

CBSE Class 12 Chemistry Question Paper 2017 with Solution PDF-Set 56-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

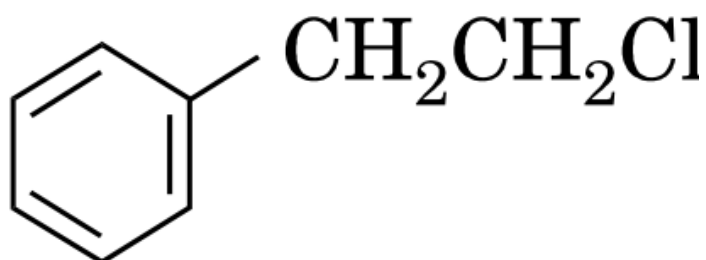
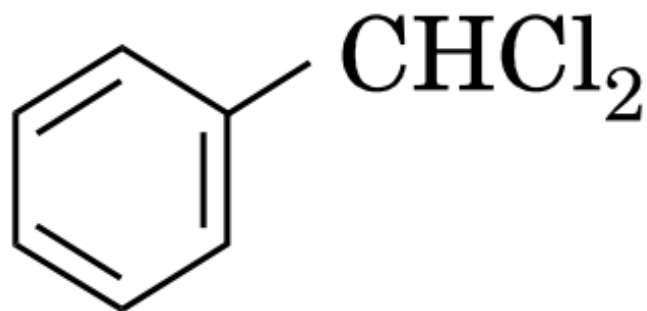
Maximum Marks: 70

General Instructions

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

1. Out of $\text{C}_6\text{H}_5\text{-CHCl}_2$ and $\text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{Cl}$, which is an example of a benzylic halide?

[1 mark]



Solution:

Concept:

- A benzylic halide has a halogen bonded to an sp^3 -hybridised carbon directly attached to a benzene ring.
- The benzylic position is the first carbon of a side chain next to the aromatic ring.

Step 1: Examine the first compound In $\text{C}_6\text{H}_5 - \text{CHCl}_2$, the carbon bearing both chlorine atoms is directly bonded to the benzene ring. Each C–Cl bond therefore occurs at a benzylic carbon.

Step 2: Compare the second compound In $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2\text{Cl}$, chlorine is bonded to the second carbon of the side chain. A CH_2 group lies between that carbon and the ring, so this is not a benzylic halide.

Step 3: Conclusion $\text{C}_6\text{H}_5 - \text{CHCl}_2$ is the benzylic halide.

Quick Tip to Solve: Locate the carbon bearing halogen: it must be directly bonded to the benzene ring.

2. What is the effect of adding a catalyst on

(a) Activation energy (E_a), and

(b) Gibbs energy (ΔG) of a reaction?

[1 mark]

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with a lower activation energy E_a .
- Gibbs energy change ΔG depends on the initial and final states, not on the reaction pathway.

Step 1: Effect on activation energy The alternative catalysed pathway has a smaller energy barrier. Hence adding a catalyst decreases E_a , enabling a larger fraction of reacting molecules to undergo successful collisions at the same temperature.

Step 2: Effect on Gibbs energy The catalyst does not change the Gibbs energies of the reactants or products. Thus $\Delta G = G_{\text{products}} - G_{\text{reactants}}$ remains unchanged. It accelerates the approach to equilibrium without changing the equilibrium constant.

Step 3: Conclusion (a) Activation energy decreases. (b) The Gibbs energy change of the reaction remains unchanged.

Quick Tip to Solve: Distinguish the pathway-dependent energy barrier from the state-dependent Gibbs energy change.

3. Write the formula of the compound of iodine which is obtained when conc. HNO_3 oxidises I_2 .

[1 mark]

Solution:

Concept:

- Concentrated nitric acid is a strong oxidising agent.
- In iodic acid, HIO_3 , iodine has oxidation state +5, whereas in I_2 it is zero.

Step 1: Identify the iodine product Concentrated HNO_3 oxidises elemental iodine to iodic acid. With hydrogen assigned +1 and each oxygen assigned -2, electrical neutrality gives $1 + x - 6 = 0$, so iodine in this product is in the +5 state.

Step 2: Represent the oxidation The balanced reaction is



Iodine is oxidised while nitrogen in nitric acid is reduced from +5 to +4 in nitrogen dioxide.

Step 3: Conclusion The compound is iodic acid, $\boxed{\text{HIO}_3}$.

Quick Tip to Solve: For iodine oxidised by concentrated nitric acid, recall iodic acid and check iodine is in the +5 state.

4. What type of colloid is formed when a gas is dispersed in a liquid? Give an example.

[1 mark]

Solution:

Concept:

- Colloids are classified by the physical states of their dispersed phase and dispersion medium.
- A gas dispersed as fine bubbles in a liquid forms a foam.

Step 1: Identify the two phases The question specifies gas as the dispersed phase and liquid as the continuous dispersion medium. This combination is classified as a foam. The gas is present as bubbles distributed throughout the liquid.

Step 2: Give a matching example Soap lather is an example: air bubbles form the dispersed gas phase, while the aqueous soap solution is the liquid dispersion medium. The liquid films surrounding the bubbles are stabilised by soap.

Step 3: Conclusion The colloid is a foam; an example is soap lather.

Quick Tip to Solve: Read the dispersed phase first: gas in liquid is foam, while liquid droplets in gas form an aerosol.

5. Write the IUPAC name of the following compound:



[1 mark]

Solution:

Concept:

- Ethers are named as alkoxyalkanes: the smaller alkyl group with oxygen is treated as an alkoxy substituent.
- The parent chain is the longest continuous carbon chain on the larger side of the ether oxygen; substituents receive the lowest locants.

Step 1: Choose the parent and alkoxy group The structure is $\text{CH}_3\text{-O-C(CH}_3)_2\text{-CH}_3$. The $\text{CH}_3\text{O-}$ portion is a methoxy group. On the larger carbon fragment, the longest continuous carbon chain contains three carbon atoms, so the parent is propane.

Step 2: Locate and order the substituents The central carbon of this propane chain is carbon 2. It carries both the methoxy group and the remaining methyl group. Both locants are therefore 2. In alphabetical order, methoxy precedes methyl, giving the name shown below.

Step 3: Conclusion The IUPAC name is 2-methoxy-2-methylpropane.

Quick Tip to Solve: For a tert-butyl ether, choose propane as the parent and put both substituents on carbon 2.

6. Draw the structures of the following:

(a) XeF_4

(b) BrF_5

[2 marks]

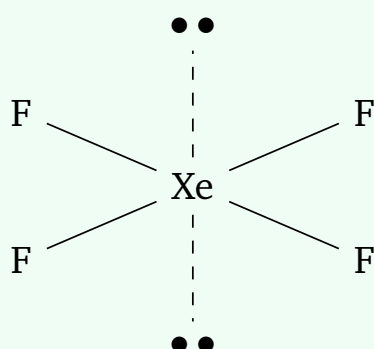
Solution:

Concept:

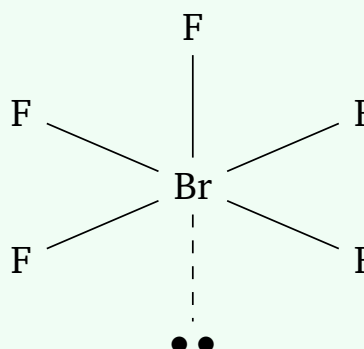
- VSEPR theory determines molecular shape from the number of bond pairs and lone pairs around the central atom. Lone pairs occupy positions that minimise repulsion.
- Six electron domains have an octahedral arrangement. Molecular shape describes the positions of atoms only; lone pairs are excluded when naming the shape.

Step 1: (a) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four form four Xe–F bonds, leaving two lone pairs on Xe. Thus XeF_4 is AX_4E_2 , with six electron domains and an octahedral electron-pair arrangement. The two lone pairs lie opposite each other, above and below the plane of the four fluorine atoms. The molecular shape is square planar, with adjacent F – Xe – F angles 90° and opposite angles 180° .

Step 2: (b) Structure of bromine pentafluoride Bromine has seven valence electrons. Five Br–F bonds leave one lone pair, giving AX_5E and six electron domains. One position of the octahedral arrangement contains the lone pair; the remaining five positions contain fluorine atoms. Four F atoms form the square base and one F atom is at the apex. Hence BrF_5 has a square-pyramidal shape, slightly distorted by lone-pair repulsion.



square planar



square pyramidal

Left: square-planar XeF_4 . Right: square-pyramidal BrF_5 . Dots denote lone pairs.

Step 3: Conclusion

XeF_4 : square planar; BrF_5 : square pyramidal

Quick Tip to Solve: Count six electron domains in both species, then remove the two opposite lone-pair positions for XeF_4 or one position for BrF_5 to identify the shape.

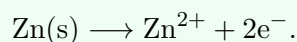
7. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell. [2 marks]

Solution:

Concept:

- A dry cell (Leclanche cell) is a primary electrochemical cell commonly used in transistors. The zinc container is the anode; a carbon rod surrounded by manganese dioxide and carbon serves as the cathode assembly.
- Oxidation releases electrons at the anode and reduction consumes them at the cathode. The electrolyte is a moist paste containing ammonium chloride and zinc chloride.

Step 1: Identify the cell and its anode reaction The cell generally used in transistors is the dry cell, also called the Leclanche cell. Its zinc container undergoes oxidation, supplying electrons to the external circuit:



Thus zinc is the negative electrode while the cell supplies current. This is a primary cell and is not normally recharged.

