CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/1 (Delhi)

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) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vi) Use Log Tables, if necessary. Use of calculators is not allowed.

1. Give one example each of 'oil in water' and 'water in oil' emulsion. [1 mark]

Solution:

Concept:

- An emulsion is a colloidal dispersion of one liquid in another immiscible liquid.
- The continuous medium determines whether the emulsion is oil-in-water or water-in-oil.

Step 1: Identify an oil-in-water example Milk is an oil-in-water emulsion: tiny droplets of liquid fat are dispersed throughout water. Thus water forms the continuous dispersion medium and fat forms the dispersed phase.

Step 2: Identify a water-in-oil example Butter is a water-in-oil emulsion: water droplets are dispersed in a continuous fat or oil phase. The distinction depends on the continuous phase, rather than simply on the presence of both oil and water.

Step 3: Conclusion Oil-in-water: milk. Water-in-oil: butter.

Quick Tip to Solve: Name the continuous phase first when checking the type: milk has a continuous aqueous phase.

2. Which reducing agent is employed to get copper from the leached low grade copper ore? [1 mark]

Solution:

Concept:

- A metal above copper in the activity series can displace copper from its aqueous salt solution.
- In displacement, the more reactive metal supplies electrons and acts as the reducing agent.

Step 1: Choose the reducing metal Scrap iron is employed to recover copper from the solution obtained by leaching low-grade copper ore. Iron is more readily oxidised than copper, so it can reduce the dissolved copper ions.

Step 2: Show the displacement reaction The reaction is $\mathrm{Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)}$. Iron loses two electrons while copper(II) ions gain them and deposit as metallic copper. Thus iron is consumed as the reducing agent.

Step 3: Conclusion Scrap iron is the reducing agent.

Quick Tip to Solve: For leached copper recovery, remember that cheaper, more reactive iron displaces copper from solution.

3. Which of the following is more stable complex and why?
$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ [1 mark]

Solution:

Concept:

- Ethylenediamine, en, is a bidentate ligand; ammonia is monodentate.

Quick Tip to Solve: When comparing similar complexes of the same metal, look for bidentate ligands and chelate rings.

- The chelate effect increases the stability of complexes formed with multidentate ligands.

Step 1: Compare the ligands In $[Co(NH_3)_6]^{3+}$, each ammonia molecule binds through one nitrogen atom. In $[Co(en)_3]^{3+}$, each en molecule binds through two nitrogen atoms, forming chelate rings around the same central cobalt(III) ion.

Step 2: Apply the chelate effect The three bidentate en ligands produce three five-membered chelate rings. Ring formation and the favourable chelate effect make this complex more stable than the corresponding complex with six separate monodentate ammonia ligands.

Step 3: Conclusion $[Co(en)_3]^{3+}$ is more stable because of the chelate effect.

Quick Tip to Solve: When comparing similar complexes of the same metal, look for bidentate ligands and chelate rings.

4. Write the IUPAC name of the compound.

$CH_3-CH(OH)-CH_2-COOH$ [1 mark]

Solution:

Concept:

- The carboxylic acid group is the principal functional group and provides the suffix -oic acid.
- Number the parent chain from the carboxyl carbon; an additional hydroxyl group is named with the prefix hydroxy-.

Step 1: Choose and number the parent chain The chain containing the $-COOH$ group has four carbon atoms, so the parent acid is butanoic acid. Numbering starts at the carboxyl carbon: $HOOC(1) - CH_2(2) - CH(OH)(3) - CH_3(4)$.

Step 2: Locate the substituent The hydroxyl group is attached to carbon 3. Since the carboxylic acid has priority, the hydroxyl is expressed as the prefix 3-hydroxy, rather than using an alcohol suffix.

Step 3: Conclusion The IUPAC name is 3-hydroxybutanoic acid.

Quick Tip to Solve: Always count the carboxyl carbon as carbon 1 before assigning the hydroxy locant.

5. Which of the following isomers is more volatile: o-nitrophenol or p-nitrophenol? [1 mark]

Solution:

Concept:

- Stronger intermolecular attraction lowers volatility because more energy is needed to separate molecules.
- Intramolecular hydrogen bonding occurs within a molecule, whereas intermolecular hydrogen bonding associates different molecules.

Step 1: Examine the ortho isomer In *o*-nitrophenol, the adjacent $-OH$ and $-NO_2$ groups form an intramolecular hydrogen bond. This reduces the extent of hydrogen bonding between separate

Quick Tip to Solve: For these two isomers, connect ortho intramolecular bonding with less association and greater volatility.

molecules and hence their association.

Step 2: Compare the para isomer In p-nitrophenol, the groups are too far apart to form this intramolecular bond. It instead forms intermolecular hydrogen bonds, producing greater association and requiring more energy for vaporisation. Therefore its volatility is lower.

Step 3: Conclusion o-Nitrophenol is more volatile than p-nitrophenol.

Quick Tip to Solve: For these two isomers, connect ortho intramolecular bonding with less association and greater volatility.

6. What are isotonic solutions? [1 mark]

Solution:

Concept:

- Osmotic pressure is the pressure required to stop solvent flow through a semipermeable membrane.
- Solutions must be compared at the same temperature when judging whether they are isotonic.

Step 1: State the defining condition Two solutions are isotonic when they have equal osmotic pressures at the same temperature. If their osmotic pressures are denoted by π_1 and π_2, the condition is $\pi_1 = \pi_2$.

Step 2: Explain the consequence When isotonic solutions are separated by a suitable semipermeable membrane, there is no net flow of solvent from one to the other. For ideal dilute solutions, $\pi = iCRT$; thus equal effective solute-particle concentrations at the same temperature give equal osmotic pressures.

Step 3: Conclusion Isotonic solutions have the same osmotic pressure at the same temperature.

Quick Tip to Solve: Include both equal osmotic pressure and the same temperature in the definition of isotonic solutions.

7. Arrange the following compounds in increasing order of solubility in water:
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ [1 mark]

Solution:

Concept:

- Water solubility of an amine depends on hydrogen bonding with water and the size of its nonpolar hydrocarbon portion.
- The nitrogen atom can accept hydrogen bonds from water; an N–H bond can also donate a hydrogen bond. Increasing the hydrophobic portion generally lowers solubility.

Step 1: Compare aniline with the aliphatic amines Aniline, $C_6H_5NH_2$, has a large hydrophobic phenyl group. This reduces its affinity for water, so it is less soluble than either of the small aliphatic amines given.

Quick Tip to Solve: Compare the hydrocarbon portions as well as hydrogen bonding; do not use basicity alone to rank solubility.

Step 2: Compare the two aliphatic amines Ethylamine, $C_2H_5NH_2$, has only one ethyl group, whereas diethylamine, $(C_2H_5)_2NH$, has two. Ethylamine has the smaller hydrophobic portion and forms hydrogen bonds effectively with water, making it more soluble in the required comparison.

Step 3: Conclusion The increasing order is

$$\boxed{C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2.}$$

Quick Tip to Solve: Compare the hydrocarbon portions as well as hydrogen bonding; do not use basicity alone to rank solubility.

8. Which of the two components of starch is water soluble? [1 mark]

Solution:

Concept:

- Starch contains two polysaccharide components: amylose and amylopectin.
- Amylose consists mainly of unbranched chains of glucose joined through $\alpha(1 \rightarrow 4)$ glycosidic linkages.

Step 1: Identify the soluble component Amylose is the water-soluble component of starch. Its chains are predominantly linear and can adopt a helical arrangement.

Step 2: Distinguish the other component Amylopectin is the branched component, with $\alpha(1 \rightarrow 6)$ branch linkages in addition to its $\alpha(1 \rightarrow 4)$ chains. It is the water-insoluble component in the standard classification of starch.

Step 3: Conclusion $\boxed{\text{Amylose}}$ is the water-soluble component of starch.

Quick Tip to Solve: Remember the pair together: amylose is soluble and largely linear; amylopectin is insoluble and branched.

9. An element with density 11.2 g cm^{-3} forms a f.c.c. lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of the element.
(Given: $N_A = 6.022 \times 10^{23}$ mol^{-1}) [2 marks]

Solution:

Concept:

- The density of a unit cell is $\rho = \dfrac{ZM}{N_A a^3}$, where Z is the number of atoms per cell, M the molar mass, N_A Avogadroś constant and a the edge length.
- For a face-centred cubic (f.c.c.) unit cell, $Z = 8(1/8) + 6(1/2) = 4$.

Step 1: Calculate the volume of one unit cell The edge is $a = 4 \times 10^{-8}$ cm, so

$$a^3 = (4 \times 10^{-8})^3 = 6.4 \times 10^{-23}\ \text{cm}^3.$$

Quick Tip to Solve: For an f.c.c. cell use four atoms, and cube both the numerical factor and the power of ten in the edge length.

Using centimetres keeps the volume consistent with the given density in g cm^{-3}.

Step 2: Use the density to obtain the molar mass Rearranging the density relation gives

$$\begin{aligned} M &= \frac{\rho a^3 N_A}{Z} \\ &= \frac{11.2 \times (6.4 \times 10^{-23}) \times (6.022 \times 10^{23})}{4} \\ &= 107.91424\,\text{g mol}^{-1}. \end{aligned}$$

The powers of ten cancel. This value is the mass of one mole of atoms; the corresponding atomic mass has the same numerical value in unified atomic mass units.

