

CBSE Class 12 Chemistry Question Paper 2008 with Solution PDF-Set 56/3 (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 nos. 1 to 8 are very short answer questions and carry 1 mark each.
- (iii) Question nos. 9 to 18 are short answer questions and carry 2 marks each.
- (iv) Question nos. 19 to 27 are also short answer questions and carry 3 marks each.
- (v) Question nos. 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. What type of substances exhibits antiferromagnetism?

[1 mark]

Solution:

Concept:

- Antiferromagnetism results from an ordered antiparallel arrangement of neighbouring magnetic moments.
- Equal moments in opposite directions cancel, giving zero resultant magnetic moment in the ordered state.

Step 1: Identify the arrangement The constituent atoms or ions possess magnetic moments, but neighbouring moments align in opposite directions. This antiparallel ordering distinguishes the material from a ferromagnet, in which moments align parallel.

Step 2: Check the resultant When the opposing magnetic moments are equal in magnitude, their vector sum is zero. Manganese(II) oxide, MnO , is a standard example of an antiferromagnetic substance below its ordering temperature.

Step 3: Conclusion Substances with equal magnetic moments aligned antiparallel exhibit antiferromagnetism; for example, MnO .

Quick Tip to Solve: Look for equal and opposite neighbouring magnetic moments: their cancellation identifies antiferromagnetism.

2. Express the relation between conductivity and molar conductivity of a solution.

[1 mark]

Solution:

Concept:

- Conductivity κ measures the conducting ability of a solution per unit geometrical factor.
- Molar conductivity Λ_m is conductivity multiplied by the volume containing one mole of electrolyte.

Step 1: Express the molar volume If the concentration is $C \text{ mol L}^{-1}$, one mole of electrolyte is contained in $1/C$ litres, or $1000/C \text{ cm}^3$, of the solution.

Step 2: Relate the two conductivities Multiplying conductivity by this volume gives

$$\Lambda_m = \frac{1000\kappa}{C}.$$

Here κ is in S cm^{-1} , so Λ_m is in $\text{S cm}^2 \text{ mol}^{-1}$. In SI units, $\Lambda_m = \kappa/c$ when c is in mol m^{-3} .

Step 3: Conclusion $\Lambda_m = 1000\kappa/C$, with C in mol L^{-1} and κ in S cm^{-1} .

Quick Tip to Solve: Use the factor 1000 only when concentration is per litre and conductivity uses centimetres.

3. Which has a higher enthalpy of adsorption, physisorption or chemisorption?

[1 mark]

Solution:

Concept:

- Physisorption is caused mainly by relatively weak van der Waals attractions.
- Chemisorption involves formation of stronger chemical bonds between adsorbate and adsorbent.

Step 1: Compare the interactions Physical adsorption does not normally form a chemical bond between the surface and the adsorbed particles. Its weak intermolecular attractions therefore release comparatively little heat.

Step 2: Compare the heat evolved Chemical adsorption involves appreciably stronger bonding and hence releases more energy per mole adsorbed. Adsorption enthalpies are negative for these exothermic processes; the usual comparison of their values means the magnitude of the heat released.

Step 3: Conclusion Chemisorption has the higher magnitude of enthalpy of adsorption (a more negative adsorption enthalpy).

Quick Tip to Solve: For adsorption comparisons, stronger bonding means a larger magnitude of heat evolved, not a more positive enthalpy.

4. Write the IUPAC name of the following compound:



[1 mark]

Solution:

Concept:

- The parent chain must contain the maximum number of hydroxyl groups.
- Number the chain to give the principal hydroxyl groups the lowest possible set of locants.

Step 1: Select and number the parent The longest chain containing both hydroxyl groups has six carbon atoms. Numbering from the terminal CH_2OH end places the hydroxyl groups at carbon atoms 1 and 3; numbering from the other end would give 4 and 6.

Step 2: Locate the substituents On this numbered hexane chain, methyl groups occur at carbon atoms 2 and 5. Use the prefix 2,5-dimethyl and the suffix -1,3-diol to represent the two hydroxyl groups. The hydroxyl locants take priority over substituent locants.

Step 3: Conclusion The IUPAC name is 2,5-dimethylhexane-1,3-diol.

Quick Tip to Solve: Start numbering at the terminal alcohol end so that the two hydroxyl groups receive locants 1 and 3.

5. In which one of the two structures, NO_2^+ and NO_2^- , the bond angle has a higher value? [1 mark]

Solution:

Concept:

- VSEPR theory relates molecular shape to repulsion between electron domains around the central atom.
- A lone pair on the central atom causes greater repulsion than a bonding pair and produces a bent molecular shape.

Step 1: Examine the nitronium ion In NO_2^+ , the central nitrogen has two bonding domains and no lone pair. The two domains lie opposite each other, so this ion is linear and its $\text{O} - \text{N} - \text{O}$ bond angle is 180° .

Step 2: Examine the nitrite ion In NO_2^- , nitrogen has two bonding domains and one lone pair. Its electron-domain arrangement is trigonal planar, but the molecular shape is bent. Lone-pair repulsion makes the bond angle less than 120° , well below the linear angle.

Step 3: Conclusion NO_2^+ has the higher bond angle: 180° .

Quick Tip to Solve: Count lone pairs on nitrogen: no lone pair gives linear nitronium, whereas one gives bent nitrite.