Step 2: Write the cathode reaction Manganese dioxide is reduced at the positive electrode in the presence of ammonium ions. The cathode reaction is represented as



Manganese changes from oxidation state +4 in MnO_2 to +3 in MnO(OH) . Multiplying this half-reaction by two balances the two electrons released by one zinc atom; the carbon rod provides electrical contact.

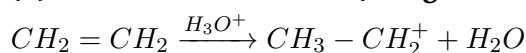
Step 3: Conclusion The required cell is the dry (Leclanche) cell. Its anode reaction is $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$, and its cathode reaction is $\text{MnO}_2 + \text{NH}_4^{+} + \text{e}^{-} \rightarrow \text{MnO(OH)} + \text{NH}_3$.

Quick Tip to Solve: Associate transistors with the zinc-container dry cell; write zinc oxidation first, then the one-electron reduction of MnO_2 at the cathode.

8(a). Arrange the following compounds in the increasing order of their acid strength:

p-cresol, p-nitrophenol, phenol

(b) Write the mechanism (using curved arrow notation) of the following reaction:



[2 marks]

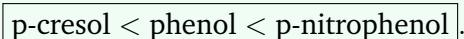
Solution:

Concept:

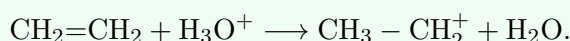
- Phenol acidity increases when a substituent stabilises the phenoxide ion. Electron-withdrawing groups stabilise the conjugate base; electron-donating groups destabilise it.
- An alkene pi bond acts as an electron-pair donor towards a proton. A curved arrow starts at the electron pair and points to the atom or bond receiving that pair.

Quick Tip to Solve: For acidity, compare the conjugate bases; for protonation, draw one arrow from the pi bond to H and a second from the O-H bond back to O.

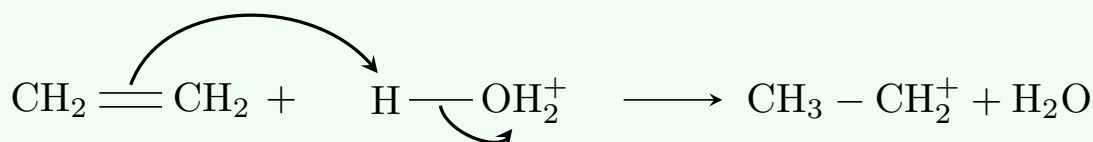
Step 1: (a) Compare the stability of the phenoxide ions The para-methyl group in p-cresol donates electron density through its positive inductive effect and hyperconjugation, destabilising the negatively charged phenoxide ion relative to phenoxide itself. The para-nitro group withdraws electron density through both inductive and resonance effects, stabilising the p-nitrophenoxide ion. Therefore the increasing order of acid strength is



Step 2: (b) Protonate the ethene double bond The printed reaction is the protonation step forming the ethyl carbocation. The pi-electron pair of ethene moves towards a hydrogen atom of H_3O^+ , forming a new C–H bond. Simultaneously, the electron pair in that hydronium O–H bond returns to oxygen, producing water. One carbon consequently gains hydrogen and the other bears the positive charge:



Either carbon may receive the proton because ethene is symmetrical. Both curved arrows represent movement of electron pairs; the positive charge is left on the carbon that loses its share of the pi bond.



Curved-arrow mechanism for protonation of ethene.

Step 3: Conclusion (a) p-cresol < phenol < p-nitrophenol. (b) Transfer of a proton from hydronium to the ethene pi bond gives $\text{CH}_3 - \text{CH}_2^+$ and water, as shown by the two curved arrows.

Quick Tip to Solve: For acidity, compare the conjugate bases; for protonation, draw one arrow from the pi bond to H and a second from the O–H bond back to O.

OR

8(b). Write the structures of the products when Butan-2-ol reacts with the following:

(a) CrO_3

(b) SOCl_2

[2 marks]

Solution:

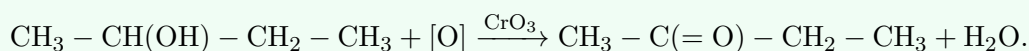
Concept:

- A secondary alcohol undergoes oxidation to a ketone: the carbon bearing the hydroxyl group loses its hydrogen while the O–H hydrogen is also removed.
- Thionyl chloride converts an alcohol into an alkyl chloride by replacing its hydroxyl group with chlorine, without changing the carbon skeleton.

Step 1: (a) Reaction with chromium trioxide Butan-2-ol is a secondary alcohol, with the hydroxyl

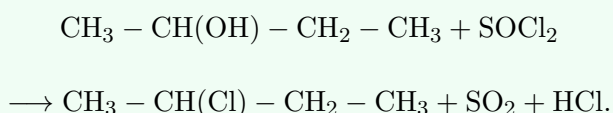
Quick Tip to Solve: Keep the four-carbon chain unchanged: CrO_3 changes $\text{CH}(\text{OH})$ into $\text{C}=\text{O}$, whereas SOCl_2 changes $\text{CH}(\text{OH})$ into $\text{CH}(\text{Cl})$.

group on carbon 2. Chromium trioxide acts as an oxidising agent and converts the secondary alcohol group into a carbonyl group. The product is butan-2-one:



The carbonyl group remains on the second carbon; no carbon atom is added or removed in this conversion.

Step 2: (b) Reaction with thionyl chloride Thionyl chloride replaces the hydroxyl group on the second carbon by a chlorine atom. Hence the organic product is 2-chlorobutane:



Sulphur dioxide and hydrogen chloride are gaseous by-products. This is substitution of the hydroxyl group, whereas the chromium trioxide reaction is oxidation to a ketone.

Step 3: Conclusion The product structures are (a) $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_3$, butan-2-one; and (b) $\text{CH}_3 - \text{CH}(\text{Cl}) - \text{CH}_2 - \text{CH}_3$, 2-chlorobutane.

Quick Tip to Solve: Keep the four-carbon chain unchanged: CrO_3 changes $\text{CH}(\text{OH})$ into $\text{C}=\text{O}$, whereas SOCl_2 changes $\text{CH}(\text{OH})$ into $\text{CH}(\text{Cl})$.

9. Using IUPAC norms write the formulae for the following:

(a) Potassium trioxalatoaluminate(III)

(b) Dichloridobis(ethane-1,2-diamine)cobalt(III)

[2 marks]

Solution:

Concept:

- A coordination formula encloses the metal and its ligands in square brackets. The charge of the coordination entity equals the metal oxidation state plus the sum of ligand charges.
- Oxalato is $\text{C}_2\text{O}_4^{2-}$, chlorido is Cl^- , and ethane-1,2-diamine, abbreviated en, is a neutral bidentate ligand.

Step 1: (a) Balance the aluminate complex with potassium ions Aluminium(III) contributes +3, while the three oxalato ligands contribute $3(-2) = -6$. Hence the complex has charge -3:

$$+3 + 3(-2) = -3.$$

Three K^+ ions are therefore required outside the brackets to make the compound electrically neutral.

Step 2: (b) Determine the charge of the cobalt coordination entity Cobalt(III) contributes +3. Two chlorido ligands contribute -2, while both en ligands are neutral. Thus

$$+3 + 2(-1) + 2(0) = +1.$$

Quick Tip to Solve: Count the ligand charges before writing any counter-ions; en contributes zero charge even though it occupies two coordination sites.

The name gives a coordination ion and specifies no counter-ion, so retain its positive charge instead of adding an unspecified anion.

Step 3: Conclusion (a) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$. (b) $[\text{CoCl}_2(\text{en})_2]^+$, where $\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.

Quick Tip to Solve: Count the ligand charges before writing any counter-ions; en contributes zero charge even though it occupies two coordination sites.

10. Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a face-centred cubic (f.c.c.) structure. (Atomic mass of Al = 27 g mol⁻¹) [2 marks]

Solution:

Concept:

- The number of atoms in a sample is $N = (m/M)N_A$, where m is its mass, M is its molar mass and $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$.
- An f.c.c. unit cell contains $Z = 4$ atoms: eight corner atoms contribute $8/8 = 1$, and six face-centred atoms contribute $6/2 = 3$.

Step 1: Calculate the number of aluminium atoms The amount of aluminium in the sample is

$$n = \frac{8.1 \text{ g}}{27 \text{ g mol}^{-1}} = 0.30 \text{ mol.}$$

Each mole contains Avogadro's number of atoms. Therefore

$$N = 0.30 \times 6.022 \times 10^{23} = 1.8066 \times 10^{23} \text{ atoms.}$$

Step 2: Divide by the number of atoms per f.c.c. cell Since each unit cell accounts for four aluminium atoms, the total number of unit cells is

$$N_{\text{cells}} = \frac{N}{Z} = \frac{1.8066 \times 10^{23}}{4} = 4.5165 \times 10^{22}.$$

Shared atoms must be counted fractionally; counting all fourteen visible lattice positions as whole atoms would give an incorrect cell population.

Step 3: Conclusion The sample contains approximately 4.52×10^{22} f.c.c. unit cells (or 4.5×10^{22} to two significant figures).

Quick Tip to Solve: For an f.c.c. sample, use $N_{\text{cells}} = mN_A/(4M)$; dividing by four converts atoms into unit cells.

11. (a) What type of isomerism is shown by the complex $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$?

(b) Why is $[\text{NiCl}_4]^{2-}$ paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic? (Atomic number of Ni = 28)

(c) Why are low spin tetrahedral complexes rarely observed?