Step 3: Conclusion The atomic mass of the element is $\boxed{107.9\,\text{u} \approx 108\,\text{u}}$, corresponding to a molar mass of about $108\,\text{g mol}^{-1}$.

Quick Tip to Solve: For an f.c.c. cell use four atoms, and cube both the numerical factor and the power of ten in the edge length.

10. Examine the given defective crystal:

A^+	B^-	A^+	B^-	A^+
B^-	0	B^-	A^+	B^-
A^+	B^-	A^+	0	A^+
B^-	A^+	B^-	A^+	B^-

Answer the following questions:

(i) What type of stoichiometric defect is shown by the crystal?

(ii) How is the density of the crystal affected by this defect?

(iii) What type of ionic substances show such defect? [2 marks]

Solution:

Concept:

- A Schottky defect is a vacancy defect in which equal numbers of cations and anions are missing from their normal lattice sites.
- Equal positive and negative vacancies preserve electrical neutrality and the stoichiometric ratio. Density is mass divided by volume.

Step 1: (i) Identify the defect from the vacant sites In the displayed alternating lattice, the vacant site in the second row should contain A^+, while the vacant site in the third row should contain B^-. Thus one cation and one anion are missing. The defect is a Schottky defect. There is no ion displaced to an interstitial site, as would occur in a Frenkel defect.

Step 2: (ii) State the effect on density Removing an ion pair decreases the mass of the crystal while its volume remains essentially unchanged. Consequently, $\rho = m/V$ decreases. Since the missing ions have opposite charges and equal numbers, the crystal remains electrically neutral.

Quick Tip to Solve: Check which ion belongs at each vacancy: equal cation and anion vacancies indicate a Schottky defect.

Step 3: (iii) Describe substances that show the defect This defect is typical of ionic solids with cations and anions of approximately similar sizes and high coordination numbers. Examples include NaCl, KCl and CsCl.

Step 4: Conclusion (i) Schottky defect. (ii) The density decreases. (iii) Ionic solids having similarly sized cations and anions and high coordination numbers show this defect.

Quick Tip to Solve: Check which ion belongs at each vacancy: equal cation and anion vacancies indicate a Schottky defect.

11. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K (K_f = 5.12 K kg mol^{-1}). [2 marks]

Solution:

Concept:

- For a dilute solution of a non-electrolyte, freezing-point depression is $\Delta T_f = K_f m$, where m is molality and K_f is the solventś molal depression constant.
- Molality is moles of solute per kilogram of solvent: $m = (w/M)/W$, where w is solute mass in grams, M its molar mass and W the solvent mass in kilograms.

Step 1: Determine the molality required The given freezing-point lowering is $\Delta T_f = 0.48\,\mathrm{K}$. Therefore,

$$m = \frac{\Delta T_f}{K_f} = \frac{0.48}{5.12} = 0.09375\,\text{mol kg}^{-1}.$$

Use the magnitude of the lowering, so the required molality is positive.

Step 2: Convert the solvent mass and find solute mass The mass of benzene is $75\,\mathrm{g} = 0.075\,\mathrm{kg}$. Hence

$$\begin{aligned} n = mW &= 0.09375 \times 0.075 \\ &= 0.00703125\,\text{mol}, \\ w = nM &= 0.00703125 \times 256 = 1.80\,\mathrm{g}. \end{aligned}$$

The calculation uses the mass of the solvent, rather than the mass or volume of the final solution. No dissociation or association is specified, so the compound is treated as a non-electrolyte.

Step 3: Conclusion The required mass of the compound is $\boxed{1.80\,\mathrm{g}}$.

Quick Tip to Solve: Convert 75 g of benzene to 0.075 kg before applying molality; use the solvent mass, not solution mass.

12. Define an ideal solution and write one of its characteristics. [2 marks]

Solution:

Concept:

- An ideal solution obeys Raoult's law throughout the entire range of composition at a specified temperature.
- For a volatile component i, $p_i = x_i p_i^\circ$, where x_i is its liquid mole fraction and p_i° is the vapour pressure of the pure component.

Step 1: Define the solution A solution is called ideal if the partial vapour pressure of each component is proportional to its mole fraction in the liquid over the whole composition range. For a binary solution, $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$; hence $p_{\text{total}} = x_A p_A^\circ + x_B p_B^\circ$. The temperature is held fixed in stating these relations.

Step 2: State a characteristic An ideal solution has zero enthalpy change on mixing: $\Delta H_{\text{mix}} = 0$. Thus mixing its components neither absorbs nor releases heat. This follows because the unlike molecular interactions are approximately equal in strength to the like interactions they replace; there is no net energetic change on mixing.

Step 3: Conclusion An ideal solution obeys Raoult's law at all compositions. One characteristic is $\boxed{\Delta H_{\text{mix}} = 0}$.

Quick Tip to Solve: State the full composition range in the definition, then give zero heat of mixing as the characteristic.

13. Write two differences between 'order of reaction' and 'molecularity of reaction'. [2 marks]

Solution:

Concept:

- Order is the sum of the powers of reactant concentrations in the experimentally determined rate law.
- Molecularity counts the reacting species taking part in a single elementary reaction step.

Step 1: Compare how they are determined If an observed rate law is $r = k[A]^m[B]^n$, the order is $m+n$, found experimentally. It cannot in general be read from the balanced overall equation. Molecularity, in contrast, is obtained by counting atoms, ions or molecules colliding in the elementary step, as specified by its mechanism. Thus order is an experimental kinetic quantity, whereas molecularity describes the elementary event.

Step 2: Compare allowed numerical values Order can be zero, fractional or an integer: its value is set by the measured concentration dependence of the rate. Molecularity must be a positive integer, usually one, two or three; it cannot be zero or fractional because a reacting event involves a whole number of species. Molecularity is defined for an elementary step, not assigned to an overall complex reaction.

Step 3: Conclusion Two differences are: order is determined experimentally whereas molecularity counts species in an elementary step; order may be zero or fractional whereas molecularity is always

Quick Tip to Solve: Use the measured rate law for order, and count species only in an elementary step for molecularity.

a positive integer.

Quick Tip to Solve: Use the measured rate law for order, and count species only in an elementary step for molecularity.

14. Outline the principles behind the refining of metals by the following methods:

(i) Zone refining method

(ii) Chromatographic method [2 marks]

Solution:

Concept:

- Zone refining depends on a difference in the solubility of impurities in molten and solid metal.
- Chromatographic separation depends on different degrees of adsorption of mixture components on an adsorbent.

Step 1: Explain zone refining The impurities are more soluble in molten metal than in its solid form. A narrow molten zone is produced by a circular heater and moved slowly along the metal rod. As the zone advances, purified metal crystallises behind it while the impurities remain preferentially in the melt and travel with it. Repeated passage concentrates impurities at one end, which is cut off. Thus preferential retention of impurities in the liquid gives very pure solid metal.

Step 2: Explain chromatographic refining Components of a mixture are adsorbed to different extents on a stationary adsorbent such as alumina. The mixture is placed on an adsorbent column and a suitable solvent is passed through it. More strongly adsorbed components move more slowly, while weakly adsorbed components move faster. Their different migration rates separate them into distinct bands, which can be eluted and collected separately to obtain the desired pure component.

Step 3: Conclusion (i) Zone refining: impurities are more soluble in molten metal than in solid metal. (ii) Chromatographic refining: components are separated by their different extents of adsorption on an adsorbent.

Quick Tip to Solve: Link zone refining to liquid-versus-solid solubility, and chromatography to differential adsorption.

15(a). Complete the following chemical equations:

(i) $Ca_3P_2 + H_2O \rightarrow$

(ii) $Cu + H_2SO_4(conc.) \rightarrow$ [2 marks]

Solution:

Concept:

- Metal phosphides react with water to produce phosphine, PH_3, and a metal hydroxide.
- Hot concentrated sulphuric acid is an oxidising agent: it oxidises copper to copper(II) and is reduced to sulphur dioxide.

Quick Tip to Solve: Remember phosphide plus water gives phosphine; concentrated sulphuric acid with copper gives sulphur dioxide.

Step 1: Complete the hydrolysis of calcium phosphide Calcium phosphide gives calcium hydroxide and phosphine on reaction with water. Balance calcium first, then phosphorus, and finally hydrogen and oxygen:

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3 \uparrow.$$

There are three calcium atoms, two phosphorus atoms, six oxygen atoms and twelve hydrogen atoms on each side, so both the products and coefficients are consistent.

Step 2: Complete the oxidation of copper With hot concentrated sulphuric acid, copper forms copper(II) sulphate, sulphur dioxide and water:

$$Cu + 2H_2SO_4(conc.) \xrightarrow{\Delta} CuSO_4 + SO_2 \uparrow + 2H_2O.$$

Copper changes from oxidation state zero to $+2$, losing two electrons. One sulphur atom changes from $+6$ in sulphuric acid to $+4$ in sulphur dioxide, gaining those two electrons; the other sulphur atom remains in sulphate. Hydrogen gas is therefore not the product of this reaction.