6. Name a substance that can be used as an antiseptic as well as a disinfectant. [1 mark]

Solution:

Concept:

- Antiseptics act against microorganisms on living tissues at suitable low concentrations.
- Disinfectants destroy microorganisms on non-living surfaces; the action of some substances depends on concentration.

Step 1: Choose a concentration-dependent agent Phenol is a standard example of a substance that can serve both purposes. The concentration controls its use: a sufficiently dilute solution is used as an antiseptic, while a stronger solution is used as a disinfectant.

Step 2: State the textbook concentrations A 0.2% phenol solution is used as an antiseptic, whereas a 1% phenol solution is used as a disinfectant. Thus the same chemical may fall into either category according to its concentration and application.

Step 3: Conclusion Phenol: 0.2% solution as an antiseptic and 1% solution as a disinfectant.

Quick Tip to Solve: Recall phenol as the dual-use example, and associate the lower concentration with antiseptic action.

7. Arrange the following compounds in an increasing order of their acid strengths:

$(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$

[1 mark]

Solution:

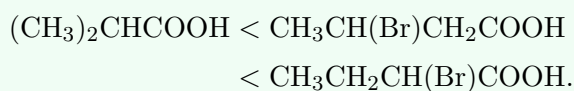
Concept:

- Acid strength increases when the conjugate carboxylate ion is stabilised. Bromine withdraws electron density through its negative inductive ($-I$) effect.
- The inductive effect decreases rapidly as the electron-withdrawing atom moves farther from the $-\text{COOH}$ group.

Step 1: Compare the substituents In $(\text{CH}_3)_2\text{CHCOOH}$, the alkyl groups show an electron-releasing effect and do not provide the stabilisation given by bromine. The bromo acids are therefore stronger acids.

Step 2: Compare the bromine positions In $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, bromine is on the beta carbon. In $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, it is on the alpha carbon, next to the carboxyl group, so its stabilising inductive effect is stronger.

Step 3: Conclusion The increasing order of acid strength is



Quick Tip to Solve: Number the chain from the carboxyl carbon: a nearer bromine atom gives the stronger acid.

8. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

[1 mark]

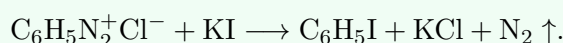
Solution:

Concept:

- An aromatic diazonium salt reacts with potassium iodide to replace the diazonium group, $-\text{N}_2^+$, by iodine.
- The aromatic carbon retains its bond position; nitrogen is released as N_2 gas.

Step 1: Choose the diazonium salt Take benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, and add aqueous potassium iodide. Iodide supplies the iodine that becomes attached to the benzene ring.

Step 2: Write the balanced replacement reaction

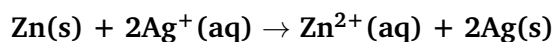


The products are iodobenzene, potassium chloride and nitrogen. Copper powder or a cuprous salt is not required for this iodide replacement.

Step 3: Conclusion Benzenediazonium chloride reacts with KI to give iodobenzene, with evolution of nitrogen gas.

Quick Tip to Solve: Use KI for the iodo product and always show nitrogen gas among the products.

9. Formulate the galvanic cell in which the following reaction takes place:



State:

- (i) Which one of its electrodes is negatively charged.
- (ii) The reaction taking place at each of its electrodes.
- (iii) The carriers of current within this cell.

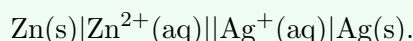
[2 marks]

Solution:

Concept:

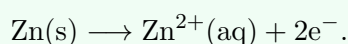
- Oxidation occurs at the anode and reduction at the cathode. In a galvanic cell the anode is negative and the cathode is positive.
- Cell notation places the anode on the left and cathode on the right; a single vertical line indicates a phase boundary and a double line the salt bridge.

Step 1: Formulate the cell and identify the negative electrode

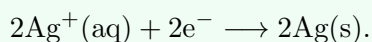


Zinc loses electrons in the spontaneous cell reaction. Hence the zinc electrode is the negatively charged anode, while silver is the positive cathode.

Step 2: Write the electrode reactions At the zinc anode, oxidation is



At the silver cathode, reduction is



Adding these equations cancels the electrons and gives the stated overall reaction.

Step 3: Identify the carriers of current Within the electrolyte solutions and the salt bridge, current is carried by moving ions: cations and anions migrate in opposite directions. Salt-bridge anions move towards the anode compartment and cations towards the cathode compartment to maintain electrical neutrality. Electrons carry current in the external metallic circuit, flowing from zinc to silver.

Step 4: Conclusion The cell is $\text{Zn}|\text{Zn}^{2+}||\text{Ag}^+|\text{Ag}$; Zn is the negative anode, Zn is oxidised, Ag^+ is reduced, and ions carry current within the electrolytes.

Quick Tip to Solve: Place the metal that loses electrons on the left; distinguish ionic conduction inside from electron flow outside.

10. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is $1500\ \Omega$. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3}\ \text{S cm}^{-1}$? [2 marks]

Solution:

Concept:

- For electrode separation l and electrode area A , the cell constant is l/A . Conductivity is $\kappa = (l/A)/R$, where R is resistance.
- Thus the cell constant equals conductivity multiplied by resistance: $l/A = \kappa R$. Using conductivity in S cm^{-1} gives the cell constant in cm^{-1} .