[3 marks]

Solution:

Concept:

- Ambidentate ligands can coordinate through either of two different donor atoms, producing linkage isomers without changing the overall composition.
- Magnetic behaviour depends on unpaired electrons. Ligand strength and coordination geometry determine the splitting and occupation of metal d orbitals.
- Electron pairing is favoured when the crystal-field splitting exceeds pairing energy P . Tetrahedral splitting Δ_t is usually too small for this condition.

Step 1: (a) Identify the linkage isomerism The ligand SCN^- is ambidentate: it can bond through sulphur or through nitrogen. Thus the S-bonded complex $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$ and its N-bonded form $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ are linkage isomers. The donor atom changes, while the ligand composition remains the same.

Step 2: (b) Compare the electronic arrangements of the nickel complexes In both complexes, four ligands each carry charge -1 , so nickel has oxidation state $+2$. Nickel is $[\text{Ar}]3d^84s^2$, hence Ni^{2+} is $[\text{Ar}]3d^8$. Chloride is a weak-field ligand and does not cause pairing of the two unpaired 3d electrons. The complex $[\text{NiCl}_4]^{2-}$ uses sp^3 hybridisation and is tetrahedral, with two unpaired electrons; it is therefore paramagnetic. Cyanide is a strong-field ligand. It causes pairing of the 3d electrons, leaving one 3d orbital available for dsp^2 hybridisation. The resulting $[\text{Ni}(\text{CN})_4]^{2-}$ complex is square planar with all electrons paired, and is therefore diamagnetic.

Step 3: (c) Explain why tetrahedral complexes usually have high spin Tetrahedral crystal-field splitting is small; for comparable metal-ligand combinations, $\Delta_t \approx \frac{4}{9}\Delta_o$. It is generally smaller than the electron-pairing energy P . Electrons therefore occupy higher-energy d orbitals singly rather than pair in the lower set. The high-spin arrangement is favoured, making low-spin tetrahedral complexes rare.

Step 4: Conclusion (a) Linkage isomerism. (b) Tetrahedral $[\text{NiCl}_4]^{2-}$ has two unpaired electrons, while square-planar $[\text{Ni}(\text{CN})_4]^{2-}$ has none. (c) Usually $\Delta_t < P$, so pairing is unfavourable.

Quick Tip to Solve: For nickel(II), first identify the d^8 configuration, then use the ligand and geometry together to decide whether its electrons are paired.

12(a). Write one difference in each of the following:

(a) Multimolecular colloid and Associated colloid

(b) Coagulation and Peptization

(c) Homogeneous catalysis and Heterogeneous catalysis

[3 marks]

Solution:

Concept:

- Colloids can be classified by how their dispersed particles form. Aggregation of many small species and micelle formation by surfactants produce different classes of colloids.
- Coagulation and peptization describe opposite changes between colloidal dispersions and precipitates. Catalysis is classified as homogeneous or heterogeneous by the phases of the reactants and catalyst.

Step 1: (a) Compare how the colloidal particles form In a multimolecular colloid, many atoms or small molecules aggregate to produce particles of colloidal size, as in gold sol or sulphur sol. In an associated colloid, amphiphilic molecules or ions behave as ordinary small solutes at low concentration but associate into micelles above the critical micelle concentration, at a suitable temperature above the Kraft temperature. Soap solution above this concentration is an example. Thus the distinction is ordinary aggregation versus concentration-dependent micelle formation.

Step 2: (b) Compare the direction of the physical change Coagulation is the aggregation and precipitation of colloidal particles, usually following loss or neutralisation of their stabilising charge, for example on adding sufficient electrolyte to a sol. 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 suitable electrolyte, called the peptizing agent. Thus coagulation changes sol into precipitate, whereas peptization changes fresh precipitate into sol.

Step 3: (c) Compare the phases present during catalysis In homogeneous catalysis, the catalyst and the reactants are in the same phase. For example, gaseous nitric oxide catalyses the oxidation of gaseous sulphur dioxide by gaseous oxygen. In heterogeneous catalysis, the catalyst and the reactants are in different phases. For example, solid iron catalyses the reaction of gaseous nitrogen and hydrogen in the Haber process. The latter reaction occurs at the solid catalyst's surface.

Step 4: Conclusion (a) Multimolecular colloids form by aggregation of small species; associated colloids form micelles above the critical micelle concentration. (b) Coagulation converts sol to precipitate; peptization converts fresh precipitate to sol. (c) Homogeneous catalysis has the same phase for catalyst and reactants; heterogeneous catalysis has different phases.

Quick Tip to Solve: Organise these three comparisons by particle formation, direction of conversion, and phases of catalyst and reactants, respectively.

12(b). (a) Write the dispersed phase and dispersion medium of milk.

(b) Write one similarity between physisorption and chemisorption.

(c) Write the chemical method by which $\text{Fe}(\text{OH})_3$ sol is prepared from FeCl_3 .

[3 marks]

Solution:

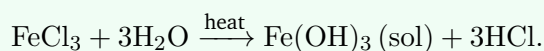
Concept:

- A colloid contains a dispersed phase distributed in a continuous dispersion medium. Milk is an emulsion: both phases are liquids.
- Adsorption is accumulation at a surface. Hydrolysis of a suitable salt is a chemical method of preparing a colloidal hydroxide sol.

Step 1: (a) Identify the two liquid phases in milk Milk contains small droplets of liquid fat dispersed throughout water. Thus its dispersed phase is liquid fat and its dispersion medium is water. It is an oil-in-water emulsion; the droplets are distributed in the continuous aqueous medium rather than forming a true molecular solution.

Step 2: (b) State a similarity of the two types of adsorption Both physisorption and chemisorption are surface phenomena: in each, particles of the adsorbate accumulate at the surface of the adsorbent, producing a higher concentration at that surface than in the bulk. Either process therefore depends on the availability of the adsorbent's surface. The forces responsible differ, but the location of adsorption provides the required similarity.

Step 3: (c) Prepare ferric hydroxide sol by hydrolysis The chemical method is hydrolysis. Add a small amount of ferric chloride solution to boiling distilled water. Ferric chloride undergoes hydrolysis, producing colloidal ferric hydroxide, which forms a reddish-brown sol:

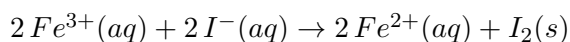


The insoluble hydroxide forms finely dispersed colloidal particles in the aqueous medium. The process is hydrolysis of the salt, rather than peptization of a pre-existing precipitate.

Step 4: Conclusion (a) Dispersed phase: liquid fat; dispersion medium: water. (b) Both are surface phenomena. (c) Ferric hydroxide sol is prepared by hydrolysis of ferric chloride in boiling water.

Quick Tip to Solve: For milk, identify the droplets first: fat is dispersed in water. For ferric chloride, boiling water points to hydrolysis.

13. (a) A cell in which the following reaction occurs:



has $E_{\text{cell}}^{\circ} = 0.236\text{ V}$ at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given: $1\text{ F} = 96,500\text{ C mol}^{-1}$)

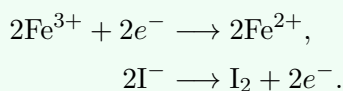
(b) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given: $1\text{ F} = 96,500\text{ C mol}^{-1}$) [3 marks]

Solution:

Concept:

- The standard Gibbs energy of a cell reaction is $\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$, where n is the number of moles of electrons transferred per mole of the reaction as written and F is the Faraday constant.
- Charge passed is $Q = It$, with current I in amperes and time t in seconds. The electron count is $N = (Q/F)N_A$, where $N_A = 6.022 \times 10^{23}\text{ mol}^{-1}$.

Step 1: (a) Determine the electron transfer The half-reactions for the reaction as written are



Two electrons are transferred overall, so $n = 2$. Electrons appearing in both half-reactions are not added together; the same electrons released by iodide are accepted by iron(III).

Step 2: (a) Calculate standard Gibbs energy Using $F = 96500\text{ C mol}^{-1}$ and $E_{\text{cell}}^{\circ} = 0.236\text{ V}$,

$$\begin{aligned}\Delta_r G^{\circ} &= -2(96500)(0.236) \\&= -45548\text{ J mol}^{-1} \\&= -45.548\text{ kJ mol}^{-1}.\end{aligned}$$

The unit follows from $\text{C V} = \text{J}$. The negative sign is consistent with a positive standard cell potential and a spontaneous forward reaction under standard conditions.

Step 3: (b) Convert the charge to a number of electrons First convert the time: $t = 2 \times 60 \times 60 = 7200\text{ s}$. Hence

$$Q = It = 0.5 \times 7200 = 3600\text{ C}.$$

One mole of electrons carries 96500 C. Therefore

$$\begin{aligned}n(e^{-}) &= \frac{3600}{96500} = 0.03731\text{ mol}, \\N &= \frac{3600}{96500}(6.022 \times 10^{23}) \\&\approx 2.25 \times 10^{22}\text{ electrons}.\end{aligned}$$

This is a particle count, obtained by multiplying the moles of electrons by Avogadro's constant.

Step 4: Conclusion (a) $\Delta_r G^{\circ} = -45.548\text{ kJ mol}^{-1}$ (approximately -45.5 kJ mol^{-1}). (b) Approximately 2.25×10^{22} electrons flow through the wire.

Quick Tip to Solve: Count two transferred electrons for the reaction as written, and convert hours into seconds before using $Q = It$.

14. (a) Based on the nature of intermolecular forces, classify the following solids:

Sodium sulphate, Hydrogen

(b) What happens when CdCl_2 is doped with AgCl ?

(c) Why do ferrimagnetic substances show better magnetism than antiferromagnetic substances?

