions and molecules to pass through but retains colloidal particles.

Step 1: (i) Peptization Peptization is the conversion of a freshly prepared precipitate into a colloidal sol by shaking it with the dispersion medium in the presence of a small amount of a suitable electrolyte, called the peptizing agent. The precipitate preferentially adsorbs one kind of ion from this electrolyte. The resulting similarly charged particles repel one another and disperse into colloidal dimensions. For example, freshly precipitated Fe(OH)_3 forms a sol on treatment with a small amount of FeCl_3; adsorption of Fe^{3+} imparts positive charge to the particles.

Step 2: (ii) Lyophobic colloids Lyophobic colloids are sols whose dispersed phase has little affinity for the dispersion medium. They require special preparation methods and are comparatively unstable: addition of even a small amount of an electrolyte can cause coagulation by reducing the stabilizing particle charge. Their formation is generally irreversible; simply mixing the separated phases does not regenerate the sol. Sols of gold, sulphur and arsenic sulphide in water are examples.

Quick Tip to Solve: Remember the distinction: peptization prepares the sol, lyophobic describes its affinity for the medium, and dialysis removes small dissolved impurities.

Step 3: (iii) Dialysis Dialysis is the purification of a colloidal sol by removing dissolved electrolytes and other small solutes through a suitable semipermeable membrane, such as parchment or cellophane. The sol is placed inside a membrane bag immersed in water. Small ions and molecules diffuse through the membrane into the surrounding water, while colloidal particles are retained. Renewing the outside water maintains the concentration difference and helps the impurities continue to diffuse out.

Step 4: Conclusion Peptization prepares a sol from a fresh precipitate; lyophobic colloids have little affinity for their medium; dialysis purifies a sol by membrane diffusion of small solutes.

Quick Tip to Solve: Remember the distinction: peptization prepares the sol, lyophobic describes its affinity for the medium, and dialysis removes small dissolved impurities.

15. Outline the principles of refining of metals by the following methods :

(i) Zone refining

(ii) Electrolytic refining

(iii) Vapour phase refining [3 marks]

Solution:

Concept:

- Refining separates a metal from its impurities by exploiting a difference in physical properties or chemical behaviour between them.
- The relevant differences here are impurity solubility in liquid and solid metal, selective anodic dissolution and cathodic deposition, and reversible formation of a volatile metal compound.

Step 1: (i) Zone refining The principle is that impurities are more soluble in the molten metal than in the solid metal. A narrow molten zone is produced in an impure metal rod by a movable heater. As the heater travels along the rod, relatively pure metal crystallizes behind it while the impurities remain concentrated in the molten zone. Repeated movement in the same direction carries the impurities towards one end, which is then cut off. This method gives very pure semiconductors such as germanium and silicon.

Step 2: (ii) Electrolytic refining The impure metal serves as the anode, a thin sheet of pure metal as the cathode, and a solution containing a suitable soluble salt of that metal as the electrolyte. On passing current, metal dissolves from the anode and deposits as pure metal on the cathode. For copper,

$$\text{Anode: } \mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\mathrm{e^-},$$

$$\text{Cathode: } \mathrm{Cu^{2+}(aq)} + 2\mathrm{e^-} \rightarrow \mathrm{Cu(s)}.$$

More reactive impurities generally remain in solution, while less reactive noble-metal impurities collect beneath the anode as anode mud.

Step 3: (iii) Vapour phase refining The impure metal is converted into a volatile compound by a suitable reagent. This compound must be readily formed and must decompose easily to give pure metal. The vapour is separated from non-volatile impurities and then decomposed. In the Mond

Quick Tip to Solve: For each method, state the separation principle first: molten-zone impurity solubility, selective electrode deposition, or a volatile compound that decomposes to pure metal.

process, nickel forms volatile nickel tetracarbonyl at about 330–350 K:

$$\mathrm{Ni} + 4\mathrm{CO} \rightarrow \mathrm{Ni(CO)_4}.$$

Heating the separated vapour to about 450–470 K decomposes it:

$$\mathrm{Ni(CO)_4} \rightarrow \mathrm{Ni} + 4\mathrm{CO}.$$

Pure nickel is thereby recovered.

Step 4: Conclusion Zone refining uses preferential impurity solubility in the melt; electrolytic refining transfers metal from an impure anode to a pure cathode; vapour phase refining uses formation and decomposition of a volatile compound.

Quick Tip to Solve: For each method, state the separation principle first: molten-zone impurity solubility, selective electrode deposition, or a volatile compound that decomposes to pure metal.

16(a). Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with oxalic acid? [3 marks]

Solution:

Concept:

- Potassium permanganate, $\mathrm{KMnO_4}$, is prepared from pyrolusite, $\mathrm{MnO_2}$, through potassium manganate, $\mathrm{K_2MnO_4}$. The oxidation state of manganese increases successively from $+4$ to $+6$ to $+7$.
- In acidic solution, permanganate is a strong oxidising agent. It is reduced to $\mathrm{Mn^{2+}}$, while oxalic acid, $\mathrm{H_2C_2O_4}$, is oxidised to carbon dioxide.

Step 1: Prepare potassium manganate Finely powdered pyrolusite is fused with potassium hydroxide in the presence of air or an oxidising agent such as potassium nitrate. With oxygen, the reaction is

$$2\,\mathrm{MnO_2} + 4\,\mathrm{KOH} + \mathrm{O_2} \longrightarrow 2\,\mathrm{K_2MnO_4} + 2\,\mathrm{H_2O}.$$

The green mass contains potassium manganate. It is extracted with water to obtain a green aqueous solution.

Step 2: Oxidise manganate to permanganate The manganate solution is electrolytically oxidised. At the anode, manganese loses one electron as its oxidation state changes from $+6$ to $+7$:

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

The resulting purple solution is concentrated and cooled to obtain crystals of potassium permanganate. Thus manganate is the intermediate, rather than the final product.

Step 3: React acidified permanganate with oxalic acid On warming oxalic acid with potassium permanganate acidified with dilute sulphuric acid, carbon dioxide is evolved and the purple colour

Quick Tip to Solve: Track manganese through $+4$, $+6$, $+7$, then $+2$; use the five-electron and two-electron changes to obtain the $2 : 5$ permanganate-to-oxalic-acid ratio.

disappears as Mn^{2+} forms. The balanced ionic equation is

$$2\,MnO_4^- + 5\,H_2C_2O_4 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O.$$

Each permanganate ion gains five electrons, whereas each oxalic acid molecule loses two electrons; hence their reacting mole ratio is $2 : 5$. The reaction is initially slow and accelerates as the Mn^{2+} product catalyses it.

Step 4: Conclusion Potassium permanganate is obtained by alkaline oxidative fusion of pyrolusite to manganate, followed by electrolytic oxidation and crystallisation. Warm acidified permanganate oxidises oxalic acid to CO_2 and is itself reduced to Mn^{2+}.

Quick Tip to Solve: Track manganese through $+4$, $+6$, $+7$, then $+2$; use the five-electron and two-electron changes to obtain the $2 : 5$ permanganate-to-oxalic-acid ratio.