Step 1: List the data and choose the relation At 298 K,

$$R = 1500\ \Omega, \quad \kappa = 0.146 \times 10^{-3}\ \text{S cm}^{-1}.$$

The resistance and conductivity refer to the same KCl solution at the same temperature. Rearranging $\kappa = (1/R)(l/A)$ gives $l/A = \kappa R$. The stated concentration identifies the calibration solution; no molar-conductivity conversion is needed.

Step 2: Substitute and check the units

$$\begin{aligned} \frac{l}{A} &= (0.146 \times 10^{-3})(1500) \\ &= (0.146 \times 10^{-3})(1.5 \times 10^3) \\ &= 0.219\ \text{cm}^{-1}. \end{aligned}$$

Since $\text{S} = \Omega^{-1}$, the product of the conductivity and resistance has unit $\text{S cm}^{-1}\ \Omega = \text{cm}^{-1}$, as required for a length divided by an area.

Step 3: Conclusion The cell constant is $0.219\ \text{cm}^{-1}$.

Quick Tip to Solve: Multiply conductivity by resistance; the siemens and ohm cancel, leaving inverse centimetres.

11(a). State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law. [2 marks]

Solution:

Concept:

- Raoult's law states that, at a fixed temperature, the partial vapour pressure of each volatile component equals its mole fraction in solution multiplied by its pure-component vapour pressure: $p_i = x_i p_i^0$.
- The total pressure is the sum of partial pressures: $P = p_A + p_B = x_A p_A^0 + x_B p_B^0$. Deviations arise when unlike-molecule attractions differ from like-molecule attractions.

Step 1: State Raoult's law For a binary solution of volatile liquids A and B,

$$p_A = x_A p_A^0, \quad p_B = x_B p_B^0.$$

Here x_A, x_B are liquid-phase mole fractions and p_A^0, p_B^0 are the vapour pressures of the pure liquids at the same temperature.

Step 2: Explain positive deviation with an example Positive deviation means that the observed vapour pressure is greater than the value predicted by Raoult's law. Unlike A–B attractions are weaker than the original A–A and B–B attractions, so molecules escape into vapour more readily. Ethanol mixed with acetone is an example: acetone disrupts the hydrogen bonding between ethanol molecules.

Step 3: Explain negative deviation with an example Negative deviation means that the observed vapour pressure is less than the Raoult-law prediction. Unlike A–B attractions are stronger, reducing the tendency to escape. Acetone mixed with chloroform is an example: hydrogen bonding forms between chloroform hydrogen and acetone oxygen.

Step 4: Conclusion Raoult's law is $p_i = x_i p_i^0$. Ethanol–acetone shows positive deviation; acetone–chloroform shows negative deviation.

Quick Tip to Solve: Weaker unlike attractions raise vapour pressure; stronger unlike attractions lower it.

OR

11(b). Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure. [2 marks]

Solution:

Concept:

- Osmosis is solvent flow through a semipermeable membrane from pure solvent into a solution, or from dilute into concentrated solution.
- For a dilute solution, $\pi V = nRT$, where π is osmotic pressure, V is solution volume, n is moles of solute and T is absolute temperature.

Step 1: Define osmotic pressure Osmotic pressure is the minimum additional pressure that must be applied to a solution to prevent solvent from entering it through a semipermeable membrane. The membrane permits solvent molecules to pass but retains solute particles. This pressure is measured at a specified temperature.

Step 2: Measure the pressure and calculate molar mass Dissolve a known mass w of the substance to prepare a dilute solution of known volume V . Separate it from pure solvent by a semipermeable membrane and measure the pressure needed to just stop osmosis at temperature T . If the solute neither associates nor dissociates, $n = w/M$, where M is its molar mass. Thus

$$\pi V = \frac{w}{M} RT, \quad M = \frac{wRT}{\pi V}.$$

Insert the measured quantities using consistent pressure and volume units with the selected gas constant R . With mass in grams, molar mass is obtained in g mol^{-1} .

Step 3: Conclusion The measured osmotic pressure gives the molar mass through $M = wRT/(\pi V)$.

Quick Tip to Solve: Use the final solution volume, not the volume of solvent added, and always convert the temperature to kelvin.

12. Assign a reason for each of the following statements:

(i) Ammonia is a stronger base than phosphine.

(ii) Sulphur in vapour state exhibits a paramagnetic behaviour.

[2 marks]

Solution:

Concept:

- A Lewis base donates a lone pair of electrons. Its basicity depends on how readily that lone pair is available for bonding to a proton.
- Paramagnetism arises from unpaired electrons; a species with all electrons paired is diamagnetic.

Step 1: Compare the availability of the lone pairs Both NH_3 and PH_3 possess a lone pair on the central atom. In ammonia, this lone pair is more readily available for donation to a proton. In phosphine, the lone pair has greater s-character and is less readily donated. Therefore ammonia accepts a proton more readily and is a stronger base than phosphine. Merely counting the lone pairs cannot explain the difference, since both molecules have one lone pair.

Step 2: Identify the paramagnetic species in sulphur vapour At high temperature sulphur vapour contains diatomic S_2 molecules. Like O_2 , each S_2 molecule has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons cause attraction towards a magnetic field, so sulphur vapour exhibits paramagnetic behaviour. The explanation concerns the diatomic species in the vapour, rather than the usual cyclic S_8 molecules of solid sulphur.

Step 3: Conclusion (i) Ammonia has a more readily available lone pair than phosphine. (ii) The S_2 molecules present in hot sulphur vapour have two unpaired electrons and are paramagnetic.