[3 marks]

Solution:

Concept:

- Ionic solids contain oppositely charged ions held by electrostatic attraction. Non-polar molecular solids contain neutral non-polar molecules held by London dispersion forces.
- Substitution by an impurity ion of a different charge requires charge compensation in an ionic crystal. Opposing magnetic moments give a net moment only when they do not cancel completely.

Step 1: (a) Classify sodium sulphate and hydrogen Sodium sulphate, Na_2SO_4 , is an ionic solid. Its lattice contains Na^+ and SO_4^{2-} ions, held together by electrostatic attraction. Although each sulphate ion has internal covalent bonds, the attraction between the ions determines this solid's classification. Solid hydrogen is a non-polar molecular solid: its constituents are non-polar H_2 molecules, held together by weak London dispersion forces.

Step 2: (b) Explain the effect of doping cadmium chloride When CdCl_2 is doped with AgCl , some Cd^{2+} ions are replaced by Ag^+ ions. Each such substitution reduces the positive charge by one unit. To maintain electrical neutrality, one Cl^- ion is absent from its normal lattice site for each substituted Ag^+ ion. Thus anion (chloride-ion) vacancies are produced as an impurity defect. The missing negative charge compensates for the smaller positive charge of the impurity cation.

Step 3: (c) Compare the cancellation of magnetic moments In an antiferromagnetic substance, neighbouring sets of magnetic moments align in opposite directions with equal magnitudes. They cancel, giving zero net magnetic moment in the ideal arrangement. In a ferrimagnetic substance, moments also align in opposite directions, but the opposing sets have unequal total magnitudes. Cancellation is incomplete and a resultant magnetic moment remains. Therefore ferrimagnetic substances exhibit greater magnetism than antiferromagnetic substances.

Step 4: Conclusion (a) Sodium sulphate is ionic; solid hydrogen is non-polar molecular. (b) Doping with AgCl produces chloride-ion vacancies in CdCl_2 . (c) Unequal opposing moments leave a net moment in ferrimagnetic substances, whereas equal opposing moments cancel in antiferromagnetic substances.

Quick Tip to Solve: For doping, compare the ion charges first: replacing Cd^{2+} by Ag^+ requires one missing Cl^- to retain neutrality.

15. (a) Write the principle of electrolytic refining.

(b) Why does copper obtained in the extraction from copper pyrites have a blistered appearance?

(c) What is the role of depressants in the froth floatation process?

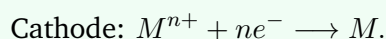
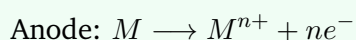
[3 marks]

Solution:

Concept:

- Electrolytic refining transfers a metal from an impure anode to a pure cathode through a solution containing a soluble salt of the metal.
- Gases escaping from molten metal can leave cavities on solidification. Selective wetting of sulphide ores permits their separation by froth floatation.

Step 1: (a) Principle of electrolytic refining The impure metal is made the anode and a thin sheet of pure metal the cathode. The electrolyte is a solution of a soluble salt of that metal. On passing current, metal atoms from the anode enter solution as ions and metal ions are reduced to pure metal at the cathode:



The applied conditions favour deposition of the desired metal. Insoluble impurities collect below the anode as anode mud, whereas soluble impurities may remain in the electrolyte.

Step 2: (b) Origin of the blistered surface of copper During extraction from copper pyrites, copper(I) sulphide reacts with copper(I) oxide in the self-reduction step:



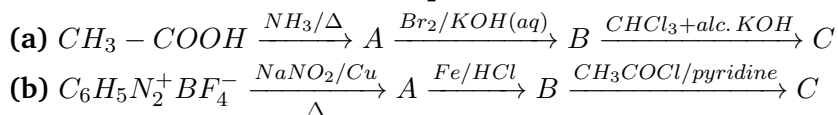
Sulphur dioxide escaping from the molten copper produces bubbles and cavities. As the metal solidifies, these leave a blistered appearance, so the product is called blister copper.

Step 3: (c) Selective action of depressants A depressant selectively prevents one sulphide ore from forming froth, enabling another sulphide ore to be floated and separated. For example, in a mixture of ZnS and PbS , $NaCN$ prevents ZnS from entering the froth, while PbS is carried by the froth. Thus depressants help separate two sulphide ores present together.

Step 4: Conclusion (a) Electrolytic refining uses selective anodic dissolution and cathodic deposition of pure metal. (b) Escaping SO_2 gives copper its blistered appearance. (c) Depressants selectively prevent one sulphide from forming froth so that sulphide ores can be separated.

Quick Tip to Solve: Link blister copper to escaping sulphur dioxide, and remember the selective pair: $NaCN$ depresses ZnS while PbS floats.

16. Write the structures of compounds A, B and C in the following reactions:



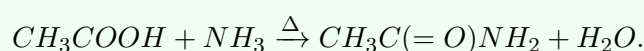
[3 marks]

Solution:

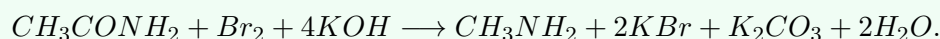
Concept:

- Heating a carboxylic acid with ammonia gives an amide. Hofmann bromamide degradation converts $RCONH_2$ into RNH_2 , removing the carbonyl carbon.
- Primary amines react with chloroform and alcoholic alkali to form isocyanides, $R - N \equiv C$. A diazonium group can be replaced by a nitro group, which is reducible to an amino group.

Step 1: (a) Identify the amide A and the amine B Ethanoic acid first forms ammonium ethanoate with ammonia; heating eliminates water to give ethanamide (acetamide):

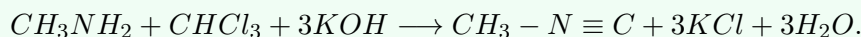


Therefore $A = CH_3C(=O)NH_2$. Treatment with bromine and aqueous potassium hydroxide causes Hofmann degradation:



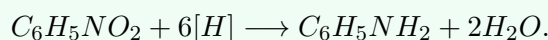
Hence $B = CH_3NH_2$, methylamine. It contains one fewer carbon atom than the starting amide.

Step 2: (a) Identify the carbylamine product C Methylamine is a primary amine, so it gives the carbylamine reaction with chloroform and alcoholic potassium hydroxide:

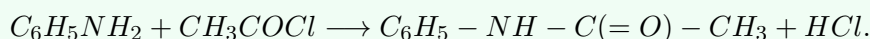


Thus $C = CH_3 - N \equiv C$, methyl isocyanide. The methyl group is bonded to nitrogen, which distinguishes this product from methyl cyanide, $CH_3 - C \equiv N$.

Step 3: (b) Replace the diazonium group, then reduce and acetylate Sodium nitrite and copper on heating replace the diazonium group by $-NO_2$, with evolution of nitrogen. Thus $A = C_6H_5 - NO_2$, nitrobenzene. Reduction with Fe/HCl converts the nitro group into an amino group:



The amine identified after work-up is $B = C_6H_5 - NH_2$, aniline. Acetyl chloride in pyridine then acetylates its amino nitrogen:



Pyridine accepts the hydrogen chloride produced. Therefore $C = C_6H_5 - NH - C(=O) - CH_3$, acetanilide.

Step 4: Conclusion (a) $A = CH_3C(=O)NH_2$, $B = CH_3NH_2$, $C = CH_3 - N \equiv C$.

(b) $A = C_6H_5NO_2$, $B = C_6H_5NH_2$, $C = C_6H_5 - NH - C(=O) - CH_3$.

Quick Tip to Solve: Track the carbonyl carbon in Hofmann degradation: it is lost. In the final carbylamine, write $R-NC$ rather than $R-CN$.

17. Give reasons for the following:

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than $\text{C}_6\text{H}_5\text{NH}_2$.

(c) Although $-\text{NH}_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline.

[3 marks]

Solution:

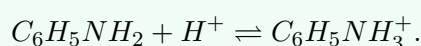
Concept:

- An amino group's activating effect depends on donation of the nitrogen lone pair into an aromatic ring. Competing delocalisation into a carbonyl group reduces that donation.
- Basicity depends on the availability of the nitrogen lone pair for protonation. Protonation also changes the directing influence of an aromatic amino group.

Step 1: (a) Acetylation reduces the activation by aniline Acetylation converts the strongly activating amino group of aniline, $\text{C}_6\text{H}_5 - \text{NH}_2$, into the acetamido group, $\text{C}_6\text{H}_5 - \text{NH} - \text{C}(=\text{O})\text{CH}_3$. In this amide group the nitrogen lone pair is delocalised towards the carbonyl group as well as towards the benzene ring. Consequently, it is less available for donation into the ring than in aniline. The electron density and hence the rate of electrophilic substitution of the ring are reduced. The acetamido group remains ortho/para directing, but its activating influence is weaker than that of $-\text{NH}_2$.

Step 2: (b) Methylamine is more basic than aniline In methylamine, CH_3NH_2 , the methyl group has a positive inductive effect, increasing electron density on nitrogen. Its lone pair is localised and readily accepts a proton. In aniline, $\text{C}_6\text{H}_5\text{NH}_2$, the nitrogen lone pair is delocalised into the benzene ring by resonance and is therefore less available to bind H^+ . The phenyl group also exerts an electron-withdrawing inductive effect. Thus proton acceptance is more favourable for methylamine, making it more basic than aniline.

Step 3: (c) Nitration gives a significant meta product The strongly acidic nitrating mixture protonates a substantial fraction of aniline:



Although free $-\text{NH}_2$ is ortho/para directing, the protonated group $-\text{NH}_3^+$ has no nitrogen lone pair available for donation into the ring. It is electron withdrawing, deactivating and meta directing. Nitration of these anilinium ions therefore produces a significant amount of meta-nitroaniline after work-up. The direction follows the group present in the acidic reaction medium.