OR

16(b). Define lanthanoid contraction. Write its two consequences. [3 marks]

Solution:

Concept:

- Across the lanthanoid series, increasing nuclear charge is accompanied by the addition of electrons to the inner $4f$ subshell. These electrons shield the outer electrons poorly.
- Greater effective nuclear attraction contracts the electron cloud. For ions of the same charge, a smaller ionic radius also increases the polarising power of the cation.

Step 1: Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic and ionic radii of the lanthanoids with increasing atomic number from lanthanum to lutetium. It is particularly evident in the radii of their trivalent ions. Each successive element has an additional proton, but the added $4f$ electron does not adequately screen this increase in nuclear charge. The stronger effective attraction therefore draws the electrons closer to the nucleus.

Step 2: Explain the similarity of zirconium and hafnium The contraction largely offsets the normal increase in atomic size expected on moving from the $4d$ to the $5d$ transition series. Consequently, zirconium and hafnium have almost identical atomic and ionic radii. They show very similar chemical properties and are difficult to separate from one another. This close size similarity is a direct consequence of the intervening lanthanoid contraction.

Step 3: Explain the decrease in hydroxide basicity From La^{3+} to Lu^{3+}, the ionic radius decreases while the charge remains $+3$. The smaller ions have greater polarising power and increase the covalent character of the metal–oxygen bond in their hydroxides. Hence the basic character decreases along the series: $La(OH)_3$ is more basic than $Lu(OH)_3$.

Step 4: Conclusion Lanthanoid contraction is the gradual decrease in lanthanoid atomic and ionic radii with increasing atomic number. Two consequences are the nearly equal sizes and similar chemistry of zirconium and hafnium, and the decreasing basicity of lanthanoid hydroxides from $La(OH)_3$ to $Lu(OH)_3$.

Quick Tip to Solve: Link poor $4f$ shielding to smaller radii first; then recall the Zr–Hf size similarity and the fall in hydroxide basicity.

17. Write the hybridization, shape and magnetic character of $[Fe(CN)_6]^{4-}$. [3 marks]

Solution:

Concept:

- In valence bond theory, coordination number six corresponds to an octahedral complex. The possible hybridisations are inner-orbital d^2sp^3 and outer-orbital sp^3d^2.
- The oxidation state determines the metal ion's d-electron count. Strong-field ligands such as CN^- favour electron pairing, and magnetic character depends on the number of unpaired electrons.

Step 1: Determine the iron oxidation state and configuration In $[Fe(CN)_6]^{4-}$, each of the six cyanide ligands has charge -1. If the oxidation state of iron is x, charge balance gives

$$x + 6(-1) = -4, \qquad x = +2.$$

Neutral iron has configuration $[Ar]\,3d^6 4s^2$. Removal of the two $4s$ electrons gives Fe^{2+} with configuration $[Ar]\,3d^6$.

Step 2: Identify the orbitals used for bonding Cyanide is a strong-field ligand. It causes the six $3d$ electrons to pair in three of the five $3d$ orbitals, leaving two $3d$ orbitals vacant. These two vacant inner $3d$ orbitals, one $4s$ orbital and three $4p$ orbitals hybridise to form six d^2sp^3 hybrid orbitals. Each accepts a lone pair from a cyanide ligand. The resulting six bonds point toward the vertices of an octahedron.

Step 3: Determine the magnetic character All six metal d electrons are paired in this low-spin complex; its octahedral crystal-field occupancy is $t_{2g}^6 e_g^0$. Thus the number of unpaired electrons is $n = 0$, and the spin-only magnetic moment is

$$\mu = \sqrt{n(n+2)}\,\mu_B = 0.$$

The absence of unpaired electrons makes the complex diamagnetic.

Step 4: Conclusion $[Fe(CN)_6]^{4-}$ has d^2sp^3 hybridisation, an octahedral shape and diamagnetic character. It is an inner-orbital, low-spin complex with no unpaired electrons.

Quick Tip to Solve: Calculate the metal charge before counting d electrons: Fe^{2+} is d^6, and strong-field cyanide pairs all six electrons in an octahedral complex.

18. What happens when :

(i) CH_3-Cl is treated with aqueous KOH?

(ii) CH_3-Cl is treated with KCN?

(iii) CH_3-Br is treated with Mg in the presence of dry ether? [3 marks]

Solution:

Concept:

- A haloalkane undergoes nucleophilic substitution when an attacking nucleophile replaces its halide ion. A methyl halide is especially suitable for the one-step S_N2 pathway.
- Aqueous hydroxide supplies OH^-; potassium cyanide supplies CN^-. Magnesium inserts into a carbon-halogen bond in anhydrous ether to form a Grignard reagent.

Step 1: (i) Reaction with aqueous potassium hydroxide The hydroxide ion attacks the methyl carbon and replaces chloride. Thus chloromethane is hydrolysed to methanol, and potassium chloride is the accompanying salt:

$$CH_3Cl + KOH(aq) \longrightarrow CH_3OH + KCl.$$

The aqueous medium favours substitution. Moreover, a methyl halide has no adjacent carbon bearing a hydrogen, so elimination to an alkene is not possible.

Step 2: (ii) Reaction with potassium cyanide The cyanide ion from ionic KCN attacks mainly through its carbon end. Chloride is displaced, producing ethanenitrile, also called methyl cyanide:

$$CH_3Cl + KCN \longrightarrow CH_3CN + KCl.$$

The nitrile carbon becomes part of the product chain, so the product has two carbon atoms although the starting haloalkane has only one. The product is a nitrile, not methyl isocyanide.

Step 3: (iii) Reaction with magnesium in dry ether Magnesium enters the carbon-bromine bond of bromomethane to give methylmagnesium bromide:

$$CH_3Br + Mg \xrightarrow{\text{dry ether}} CH_3MgBr.$$

This is a Grignard reagent. Ether coordinates to magnesium and stabilises the reagent. Moisture must be excluded because water destroys it, forming methane: $CH_3MgBr + H_2O \longrightarrow CH_4 + Mg(OH)Br$.

Step 4: Conclusion The respective organic products are $\boxed{CH_3OH}$ (methanol), $\boxed{CH_3CN}$ (ethanenitrile) and $\boxed{CH_3MgBr}$ (methylmagnesium bromide).

Quick Tip to Solve: Identify the reagent first: aqueous OH replaces halide by OH, KCN adds a carbon through CN, and Mg in dry ether gives RMgX.

19. Explain the following with an example in each :

(i) Kolbe's reaction

(ii) Reimer-Tiemann reaction

(iii) Williamson ether synthesis [3 marks]

Solution:

Concept:

- Phenoxide ions undergo electrophilic substitution mainly at the ortho position. Carbon dioxide introduces $-\mathrm{COOH}$ after acidification, whereas chloroform and alkali introduce $-\mathrm{CHO}$.
- Williamson ether synthesis is an $S_{\mathrm{N}}2$ reaction of an alkoxide ion RO^- with a suitable alkyl halide $\mathrm{R'X}$, producing $\mathrm{ROR'}$.