Quick Tip to Solve: For basicity compare lone-pair availability; for sulphur vapour first identify S_2 and then count its unpaired electrons.

13. Draw the structures of the following molecules:

(i) SF_4

(ii) XeF_4

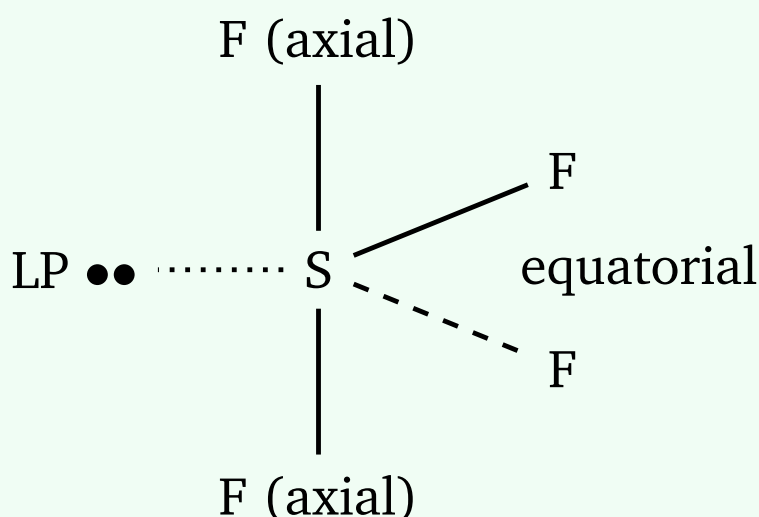
[2 marks]

Solution:

Concept:

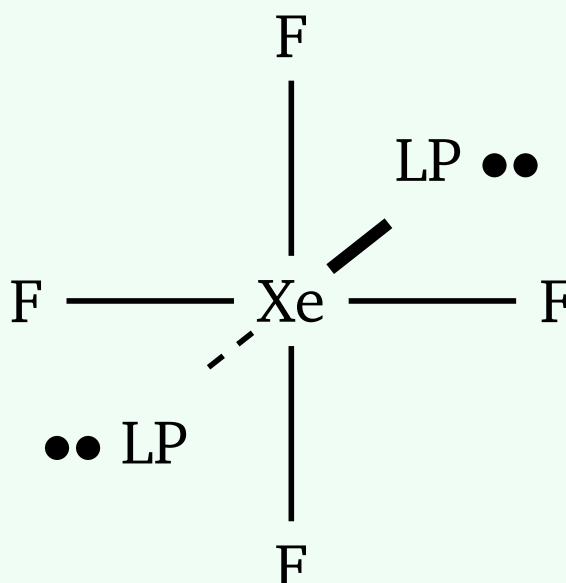
- VSEPR theory assigns molecular shape by arranging bond pairs and lone pairs to minimise electron-pair repulsion. Lone pairs repel more strongly than bond pairs.
- Count the electron domains around the central atom: SF_4 has five domains, whereas XeF_4 has six domains.

Step 1: Construct the structure of sulphur tetrafluoride Sulphur has six valence electrons. Four are used in the four S–F bonds, leaving one lone pair on sulphur. Thus SF_4 is an AX_4E molecule with trigonal-bipyramidal electron-pair geometry and sp^3d hybridisation in the usual school description. The lone pair occupies an equatorial position, reducing the number of strong right-angle repulsions. Two fluorine atoms occupy axial sites and two occupy the remaining equatorial sites, giving a see-saw molecular shape.



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

Step 2: Construct the structure of xenon tetrafluoride Xenon has eight valence electrons. Four single Xe–F bonds leave two lone pairs on xenon, so XeF_4 is AX_4E_2 . Its six electron domains have octahedral geometry, described by sp^3d^2 hybridisation. The two lone pairs occupy opposite positions to minimise their mutual repulsion. All four fluorine atoms then lie in one plane at the corners of a square, with xenon at its centre. Adjacent F–Xe–F angles are 90° .



Square-planar XeF_4 ; the lone pairs lie above and below the molecular plane.

Step 3: Conclusion SF_4 is see-saw shaped with one equatorial lone pair; XeF_4 is square planar with two mutually trans lone pairs.

Quick Tip to Solve: Count lone pairs before naming the shape: five domains with one lone pair give see-saw, while six domains with two opposite lone pairs give square planar.

14(a). Explain as to why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions. [2 marks]

Solution:

Concept:

- Haloarenes have halogen bonded directly to an aromatic, sp^2 -hybridised carbon; haloalkanes usually have an sp^3 carbon bonded to halogen.
- Nucleophilic substitution requires cleavage of the carbon–halogen bond; bond strength and the accessibility of the reaction pathway control reactivity.

Step 1: Explain the strong aryl carbon–halogen bond In a haloarene, a lone pair on the halogen overlaps with the aromatic π -system. Resonance therefore gives the carbon–halogen bond partial double-bond character. Also, an sp^2 carbon has greater s-character than an sp^3 carbon and holds the bonding electrons more closely. The aryl carbon–halogen bond is consequently shorter and stronger than the corresponding alkyl bond, so it is harder to break.

Step 2: Explain the substitution pathways The S_N1 pathway would require an extremely unstable phenyl carbocation, so ionisation is unfavourable. The usual S_N2 backside attack is also difficult at an aromatic sp^2 carbon because of the ring geometry and its electron cloud. Thus ordinary nucleophilic substitution occurs far less readily in haloarenes.