Step 3: Conclusion

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3 \uparrow,$$

$$Cu + 2H_2SO_4(conc.) \xrightarrow{\Delta} CuSO_4 + SO_2 \uparrow + 2H_2O.$$

Quick Tip to Solve: Remember phosphide plus water gives phosphine; concentrated sulphuric acid with copper gives sulphur dioxide.

OR

15(b). Arrange the following in the order of property indicated against each set:

(i) HF, HCl, HBr, HI – increasing bond dissociation enthalpy.

(ii) H_2O, H_2S, H_2Se, H_2Te – increasing acidic character. [2 marks]

Solution:

Concept:

- Bond dissociation enthalpy is the energy required to break one mole of gaseous bonds. A longer, weaker bond generally has a smaller dissociation enthalpy.
- For group 16 hydrides, acidic character increases as the central atom becomes larger and the bond to hydrogen becomes weaker down the group.

Step 1: (i) Compare hydrogen halide bond strengths Atomic size increases from fluorine to iodine, so the $H - X$ bond length increases from HF to HI. Orbital overlap becomes less effective and the bond becomes weaker. Thus HI requires the least energy for bond cleavage and HF the most. The increasing bond dissociation enthalpy is

$$HI < HBr < HCl < HF.$$

Step 2: (ii) Compare the acidic character of group 16 hydrides From oxygen to tellurium, the $E - H$

Quick Tip to Solve: Down each group the hydrogen bond weakens: bond dissociation enthalpy falls, while ease of proton release increases.

bond becomes longer and weaker. The release of a proton therefore becomes progressively easier, so the increasing acidic character is

$$H_2O < H_2S < H_2Se < H_2Te.$$

The bond-strength trend governs this comparison down the group; oxygen's high electronegativity alone must not be used to place water as the strongest acid.

Step 3: Conclusion (i) Increasing bond dissociation enthalpy: $HI < HBr < HCl < HF$.
(ii) Increasing acidic character: $H_2O < H_2S < H_2Se < H_2Te$.

Quick Tip to Solve: Down each group the hydrogen bond weakens: bond dissociation enthalpy falls, while ease of proton release increases.

16. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit?

[2 marks]

Solution:

Concept:

- In coordination nomenclature, ligand names precede the metal name and are arranged alphabetically, ignoring multiplicative prefixes. Neutral NH_3 is named ammine and coordinated Cl^- is named chlorido.
- An octahedral complex of type $[MA_4B_2]$ exhibits geometrical isomerism because its two B ligands may be adjacent or opposite.

Step 1: Find the oxidation state and name the complex Let the chromium oxidation state be x. Each ammine ligand is neutral and each chlorido ligand has charge -1. Since the complex has charge $+1$,

$$x + 4(0) + 2(-1) = +1 \quad \Rightarrow \quad x = +3.$$

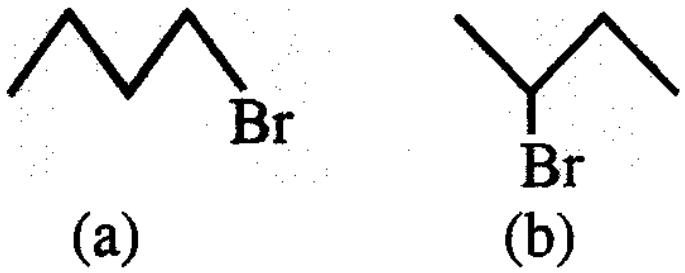
The four ammine ligands give tetraammine, followed alphabetically by dichlorido. As the complex is cationic, the metal retains the name chromium. Its IUPAC name is tetraamminedichloridochromium(III) ion.

Step 2: Identify the possible geometrical arrangements There are six donor atoms around chromium, giving an octahedral arrangement. The two chlorido ligands can occupy adjacent positions with a 90° angle between them (cis), or opposite positions with a 180° angle (trans). These distinct arrangements give geometrical, or cis-trans, isomerism.

Step 3: Conclusion The name is tetraamminedichloridochromium(III) ion. It exhibits geometrical (cis-trans) isomerism.

Quick Tip to Solve: For octahedral $[MA_4B_2]$, place the two B ligands adjacent for cis and opposite for trans; calculate the metal charge before naming it.

17. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?
(ii) Out of S_N1 and S_N2, which reaction occurs with
(a) Inversion of configuration
(b) Racemisation [2 marks]



(a) (b)

Solution:

Concept:

- A tetrahedral carbon bonded to four different groups is a chiral centre. The rate of S_N2 substitution decreases as steric hindrance at the carbon bearing the leaving group increases.
- Backside attack in S_N2 causes inversion. A planar carbocation intermediate in S_N1 permits attack from either face, producing racemisation for a suitable chiral substrate.

Step 1: (i) Identify chirality and compare substitution rates separately Structure (a) is 1-bromobutane, $CH_3CH_2CH_2CH_2Br$; structure (b) is 2-bromobutane, $CH_3CH(Br)CH_2CH_3$. In (b), carbon 2 bears four different groups: Br, H, methyl and ethyl. Hence (b) is chiral. Structure (a) has no such centre and is achiral.

However, (a) is a primary halide whereas (b) is secondary. Backside approach of the nucleophile is less hindered in (a), so (a) undergoes the faster S_N2 reaction under comparable conditions. The two properties asked about belong to different members of the pair.

Step 2: (ii) Relate each stereochemical result to the mechanism (a) Inversion of configuration occurs in S_N2: the nucleophile attacks from the face opposite the leaving group in a single concerted step, reversing the configuration at the reacting chiral centre.

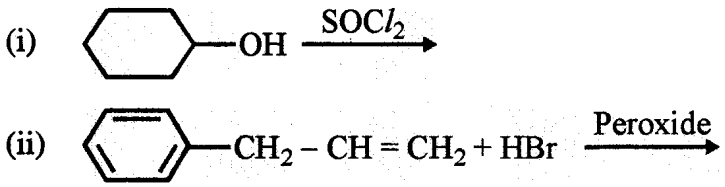
(b) Racemisation occurs in S_N1: loss of the leaving group creates a planar carbocation. Attack from its two faces gives both configurations. The textbook result is racemisation, although ion-pair effects can make it incomplete in practice.

Step 3: Conclusion (i) (b), 2-bromobutane, is chiral; (a), 1-bromobutane, undergoes faster S_N2 reaction.

(ii) Inversion: S_N2; racemisation: S_N1.

Quick Tip to Solve: Check four different groups for chirality, but compare crowding at the C-Br carbon for the substitution rate; these are separate tests.

18. Draw the structure of major monohalo product in each of the following reactions: [2 marks]



Solution:

Concept:

- Thionyl chloride converts an alcohol into an alkyl chloride by replacing its hydroxyl group with chlorine; the carbon skeleton remains unchanged.
- In the presence of peroxide, HBr adds to an unsymmetrical alkene by the free-radical mechanism, giving the anti-Markovnikov product. Bromine bonds to the less substituted carbon of the original double bond.

Step 1: (i) Reaction with thionyl chloride The carbon bearing the $-OH$ group becomes bonded to $-Cl$. Thus, the six-membered saturated ring is retained and chlorocyclohexane is formed:

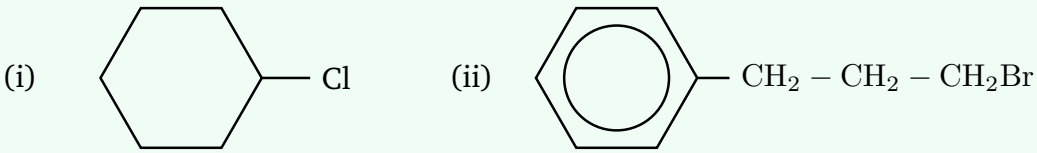
$$C_6H_{11}OH + SOCl_2 \longrightarrow C_6H_{11}Cl + SO_2 + HCl.$$

There is only one halogen atom in the organic product. The first structure below shows the required ring and its chlorine substituent.

Step 2: (ii) Peroxide-directed addition The reactant is $C_6H_5 - CH_2 - CH = CH_2$. Addition of a bromine radical to the terminal carbon gives the more stable secondary radical at the internal carbon. This radical abstracts hydrogen from HBr. Consequently, Br attaches to the terminal carbon and H to the internal carbon:

$$C_6H_5 - CH_2 - CH = CH_2 + HBr \xrightarrow{\text{peroxide}} C_6H_5 - CH_2 - CH_2 - CH_2Br.$$

The benzene ring is unaffected; the product is 1-bromo-3-phenylpropane, shown in the second structure below.



Structures of the major monohalo products

Step 3: Conclusion The major monohalo products are (i) chlorocyclohexane and (ii) 1-bromo-3-phenylpropane, with the structures drawn above.

Quick Tip to Solve: For HBr with peroxide, place Br on the terminal carbon of this side-chain double bond; do not brominate the benzene ring.

19. (a) In reference to Freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of an equation.

(b) Write an important characteristic of lyophilic sols.