Step 1: (i) Kolbe's reaction Sodium phenoxide is heated with carbon dioxide at about $400\,\mathrm{K}$ under a pressure of about 4 to $7\,\mathrm{atm}$. Carboxylation occurs mainly ortho to the phenoxide group, giving sodium salicylate. Acidification produces salicylic acid (2-hydroxybenzoic acid):

$$\mathrm{C_6H_5ONa} + \mathrm{CO_2} \xrightarrow[\text{pressure}]{400\,\mathrm{K}} \mathrm{o-HOC_6H_4COONa},$$

$$\mathrm{o-HOC_6H_4COONa} + \mathrm{HCl} \longrightarrow \mathrm{o-HOC_6H_4COOH} + \mathrm{NaCl}.$$

In the context of phenols, this carboxylation is called the Kolbe or Kolbe-Schmitt reaction.

Step 2: (ii) Reimer-Tiemann reaction Phenol, on heating with chloroform and aqueous sodium hydroxide followed by acidification, gives mainly salicylaldehyde (2-hydroxybenzaldehyde). A formyl group replaces an ortho hydrogen of phenol. The overall reaction after work-up is

$$\mathrm{C_6H_5OH} + \mathrm{CHCl_3} + 3\mathrm{NaOH}$$

$$\xrightarrow[\text{then } \mathrm{H^+}]{\text{heat}} \mathrm{o-HOC_6H_4CHO} + 3\mathrm{NaCl} + 2\mathrm{H_2O}.$$

The electrophile generated from chloroform and alkali is dichlorocarbene, $:\mathrm{CCl_2}$. The para product may also form in a smaller amount.

Step 3: (iii) Williamson ether synthesis An alkoxide reacts with a methyl or primary alkyl halide by nucleophilic displacement of halide, forming an ether. For example, sodium ethoxide and bromoethane give ethoxyethane:

$$\mathrm{C_2H_5ONa} + \mathrm{C_2H_5Br} \longrightarrow \mathrm{C_2H_5OC_2H_5} + \mathrm{NaBr}.$$

The alkoxide provides the oxygen-containing fragment and the alkyl halide provides the other alkyl group. Primary halides are preferred because steric hindrance is small; tertiary halides favour elimination instead of the desired substitution.

Step 4: Conclusion Kolbe's reaction gives salicylic acid, Reimer-Tiemann reaction gives salicylaldehyde, and Williamson synthesis gives an ether such as ethoxyethane.

Quick Tip to Solve: Remember the new group: Kolbe introduces COOH, Reimer-Tiemann introduces CHO, and Williamson links two carbon groups through oxygen.

20. Write the products A and B in the following :

(i) 4-Nitrobenzoic acid $\xrightarrow{Sn/HCl}$ **A** $\xrightarrow{CHCl_3+aq.\ NaOH}$ **B**

(ii) Benzoic acid $\xrightarrow{NH_3}$ **A** $\xrightarrow{Heat}$ **B**

(iii) $C_6H_5N_2^+Cl^-$ $\xrightarrow{Cu/HCl}$ **A** $\xrightarrow{Cl_2/FeCl_3}$ **B** [3 marks]

Solution:

Concept:

- Tin and hydrochloric acid reduce an aromatic nitro group $-NO_2$ to $-NH_2$, leaving the carboxyl group intact. A primary amine reacts with chloroform and strong alkali in the carbylamine transformation to give an isocyanide $-N \equiv C$.
- A carboxylic acid first forms an ammonium carboxylate with ammonia; heating removes water to form an amide. Chlorine on a benzene ring deactivates the ring but directs further electrophilic substitution to ortho and para positions.

Step 1: (i) Reduction followed by the carbylamine transformation Reduction of 4-nitrobenzoic acid converts only the nitro group into an amino group:

$$\mathrm{p-O_2NC_6H_4COOH} + 6[\mathrm{H}] \xrightarrow{\mathrm{Sn/HCl}} \mathrm{p-H_2NC_6H_4COOH} + 2\mathrm{H_2O}.$$

Thus A is 4-aminobenzoic acid. Its primary amino group undergoes the carbylamine transformation with chloroform and strong alkali, giving the isocyano group:

$$\mathrm{p-H_2NC_6H_4COOH} + \mathrm{CHCl_3} + 3\mathrm{NaOH}$$

$$\longrightarrow \mathrm{p-(NC)C_6H_4COOH} + 3\mathrm{NaCl} + 3\mathrm{H_2O}.$$

Here $-NC$ means $-N \equiv C$, with nitrogen bonded to the ring. B is 4-isocyanobenzoic acid in its acid form. In the alkaline reaction mixture its carboxyl group is present as the sodium carboxylate; acidification gives the acid shown.

Step 2: (ii) Reaction of benzoic acid with ammonia and heating Acid-base reaction occurs first, producing ammonium benzoate:

$$\mathrm{C_6H_5COOH} + \mathrm{NH_3} \longrightarrow \mathrm{C_6H_5COO^-NH_4^+}.$$

Therefore A is ammonium benzoate, not benzamide at this first stage. Heating the ammonium salt causes dehydration:

$$\mathrm{C_6H_5COO^-NH_4^+} \xrightarrow{\mathrm{heat}} \mathrm{C_6H_5CONH_2} + \mathrm{H_2O}.$$

Hence B is benzamide. The carbonyl carbon stays attached to the benzene ring throughout.

Step 3: (iii) Replacement of the diazonium group and ring chlorination Copper and hydrochloric acid replace the diazonium group by chlorine, with liberation of nitrogen:

$$\mathrm{C_6H_5N_2^+Cl^-} \xrightarrow{\mathrm{Cu/HCl}} \mathrm{C_6H_5Cl} + \mathrm{N_2}.$$

Quick Tip to Solve: Keep the two arrows separate: identify the intermediate A first, then apply only the second reagent to obtain B. In isocyanides, the ring bonds to nitrogen.

Thus A is chlorobenzene. Chlorination with $Cl_2/FeCl_3$ then substitutes a ring hydrogen:

$$C_6H_5Cl + Cl_2 \xrightarrow{FeCl_3} C_6H_4Cl_2 + HCl.$$

The attached chlorine directs the incoming chlorine to the ortho and para positions. Consequently B is a mixture of 1,2-dichlorobenzene and 1,4-dichlorobenzene, with the para isomer generally the major product because it has less steric crowding.

Step 4: Conclusion (i) A: 4-aminobenzoic acid; B: 4-isocyanobenzoic acid (its carboxylate in alkali). (ii) A: ammonium benzoate; B: benzamide. (iii) A: chlorobenzene; B: ortho- and para-dichlorobenzene, para major.

Quick Tip to Solve: Keep the two arrows separate: identify the intermediate A first, then apply only the second reagent to obtain B. In isocyanides, the ring bonds to nitrogen.