Step 3: Conclusion Haloarenes are less reactive because their carbon–halogen bond is strengthened by resonance and sp^2 hybridisation, while the usual S_N1 and S_N2 pathways are unfavourable.

Quick Tip to Solve: For aryl halides, mention resonance-strengthened C–X first, then the difficulty of the substitution pathway.

OR

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

(i) CH_3Br or CH_3I

(ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

[2 marks]

Solution:

Concept:

- An S_N2 reaction occurs in one step by backside attack of the nucleophile, here OH^- , with simultaneous departure of the leaving group.
- Faster substitution is favoured by a better leaving group and less steric obstruction around the carbon being attacked.

Step 1: Compare methyl bromide and methyl iodide Both compounds are methyl halides and have essentially the same steric environment. The C – I bond is weaker than the C – Br bond, and I^- is a better leaving group than Br^- . Therefore CH_3I undergoes S_N2 substitution with hydroxide faster than CH_3Br . The difference here is leaving-group ability, rather than crowding.

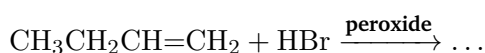
Step 2: Compare tert-butyl chloride and methyl chloride In $(\text{CH}_3)_3\text{CCl}$, three methyl groups crowd the carbon attached to chlorine and strongly hinder backside attack by hydroxide. In CH_3Cl , the carbon bears only three small hydrogen atoms, so the nucleophile can approach readily. Hence CH_3Cl reacts faster by $\text{S}_{\text{N}}2$; the tertiary halide is essentially unreactive through this pathway. Any tendency of a tertiary halide toward elimination or $\text{S}_{\text{N}}1$ does not change this comparison.

Step 3: Conclusion (i) CH_3I , owing to the weaker C–I bond and better leaving group; (ii) CH_3Cl , owing to minimal steric hindrance.

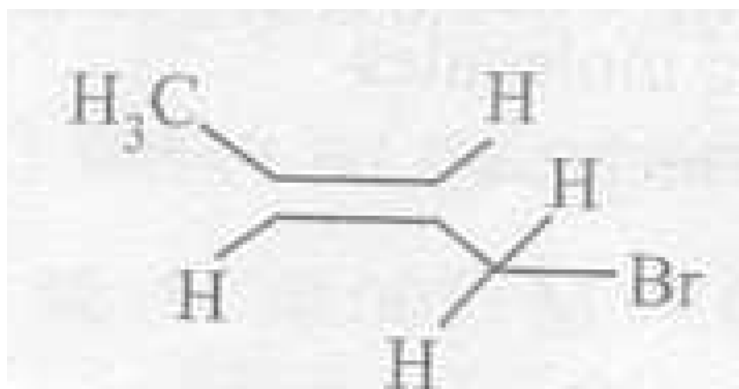
Quick Tip to Solve: Compare leaving groups when the carbon skeleton is the same; compare crowding when the leaving group is the same.

15. (a) State the IUPAC name of the following compound:

(b) Complete the following chemical equation:



[2 marks]



Solution:

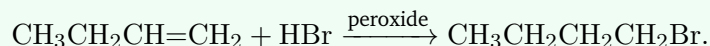
Concept:

- For naming an unsaturated halide, choose the longest chain containing the double bond and give the double bond the lowest possible locant; resolve a tie using the substituent locant.
- With peroxide, HBr adds to an unsymmetrical alkene by a radical mechanism, placing bromine on the less substituted carbon (anti-Markovnikov addition).

Step 1: Name the displayed compound The displayed structure is $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br}$. Its four-carbon parent chain is but-2-ene. Numbering from the brominated end gives the double bond locant 2 and bromine locant 1, rather than 4. Thus the required name is 1-bromobut-2-ene. The higher-priority groups at the double bond, CH_3 and CH_2Br , lie on opposite sides; including the shown configuration gives (E)-1-bromobut-2-ene.

Step 2: Complete the peroxide addition In but-1-ene, $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$, bromine radical adds at the terminal carbon so that the radical intermediate is secondary rather than primary. This radical

abstracts hydrogen from HBr. The resulting product is 1-bromobutane:



The carbon skeleton remains unchanged, and one H and one Br are added across the double bond.

Step 3: Conclusion (a) 1-Bromobut-2-ene, more fully (E)-1-bromobut-2-ene. (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, 1-bromobutane.

Quick Tip to Solve: First locate the double bond for naming; for HBr with peroxide, put Br on the terminal alkene carbon.

16. What are biodegradable and non-biodegradable detergents? Give one example of each class.

[2 marks]

Solution:

Concept:

- Biodegradation means breakdown of a substance by microorganisms, such as bacteria, into simpler products.
- The structure of the hydrocarbon chain controls how readily microbial enzymes can attack many synthetic detergents: straight chains are more readily degraded than highly branched chains.

Step 1: Define and exemplify biodegradable detergents Biodegradable detergents are detergents that microorganisms can decompose into simpler substances. They generally contain a straight, unbranched hydrocarbon chain, which is accessible to enzyme action. One example is sodium n-dodecyl sulphate (sodium lauryl sulphate), $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$. Its linear alkyl chain permits microbial degradation, so it does not persist in the environment in the same manner as a resistant branched detergent.