(c) Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid. [3 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance at a surface. At a fixed temperature, an adsorption isotherm relates the amount adsorbed per unit mass of adsorbent to the equilibrium gas pressure.
- Lyophilic colloids have a strong affinity between dispersed particles and the dispersion medium. Associated and multimolecular colloids differ in the nature of the aggregates forming their dispersed particles.

Step 1: (a) Write the Freundlich adsorption isotherm For adsorption of a gas on a solid at constant temperature,

$$\boxed{\frac{x}{m} = kp^{1/n}}, \qquad 0 < \frac{1}{n} < 1.$$

Here x is the mass of gas adsorbed, m is the mass of solid adsorbent, p is the equilibrium gas pressure, and k and n are empirical constants for the given gas, adsorbent and temperature. Its logarithmic form is

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p.$$

The empirical power law describes adsorption over a limited pressure range; it is not extrapolated indefinitely to very high pressure.

Step 2: (b) State a characteristic of lyophilic sols Lyophilic sols are reversible: if the dispersion medium is removed, the sol can be re-formed by adding the medium again. This behaviour follows from the strong affinity of the dispersed phase for the medium and the solvation of its particles. Starch sol in water is a familiar example of this class.

Step 3: (c) Give one example of each colloid type An associated colloid is soap in water above its critical micelle concentration and Krafft temperature. Many soap ions associate into micelles that behave as colloidal particles, although at low concentration they behave as ordinary solute particles. A multimolecular colloid is gold sol. Its colloidal particles consist of aggregates of many gold atoms held together by attractive forces. Thus, soap micelles illustrate association of amphiphilic species, whereas gold sol illustrates aggregation of many small atomic units.

Step 4: Conclusion (a) $x/m = kp^{1/n}$ at fixed temperature. (b) Lyophilic sols are reversible. (c) Associated colloid: soap micelles in water; multimolecular colloid: gold sol.

Quick Tip to Solve: Remember the contrast: soap molecules or ions associate into micelles, while many gold atoms aggregate to form particles of gold sol.

20. (a) Draw the structures of the following molecules:

(i) $XeOF_4$

(ii) H_2SO_4

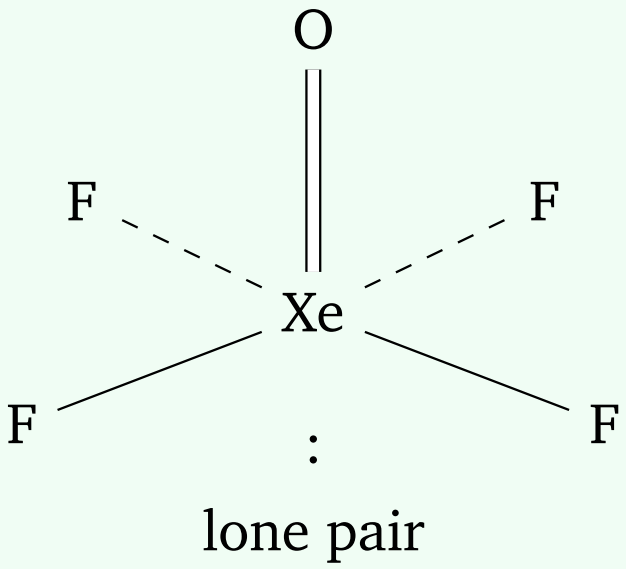
(b) Write the structural difference between white phosphorus and red phosphorus. [3 marks]

Solution:

Concept:

- VSEPR theory counts each bond, whether single or double, as one region of electron density. Lone pairs affect molecular shape but are omitted when naming the arrangement of atoms.
- An allotrope has the same constituent element but a different arrangement of atoms. White phosphorus contains discrete P_4 molecules, whereas red phosphorus has a polymeric network.

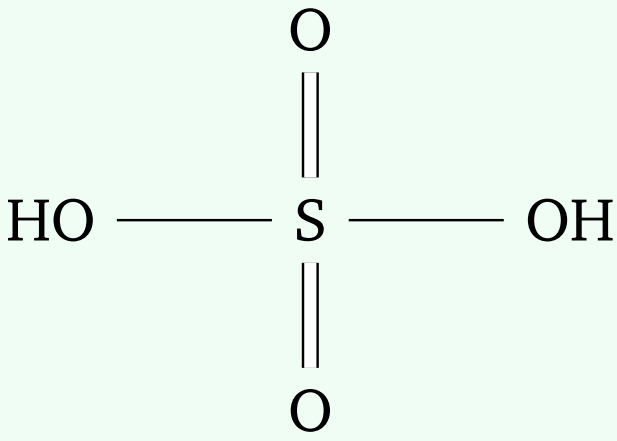
Step 1: (a)(i) Structure of xenon oxytetrafluoride In $XeOF_4$, xenon has four Xe–F bonds, one Xe=O bond and one lone pair. These constitute six electron-pair regions, with an octahedral electron-pair arrangement. The four fluorine atoms occupy the corners of a square base; oxygen occupies the apex and the lone pair lies opposite oxygen. Thus the molecular shape is square pyramidal. The dashed bonds below indicate the two bonds directed behind the plane of the page.



Square-pyramidal XeOF4: oxygen is above the square of fluorine atoms.

Step 2: (a)(ii) Structure of sulphuric acid Sulphuric acid has the connectivity $HO-S(=O)_2-OH$. The central sulphur atom is bonded to four oxygen atoms: two are conventionally shown by double bonds and two belong to hydroxyl groups. The oxygen atoms have an approximately tetrahedral arrangement around sulphur; the drawing displays the connectivity, rather than a planar molecular geometry. Both hydrogen atoms are attached to oxygen, not directly to sulphur.

Quick Tip to Solve: For XeOF4, place the lone pair opposite oxygen; in H2SO4 always attach both hydrogens through oxygen.



Bond connectivity in sulphuric acid.

Step 3: (b) Compare the phosphorus allotropes White phosphorus consists of separate tetrahedral P_4 molecules. Each phosphorus atom is bonded to the other three atoms of its tetrahedron, producing small 60° bond angles and considerable strain. Red phosphorus has a polymeric structure in which phosphorus tetrahedral units are linked together into an extended network, rather than remaining as isolated P_4 molecules. This difference in connectivity distinguishes the two allotropes structurally.

Step 4: Conclusion $XeOF_4$ is square pyramidal; H_2SO_4 has a tetrahedral arrangement of oxygen atoms around sulphur with two S=O and two S–OH linkages. White phosphorus contains discrete tetrahedral P_4 molecules, while red phosphorus is polymeric.

Quick Tip to Solve: For XeOF4, place the lone pair opposite oxygen; in H2SO4 always attach both hydrogens through oxygen.

21. Account for the following:

(i) PCl_5 is more covalent than PCl_3.

(ii) Iron on reaction with HCl forms $FeCl_2$ and not $FeCl_3$.

(iii) The two O-O bond lengths in the ozone molecule are equal. [3 marks]

Solution:

Concept:

- According to Fajans' rule, a higher positive charge and smaller size increase a cation's polarising power, increasing covalent character. For phosphorus chlorides, this supplies the conventional comparison using the formal oxidation states of phosphorus.
- A non-oxidising acid liberates hydrogen on reaction with suitable metals; resonance makes equivalent bonds acquire an intermediate bond order.

Step 1: (i) Greater covalent character of PCl5 The formal oxidation state of phosphorus is $+5$ in PCl_5, compared with $+3$ in PCl_3. The higher formal positive charge corresponds to a greater polarising power of the phosphorus centre. It distorts the electron cloud associated with chlorine more strongly,

Quick Tip to Solve: Match each observation with its principle: polarisation for covalency, acid oxidising ability for iron, and resonance for ozone bond equivalence.

increasing electron sharing and hence covalent character. This is the Fajans'-rule explanation for the stated comparison; the oxidation-state notation is a formal model and does not imply free P^{5+} ions in a molecular sample.

Step 2: (ii) Formation of ferrous chloride with hydrochloric acid Hydrochloric acid is a non-oxidising acid. Iron displaces hydrogen ions to give iron(II) chloride:

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2 \uparrow.$$

Under these conditions HCl does not oxidise Fe^{2+} further to Fe^{3+}. Moreover, any ferric ions in contact with excess metallic iron are reduced to ferrous ions:

$$2Fe^{3+} + Fe \longrightarrow 3Fe^{2+}.$$

Consequently the chloride obtained from iron and dilute HCl is $FeCl_2$, not $FeCl_3$.

Step 3: (iii) Equal bond lengths in ozone Ozone has two equivalent resonance contributors:

$$O = O^+ - O^- \longleftrightarrow {}^-O - O^+ = O.$$

Neither contributor alone describes the molecule. The actual molecule is a resonance hybrid with delocalised pi bonding across the three oxygen atoms. Thus neither O–O linkage remains a localised single bond or a localised double bond. Each has the same average bond order, $(1 + 2)/2 = 1.5$, so both have equal lengths, intermediate between typical O–O single and O=O double bonds. Resonance does not mean that the molecule alternates between two structures.

Step 4: Conclusion The comparison of phosphorus chlorides follows the greater polarising power of phosphorus in its higher oxidation state; non-oxidising HCl gives iron(II) chloride; and resonance makes the two O–O bonds in ozone equivalent.