21. Write two uses of each of the following polymers.

(i) Polypropylene

(ii) PVC

(iii) Nylon-6,6 [3 marks]

Solution:

Concept:

- A polymer's uses depend on properties such as strength, flexibility, resistance to chemicals and ability to form fibres or moulded articles.
- Polypropylene and polyvinyl chloride (PVC) are thermoplastics, whereas nylon-6,6 is a strong synthetic polyamide widely used as a fibre.

Step 1: (i) Uses of polypropylene Two uses of polypropylene are the manufacture of **ropes** and **packaging films**. Its low density and resistance to moisture make ropes light and suitable for handling in wet conditions. It can also be processed into thin, tough films for wrapping and protecting goods. These are two distinct applications of the same polymer.

Step 2: (ii) Uses of PVC Two uses of PVC are the manufacture of **water pipes** and **electrical cable insulation**. Rigid PVC is durable and resists corrosion, which makes it useful for pipes carrying water. Flexible PVC formulations are used around electrical wires because PVC is a good electrical insulator. The flexibility needed for cable coverings can be obtained by adding suitable plasticisers.

Step 3: (iii) Uses of nylon-6,6 Two uses of nylon-6,6 are the manufacture of **textile fibres** and **tyre cords**. Its fibres have high tensile strength and good resistance to abrasion. They can therefore be woven into durable fabrics and used to reinforce tyres, where the cords must withstand repeated mechanical stress during use.

Step 4: Conclusion Polypropylene: ropes and packaging films. PVC: water pipes and electrical cable insulation. Nylon-6,6: textile fibres and tyre cords.

Quick Tip to Solve: Recall two separate finished products for each polymer; linking each pair to a material property helps keep the uses distinct.

22. What are enzymes? Describe their functions. Name two diseases which are caused due to deficiency of enzymes. [3 marks]

Solution:

Concept:

- Enzymes are biological catalysts produced by living cells. Most enzymes are globular proteins and catalyse specific biochemical reactions.
- A catalyst lowers the activation energy of a reaction, increasing its rate without being consumed overall. Deficiency of a specific enzyme can block a metabolic pathway.

Step 1: Define enzymes Enzymes are biological catalysts that accelerate chemical reactions in living organisms. They are generally protein molecules with a specific three-dimensional structure and an active site to which the appropriate substrate binds. Their specificity allows different cellular reactions to be catalysed by different enzymes.

Step 2: Describe their functions Enzymes make biochemical reactions proceed rapidly under the mild temperature and pH conditions of living cells by lowering the activation energy. They catalyse both the breakdown and the synthesis of biomolecules. For example, amylase catalyses the hydrolysis of starch during digestion, while proteases catalyse the hydrolysis of proteins. Other enzymes catalyse reactions involved in respiration and the synthesis of cellular constituents. The enzyme is regenerated after the reaction and can act again.

Step 3: Name two diseases caused by enzyme deficiency **Phenylketonuria** results from deficiency of phenylalanine hydroxylase, the enzyme required for conversion of phenylalanine to tyrosine. Phenylalanine then accumulates in the body. **Albinism**, specifically its tyrosinase-deficient form, results from deficient activity of tyrosinase in the pathway that produces the pigment melanin from tyrosine. Consequently, pigmentation of the skin, hair and eyes is reduced or absent.

Step 4: Conclusion Enzymes are biological catalysts that speed up specific metabolic reactions. Two enzyme-deficiency diseases are phenylketonuria and tyrosinase-deficient albinism.

Quick Tip to Solve: Pair each disease with its missing enzyme: phenylketonuria with phenylalanine hydroxylase, and albinism with tyrosinase.

23. Ankit's grandfather is not only obese but he is also a diabetic patient. Seeing his fondness for sweets, Ankit suggested him to replace sugar with artificial sweeteners. After few days, Ankit observed a controlled level of sugar in his grandfather.

Answer the following:

(i) What are the values displayed by Ankit?

(ii) What are artificial sweeteners?

(iii) Give two examples of artificial sweeteners.

(iv) Name an artificial sweetener which is unstable at cooking temperature. [4 marks]

Solution:

Concept:

- Artificial sweeteners are substances used in place of sugar to impart a sweet taste. They are generally much sweeter than sucrose, so small quantities are sufficient.
- The thermal stability of a sweetener determines whether it can be used during cooking. Aspartame is unstable at cooking temperatures and is therefore used in cold foods and drinks.

Step 1: (i) Identify the values displayed by Ankit Ankit shows care and concern for his grandfather's health, respect for elders and a sense of responsibility. He also applies scientific knowledge to a practical problem: he recognises his grandfather's fondness for sweets and suggests a sugar substitute in view of his diabetes and obesity.

Step 2: (ii) Define artificial sweeteners Artificial sweeteners are chemical substances used as substitutes for sugar to provide sweetness to food and beverages. Because they are intensely sweet, they are used in very small quantities and can reduce the amount of ordinary sugar consumed. They provide the desired sweet taste without requiring the usual quantity of sucrose.

Step 3: (iii) Give two examples Two examples are saccharin and aspartame. Both are artificial sweeteners used to impart sweetness. Saccharin is an early sugar substitute, while aspartame is a methyl ester of a dipeptide formed from aspartic acid and phenylalanine.

Step 4: (iv) Identify the heat-sensitive sweetener Aspartame is unstable at cooking temperatures. On heating it decomposes and loses its suitability as a sweetening agent; consequently it is used mainly in cold foods and soft drinks rather than in foods that must be cooked.

Step 5: Conclusion (i) Care for elders, responsibility and scientific awareness; (ii) substances used instead of sugar to impart sweetness; (iii) saccharin and aspartame; (iv) aspartame is unstable at cooking temperatures.

Quick Tip to Solve: Link aspartame with cold foods: it is heat-sensitive, so do not choose it as the sweetener for cooking.

24(a). What are the two classifications of batteries? What is the difference between them?

(b) The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell is unity. Calculate the molar conductivity of the solution. [5 marks]

Solution:

Concept:

- Batteries are classified as primary batteries and secondary (storage) batteries according to whether their cell reactions can be reversed by supplying electrical energy.
- Conductance is the reciprocal of resistance: $G = 1/R$. Conductivity is $\kappa = G(l/A)$, where l/A is the cell constant.
- For concentration c in mol L^{-1} and conductivity in S cm^{-1}, molar conductivity is $\Lambda_m = 1000\kappa/c$, in S cm^2 mol^{-1}.

Step 1: (a) Classify batteries and explain the distinction The two classes are **primary batteries** and **secondary batteries**. In a primary battery, the cell reaction is essentially irreversible under normal operating conditions. Once its active reactants are consumed, it cannot be restored for reuse by passing a charging current. A dry cell is an example.

In a secondary battery, the cell reaction is reversible. After discharge, an external source drives current in the opposite direction and regenerates the original active materials. Thus it can be recharged and used repeatedly. A lead storage battery is an example.