Step 4: Conclusion (a) Acetylation diverts the nitrogen lone pair towards a carbonyl group and weakens ring activation. (b) The lone pair is more available in methylamine than in resonance-stabilised aniline. (c) Acidic nitration forms meta-directing anilinium ions, accounting for the significant meta product.

Quick Tip to Solve: Before predicting aniline's behaviour, check the nitrogen: free NH_2 donates, acetylation weakens donation, and protonation removes the lone pair from donation.

18. Give reasons for the following:

- (a) Red phosphorus is less reactive than white phosphorus.
(b) Electron gain enthalpies of halogens are largely negative.
(c) N_2O_5 is more acidic than N_2O_3 .

[3 marks]

Solution:

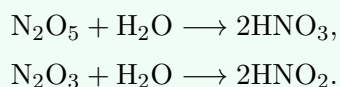
Concept:

- Allotrope reactivity depends on structure and bond strain; a less strained, extended structure is more stable.
- Electron gain enthalpy is the enthalpy change for $\text{X}(\text{g}) + \text{e}^- \rightarrow \text{X}^-(\text{g})$; a negative value indicates energy release.
- For oxides of the same non-metal, acidic character generally increases with its oxidation state.

Step 1: (a) Compare the structures of phosphorus White phosphorus consists of discrete tetrahedral P_4 molecules. The $\text{P} - \text{P} - \text{P}$ angles are only 60° , making these molecules highly strained and readily attacked by other substances. Red phosphorus has a polymeric network with much less angular strain and greater structural stability. Consequently, breaking and rearranging its bonds is less favourable, so red phosphorus is less reactive than white phosphorus.

Step 2: (b) Explain favourable electron gain by halogens Halogen atoms have the valence-shell configuration ns^2np^5 . Each needs only one electron to attain the stable noble-gas configuration ns^2np^6 . Their high effective nuclear attraction favours capture of an electron; formation of the halide ion releases considerable energy. Their first electron gain enthalpies are therefore largely negative. This statement concerns addition of one electron to a gaseous atom.

Step 3: (c) Compare the two nitrogen oxides Nitrogen is in the +5 oxidation state in N_2O_5 , but in the +3 state in N_2O_3 . The higher oxidation state increases the acidic character of the oxide. The corresponding acids also illustrate this difference:



Nitric acid is stronger than nitrous acid, consistent with the greater acidity of its anhydride, N_2O_5 .

Step 4: Conclusion (a) Red phosphorus has a more stable, less strained polymeric structure. (b) Halogens release energy on gaining an electron to complete their valence shell. (c) Nitrogen's higher oxidation state in N_2O_5 gives it greater acidic character.

Quick Tip to Solve: Link each reason to the relevant feature: phosphorus structure, halogen octet completion, and nitrogen oxidation state.

19. Define the following:

(a) Cationic detergents

(b) Broad spectrum antibiotics

(c) Tranquilizers

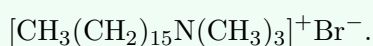
[3 marks]

Solution:

Concept:

- Detergents contain a water-attracting ionic head and a water-repelling hydrocarbon tail; the charge of the active head determines their class.
- The spectrum of an antibiotic describes the range of bacteria against which it acts.
- Tranquilizers are drugs that act on the central nervous system to relieve mental stress and related disturbances.

Step 1: (a) Cationic detergents Cationic detergents are generally quaternary ammonium salts containing a long hydrocarbon chain. Their positively charged organic ion is the surface-active, cleansing component; the counter-ion is commonly chloride or bromide. For example, cetyltrimethylammonium bromide has the formula



Its long chain associates with grease, while the charged ammonium head interacts with water. Thus the word cationic refers to the detergent's active positive ion.

Step 2: (b) Broad spectrum antibiotics Broad spectrum antibiotics are antibiotics that kill or inhibit the growth of a wide range of bacteria, including both Gram-positive and Gram-negative bacteria. Chloramphenicol is a standard example. The defining feature is the range of susceptible bacterial types, rather than merely the strength of action against a single species. These antibiotics act against bacteria; the term does not mean that they cure all microbial or viral diseases.

Step 3: (c) Tranquilizers Tranquilizers are a class of drugs used to treat stress and mild or severe mental diseases. They act on the central nervous system and relieve anxiety, tension, irritability or excitement, producing a sense of well-being. Diazepam is an example. Their defining role is to reduce mental tension and disturbance; they are distinct from analgesics, whose principal role is relief of pain.

Step 4: Conclusion Cationic detergents have a positively charged surface-active ion; broad spectrum antibiotics act against a wide range of Gram-positive and Gram-negative bacteria; tranquilizers relieve stress, anxiety and related mental disturbances.

Quick Tip to Solve: For definitions, state the distinguishing feature first: positive active ion, wide bacterial range, or relief of mental tension.

20. Write the structures of the monomers used for getting the following polymers:

(a) Teflon

(b) Melamine-formaldehyde polymer

(c) Neoprene

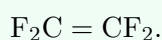
[3 marks]

Solution:

Concept:

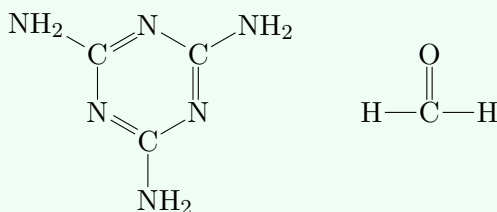
- An addition polymer is formed by repeated addition of unsaturated monomers without eliminating a small molecule.
- A condensation polymer is formed from reactive functional groups of monomers, commonly with elimination of small molecules such as water.

Step 1: (a) Monomer of Teflon Teflon is polytetrafluoroethene. Its monomer is tetrafluoroethene (tetrafluoroethylene), whose structure is



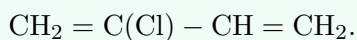
The double bond opens during addition polymerisation to give the repeating unit $-\text{CF}_2 - \text{CF}_2-$. All four substituents on the two carbon atoms are fluorine atoms; the monomer contains no hydrogen.

Step 2: (b) Monomers of melamine-formaldehyde polymer Two monomers are required: melamine and formaldehyde (methanal). Their structures are shown below.



Melamine is 2,4,6-triamino-1,3,5-triazine: its ring contains alternating carbon and nitrogen atoms, with an $-\text{NH}_2$ group attached to each carbon. Formaldehyde has the condensed structural formula $\text{H} - \text{C}(=\text{O}) - \text{H}$. Their amino and carbonyl groups participate in condensation, ultimately producing a cross-linked thermosetting resin.

Step 3: (c) Monomer of neoprene Neoprene is made from chloroprene, or 2-chlorobuta-1,3-diene. Its structure is



This is a conjugated diene with chlorine on carbon 2. Polymerisation mainly occurs by 1,4-addition to yield the repeating unit $-\text{CH}_2 - \text{C}(\text{Cl}) = \text{CH} - \text{CH}_2-$. Thus chloroprene, rather than unsubstituted butadiene or vinyl chloride, is the required monomer.

Step 4: Conclusion (a) Tetrafluoroethene, $\text{CF}_2 = \text{CF}_2$. (b) Melamine, the triazine ring with three $-\text{NH}_2$ groups shown above, and formaldehyde, $\text{H} - \text{C}(=\text{O}) - \text{H}$. (c) Chloroprene, $\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$.

Quick Tip to Solve: Recover the unsaturated monomer from an addition polymer; for the melamine resin remember that both melamine and methanal must be supplied.

21. The following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(a) Write the compound which is most reactive towards S_N2 reaction.

(b) Write the compound which is optically active.

(c) Write the compound which is most reactive towards β -elimination reaction.

[3 marks]

Solution:

Concept:

- In an S_N2 reaction the nucleophile attacks the carbon bearing the leaving group from the back. Increasing steric crowding slows this attack: primary halides react faster than secondary and tertiary halides.
- A tetrahedral carbon attached to four different groups is a chiral centre; a single enantiomer of such a molecule can rotate plane-polarised light.
- In the usual comparison of alkyl halides, the tendency towards β -elimination increases in the order primary < secondary < tertiary. Elimination removes hydrogen from a neighbouring carbon and halogen from the carbon bearing it.

Step 1: (a) Compare steric hindrance for substitution In 1-bromopentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, the carbon bonded to bromine is primary and is least crowded. The corresponding carbons in 2-bromopentane and 2-bromo-2-methylbutane are secondary and tertiary, respectively. Thus the backside approach required for S_N2 is easiest in 1-bromopentane; the tertiary compound is especially hindered.

Step 2: (b) Identify the chiral carbon The structure of 2-bromopentane is $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_2\text{CH}_3$. Its second carbon is bonded to four different groups: H, Br, CH_3 and $\text{CH}_2\text{CH}_2\text{CH}_3$. Hence it is chiral and its individual enantiomers are optically active. In contrast, 1-bromopentane has no chiral centre, while the carbon bearing bromine in 2-bromo-2-methylbutane has two identical methyl groups. As usual, an equal mixture of the two enantiomers of 2-bromopentane would show no net rotation.

Step 3: (c) Compare the tendency towards elimination 2-Bromo-2-methylbutane, $(\text{CH}_3)_2\text{C}(\text{Br})\text{CH}_2\text{CH}_3$, is a tertiary alkyl halide with available β -hydrogens. Its substitution by the S_N2 route is sterically hindered and it has the greatest tendency towards elimination among these three compounds. Loss of hydrogen bromide can give the stable, more substituted alkene 2-methylbut-2-ene as the major product under the usual elimination conditions.