Quick Tip to Solve: Match each observation with its principle: polarisation for covalency, acid oxidising ability for iron, and resonance for ozone bond equivalence.

22. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given: log 4 = 0.6021, log 2 = 0.3010) [3 marks]

Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log\dfrac{p_0}{p_A}$, where p_0 is the initial reactant pressure and p_A its partial pressure at time t.
- At constant temperature and volume, gas pressure is proportional to amount. For $A(g) \rightarrow B(g) + C(g)$, each amount decomposed produces an equal increase in total pressure.

Step 1: Relate total pressure to the extent of decomposition Initially only SO_2Cl_2 is present, so $p_0 = 0.4\,\text{atm}$. Let x be the pressure equivalent of reactant decomposed after $100\,\text{s}$. The partial pressures of SO_2Cl_2, SO_2 and Cl_2 are respectively $0.4 - x$, x and x. Hence

$$P_t = (0.4 - x) + x + x = 0.4 + x.$$

Since $P_t = 0.7\,\text{atm}$, $x = 0.3\,\text{atm}$.

Step 2: Find the remaining reactant pressure The reactant partial pressure, which must be used in the integrated rate equation, is

$$p_A = p_0 - x = 0.4 - 0.3 = 0.1\,\text{atm}.$$

Equivalently, $p_A = 2p_0 - P_t$. Thus one-quarter of the initial reactant remains after $100\,\text{s}$; the total pressure itself is not the reactant pressure.

Step 3: Apply the integrated first-order equation Substitution gives

$$\begin{aligned} k &= \frac{2.303}{100}\log\frac{0.4}{0.1} \\ &= \frac{2.303}{100}\log 4 \\ &= \frac{2.303 \times 0.6021}{100} \\ &= 0.013866\,\text{s}^{-1}. \end{aligned}$$

The pressure ratio is dimensionless and time is in seconds, so the rate constant has units s^{-1}.

Step 4: Conclusion The rate constant is $\boxed{k \approx 1.39 \times 10^{-2}\,\text{s}^{-1}}$.

Quick Tip to Solve: For a one-to-two gaseous decomposition, first calculate the reactant pressure as $2p_0 - P_t$; never insert total pressure directly.

23. (i) Give two examples of macromolecules that are chosen as drug targets.

(ii) What are antiseptics? Give an example.

(iii) Why is use of aspartame limited to cold foods and soft drinks? [3 marks]

Solution:

Concept:

- Drugs act by interacting with biological macromolecules, including proteins and nucleic acids; their action depends on the target and its biological role.
- Antiseptics control microorganisms on living tissues. Artificial sweeteners must remain chemically stable under the conditions in which the food is prepared.

Step 1: Identify two macromolecular drug targets (i) Two examples are **proteins** and **nucleic acids**. Proteins include enzymes that catalyse reactions and receptors involved in communication between cells. A drug can alter biological activity by binding to such a target. Nucleic acids are another class of large biomolecules with which drugs can interact. These names identify the target macromolecules, rather than small molecules used as medicines.

Step 2: Define antiseptics and give an example (ii) Antiseptics are substances that kill microorganisms or prevent their growth and can be applied to **living tissues**, such as wounds, cuts and diseased skin. **Dettol** is an example; it contains chloroxylenol and terpineol. Their use on living tissue distinguishes antiseptics from disinfectants intended for non-living surfaces. The concentration and intended application matter when an antimicrobial chemical is used.

Step 3: Explain the temperature restriction on aspartame (iii) Aspartame is an artificial sweetener that is **unstable at cooking temperature**. It decomposes on heating, so it cannot retain its intended sweetening effect reliably in hot preparations. Its use is therefore limited to cold foods and soft drinks, where exposure to the high temperatures of cooking is avoided. This limitation concerns thermal stability, rather than an inability to sweeten a cold food.

Step 4: Conclusion (i) Proteins and nucleic acids. (ii) Antiseptics kill or inhibit microorganisms on living tissues; example: Dettol. (iii) Aspartame decomposes at cooking temperature.

Quick Tip to Solve: For antiseptics, include the phrase living tissues; for aspartame, connect cold-food use directly to decomposition on heating.

24. (i) Deficiency of which vitamin causes night-blindness?

(ii) Name the base that is found in nucleotide of RNA only.

(iii) Glucose on reaction with HI gives n-hexane. What does it suggest about the structure of glucose? [3 marks]

Solution:

Concept:

- Vitamins support specific physiological functions; characteristic deficiency symptoms identify the vitamin involved.
- RNA and DNA differ in one of their usual pyrimidine bases. Reduction with HI can reveal the

Quick Tip to Solve: Read HI reduction as a carbon-skeleton test: formation of n-hexane identifies an unbranched chain of six carbons.

connectivity of the carbon skeleton of a carbohydrate.

Step 1: Identify the vitamin related to night vision (i) Deficiency of **vitamin A** causes night-blindness. Vitamin A is associated with the visual process and enables normal vision in dim light. Therefore impaired vision under low-light conditions points to its deficiency. Night-blindness is the characteristic symptom asked for here; it should not be confused with scurvy from vitamin C deficiency or rickets associated with vitamin D deficiency.

Step 2: Identify the base characteristic of RNA (ii) The base is **uracil**. In the usual nucleotide composition, RNA contains adenine, guanine, cytosine and uracil, whereas DNA contains thymine in place of uracil. Adenine, guanine and cytosine occur in both nucleic acids, so none of those three distinguishes RNA from DNA in this question. The required answer is the nitrogenous base, rather than the sugar ribose.

Step 3: Interpret formation of n-hexane from glucose (iii) Prolonged heating of glucose with HI gives n-hexane, whose carbon skeleton is

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3.$$

This suggests that all **six carbon atoms of glucose are joined in one straight, unbranched chain**. Under this reduction the oxygen-containing groups are removed while the carbon skeleton is retained. The product therefore supplies evidence about carbon connectivity; this observation alone does not locate every hydroxyl group or establish all stereochemical details of glucose.

Step 4: Conclusion (i) Vitamin A. (ii) Uracil. (iii) The six carbon atoms of glucose form a straight, unbranched carbon chain.

Quick Tip to Solve: Read HI reduction as a carbon-skeleton test: formation of n-hexane identifies an unbranched chain of six carbons.

25. After the ban on plastic bags, students of one school decided to make the people aware of the harmful effects of plastic bags on environment and Yamuna River. To make the awareness more impactful, they organized rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All students pledged not to use polythene bags in future to save Yamuna River.

After reading the above passage, answer the following questions:

(i) What values are shown by the students?

(ii) What are biodegradable polymers? Give one example.

(iii) Is polythene a condensation or an addition polymer? [3 marks]

Solution:

Concept:

- Environmental responsibility means choosing and promoting practices that reduce pollution and conserve natural resources.
- Biodegradable polymers are polymers that microorganisms can break down through biological

Quick Tip to Solve: Classify polythene by opening the ethene double bond: no water or other small molecule is lost.

processes; susceptible linkages in their chains allow degradation.

- Addition polymerisation joins unsaturated monomers without eliminating small molecules; condensation polymerisation generally eliminates small molecules such as water.

Step 1: (i) Identify the values shown The students show environmental awareness, social responsibility, concern for public health and respect for natural resources. Joining hands with other schools demonstrates cooperation and collective action. Distributing paper bags shows initiative and a practical commitment to reducing plastic waste, while the pledge reflects responsible citizenship and concern for the Yamuna River.

Step 2: (ii) Define a biodegradable polymer and give an example A biodegradable polymer is one that can be decomposed by microorganisms, such as bacteria, through enzymatic action. An example is PHBV, poly(β-hydroxybutyrate-co-β-hydroxyvalerate), a biodegradable polyester. Its ester linkages can undergo cleavage during biological degradation; hence it does not persist in the same manner as ordinary polythene.

Step 3: (iii) Classify polythene Polythene forms by addition polymerisation of ethene. The carbon-carbon double bonds open and the monomer units link into a long chain:

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

No small molecule is eliminated during this process. The formation of the saturated carbon-chain backbone therefore identifies it as an addition polymer.

Step 4: Conclusion (i) Environmental awareness, cooperation and social responsibility; (ii) a polymer decomposed by microorganisms, for example PHBV; (iii) polythene is an addition polymer.

Quick Tip to Solve: Classify polythene by opening the ethene double bond: no water or other small molecule is lost.

26. (a) Write the mechanism of the following reaction:

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

(b) Write the equation involved in Reimer-Tiemann reaction. [3 marks]

Solution:

Concept:

- An alcohol reacts with hydrogen bromide after protonation converts its poor leaving group into water.
- For a primary alcohol such as ethanol, bromide displaces water by a concerted nucleophilic substitution mechanism.
- The Reimer–Tiemann reaction introduces a formyl group mainly ortho to the hydroxyl group of phenol using chloroform and aqueous alkali, followed by acidification.

Step 1: (a) Protonate the hydroxyl group Hydrogen bromide provides H^+ and Br^-. The oxygen lone pair accepts a proton:

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2^+.$$

Quick Tip to Solve: For ethanol with HBr, protonate oxygen first and show bromide displacing water without a primary carbocation.