Step 2: (b) Calculate the conductance and conductivity The resistance is $R = 200\,\Omega$. Hence

$$G = \frac{1}{R} = \frac{1}{200} = 5.0 \times 10^{-3}\,\text{S}.$$

Taking the given unit cell constant as $l/A = 1\,\text{cm}^{-1}$,

$$\kappa = G\frac{l}{A} = (5.0 \times 10^{-3})(1) = 5.0 \times 10^{-3}\,\text{S cm}^{-1}.$$

Step 3: (b) Convert conductivity to molar conductivity Here $c = 0.01$ mol L^{-1}. Therefore

$$\begin{aligned}\Lambda_m &= \frac{1000\kappa}{c} \\ &= \frac{1000(5.0 \times 10^{-3})}{0.01} \\ &= 500\,\text{S cm}^2\,\text{mol}^{-1}.\end{aligned}$$

The factor 1000 converts the litre in the concentration unit to cubic centimetres, so that the volume unit is consistent with conductivity expressed per centimetre.

Step 4: Conclusion (a) Batteries are primary (essentially irreversible and not rechargeable) or secondary (reversible and rechargeable). (b) The molar conductivity of the given NaCl solution is $\boxed{500\,\text{S cm}^2\,\text{mol}^{-1}}$.

Quick Tip to Solve: First invert the resistance, multiply by the cell constant, and only then use $1000\kappa/c$; keep $c = 0.01$ in molarity throughout.

OR

24(b). What are fuel cells? Give an example of a fuel cell.

Calculate the equilibrium constant (log K_c) and $\Delta_r G^\circ$ for the following reaction at 298 K.

$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$

Given $E^\circ_{cell} = 0.46$ V and 1F = 96500 C mol^{-1} [5 marks]

Solution:

Concept:

- Fuel cells are galvanic cells in which the chemical energy of continuously supplied fuel and oxidant is converted directly into electrical energy.
- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred per balanced reaction and F is the Faraday constant.
- At equilibrium, $\Delta_r G^\circ = -RT \ln K_c$. Thus the logarithm of the equilibrium constant follows from the standard cell potential and temperature.

Step 1: Define fuel cells and give an example A fuel cell produces electricity by the electrochemical reaction of a fuel with an oxidant, both of which are supplied continuously to its electrodes. It can keep operating while these reactants are supplied and the products are removed. Unlike combustion followed by mechanical generation, the conversion to electrical energy is direct.

An example is the hydrogen–oxygen fuel cell. In an alkaline electrolyte, its electrode reactions are

$$\text{Anode: } 2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-,$$
$$\text{Cathode: } O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-.$$

Adding these gives $2H_2 + O_2 \longrightarrow 2H_2O$. Thus hydrogen is the fuel, oxygen is the oxidant, and water is the net reaction product.

Step 2: Determine the electron transfer for the copper–silver reaction The oxidation and reduction half-reactions are

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-,$$
$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s).$$

Therefore $n = 2$ for the reaction as written. The pure solids have unit activity, so the equilibrium expression involves the aqueous ions: $K_c = [Cu^{2+}]/[Ag^+]^2$, with concentrations understood relative to their standard state.

Step 3: Calculate the standard Gibbs energy change Substitute the given standard cell potential and Faraday constant:

$$\begin{aligned}\Delta_r G^\circ &= -2 \times 96500 \times 0.46 \\ &= -88780\,\text{J mol}^{-1} \\ &= -88.78\,\text{kJ mol}^{-1}.\end{aligned}$$

The negative sign is consistent with the positive standard cell potential: the forward reaction is thermodynamically favourable under standard conditions.

Step 4: Calculate the equilibrium constant at 298 K Taking $R = 8.314\,\text{J mol}^{-1}\text{K}^{-1}$, the relation

Quick Tip to Solve: Balance the half-reactions first: copper loses two electrons, so use $n = 2$. Keep Gibbs energy in joules when combining it with RT, and divide by 2.303 when converting a natural logarithm to $\log_{10}$.

between electrical work and equilibrium gives

$$\log_{10} K_c = \frac{2 \times 96500 \times 0.46}{2.303 \times 8.314 \times 298} \approx 15.56.$$

Consequently, $K_c = 10^{15.56} \approx 3.6 \times 10^{15}$. The very large value agrees with the negative standard Gibbs energy change and indicates that equilibrium strongly favours formation of copper(II) ions and silver metal.

Step 5: Conclusion Fuel cells convert the chemical energy of continuously supplied fuel and oxidant directly into electricity; the hydrogen–oxygen fuel cell is an example. For the given reaction at $298\,\text{K}$, $\boxed{\log_{10} K_c \approx 15.56}$, $K_c \approx 3.6 \times 10^{15}$, and $\boxed{\Delta_r G^\circ = -88.78\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Balance the half-reactions first: copper loses two electrons, so use $n = 2$. Keep Gibbs energy in joules when combining it with RT, and divide by 2.303 when converting a natural logarithm to $\log_{10}$.

25(a). Draw the structure of

(i) BrF_3

(ii) $XeOF_4$

(b) Explain giving reason in each case:

(i) Why H_2Te is more acidic than H_2S?

(ii) Why are halogens strong oxidising agents?

(iii) Why does nitrogen show catenation tendency less than phosphorus? [5 marks]

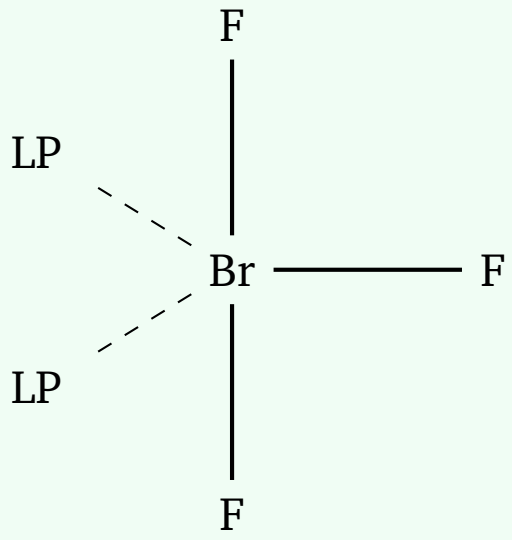
Solution:

Concept:

- In VSEPR theory, electron domains around the central atom arrange themselves to minimise repulsion. A multiple bond counts as one domain; lone pairs influence the molecular shape but are not included among its vertices.
- Acidity of group 16 hydrides increases as the strength of the element–hydrogen bond decreases down the group. Oxidising agents accept electrons, while catenation depends on the stability of bonds between like atoms.