Step 2: Define and exemplify non-biodegradable detergents Non-biodegradable detergents are detergents that resist decomposition by microorganisms and therefore persist for a long time in water and soil. Highly branched hydrocarbon chains hinder the usual microbial breakdown. An example is sodium branched-chain dodecylbenzene sulphonate, a branched alkylbenzene sulphonate detergent. The word branched is essential: a linear alkylbenzene sulphonate is a biodegradable alternative, so alkylbenzene sulphonate alone would not specify the resistant class.

Step 3: Conclusion Biodegradable: readily decomposed by microbes, e.g. sodium n-dodecyl sulphate. Non-biodegradable: resists microbial decomposition, e.g. sodium branched-chain dodecylbenzene sulphonate.

Quick Tip to Solve: Use a straight-chain example for biodegradable detergents and explicitly say branched-chain for the resistant example.

17. Define the following terms in relation to proteins:

(i) Peptide linkage

(ii) Denaturation

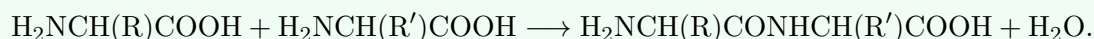
[2 marks]

Solution:

Concept:

- Amino acids join through covalent amide bonds to form the primary structure of proteins.
- The biological activity of a protein depends on its specific folded secondary and tertiary structures, stabilised by interactions such as hydrogen bonds.

Step 1: (i) Peptide linkage A peptide linkage is the amide bond, $-\text{CO}-\text{NH}-$, formed when the carboxyl group of one amino acid reacts with the amino group of another, eliminating one molecule of water. For example,



The resulting molecule is a dipeptide; repeated peptide-bond formation produces a polypeptide chain.

Step 2: (ii) Denaturation Denaturation is the loss of a protein's native conformation and biological activity when its secondary and tertiary structures are disrupted by heating, a change in pH, or suitable chemicals. The primary structure and peptide bonds remain intact. For example, the coagulation of egg white on boiling results from denaturation of its proteins. It is therefore a change in folding rather than hydrolysis into amino acids.

Step 3: Conclusion A peptide linkage is the $-\text{CO}-\text{NH}-$ bond joining amino-acid residues. Denaturation destroys the native folding and biological activity of a protein without changing its primary structure.

Quick Tip to Solve: Distinguish denaturation from hydrolysis: folding is disrupted in denaturation, whereas peptide bonds are broken in hydrolysis.

18. List the reactions of glucose which cannot be explained by its open chain structure.

[2 marks]

Solution:

Concept:

- The open-chain formula $\text{CHO}-(\text{CHOH})_4-\text{CH}_2\text{OH}$ gives glucose a free aldehyde group and five hydroxyl groups.
- A free aldehyde normally gives characteristic carbonyl reactions; the following observations show why this formula alone is inadequate.

Step 1: Absence of expected aldehyde reactions Despite the aldehyde group suggested by its open-chain formula, glucose does not give Schiff's test. It also does not form the usual hydrogen sulphite addition product with NaHSO_3 . These negative reactions cannot be explained satisfactorily if glucose is regarded as existing only as a molecule with a freely available $-\text{CHO}$ group.

Step 2: Behaviour of glucose pentaacetate Glucose pentaacetate does not react with hydroxylamine,

NH_2OH , to form an oxime. If acetylation had merely converted the five hydroxyl groups of an open-chain glucose molecule into acetate groups, its aldehyde group would still be available for oxime formation. The absence of this reaction therefore indicates the absence of a free aldehyde group in the pentaacetate. These observations are explained by the predominantly cyclic hemiacetal structure of glucose.

Step 3: Conclusion The unexplained observations are: no Schiff's test, no NaHSO_3 addition product, and no oxime formation when glucose pentaacetate is treated with hydroxylamine.

Quick Tip to Solve: For the open-chain limitations, recall two negative aldehyde tests and the failure of glucose pentaacetate to form an oxime.

19(a). How would you account for the following?

(i) Frenkel defects are not found in alkali metal halides.

(ii) Schottky defects lower the density of related solids.

(iii) Impurity doped silicon is a semiconductor.

[3 marks]

Solution:

Concept:

- A Frenkel defect displaces an ion from its normal lattice site to an interstitial site; a Schottky defect creates stoichiometric cation and anion vacancies.
- Density is mass divided by volume, $\rho = m/V$. Doping silicon introduces additional mobile charge carriers into its covalent lattice.

Step 1: (i) Absence of Frenkel defects in alkali metal halides Frenkel defects are favoured when a small cation can fit into an interstitial space between relatively large anions. Alkali-metal cations are too large to occupy the available interstitial spaces readily. Thus displacement of such a cation into an interstitial site is unfavourable, so alkali metal halides do not exhibit Frenkel defects.

Step 2: (ii) Decrease in density due to Schottky defects In a Schottky defect, the requisite numbers of cations and anions are missing from their lattice sites so that electrical neutrality is maintained. The missing ions reduce the mass of the crystal, while its volume remains essentially unchanged. Hence, from $\rho = m/V$, the density decreases. This differs from a Frenkel defect, in which ions are displaced within the crystal and the mass is unchanged.