This changes the leaving group from hydroxide, which is a poor leaving group, to neutral water. The oxygen now bears the positive charge.

Step 2: (a) Bromide attacks the primary carbon The bromide ion attacks the carbon bonded to oxygen from the side opposite the carbon-oxygen bond. Bond formation with bromide and cleavage of the carbon-oxygen bond occur together:

$$Br^- + CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2Br + H_2O.$$

This is an S_N2 step; a free primary ethyl carbocation is not required. Adding the two steps gives the reaction stated in the question.

Step 3: (b) Write the Reimer–Tiemann equation Phenol reacts with chloroform and aqueous sodium hydroxide on heating. Acidification gives predominantly 2-hydroxybenzaldehyde (salicylaldehyde):

$$C_6H_5OH + CHCl_3 + 3NaOH$$

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

The hydroxyl and formyl groups in the major product occupy adjacent ring positions. A small amount of the para isomer may also form.

Step 4: Conclusion Ethanol gives bromoethane through protonation followed by bromide displacement of water. The Reimer–Tiemann reaction gives mainly ortho-hydroxybenzaldehyde from phenol.

Quick Tip to Solve: For ethanol with HBr, protonate oxygen first and show bromide displacing water without a primary carbocation.

27(a). Give the structures of A, B and C in the following reactions:

(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\,K]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2+KOH} B \xrightarrow{CHCl_3+NaOH} C$ [3 marks]

Solution:

Concept:

- KCN replaces bromide by carbon-bonded cyanide, adding one carbon. $LiAlH_4$ reduces nitriles to primary amines.
- Aliphatic primary amines react with nitrous acid to give alcohols. Hofmann degradation removes the carbonyl carbon of an amide.
- The carbylamine reaction converts a primary amine into an isocyanide, $R - N \equiv C$.

Step 1: (i) Follow cyanide substitution and reduction Methyl bromide undergoes nucleophilic substitution with KCN: $CH_3Br + KCN \longrightarrow CH_3C \equiv N + KBr$. Thus A is ethanenitrile, $CH_3C \equiv N$. Reduction of its nitrile group by $LiAlH_4$, followed by hydrolysis, gives $CH_3CN + 4[H] \longrightarrow CH_3CH_2NH_2$. Therefore B is ethanamine.

Step 2: (i) Treat the amine with nitrous acid At 273 K, the primary aliphatic amine reacts with nitrous

Quick Tip to Solve: Count carbons: KCN adds one carbon; Hofmann degradation removes one; carbylamine gives R-NC, not R-CN.

acid to give ethanol: $CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O$. Hence C is CH_3CH_2OH. Nitrogen evolution accompanies replacement of the amino group by hydroxyl.

Step 3: (ii) Form the amide, then shorten the carbon chain Heating ammonium ethanoate, formed from ethanoic acid and ammonia, gives ethanamide:

$$CH_3COOH + NH_3 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Thus A is CH_3CONH_2. Hofmann degradation gives

$$CH_3CONH_2 + Br_2 + 4KOH$$

$$\longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Therefore B is methanamine, containing one fewer carbon than the amide.

Step 4: (ii) Apply the carbylamine reaction Methanamine reacts with chloroform and sodium hydroxide on heating:

$$CH_3NH_2 + CHCl_3 + 3NaOH$$

$$\longrightarrow CH_3N \equiv C + 3NaCl + 3H_2O.$$

Thus C is methyl isocyanide, $CH_3 - N \equiv C$. The methyl group is attached through nitrogen, unlike the nitrile in (i).

Step 5: Conclusion (i) $A = CH_3CN$, $B = CH_3CH_2NH_2$, $C = CH_3CH_2OH$. (ii) $A = CH_3CONH_2$, $B = CH_3NH_2$, $C = CH_3NC$.

Quick Tip to Solve: Count carbons: KCN adds one carbon; Hofmann degradation removes one; carbylamine gives R-NC, not R-CN.

OR

27(b). How will you convert the following:

(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine

(iii) Aniline into N-phenylethanamide (Write the chemical equations involved.) [3 marks]

Solution:

Concept:

- A nitro group is reduced to a primary amino group without changing the benzene ring; acidic reduction initially gives an anilinium salt, which is liberated with alkali.
- Hofmann bromamide degradation converts an amide into a primary amine containing one carbon atom fewer. Acylation replaces one amino hydrogen by an acetyl group.

Step 1: (i) Reduce nitrobenzene and liberate aniline Heat nitrobenzene with tin and hydrochloric

Quick Tip to Solve: For ethanoic acid to methanamine, form the amide first: Hofmann degradation removes its carbonyl carbon.

acid, then add sodium hydroxide. The balanced reduction and liberation equations are

$$C_6H_5NO_2 + 3Sn + 7HCl \longrightarrow C_6H_5NH_3Cl + 3SnCl_2 + 2H_2O,$$

$$C_6H_5NH_3Cl + NaOH \longrightarrow C_6H_5NH_2 + NaCl + H_2O.$$

The final alkali treatment is needed because aniline is protonated in the acidic reaction mixture.

Step 2: (ii) Form ethanamide, then use Hofmann degradation First react ethanoic acid with ammonia to form ammonium ethanoate, which loses water on heating:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Heat ethanamide with bromine and aqueous potassium hydroxide:

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

The carbonyl carbon is removed during degradation, so the two-carbon acid yields one-carbon methanamine.

Step 3: (iii) Acetylate aniline Treat aniline with ethanoic anhydride. The amino nitrogen undergoes acylation to give N-phenylethanamide (acetanilide):

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

The phenyl group remains bonded to nitrogen; the new group attached to nitrogen is CH_3CO-.

Step 4: Conclusion The required conversions use (i) Sn/HCl, then $NaOH$; (ii) NH_3, heat, then Br_2/KOH; and (iii) ethanoic anhydride, giving aniline, methanamine and N-phenylethanamide respectively.

Quick Tip to Solve: For ethanoic acid to methanamine, form the amide first: Hofmann degradation removes its carbonyl carbon.

28(a). Define the following terms:

(i) Limiting molar conductivity

(ii) Fuel cell

(b) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 $\times$ 10^{-2} Ω^{-1} cm^{-1}. [5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in $S\,cm^{-1}$ and concentration c in $mol\,L^{-1}$. Its limiting value is obtained as concentration tends to zero.

Quick Tip to Solve: Calibrate the cell once using $\kappa_1 R_1$; divide that constant by the new resistance before applying $1000\kappa/c$.

- For a cell with electrode separation l and area A, the cell constant is $G^* = l/A = \kappa R$, where R is the measured resistance. It is unchanged when the same cell is filled with another solution.

Step 1: (a)(i) Define limiting molar conductivity Limiting molar conductivity, Λ_m°, is the molar conductivity of an electrolyte at infinite dilution, that is, in the limit as its concentration approaches zero:

$$\Lambda_m^\circ = \lim_{c \to 0} \Lambda_m.$$

At this limit, interactions between ions are negligible and each ion makes its independent contribution to the total molar conductivity. Its unit is $\mathrm{S\,cm^2\,mol^{-1}}$ when centimetre-based conductivity units are used.

Step 2: (a)(ii) Define a fuel cell A fuel cell is a galvanic cell that converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy. It operates as long as these reactants are supplied and products are removed. For example, a hydrogen-oxygen fuel cell uses hydrogen as fuel and oxygen as oxidant, with the overall reaction

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

Step 3: (b) Determine the cell constant using the standard solution The known conductivity and resistance of the $0.1\,\mathrm{mol\,L^{-1}}$ KCl solution give

$$\begin{aligned} G^* &= \kappa_1 R_1 \\ &= (1.29 \times 10^{-2}\,\mathrm{S\,cm^{-1}})(100\,\Omega) \\ &= 1.29\,\mathrm{cm^{-1}}. \end{aligned}$$

Here $\mathrm{S} = \Omega^{-1}$, so the resistance unit cancels. The geometry of the cell, and hence this constant, remains the same for the second solution.

Step 4: Calculate conductivity of the dilute solution Using $R_2 = 520\,\Omega$,

$$\begin{aligned} \kappa_2 &= \frac{G^*}{R_2} = \frac{1.29}{520}\,\mathrm{S\,cm^{-1}} \\ &= 2.48077 \times 10^{-3}\,\mathrm{S\,cm^{-1}}. \end{aligned}$$

The larger resistance is consistent with a smaller conductivity for the more dilute KCl solution.

Step 5: Convert conductivity to molar conductivity For $c_2 = 0.02\,\mathrm{mol\,L^{-1}}$, the factor 1000 converts the volume from litres to cubic centimetres:

$$\begin{aligned} \Lambda_{m,2} &= \frac{1000\kappa_2}{c_2} \\ &= \frac{1000(2.48077 \times 10^{-3})}{0.02} \\ &= 124.04\,\mathrm{S\,cm^2\,mol^{-1}}. \end{aligned}$$

Keep the unrounded conductivity until this final calculation to avoid rounding error.