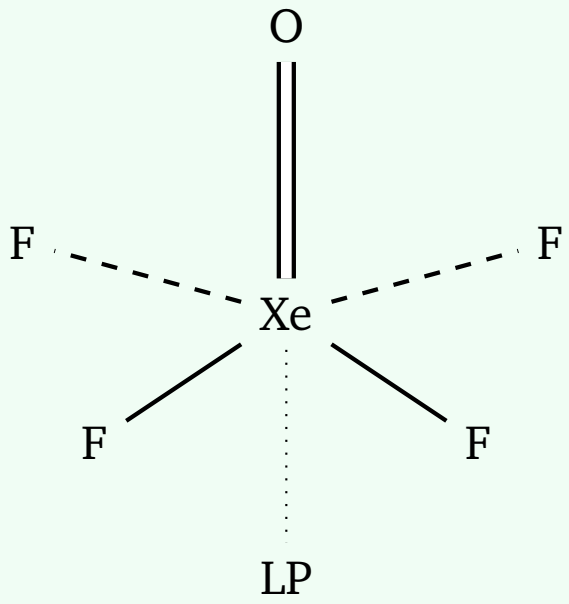
Step 1: (a)(i) Structure of BrF_3 Bromine has seven valence electrons. Three Br–F bonds and two lone pairs surround Br, giving five electron domains and a trigonal-bipyramidal electron-pair arrangement. Both lone pairs occupy equatorial sites, where they experience fewer 90° interactions than at axial sites. The remaining three bonding sites form a T-shaped molecule, with two axial F atoms and one equatorial F atom. Its conventional hybridisation is sp^3d. Lone-pair repulsion makes the axial–equatorial bond angles slightly less than 90°.

Quick Tip to Solve: Count electron domains before naming the shape: Br has two lone pairs in BrF3, whereas Xe has one in XeOF4. For catenation, compare single bonds rather than the nitrogen triple bond.



T-shaped BrF_3; the two lone pairs occupy equatorial sites.

Step 2: (a)(ii) Structure of $XeOF_4$ Xenon has four Xe–F single bonds, one Xe=O double bond and one lone pair. These constitute six electron domains: the double bond counts as one domain. Their arrangement is octahedral. The lone pair lies opposite the oxygen atom, leaving four fluorine atoms in a square plane and oxygen at the apex. Thus, the molecular shape is square pyramidal, conventionally associated with sp^3d^2 hybridisation. The perspective drawing shows the square base and the axial oxygen; LP denotes a lone pair.



Square-pyramidal $XeOF_4$; oxygen and the lone pair occupy opposite axial sites.

Step 3: (b)(i) Greater acidity of H_2Te Tellurium is larger than sulphur, so the H–Te bond is longer and weaker than the H–S bond. Consequently, ionisation involving release of H^+ occurs more readily for H_2Te. The decrease in bond strength down the group outweighs the decrease in electronegativity,

Quick Tip to Solve: Count electron domains before naming the shape: Br has two lone pairs in BrF3, whereas Xe has one in XeOF4. For catenation, compare single bonds rather than the nitrogen triple bond.

explaining the increase in acidity from H_2S to H_2Te.

Step 4: (b)(ii) Oxidising action of halogens A halogen atom has the valence-shell configuration ns^2np^5 and needs one additional electron to attain a stable noble-gas configuration. Halogens therefore readily accept electrons and are reduced to halide ions:

$$X_2 + 2e^- \longrightarrow 2X^-.$$

By accepting electrons they oxidise the other reactant, so they act as strong oxidising agents. Their high electronegativity and favourable tendency to form halide ions account for this behaviour.

Step 5: (b)(iii) Catenation of nitrogen and phosphorus The small size of nitrogen brings the lone pairs on adjacent N atoms very close together in an N–N single bond. Strong lone-pair repulsion weakens this bond and destabilises long nitrogen chains. Phosphorus atoms are larger, so the corresponding repulsion is smaller and P–P single bonds are stronger than N–N single bonds. Phosphorus therefore exhibits greater catenation. The high strength of the $N \equiv N$ triple bond does not imply a strong N–N single bond, which is the bond relevant to ordinary chain formation.

Step 6: Conclusion BrF_3 is T-shaped and $XeOF_4$ is square pyramidal. The weaker H–Te bond makes H_2Te more acidic; halogens oxidise by accepting electrons; weak N–N single bonds make nitrogen less prone to catenation than phosphorus.

Quick Tip to Solve: Count electron domains before naming the shape: Br has two lone pairs in BrF3, whereas Xe has one in XeOF4. For catenation, compare single bonds rather than the nitrogen triple bond.

OR

25(b). (a) (i) Why PCl_5 gives fumes in moisture?
(ii) Why Interhalogens are more reactive than pure halogens?
(b) Draw the structures of the following :
(i) PCl_5(s)
(ii) $H_2S_2O_8$
(iii) XeF_4 [5 marks]

Solution:

Concept:

- Hydrolysis is reaction with water. Chlorides such as PCl_5 release hydrogen chloride when they react with atmospheric moisture.
- An interhalogen contains two different halogens. Its bond is generally weaker than the corresponding bonds in the parent halogens (except F_2), so it reacts more readily.
- Structure depends on the physical state: solid PCl_5 is ionic. A peroxide linkage is an $O - O$ bond; VSEPR predicts molecular shape from bond pairs and lone pairs.

Step 1: (a)(i) Fuming of phosphorus pentachloride PCl_5 reacts with water vapour in air, liberating

Quick Tip to Solve: Check the state symbol first: PCl5(s) needs two ionic structures, and the extra oxygen in peroxodisulphuric acid belongs to an O–O bridge.

hydrogen chloride:

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl.$$

The HCl dissolves in atmospheric moisture, producing fine droplets of hydrochloric acid that appear as white fumes. With excess water, hydrolysis proceeds further:

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl.$$

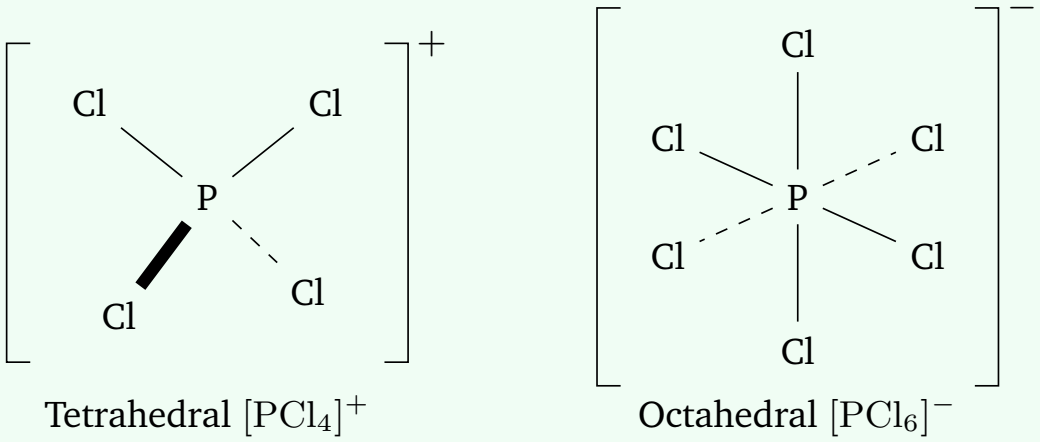
Thus the visible fumes arise from the hydrogen chloride formed by hydrolysis.

Step 2: (a)(ii) Reactivity of interhalogens The two atoms in an interhalogen differ in size and electronegativity. Their orbital overlap is less effective, making the interhalogen bond generally weaker and easier to break than the bonds in the constituent halogens. Consequently, interhalogens are generally more reactive than the parent halogens, with F_2 as the usual exception because its bond is unusually weak and fluorine is extremely reactive.