Step 4: Conclusion (a) Most reactive towards S_N2 : 1-bromopentane.

(b) Optically active compound: 2-bromopentane.

(c) Most reactive towards β -elimination: 2-bromo-2-methylbutane.

Quick Tip to Solve: Classify the carbon bearing bromine first: primary favours backside substitution, tertiary favours elimination; then check four different groups for chirality.

22. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.

(Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

[3 marks]

Solution:

Concept:

- For a first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$, where a is the initial reactant concentration, x is the concentration decomposed in time t , and k is the rate constant.
- The logarithm uses the fraction of reactant remaining. At 25% decomposition, 75% remains; at 75% completion, 25% remains. The same rate constant applies at both stages under the same conditions.

Step 1: Calculate the rate constant from 25% decomposition Take the initial amount as 100 units. After 20 minutes, 25 units have decomposed and 75 units remain. Therefore,

$$\begin{aligned}k &= \frac{2.303}{20} \log \frac{100}{75} \\&= \frac{2.303}{20} \log \frac{4}{3} \\&= \frac{2.303}{20} (\log 4 - \log 3) \\&= \frac{2.303}{20} (0.6021 - 0.4771) \\&= 0.01439375 \text{ min}^{-1}.\end{aligned}$$

The initial amount cancels in the ratio, which is characteristic of first order kinetics. The unit of k is inverse minutes because the given time is in minutes.

Step 2: Find the total time for 75% completion When 75% has decomposed, only 25% of the original reactant remains. Inserting this remaining amount into the integrated rate equation gives

$$\begin{aligned}t_{75\%} &= \frac{2.303}{k} \log \frac{100}{25} \\&= \frac{2.303}{0.01439375} \log 4 \\&= \frac{2.303 \times 0.6021}{0.01439375} \\&= 96.336 \text{ min}.\end{aligned}$$

Equivalently, cancellation of 2.303 gives $t_{75\%} = 20(0.6021)/(0.1250)$. This is the elapsed time measured from the start of the reaction. It exceeds three times 20 minutes because the reaction slows as the reactant concentration decreases; equal amounts do not decompose in equal times.

Step 3: Conclusion The time required for 75% completion, measured from the start, is 96.34 min, using the supplied logarithms.

Quick Tip to Solve: Convert percentage decomposed to percentage remaining before using the logarithm: the two ratios here are 100/75 and 100/25, not 100/25 and 100/75.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Rupali a Class XII student decided to make others aware about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct the canteen contractor to stop selling sandwiches, pizzas, burgers and other bakery products to the students. The principal took an immediate action and instructed the canteen contractor to replace the bakery products with some protein and vitamin rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and the students.

After reading the above passage, answer the following questions:

- (a) What are the values (at least two) displayed by Rupali?
- (b) Which polysaccharide component of carbohydrates is commonly present in bread?
- (c) Write the two types of secondary structures of proteins.
- (d) Give two examples of water soluble vitamins.

[4 marks]

Solution:

Concept:

- Food awareness and responsible action can protect the health of a school community. Values should be identified from what Rupali actually does in the passage.
- Starch is the storage polysaccharide of plants and is abundant in cereal flour. Protein secondary structure describes regular folding of the polypeptide backbone, stabilised mainly by hydrogen bonds.
- Vitamins are classified by solubility: vitamin C and members of the vitamin B group are water soluble.

Step 1: (a) Values displayed by Rupali Rupali displays health awareness and concern for the welfare of others: she recognises the food-safety concern described in the programme and wishes to protect her fellow students. She also shows social responsibility and initiative by approaching the principal and seeking practical action. Any two of these values, supported by her conduct, answer this part.

Step 2: (b) Polysaccharide present in bread The polysaccharide commonly present in bread is starch. Bread is made mainly from cereal flour, which contains starch as its major storage carbohydrate. Starch consists of the glucose polymers amylose and amylopectin; glucose itself is a monosaccharide, so it is not the polysaccharide asked for here.

Step 3: (c) Secondary structures of proteins The two common secondary structures are the α -helix and the β -pleated sheet. In the helix, a polypeptide backbone coils regularly; in the pleated sheet, extended backbone segments lie alongside one another. Hydrogen bonding between backbone C = O and N – H groups stabilises these arrangements. These are folding patterns, whereas the amino-acid sequence is the primary structure.

Step 4: (d) Examples of water-soluble vitamins Two examples are vitamin B₁ (thiamine) and vitamin C (ascorbic acid). Both belong to the water-soluble category. Vitamins A, D, E and K instead belong to the fat-soluble category and therefore do not answer this part.

Step 5: Conclusion (a) Health awareness, concern for others, social responsibility and initiative (any two). (b) Starch. (c) α -helix and β -pleated sheet. (d) Vitamin B₁ and vitamin C.

Quick Tip to Solve: Link values to Rupali's actions, identify bread with starch, and remember that the B group and C are the water-soluble vitamins.

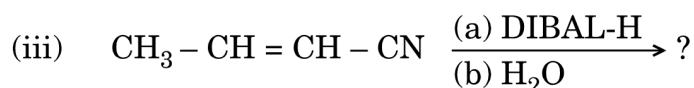
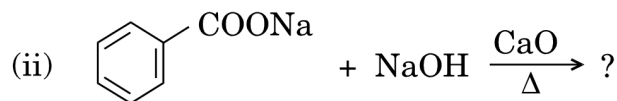
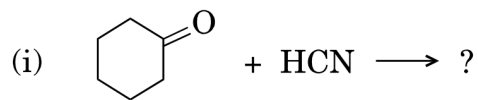
24(a). Write the product(s) in the following reactions (i)–(iii), shown in the reaction schemes below.

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Butanal and Butan-2-one

(ii) Benzoic acid and Phenol

[5 marks]



Solution:

Concept:

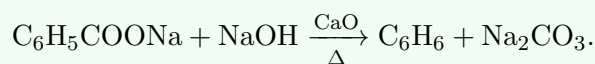
- Hydrogen cyanide adds across the carbonyl group: the carbonyl carbon acquires $-\text{CN}$ and the oxygen becomes $-\text{OH}$, producing a cyanohydrin.
- Soda lime, NaOH/CaO , removes the carboxylate carbon on heating. DIBAL-H followed by hydrolysis converts a nitrile group into an aldehyde group.
- Aldehydes reduce Tollens' reagent, whereas ordinary ketones do not. A carboxylic acid liberates CO_2 from sodium hydrogen carbonate; phenol is too weak an acid to do so.

Step 1: (a)(i) Addition of HCN to cyclohexanone The nucleophile CN^- attacks the carbonyl carbon of cyclohexanone. Protonation of the resulting oxygen anion gives the cyanohydrin. The former carbonyl carbon remains within the six-membered ring and bears both $-\text{OH}$ and $-\text{CN}$.



Thus the product is cyclohexanone cyanohydrin; the ring is not opened in this addition.

Step 2: (a)(ii) Decarboxylation of sodium benzoate On heating sodium benzoate with soda lime, the $-\text{COONa}$ group is replaced by hydrogen. The organic product is benzene, and sodium carbonate is the inorganic product:

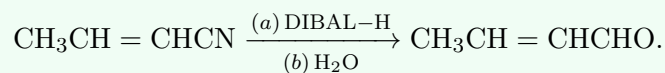


Calcium oxide is a component of soda lime and is written over the arrow; it is not consumed in the net equation.

Step 3: (a)(iii) Controlled reduction of the nitrile DIBAL-H partially reduces the nitrile, and subsequent hydrolysis gives an aldehyde. The carbon of the nitrile is retained as the aldehyde carbon; the

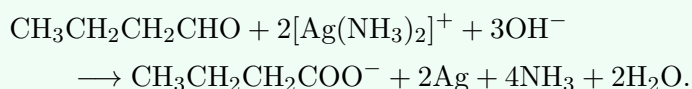
Quick Tip to Solve: Track the functional-group carbon: soda lime removes it, while DIBAL-H retains the nitrile carbon as CHO . Use Tollens' reagent for aldehyde versus ketone and bicarbonate for carboxylic acid versus phenol.

carbon-carbon double bond remains:



The product is but-2-enal. The controlled reagent sequence stops at the aldehyde rather than giving the primary amine obtained with stronger nitrile-reducing conditions.

Step 4: (b)(i) Distinguish butanal and butan-2-one Warm separate samples gently with freshly prepared Tollens' reagent (ammoniacal silver nitrate). Butanal gives a silver mirror because its aldehyde group is oxidised to carboxylate while silver(I) is reduced to metallic silver:



Butan-2-one gives no silver mirror under these conditions. These contrasting observations identify the aldehyde and ketone.

Step 5: (b)(ii) Distinguish benzoic acid and phenol Add aqueous sodium hydrogen carbonate to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide:



The evolved gas turns limewater milky. Phenol gives no effervescence with sodium hydrogen carbonate, because it is weaker than carbonic acid and cannot displace it from its salt.

Step 6: Conclusion (a) The products are (i) cyclohexanone cyanohydrin, (ii) benzene (with sodium carbonate), and (iii) $\text{CH}_3\text{CH}=\text{CHCHO}$, but-2-enal. (b) Tollens' reagent gives a silver mirror with butanal only; sodium hydrogen carbonate gives CO_2 effervescence with benzoic acid only.

Quick Tip to Solve: Track the functional-group carbon: soda lime removes it, while DIBAL-H retains the nitrile carbon as CHO. Use Tollens' reagent for aldehyde versus ketone and bicarbonate for carboxylic acid versus phenol.