Step 3: (iii) Semiconductor behaviour of impurity-doped silicon Each silicon atom normally forms four covalent bonds. Doping with a small amount of a pentavalent element such as phosphorus supplies an extra, weakly bound electron that can move through the crystal, producing an *n*-type semiconductor. Doping with a trivalent element such as boron leaves an electron-deficient bond, or hole; movement of holes produces a *p*-type semiconductor. These electrons or holes act as charge carriers and increase conductivity, while the material retains semiconductor behaviour.

Step 4: Conclusion Alkali-metal cations cannot readily occupy interstitial sites; Schottky vacancies reduce crystal mass and density; suitable doping of silicon supplies mobile electrons or holes, giving *n*-type or *p*-type semiconductors.

Quick Tip to Solve: For defect questions ask whether ions move or leave; for silicon doping compare the impurity valence with silicon's four valence electrons.

19(b). Explain the following properties giving suitable examples:

(i) Ferromagnetism

(ii) Paramagnetism

(iii) Ferrimagnetism

[3 marks]

Solution:

Concept:

- Magnetic behaviour depends on the magnetic moments associated with electrons, especially unpaired electrons, and on how these moments are arranged in the solid.
- Parallel moments reinforce one another, whereas antiparallel moments may cancel completely or leave a resultant moment if their magnitudes are unequal.

Step 1: Explain ferromagnetism Ferromagnetic substances are strongly attracted by a magnetic field. Their atomic magnetic moments align parallel within regions called domains. In an unmagnetised specimen the domains have different orientations; an applied field aligns more domains along itself, producing strong magnetisation. Some alignment can persist after the field is removed, so these substances can form permanent magnets. Examples are iron, cobalt and nickel.

Step 2: Explain paramagnetism Paramagnetic substances contain one or more unpaired electrons and are weakly attracted by a magnetic field. Without the field, thermal motion makes their magnetic moments randomly oriented. In an applied field they acquire a small preferential alignment along the field, but this magnetisation disappears when the field is removed. Molecular oxygen, O_2 , and Cu^{2+} ions are examples.

Step 3: Explain ferrimagnetism In ferrimagnetic substances, magnetic moments on different sets of sites align in opposite directions, but their magnitudes are unequal. Consequently, the opposing moments do not cancel completely and the solid possesses a net magnetic moment. Magnetite, Fe_3O_4 , and ferrites such as $MgFe_2O_4$ are examples.

Step 4: Conclusion Ferromagnetism involves parallel domain moments; paramagnetism involves weak field alignment of unpaired-electron moments; ferrimagnetism involves unequal opposing moments with a nonzero resultant.

Quick Tip to Solve: For ferrimagnetism, always state both antiparallel alignment and unequal moments; opposite directions alone do not establish a net moment.

20. Calculate the temperature at which a solution containing 54 g of glucose, ($\text{C}_6\text{H}_{12}\text{O}_6$), in 250 g of water will freeze.

(K_f for water = $1.86 \text{ K mol}^{-1} \text{ kg}$)

[3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_fm$, where m is the molality and i is the van't Hoff factor.
- Glucose is a nonelectrolyte and does not dissociate in water, so $i = 1$. Molality uses the mass of solvent in kilograms, not the mass of solution.

Step 1: Calculate the amount of glucose Using atomic masses C = 12, H = 1 and O = 16, the molar mass of glucose is

$$M(\text{C}_6\text{H}_{12}\text{O}_6) = 6(12) + 12(1) + 6(16) = 180 \text{ g mol}^{-1}.$$

Hence the amount of glucose is

$$n = \frac{54 \text{ g}}{180 \text{ g mol}^{-1}} = 0.300 \text{ mol}.$$

Step 2: Find molality and freezing-point depression The mass of water is $250 \text{ g} = 0.250 \text{ kg}$. Therefore

$$m = \frac{0.300}{0.250} = 1.20 \text{ mol kg}^{-1}.$$

Substituting in the colligative-property relation gives

$$\Delta T_f = 1 \times 1.86 \times 1.20 = 2.232 \text{ K}.$$

The units cancel as $(\text{K kg mol}^{-1})(\text{mol kg}^{-1}) = \text{K}$.

Step 3: Determine the solution freezing temperature Pure water freezes at 0°C , or 273.15 K , under ordinary atmospheric pressure. A positive depression means that the solution freezes below this temperature. Since a temperature interval of one kelvin equals an interval of one degree Celsius,

$$T_f(\text{solution}) = 0 - 2.232 = -2.232^\circ\text{C}.$$

Equivalently, $T_f = 273.15 - 2.232 = 270.918 \text{ K}$.

Step 4: Conclusion The solution freezes at -2.23°C (approximately 270.92 K).

Quick Tip to Solve: Convert 250 g of water to 0.250 kg before calculating molality, then subtract the depression from the freezing point of pure water.

21. Explain the basic principles of following metallurgical operations:

(i) Zone refining

(ii) Vapour phase refining

(iii) Electrolytic refining

[3 marks]

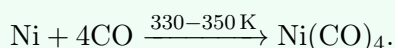
Solution:

Concept:

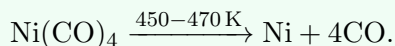
- Refining removes impurities from a crude metal by exploiting differences in solubility, volatility or electrochemical behaviour.
- The suitable process must selectively transfer or retain the desired metal while separating the associated impurities.

Step 1: Zone refining: different solubilities in melt and solid Zone refining is based on impurities being more soluble in the molten metal than in the solid metal. A narrow region of an impure metal rod is melted with a movable heater. As the heater moves, pure metal crystallises behind the molten zone, while impurities remain preferentially in the liquid and move with it. Repeated passes concentrate impurities at one end, which is cut off. This method gives very pure semiconductors such as silicon and germanium.