Step 3: (b)(i) Structure of solid phosphorus pentachloride In the solid state, phosphorus pentachloride consists of $[PCl_4]^+$ and $[PCl_6]^-$ ions:

$$2PCl_5(s) \longrightarrow [PCl_4]^+[PCl_6]^-.$$

The cation has four P–Cl bonds arranged tetrahedrally, while the anion has six P–Cl bonds arranged octahedrally. The wedge and dashed bond in the cation indicate bonds directed out of and behind the plane of the paper. Solid PCl_5 must therefore be represented by these ions; the trigonal bipyramidal molecule describes gaseous PCl_5.



Ionic structures in solid phosphorus pentachloride

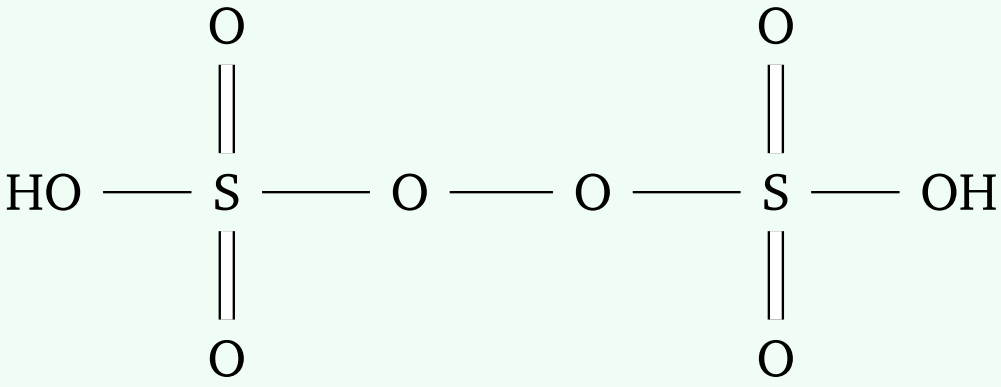
Step 4: (b)(ii) Structure of peroxodisulphuric acid $H_2S_2O_8$ contains two sulphur centres joined through a peroxide bridge:

$$HO - S(=O)_2 - O - O - S(=O)_2 - OH.$$

Each sulphur is bonded to two terminal oxygen atoms by double bonds, one hydroxyl oxygen and one oxygen of the peroxide bridge. The $O - O$ single bond is the characteristic structural feature; there is

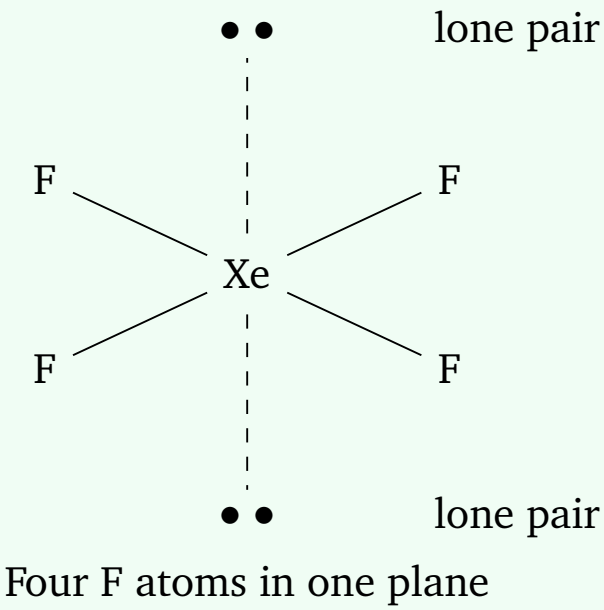
Quick Tip to Solve: Check the state symbol first: PCl5(s) needs two ionic structures, and the extra oxygen in peroxodisulphuric acid belongs to an O–O bridge.

no direct S–S bond. Counting the atoms gives two hydrogen, two sulphur and eight oxygen atoms.



Peroxodisulphuric acid: the peroxide bridge is O–O

Step 5: (b)(iii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four are used to form four Xe–F bonds, leaving two lone pairs on xenon. Thus there are six electron pairs around the central atom, with an octahedral electron-pair arrangement. The two lone pairs occupy opposite positions to minimise repulsion, leaving the four fluorine atoms in one square plane. Therefore XeF_4 is square planar, with adjacent F–Xe–F angles of 90° and opposite angles of 180°. The lone pairs lie above and below the molecular plane.



Square planar XeF4; the two lone pairs are normal to the fluorine plane

Step 6: Conclusion PCl_5 fumes because moisture hydrolyses it to release HCl; interhalogens are generally more reactive because their bonds are weaker. Solid PCl_5 contains tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$; $H_2S_2O_8$ has an $S-O-O-S$ bridge; XeF_4 is square planar.

Quick Tip to Solve: Check the state symbol first: PCl5(s) needs two ionic structures, and the extra oxygen in peroxodisulphuric acid belongs to an O–O bridge.

26(a). Complete the following equations :

(i) $C_6H_5CHO \xrightarrow{conc.\ NaOH}$ **?**

(ii) $CH_3COCH_3 \xrightarrow{LiAlH_4}$ **?**

(iii) $CH_3-COOH \xrightarrow{(a)\ Cl_2/P\ (b)\ H_2O}$ **?**

(b) Distinguish between :

(i) CH_3COOH **and phenol**

(ii) CH_3CHO **and** CH_3COCH_3 [5 marks]

Solution:

Concept:

- An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction with concentrated alkali: one molecule is oxidised to a carboxylate ion and another is reduced to an alcohol.
- Lithium aluminium hydride reduces a ketone to a secondary alcohol after hydrolysis. Chlorine with phosphorus followed by water gives alpha halogenation of a carboxylic acid containing an alpha hydrogen (Hell–Volhard–Zelinsky reaction).
- Carboxylic acids release carbon dioxide from sodium hydrogencarbonate, whereas phenol does not. Tollens' reagent oxidises an aldehyde and deposits metallic silver; a simple ketone gives no silver mirror.

Step 1: (a)(i) Reaction of benzaldehyde with concentrated sodium hydroxide Benzaldehyde has no alpha hydrogen and therefore undergoes disproportionation, called the Cannizzaro reaction. The balanced equation is

$$2C_6H_5CHO + NaOH \xrightarrow{conc.} C_6H_5COONa + C_6H_5CH_2OH.$$

The products are sodium benzoate and benzyl alcohol. Sodium benzoate, rather than free benzoic acid, is obtained in the alkaline reaction mixture.

Step 2: (a)(ii) Reduction of propanone Lithium aluminium hydride reduces the carbonyl group; subsequent hydrolysis gives propan-2-ol:

$$CH_3COCH_3 \xrightarrow[\text{2. hydrolysis}]{\text{1. } LiAlH_4\text{, dry ether}} CH_3CH(OH)CH_3.$$

The carbon skeleton is retained and the carbonyl carbon acquires a hydrogen atom. Since this carbon is bonded to two methyl groups, the product is a secondary alcohol.