24(b). (a) Write the reactions involved in the following:

(i) Etard reaction

(ii) Stephen reduction

(b) How will you convert the following in not more than two steps:

(i) Benzoic acid to Benzaldehyde

(ii) Acetophenone to Benzoic acid

(iii) Ethanoic acid to 2-Hydroxyethanoic acid

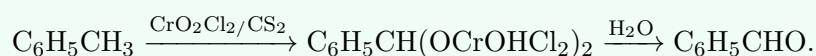
[5 marks]

Solution:

Concept:

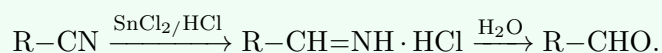
- Etard oxidation converts the methyl group of toluene to an aldehyde using chromyl chloride, CrO_2Cl_2 , followed by hydrolysis. Stephen reduction converts a nitrile to an aldehyde through an iminium salt.
- Rosenmund reduction uses hydrogen over poisoned palladium on barium sulphate to reduce an acid chloride selectively to an aldehyde.
- A methyl ketone undergoes the haloform reaction, giving a carboxylate with one fewer carbon atom. The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen; aqueous alkali then replaces that halogen by hydroxyl.

Step 1: (a)(i) Write the Etard reaction Treat toluene with chromyl chloride in carbon disulphide. An Etard complex forms; hydrolysis of this complex gives benzaldehyde:



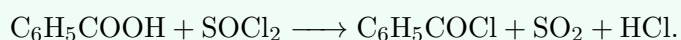
The controlled oxidation stops at the aldehyde stage instead of converting the side chain to a carboxylic acid.

Step 2: (a)(ii) Write the Stephen reduction Reduce a nitrile with stannous chloride and hydrochloric acid to its iminium chloride, then hydrolyse it to the corresponding aldehyde:

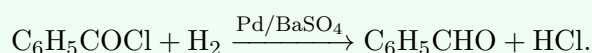


Here R denotes an alkyl or aryl group. The carbon of the nitrile group becomes the aldehyde carbon, so this conversion retains the carbon skeleton. Hydrolysis of the intermediate also produces ammonium chloride.

Step 3: (b)(i) Convert benzoic acid to benzaldehyde First convert the acid to benzoyl chloride with thionyl chloride:



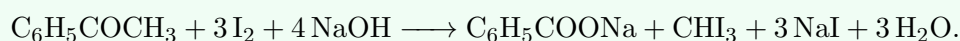
Then carry out Rosenmund reduction:



Quick Tip to Solve: For an acid-to-aldehyde conversion, use its acid chloride and Rosenmund reduction. Spot the methyl ketone in acetophenone for haloform cleavage, and use alpha halogenation before introducing hydroxyl into ethanoic acid.

The poisoned catalyst prevents further reduction of the aldehyde to benzyl alcohol. Thus the acid chloride provides a suitable intermediate in a two-step conversion.

Step 4: (b)(ii) Convert acetophenone to benzoic acid Acetophenone contains the methyl ketone group $-\text{COCH}_3$, so use iodine and aqueous sodium hydroxide for the iodoform reaction:

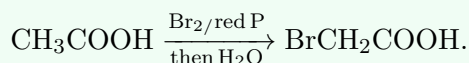


Acidify the sodium benzoate with dilute hydrochloric acid:

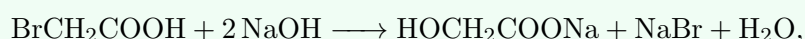


The methyl carbon is removed as iodoform, while the carbonyl carbon remains in the benzoic acid product.

Step 5: (b)(iii) Convert ethanoic acid to 2-hydroxyethanoic acid Brominate the alpha carbon using bromine and red phosphorus in the Hell-Volhard-Zelinsky reaction, followed by hydrolysis of the acyl halide formed:



Heat bromoethanoic acid with aqueous sodium hydroxide and acidify the resulting salt during work-up:



Aqueous alkali substitutes hydroxyl for bromine. Acidification is the work-up of this second conversion and yields 2-hydroxyethanoic acid, also called glycolic acid.

Step 6: Conclusion Etard oxidation and Stephen reduction give aldehydes. The required conversion routes are benzoic acid through benzoyl chloride followed by Rosenmund reduction; acetophenone through sodium benzoate by the iodoform reaction followed by acidification; and ethanoic acid through bromoethanoic acid followed by aqueous-alkali hydrolysis and acidic work-up.

Quick Tip to Solve: For an acid-to-aldehyde conversion, use its acid chloride and Rosenmund reduction. Spot the methyl ketone in acetophenone for haloform cleavage, and use alpha halogenation before introducing hydroxyl into ethanoic acid.

25(a). Account for the following:

(i) Transition metals show variable oxidation states.

(ii) Zn, Cd and Hg are soft metals.

(iii) E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is highly positive (+1.57 V) as compared to $\text{Cr}^{3+}/\text{Cr}^{2+}$.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

[5 marks]

Solution:

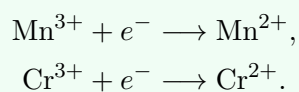
Concept:

- Oxidation states depend on which valence electrons can take part in bonding. In transition metals, the $(n-1)d$ and ns subshells have comparable energies.
- Metallic bonding depends on the availability of valence electrons for delocalisation. A completely filled d^{10} subshell contributes little to metallic bonding.
- A positive standard reduction potential, E° , indicates a favourable reduction under standard conditions. Particularly stable electronic configurations influence the relative stability of the oxidised and reduced ions.
- Lanthanoids involve progressive filling of $4f$ orbitals, whereas actinoids involve progressive filling of $5f$ orbitals.

Step 1: (a)(i) Explain variable oxidation states The energies of the outer ns and inner $(n-1)d$ electrons in transition metals are close. Consequently, both kinds of electrons can participate in bond formation or be removed during ion formation. Different numbers of these electrons can therefore be used in different compounds, giving several oxidation states. For example, manganese can show oxidation states from +2 to +7, because different numbers of its $3d$ and $4s$ electrons take part in bonding.

Step 2: (a)(ii) Explain the softness of Zn, Cd and Hg Zinc, cadmium and mercury have valence configurations of the form $(n-1)d^{10}ns^2$. Their completely filled d subshells do not effectively contribute electrons to metallic bonding. Thus, their metallic bonds are relatively weak compared with those in metals with partially filled d subshells and more electrons available for bonding. This weak cohesion accounts for their softness; mercury is liquid at room temperature.

Step 3: (a)(iii) Compare the two reduction couples The reductions being compared are



In the first reduction, Mn^{3+} , with configuration $3d^4$, gains an electron to form Mn^{2+} , with the especially stable half-filled configuration $3d^5$. Reduction is therefore strongly favoured, giving the highly positive value $E^\circ = +1.57\text{ V}$. By contrast, Cr^{3+} has configuration $3d^3$, which is particularly stable in aqueous solution because of its stable t_{2g}^3 arrangement in an octahedral field. Its reduction gives Cr^{2+} , with configuration $3d^4$, losing this stability. Hence, the $\text{Cr}^{3+}/\text{Cr}^{2+}$ reduction potential is much less positive than that of $\text{Mn}^{3+}/\text{Mn}^{2+}$.

Step 4: (b) State one similarity and one difference **Similarity:** Both lanthanoids and actinoids commonly exhibit the +3 oxidation state in their compounds.

Quick Tip to Solve: Write the ionic d -electron configurations before comparing reduction potentials: Mn(III) to Mn(II) produces $d5$, whereas Cr(III) to Cr(II) destroys the stable $d3$ arrangement.

Difference: Actinoids exhibit a wider range of oxidation states than lanthanoids. In actinoids, the $5f$, $6d$ and $7s$ orbitals have sufficiently comparable energies for different numbers of electrons to participate in bonding. Lanthanoids predominantly show +3, with only a few also showing +2 or +4, because their $4f$ electrons are less available for bonding.

Step 5: Conclusion The comparable energies of d and s electrons explain variable oxidation states; filled d^{10} subshells produce weak metallic bonding in Zn, Cd and Hg. Formation of stable Mn^{2+} explains the high Mn^{3+}/Mn^{2+} potential. Both f-block series commonly show +3, but actinoids show a wider range of oxidation states.

Quick Tip to Solve: Write the ionic d-electron configurations before comparing reduction potentials: $Mn(III)$ to $Mn(II)$ produces d^5 , whereas $Cr(III)$ to $Cr(II)$ destroys the stable d^3 arrangement.

OR

25(b). (a) Following are the transition metal ions of 3d series:

Ti^{4+} , V^{2+} , Mn^{3+} , Cr^{3+}

(Atomic numbers: Ti = 22, V = 23, Mn = 25, Cr = 24)

Answer the following:

(i) Which ion is most stable in an aqueous solution and why?

(ii) Which ion is a strong oxidising agent and why?

(iii) Which ion is colourless and why?

(b) Complete the following equations:

(i) $2 MnO_4^- + 16 H^+ + 5 S^{2-} \rightarrow$

(ii) $KMnO_4 \xrightarrow{\text{heat}}$

[5 marks]

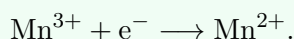
Solution:

Concept:

- Remove the $4s$ electrons before the $3d$ electrons when forming the ions of the first transition series. The resulting configurations are $Ti^{4+} : 3d^0$, $V^{2+} : 3d^3$, $Mn^{3+} : 3d^4$, and $Cr^{3+} : 3d^3$.
- An oxidising agent accepts electrons and is itself reduced. Formation of a particularly stable half-filled $3d^5$ configuration favours reduction of Mn^{3+} to Mn^{2+} .
- Colour in aqueous transition-metal ions commonly arises from absorption of visible light in $d-d$ transitions. A d^0 ion has no d electron available for such a transition.