Step 6: Conclusion For $0.02\,\mathrm{mol\,L^{-1}}$ KCl, $\boxed{\kappa = 2.48 \times 10^{-3}\,\Omega^{-1}\mathrm{cm^{-1}}}$ and $\boxed{\Lambda_m = 124\,\Omega^{-1}\mathrm{cm^2\,mol^{-1}}}$.

Quick Tip to Solve: Calibrate the cell once using $\kappa_1 R_1$; divide that constant by the new resistance before applying $1000\kappa/c$.

OR

28(b). (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu.

(b) Calculate emf of the following cell at 298 K:

Mg(s) | Mg^{2+}(0.1 M) || Cu^{2+}(0.01) | Cu(s)

[Given E°_{cell} = +2.71 V, 1 F = 96500 C mol^{-1}] [5 marks]

Solution:

Concept:

- Faraday's first law states that the mass m of a substance deposited or liberated at an electrode is directly proportional to the charge Q passed through the electrolyte: $m = ZQ = ZIt$, where Z is its electrochemical equivalent, I is current and t is time.
- One faraday is the charge carried by one mole of electrons, $F = 96500\,\text{C mol}^{-1}$. The electrode equation determines how many moles of electrons a reduction needs.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q_r$, where n is the number of electrons transferred per cell reaction and Q_r is its reaction quotient. Pure solids have unit activity.

Step 1: (a) State the law and determine the electron requirement Faraday's first law gives $m \propto Q$. Thus doubling the charge passed doubles the mass deposited for the same electrode reaction. Since $Q = It$, a constant current deposits mass proportional to the electrolysis time. For copper deposition the balanced half-reaction is

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

Each copper ion gains two electrons. Therefore, reduction of 1 mol of Cu^{2+} requires 2 mol of electrons. The required charge is

$$Q = 2F = 2(96500) = 193000\,\text{C}.$$

Step 2: (b) Write the spontaneous cell reaction and its quotient Magnesium is oxidised at the left electrode and copper ions are reduced at the right electrode:

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

On adding, $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$. Hence $n = 2$. Omitting the pure solids and using the given molar concentrations,

$$Q_r = \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.1}{0.01} = 10.$$

Step 3: Substitute in the Nernst equation With $E^{\circ}_{\text{cell}} = 2.71\,\text{V}$ and $\log 10 = 1$,

$$E_{\text{cell}} = 2.71 - \frac{0.0591}{2}\log 10$$
$$= 2.71 - 0.02955 = 2.68045\,\text{V}.$$

Quick Tip to Solve: Balance the electrode equations first: their two-electron transfer fixes both the copper charge and the denominator in the Nernst correction.

The product-ion concentration exceeds the reactant-ion concentration, so the reaction quotient is greater than unity and the emf is slightly below the standard emf, as expected.

Step 4: Conclusion (a) $m = ZQ = ZIt$; the required charge is $\boxed{2F = 1.93 \times 10^5\,\text{C}}$. (b) The cell emf at 298 K is $\boxed{2.68\,\text{V}}$.

Quick Tip to Solve: Balance the electrode equations first: their two-electron transfer fixes both the copper charge and the denominator in the Nernst correction.

29(a). **How do you prepare:**

(i) K_2MnO_4 from MnO_2?

(ii) $Na_2Cr_2O_7$ from Na_2CrO_4? [2 marks]

Solution:

Concept:

- Manganese dioxide contains manganese in oxidation state $+4$; potassium manganate contains manganese in oxidation state $+6$. Its preparation therefore requires oxidation in an alkaline medium.
- Acidification shifts the chromate-dichromate equilibrium towards dichromate. Chromium remains in oxidation state $+6$, so this conversion is not a redox reaction.

Step 1: (i) Prepare potassium manganate from manganese dioxide Fuse MnO_2 with potassium hydroxide in the presence of air or oxygen. Oxygen oxidises manganese from $+4$ to $+6$, producing green potassium manganate:

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

The strongly alkaline conditions supply potassium ions and favour formation of the manganate ion. The oxygen supplied during fusion is the oxidising agent.

Step 2: (ii) Prepare sodium dichromate from sodium chromate Acidify an aqueous solution of sodium chromate with sulphuric acid:

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

The underlying ionic equilibrium is

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O.$$

Addition of acid consumes chromate to form dichromate; the yellow chromate solution becomes orange. No oxidising agent is needed because chromium's oxidation state does not change.

Step 3: Conclusion K_2MnO_4 is obtained by oxidative alkaline fusion of MnO_2 with KOH in oxygen; $Na_2Cr_2O_7$ is obtained by acidifying Na_2CrO_4 with sulphuric acid.

Quick Tip to Solve: Remember the conditions: manganate requires hot alkali and oxygen, whereas dichromate formation requires acidification of chromate.

29(b). Account for the following:

(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

(ii) The enthalpy of atomization is lowest for Zn in 3d series of the transition elements.

(iii) Actinoid elements show wide range of oxidation states. [3 marks]

Solution:

Concept:

- A half-filled d^5 subshell has extra stability. Oxidation removes an electron, so the relative stability of the initial and final electronic configurations determines how readily a metal ion is oxidised.
- Enthalpy of atomisation measures the energy needed to separate a metal into gaseous atoms; stronger metallic bonding gives a higher value. Comparable orbital energies allow different numbers of electrons to participate in bonding.

Step 1: (i) Compare the configurations before and after oxidation Mn^{2+} has configuration $[Ar]3d^5$, whereas Fe^{2+} has $[Ar]3d^6$. Oxidising Mn^{2+} to Mn^{3+} destroys its stable half-filled configuration and produces $3d^4$. In contrast, oxidation of Fe^{2+} produces Fe^{3+}, which has the stable half-filled $3d^5$ configuration. Hence Mn^{2+} resists oxidation more strongly.

Step 2: (ii) Relate zinc's configuration to metallic bonding Zinc has the configuration $[Ar]3d^{10}4s^2$. Its completely filled $3d$ subshell contains no unpaired electrons and contributes little to the strong metallic bonding associated with partially filled d subshells. The metallic bonding in zinc is consequently weak compared with the other members of this series, so the energy required to form separated gaseous atoms is the lowest.

Step 3: (iii) Explain the variable valencies of actinoids In actinoids, the energies of the $5f$, $6d$ and $7s$ orbitals are relatively close. Therefore, electrons from these subshells can participate in bonding or be removed in different numbers. This availability of both inner $5f$ and outer electrons accounts for the wide range of oxidation states exhibited by actinoid elements.

Step 4: Conclusion The reasons are the half-filled $3d^5$ stability of Mn^{2+}, weak metallic bonding associated with zinc's filled $3d^{10}$ subshell, and the comparable energies of actinoid $5f$, $6d$ and $7s$ orbitals, respectively.

Quick Tip to Solve: Write the d-electron configurations on both sides of an oxidation before comparing the stability of metal ions.

OR

29(b). (i) Name the element of 3d transition series which shows maximum number of oxidation states. Why does it show so?

(ii) Which transition metal of 3d series has positive $E^\circ(M^{2+}/M)$ value and why?

(iii) Out of Cr^{3+} and Mn^{3+}, which is a stronger oxidizing agent and why?

(iv) Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

(v) Complete the following equation: $MnO_4^- + 8H^+ + 5e^- \rightarrow$ [5 marks]

Solution:

Concept:

- Transition-metal oxidation states depend on the availability of both $(n-1)d$ and ns electrons. Half-filled d^5 and certain other configurations such as d^3 provide enhanced stability.
- The standard electrode potential $E^\circ(\mathrm{M^{2+}/M})$ describes the reduction $\mathrm{M^{2+} + 2e^- \rightarrow M}$. Its sign reflects the combined effects of atomisation, ionisation and hydration energies.
- A reduction half-equation must conserve every element and electric charge; in acidic medium, oxygen is balanced with water and hydrogen with $\mathrm{H^+}$.

Step 1: (i) Identify the element with the greatest variety of oxidation states Manganese shows the maximum number of oxidation states in the $3d$ series, commonly from $+2$ to $+7$. Its electronic configuration is $[\mathrm{Ar}]3d^5 4s^2$. The five $3d$ electrons and two $4s$ electrons can participate in bonding because their orbital energies are sufficiently close; hence different numbers of these seven electrons can be used.

Step 2: (ii) Explain the positive potential of copper Copper has a positive $E^\circ(\mathrm{Cu^{2+}/Cu})$, approximately $+0.34\,\mathrm{V}$. The energy required for atomisation and removal of two electrons from copper is high, particularly because the second electron must be removed from the stable $3d^{10}$ configuration of $\mathrm{Cu^+}$. The hydration energy released on forming $\mathrm{Cu^{2+}(aq)}$ does not compensate for this energy requirement. Thus conversion of the metal to aqueous $\mathrm{Cu^{2+}}$ is unfavourable under standard conditions, giving a positive reduction potential.

Step 3: (iii) Compare the oxidising powers $\mathrm{Mn^{3+}}$ is the stronger oxidising agent. It accepts an electron readily to change from $3d^4$ to the stable half-filled $3d^5$ configuration of $\mathrm{Mn^{2+}}$. By contrast, $\mathrm{Cr^{3+}}$ already has a stable $3d^3$ configuration; reduction to $\mathrm{Cr^{2+}}$, which is $3d^4$, is less favourable. Therefore $\mathrm{Mn^{3+}}$ has the greater tendency to be reduced and to oxidise another species.