Step 3: (a)(iii) Alpha chlorination of ethanoic acid The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of ethanoic acid by chlorine. Hydrolysis restores the carboxylic acid group:

$$CH_3COOH \xrightarrow[\text{(b) } H_2O]{\text{(a) } Cl_2/P} ClCH_2COOH.$$

The organic product is 2-chloroethanoic acid (chloroacetic acid). The net substitution also produces hydrogen chloride: $CH_3COOH + Cl_2 \longrightarrow ClCH_2COOH + HCl$.

Step 4: (b)(i) Distinguish ethanoic acid from phenol Add aqueous sodium hydrogencarbonate

Quick Tip to Solve: Use sodium hydrogencarbonate for the acid–phenol pair and Tollens' reagent for the aldehyde–ketone pair; avoid iodoform here because both carbonyl compounds respond positively.

separately to the two samples. Ethanoic acid produces brisk effervescence of carbon dioxide:

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2 \uparrow .$$

Phenol produces no effervescence under these conditions. Ethanoic acid is sufficiently acidic to liberate carbon dioxide from hydrogencarbonate; phenol is too weak an acid to do so. The gas from the positive test turns limewater milky.

Step 5: (b)(ii) Distinguish ethanal from propanone Warm the samples separately with freshly prepared Tollens' reagent in clean test tubes. Ethanal gives a silver mirror on the inner wall because it reduces the silver(I) complex to silver metal:

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

Propanone gives no silver mirror because it is not oxidised by Tollens' reagent under these conditions. The iodoform test would not distinguish this pair, since both ethanal and propanone give a positive test.

Step 6: Conclusion (a) The products are (i) sodium benzoate and benzyl alcohol, (ii) propan-2-ol, and (iii) 2-chloroethanoic acid. (b) Sodium hydrogencarbonate gives carbon dioxide with ethanoic acid but not with phenol; Tollens' reagent gives a silver mirror with ethanal but not with propanone.

Quick Tip to Solve: Use sodium hydrogencarbonate for the acid–phenol pair and Tollens' reagent for the aldehyde–ketone pair; avoid iodoform here because both carbonyl compounds respond positively.

OR

26(b). (a) What is meant by the following terms? Give an example of the reaction in each case.

(i) Aldol

(ii) Semicarbazone

(b) Complete the following :

(i) $CH_3COCl \xrightarrow{H_2,\ Pd-BaSO_4}$ **?**

(ii) $CH_3-CH=CH-CN \xrightarrow{DIBAL-H}$ **?**

(iii) $C_6H_5CHO \xrightarrow{conc.\ HNO_3+H_2SO_4}$ **?** [5 marks]

Solution:

Concept:

- An aldol is a β-hydroxy aldehyde or ketone formed by addition between two molecules of a carbonyl compound having an α-hydrogen in dilute alkali.
- A semicarbazone contains the group $C = N - NHCONH_2$, formed by condensation of an aldehyde or ketone with semicarbazide, $H_2NNHCONH_2$.
- Controlled reduction converts an acid chloride or a nitrile into an aldehyde. The $-CHO$ group deactivates an aromatic ring and directs electrophilic substitution mainly to the meta position.

Quick Tip to Solve: Keep the nitrile carbon when replacing CN by CHO after DIBAL-H hydrolysis; for benzaldehyde nitration, place the new nitro group meta to CHO.

Step 1: (a)(i) Define aldol and illustrate its formation An aldol has a hydroxyl group on the β-carbon relative to a carbonyl group. For example, ethanal undergoes aldol addition in cold, dilute sodium hydroxide:

$$2CH_3CHO \xrightarrow{\text{dil. NaOH, cold}} CH_3CH(OH)CH_2CHO.$$

The product is 3-hydroxybutanal, an aldol. The base removes an α-hydrogen from one ethanal molecule; the resulting nucleophile adds to the carbonyl carbon of a second molecule. Protonation gives the hydroxyl group. Heating can cause dehydration, so the hydroxy compound is the product used to illustrate an aldol here.

Step 2: (a)(ii) Define semicarbazone and give its reaction A semicarbazone is the condensation derivative obtained when an aldehyde or ketone reacts with semicarbazide, with elimination of water. For example, ethanal gives ethanal semicarbazone:

$$CH_3CHO + H_2NNHCONH_2 \longrightarrow CH_3CH = NNHCONH_2 + H_2O.$$

The terminal $-NH_2$ group of semicarbazide takes part in the reaction. The $-CONH_2$ group remains intact; its nitrogen lone pair is delocalised towards the carbonyl group. These derivatives are generally crystalline solids useful in identifying carbonyl compounds.

Step 3: (b)(i) Reduce ethanoyl chloride by the Rosenmund reaction Hydrogen with palladium supported on barium sulphate reduces the acid chloride to the corresponding aldehyde:

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

The organic product is ethanal. The controlled catalyst allows the reduction to stop at the aldehyde stage rather than proceeding to the primary alcohol.

Step 4: (b)(ii) Reduce the nitrile selectively with DIBAL-H DIBAL-H partially reduces the nitrile group. Hydrolysis of the intermediate then gives an aldehyde, while the carbon-carbon double bond is retained:

$$CH_3CH = CHCN \xrightarrow[\text{2. hydrolysis}]{\text{1. DIBAL-H}} CH_3CH = CHCHO.$$

The product is but-2-enal. The carbon of the original $-CN$ group becomes the aldehyde carbon, so the four-carbon skeleton is preserved.

Step 5: (b)(iii) Nitrate benzaldehyde Concentrated nitric acid and sulphuric acid generate the nitronium electrophile, NO_2^+. Since $-CHO$ is an electron-withdrawing, meta-directing group, nitration gives mainly 3-nitrobenzaldehyde:

$$C_6H_5CHO + HNO_3 \xrightarrow{\text{conc. } H_2SO_4} 3\text{-}NO_2C_6H_4CHO + H_2O.$$

Numbering the ring carbon attached to $-CHO$ as 1 places the nitro group at position 3. The aldehyde group remains present in the nitration product.

Step 6: Conclusion (a) Aldol: a β-hydroxy carbonyl compound, for example 3-hydroxybutanal

Quick Tip to Solve: Keep the nitrile carbon when replacing CN by CHO after DIBAL-H hydrolysis; for benzaldehyde nitration, place the new nitro group meta to CHO.

from ethanal. Semicarbazone: the $C = N - NHCONH_2$ derivative of an aldehyde or ketone, for example $CH_3CH = NNHCONH_2$. (b) The products are (i) ethanal, CH_3CHO; (ii) but-2-enal, $CH_3CH = CHCHO$; (iii) 3-nitrobenzaldehyde, $3\text{-}NO_2C_6H_4CHO$.

Quick Tip to Solve: Keep the nitrile carbon when replacing CN by CHO after DIBAL-H hydrolysis; for benzaldehyde nitration, place the new nitro group meta to CHO.