Step 1: (a)(i) Identify the most stable aqueous ion The most stable ion among those listed is Cr^{3+} . Its configuration is $[Ar]3d^3$; in its octahedral aqueous complex the three electrons occupy the lower-energy t_{2g} orbitals singly, giving t_{2g}^3 . This arrangement has substantial crystal-field stabilisation. Although V^{2+} is also d^3 , it readily undergoes oxidation to higher oxidation states in aqueous solution, whereas the +3 state of chromium is particularly stable.

Step 2: (a)(ii) Identify the strong oxidising agent Mn^{3+} , with configuration $3d^4$, readily accepts one electron:

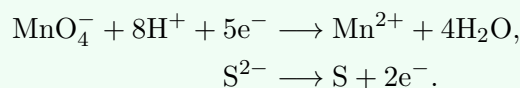


Quick Tip to Solve: Write the ionic d-electron counts first; for acidic permanganate use $Mn(II)$, then balance electrons before atoms and charge.

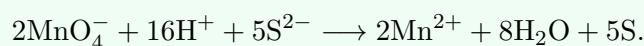
The product Mn^{2+} has the especially stable half-filled $3d^5$ configuration. Thus the tendency of Mn^{3+} to be reduced makes it a strong oxidising agent.

Step 3: (a)(iii) Identify the colourless ion Ti^{4+} has configuration $[\text{Ar}]3d^0$. Since it contains no d electrons, it cannot undergo the $d-d$ transitions responsible for the characteristic colours of these aqueous ions. It is therefore colourless. The other listed ions have partially occupied d subshells.

Step 4: (b)(i) Balance the acidic permanganate reaction In acidic medium manganese is reduced from +7 to +2, whereas sulphide is oxidised from -2 to elemental sulphur. The half-reactions are



Multiplying the first by 2 and the second by 5 cancels ten electrons, yielding



Both sides contain two manganese atoms, eight oxygen atoms, sixteen hydrogen atoms and five sulphur atoms; both have net charge +4.

Step 5: (b)(ii) Write the thermal decomposition Heating potassium permanganate produces potassium manganate, manganese dioxide and oxygen:



The two manganese atoms initially have oxidation state +7; the products contain manganese in +6 and +4 states. Oxygen evolution accompanies this internal redox decomposition. The coefficients conserve two potassium atoms, two manganese atoms and eight oxygen atoms.

Step 6: Conclusion (a) (i) Cr^{3+} : stable aqueous $3d^3$ configuration; (ii) Mn^{3+} : reduction gives stable $3d^5$ Mn^{2+} ; (iii) Ti^{4+} : colourless because it is $3d^0$. (b) The products are (i) $2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$, and (ii) $\text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$ from 2KMnO_4 .

Quick Tip to Solve: Write the ionic d-electron counts first; for acidic permanganate use Mn(II) , then balance electrons before atoms and charge.

26(a). A 10% solution (by mass) of sucrose in water has a freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15 K.

Given:

(Molar mass of sucrose = 342 g mol⁻¹)

(Molar mass of glucose = 180 g mol⁻¹)

(b) Define the following terms:

(i) Molality (m)

(ii) Abnormal molar mass

[5 marks]

Solution:

Concept:

- Depression in freezing point is a colligative property: $\Delta T_f = K_f m$, where K_f is the molal depression constant of the solvent and m is the molality of the solute. Sucrose and glucose are non-electrolytes and do not dissociate in water, so their van't Hoff factors are taken as unity.
- A 10% solution by mass contains 10 g of solute in 100 g of solution, hence 90 g of water. For equal solute masses in equal solvent masses, molality is inversely proportional to solute molar mass.
- Association or dissociation changes the number of solute particles and therefore changes the molar mass inferred from a colligative-property measurement.

Step 1: (a) Find the freezing point depression of sucrose The depression is measured relative to the freezing point of pure water:

$$\Delta T_{f,s} = 273.15 - 269.15 = 4.00 \text{ K.}$$

Taking 100 g of each solution, the mass of water in each is $100 - 10 = 90 \text{ g} = 0.090 \text{ kg}$. Thus

$$m_s = \frac{10/342}{0.090} = 0.3249 \text{ mol kg}^{-1}, \quad m_g = \frac{10/180}{0.090} = 0.6173 \text{ mol kg}^{-1}.$$

The denominator is the mass of water, not the mass of the solution.

Step 2: (a) Calculate the freezing point of the glucose solution Since water is the solvent in both solutions, K_f is the same. Dividing their freezing-point-depression equations eliminates it:

$$\begin{aligned} \frac{\Delta T_{f,g}}{\Delta T_{f,s}} &= \frac{m_g}{m_s} = \frac{342}{180} = 1.90, \\ \Delta T_{f,g} &= 4.00 \times 1.90 = 7.60 \text{ K,} \\ T_{f,g} &= 273.15 - 7.60 = 265.55 \text{ K.} \end{aligned}$$

Glucose has the lower molar mass, so the same mass supplies more particles. Its larger depression and lower freezing point are therefore consistent with the colligative-property relation.

Step 3: (b)(i) Define molality Molality, m , is the number of moles of solute dissolved in one kilogram of solvent:

$$m = \frac{n_{\text{solute}}}{w_{\text{solvent in kg}}}.$$

Its unit is mol kg⁻¹. Because it is defined using masses rather than volume, it does not change with

Quick Tip to Solve: For equal mass percentages in the same solvent, divide the two depression equations: the solvent mass cancels and the depression ratio is the inverse molar-mass ratio.

temperature for a solution of fixed composition.

Step 4: (b)(ii) Define abnormal molar mass Abnormal molar mass is the molar mass obtained from a colligative property that differs from the normal molar mass because the solute associates or dissociates in solution. If M_{normal} is the normal molar mass and M_{observed} is the value calculated assuming no association or dissociation, then

$$i = \frac{M_{\text{normal}}}{M_{\text{observed}}}.$$

Association reduces the particle count and gives an observed molar mass greater than the normal value; dissociation increases the particle count and gives an observed molar mass smaller than the normal value.

Step 5: Conclusion (a) The freezing point of the 10% glucose solution is 265.55 K. (b) Molality is moles of solute per kilogram of solvent; abnormal molar mass is a colligatively determined molar mass that differs from the normal value owing to association or dissociation.

Quick Tip to Solve: For equal mass percentages in the same solvent, divide the two depression equations: the solvent mass cancels and the depression ratio is the inverse molar-mass ratio.

OR

26(b). (a) 30 g of urea ($M = 60 \text{ g mol}^{-1}$) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg.

(b) Write two differences between ideal solutions and non-ideal solutions.

[5 marks]

Solution:

Concept:

- For a solution containing a non-volatile solute, Raoult's law gives $p_w = x_w p_w^\circ$, where p_w is the vapour pressure of water over the solution, x_w is its mole fraction and p_w° is the vapour pressure of pure water at the same temperature.
- The mole fraction of water is $x_w = n_w / (n_w + n_u)$, with n_w and n_u denoting moles of water and urea. Urea is a non-volatile, non-electrolyte solute, so it does not contribute appreciably to the vapour pressure.
- Ideal solutions obey Raoult's law over the entire composition range and have zero enthalpy and volume changes on mixing. Non-ideal solutions show deviations because unlike-molecule interactions differ from like-molecule interactions.

Step 1: (a) Calculate the moles and mole fraction of water Using the molar masses of urea and water, respectively,

$$n_u = \frac{30 \text{ g}}{60 \text{ g mol}^{-1}} = 0.50 \text{ mol},$$
$$n_w = \frac{846 \text{ g}}{18 \text{ g mol}^{-1}} = 47.0 \text{ mol}.$$

Quick Tip to Solve: For a non-volatile solute, calculate moles of both solute and solvent first, then multiply the pure-solvent pressure by the solvent mole fraction.

Hence the mole fraction needed in Raoult's law is

$$x_w = \frac{47.0}{47.0 + 0.50} = \frac{94}{95} = 0.98947.$$

The denominator includes both components; a mass fraction cannot replace a mole fraction here.

Step 2: (a) Apply Raoult's law at 298 K The supplied pure-water vapour pressure is 23.8 mm Hg. Therefore,

$$p_w = \frac{94}{95} \times 23.8 = 23.5495 \text{ mm Hg.}$$

As a check, the relative lowering is the solute mole fraction:

$$\frac{23.8 - p_w}{23.8} = \frac{0.50}{47.50} = \frac{1}{95}.$$

Thus dissolving urea lowers the pressure by approximately 0.251 mm Hg, consistent with the water mole fraction being slightly below unity.

Step 3: (b) State two differences between ideal and non-ideal solutions First, an ideal solution obeys Raoult's law, $p_i = x_i p_i^\circ$, for each volatile component throughout the composition range. A non-ideal solution deviates positively or negatively from Raoult's law.

Second, for an ideal solution $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$: mixing causes neither heat absorption/evolution nor volume change. For a non-ideal solution these changes are generally non-zero. Positive deviations are associated with weaker unlike-molecule attractions, whereas negative deviations are associated with stronger unlike-molecule attractions.

Step 4: Conclusion (a) The vapour pressure of water over the urea solution at 298 K is 23.55 mm Hg.
(b) Ideal solutions obey Raoult's law at all compositions and have zero enthalpy and volume changes of mixing; non-ideal solutions deviate from this law and generally have non-zero mixing changes.

Quick Tip to Solve: For a non-volatile solute, calculate moles of both solute and solvent first, then multiply the pure-solvent pressure by the solvent mole fraction.