Step 4: (iv) Give a lanthanoid exhibiting the +2 state Europium, Eu, is well known to exhibit the $+2$ oxidation state. Loss of its two $6s$ electrons gives $\mathrm{Eu^{2+}}$ with the particularly stable half-filled $4f^7$ configuration, $[\mathrm{Xe}]4f^7$.

Step 5: (v) Complete and check the acidic permanganate half-equation Manganese changes from $+7$ in permanganate to $+2$, accepting five electrons. The four oxygen atoms form four water molecules using the eight protons:

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

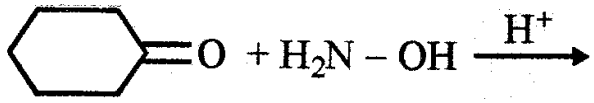
There is one manganese atom, four oxygen atoms and eight hydrogen atoms on each side. The net charge on the left is $-1+8-5=+2$, equal to the charge on the right, so the half-equation is balanced.

Quick Tip to Solve: For oxidising power, compare the configuration produced by electron gain, since the stronger oxidising agent is more readily reduced.

Step 6: Conclusion (i) Manganese; (ii) copper; (iii) Mn^{3+}; (iv) europium; (v) the products are $Mn^{2+} + 4H_2O$.

Quick Tip to Solve: For oxidising power, compare the configuration produced by electron gain, since the stronger oxidising agent is more readily reduced.

30(a). Write the products of the following reactions: [3 marks]

(i) 

(ii) $2\,C_6H_5CHO + \text{conc. } NaOH \longrightarrow$

(iii) $CH_3COOH \xrightarrow{Cl_2/P}$

Solution:

Concept:

- A carbonyl compound reacts with hydroxylamine, NH_2OH, to form an oxime by condensation, eliminating one molecule of water.
- An aldehyde without an alpha hydrogen undergoes Cannizzaro disproportionation in concentrated alkali. The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen.

Step 1: Hydroxylamine gives cyclohexanone oxime The carbonyl oxygen of cyclohexanone is replaced by the $=N-OH$ group. The ring remains unchanged, and water is eliminated:

$$C_6H_{10}O + NH_2OH \xrightarrow{H^+} C_6H_{11}NO + H_2O.$$

The organic product is cyclohexanone oxime; its ring carbon that originally carried $=O$ now carries $=N-OH$.

Step 2: Concentrated alkali gives Cannizzaro products Benzaldehyde has no alpha hydrogen, so it does not undergo aldol condensation. Two molecules disproportionate: one is reduced to benzyl alcohol and the other is oxidised to the benzoate ion.

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa.$$

The medium is alkaline, so the oxidation product is sodium benzoate rather than free benzoic acid.

Step 3: Chlorination at the alpha carbon Chlorine in the presence of phosphorus brings about the Hell–Volhard–Zelinsky reaction of ethanoic acid. An alpha hydrogen is replaced by chlorine:

$$CH_3COOH + Cl_2 \xrightarrow{P} ClCH_2COOH + HCl.$$

The organic product is 2-chloroethanoic acid, commonly called chloroacetic acid.

Step 4: Conclusion The products are (i) cyclohexanone oxime, (ii) benzyl alcohol and sodium

Quick Tip to Solve: In concentrated NaOH, write the carboxylate salt for the Cannizzaro oxidation product.

benzoate, and (iii) chloroacetic acid.

Quick Tip to Solve: In concentrated NaOH, write the carboxylate salt for the Cannizzaro oxidation product.

30(b). Give simple chemical tests to distinguish between the following pairs of compounds:
(i) Benzaldehyde and Benzoic acid
(ii) Propanal and Propanone [2 marks]

Solution:

Concept:

- Carboxylic acids release carbon dioxide with aqueous sodium hydrogen carbonate; aldehydes do not.
- Tollens' reagent oxidises an aldehyde to a carboxylate ion and deposits silver. Simple ketones do not give this test.

Step 1: Benzaldehyde and benzoic acid Add aqueous sodium hydrogen carbonate separately to the two compounds. Benzoic acid gives brisk effervescence of carbon dioxide, whereas benzaldehyde gives no effervescence.

$$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2 \uparrow + H_2O.$$

The evolved gas turns limewater milky, confirming carbon dioxide.

Step 2: Propanal and propanone Warm separate samples gently with freshly prepared Tollens' reagent. Propanal gives a silver mirror because its aldehyde group is oxidised; propanone gives no silver mirror. The ionic equation for propanal is

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Thus the visible observations distinguish the members of each pair directly.

Step 3: Conclusion Benzoic acid alone effervesces with $NaHCO_3$; propanal alone gives a silver mirror with Tollens' reagent.

Quick Tip to Solve: Use bicarbonate for an acid versus aldehyde, and Tollens reagent for an aldehyde versus ketone.

OR

30(a). Account for the following:

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(ii) Carboxylic acid is a stronger acid than phenol. [2 marks]

Solution:

Concept:

- Nucleophilic addition is favoured by greater positive character at the carbonyl carbon and by lower steric hindrance.
- Acid strength increases with the stability of the conjugate base produced after loss of H^+.

Step 1: Ethanal reacts faster with HCN In addition of HCN, CN^- attacks the electrophilic carbonyl carbon. Ethanal has one methyl group and one hydrogen attached to this carbon; propanone has two methyl groups. The extra electron-releasing methyl group in propanone decreases the positive character at its carbonyl carbon through the $+I$ effect. It also creates greater steric hindrance to attack by CN^-. Ethanal therefore undergoes nucleophilic addition more readily.

Step 2: Carboxylic acid is stronger than phenol A carboxylic acid forms a carboxylate ion, $RCOO^-$, whose negative charge is delocalised equally over two electronegative oxygen atoms in two equivalent resonance structures. Phenol forms the phenoxide ion, in which delocalisation puts some negative charge on less electronegative ring carbon atoms; its resonance structures are not equivalent. The carboxylate ion is consequently more effectively stabilised than phenoxide, so loss of a proton is more favourable for a carboxylic acid.

Step 3: Conclusion Ethanal is more reactive because it has less electron donation and less steric hindrance. Carboxylic acids are stronger because their conjugate bases have greater resonance stabilisation.

Quick Tip to Solve: For acidity, compare the stability of the conjugate bases; for carbonyl addition, compare both electronic and steric effects.

30(b). Write the chemical equations to illustrate the following name reactions:

(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction [3 marks]

Solution:

Concept:

- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine and a strong base on heating.
- Aldol condensation requires an aldehyde or ketone containing an α-hydrogen. The initial β-hydroxy carbonyl compound loses water on heating.
- Cannizzaro reaction is the disproportionation of an aldehyde having no α-hydrogen in concentrated alkali: one molecule is oxidised and another is reduced.

Quick Tip to Solve: Remember the conditions: hydrazine/KOH and heat for Wolff-Kishner, dilute alkali then heat for aldol condensation, and concentrated alkali with no alpha-hydrogen for Cannizzaro.

Step 1: (i) Wolff-Kishner reduction Acetone reacts with hydrazine to form its hydrazone, which on heating with potassium hydroxide in a high-boiling solvent such as ethylene glycol gives propane. The overall equation is

$$CH_3COCH_3 + H_2NNH_2 \xrightarrow[\text{ethylene glycol, heat}]{\text{KOH}} CH_3CH_2CH_3 + N_2 + H_2O.$$

Thus, the carbonyl oxygen is removed and the carbonyl carbon acquires two hydrogen atoms; the carbon skeleton remains unchanged.

Step 2: (ii) Aldol condensation Ethanal contains α-hydrogen atoms. Two molecules combine in cold dilute sodium hydroxide to give 3-hydroxybutanal (aldol):

$$2CH_3CHO \xrightarrow{\text{dilute NaOH}} CH_3CH(OH)CH_2CHO.$$

On heating, this aldol loses water and forms but-2-enal (crotonaldehyde), an α,β-unsaturated aldehyde:

$$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3CH{=}CHCHO + H_2O.$$

Showing dehydration completes the illustration of aldol condensation.

Step 3: (iii) Cannizzaro reaction Benzaldehyde has no α-hydrogen and undergoes self-oxidation and reduction with concentrated sodium hydroxide:

$$2C_6H_5CHO + NaOH \xrightarrow{\text{concentrated alkali}} C_6H_5COONa + C_6H_5CH_2OH.$$

One molecule gives sodium benzoate by oxidation, while the other gives benzyl alcohol by reduction. The carboxylic product remains a salt in the alkaline reaction mixture.

Step 4: Conclusion The equations illustrate carbonyl reduction to an alkane, aldol formation followed by dehydration, and aldehyde disproportionation to a carboxylate salt and an alcohol, respectively.

Quick Tip to Solve: Remember the conditions: hydrazine/KOH and heat for Wolff-Kishner, dilute alkali then heat for aldol condensation, and concentrated alkali with no alpha-hydrogen for Cannizzaro.