Step 2: Vapour phase refining: volatile compound formation The impure metal is converted selectively into a volatile compound, which is separated from nonvolatile impurities and then decomposed to yield pure metal. The compound must form readily and decompose under suitable conditions. In Mond refining of nickel,

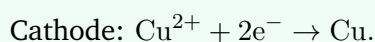
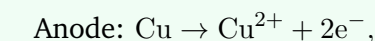


The volatile nickel carbonyl is heated to a higher temperature:



Pure nickel is deposited while carbon monoxide is released.

Step 3: Electrolytic refining: selective dissolution and deposition The impure metal acts as the anode, a thin sheet of pure metal as the cathode, and a solution of a suitable metal salt as the electrolyte. On passing current, metal dissolves from the anode and deposits in pure form on the cathode. For copper,



More reactive impurities generally remain dissolved; less reactive impurities such as silver and gold collect as anode mud instead of depositing under the chosen conditions.

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

Quick Tip to Solve: Connect each process to its separation principle first: melt solubility, volatile compound formation, or selective electrode reactions.

22. Explain what is observed when:

- (i) an electrolyte, KCl, is added to hydrated ferric oxide sol
- (ii) an electric current is passed through a colloidal solution
- (iii) a beam of strong light is passed through a colloidal solution

[3 marks]

Solution:

Concept:

- A colloidal sol is stabilised by the like charges on its particles; neutralising these charges permits aggregation and coagulation.
- Charged colloidal particles migrate in an electric field (electrophoresis), while scattering of light by these particles produces the Tyndall effect.

Step 1: (i) Addition of KCl Hydrated ferric oxide sol contains positively charged colloidal particles. On adding sufficient KCl, its negatively charged chloride ions, Cl^- , neutralise the positive charge on the particles. The particles lose their mutual repulsion, aggregate into larger particles and settle. Thus coagulation (precipitation) of the sol is observed; K^+ is not the coagulating ion for this positive sol.

Step 2: (ii) Passage of electric current The colloidal particles move towards the electrode carrying the opposite charge. Positively charged particles migrate towards the cathode and negatively charged particles towards the anode. This directed movement is called electrophoresis. At the electrode, particles may lose their charge and coagulate; the direction of movement therefore reveals the sign of their charge.

Step 3: (iii) Passage of a strong beam of light The path of the light beam becomes visible as a luminous cone when viewed from the side. The colloidal particles scatter the incident light in different directions, so some scattered light reaches the observer. This is the Tyndall effect and distinguishes a colloidal dispersion from a true solution under comparable conditions.

Step 4: Conclusion (i) KCl coagulates the positive hydrated ferric oxide sol through chloride ions. (ii) Electrophoresis occurs. (iii) The visible light path is due to the Tyndall effect.

Quick Tip to Solve: Match each stimulus to its effect: electrolyte neutralises charge, electric field moves particles, and light is scattered.

23. Write the names and structures of the monomers of the following polymers:

- (i) Buna-S
- (ii) Neoprene
- (iii) Nylon-6

[3 marks]

Solution:

Concept:

- A monomer is a small molecule that supplies the repeating units of a polymer. A copolymer is formed from two different monomers.
- Buna-S and neoprene are diene-based elastomers. Nylon-6 is a polyamide obtained by ring-opening

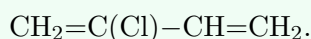
polymerisation of caprolactam.

Step 1: (i) Monomers of Buna-S Buna-S is a copolymer of 1,3-butadiene and styrene (phenylethene). Their structures are



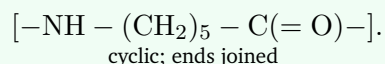
Both monomers contain carbon-carbon double bonds that participate in addition copolymerisation. The letter S in Buna-S identifies the styrene component.

Step 2: (ii) Monomer of neoprene Neoprene is obtained by polymerising chloroprene, whose systematic name is 2-chlorobuta-1,3-diene. Its structure is



The chlorine atom is attached to carbon 2 of the conjugated diene chain; chloroprene must not be confused with unsubstituted 1,3-butadiene.

Step 3: (iii) Monomer of Nylon-6 The monomer is caprolactam, specifically ϵ -caprolactam, a cyclic amide. Its ring contains one nitrogen atom, five methylene groups and one carbonyl carbon. Its structure is represented by



Here the terminal carbonyl carbon is bonded back to the initial nitrogen, closing the seven-membered ring. Ring opening produces the polyamide chain with repeating unit $[-\text{NH} - (\text{CH}_2)_5 - \text{CO}-]_n$.

Step 4: Conclusion Buna-S: 1,3-butadiene and styrene; neoprene: chloroprene; Nylon-6: ϵ -caprolactam, with the structures given above.

Quick Tip to Solve: Remember that Nylon-6 uses one six-carbon monomer; Nylon-6,6 instead uses a diamine and a dicarboxylic acid.

24. Account for the following observations:

(i) pK_b for aniline is more than that for methylamine.

(ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

(iii) Aniline does not undergo Friedel-Crafts reaction.

[3 marks]

Solution:

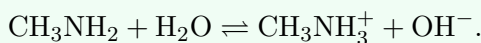
Concept:

- Basic strength depends on the availability of the nitrogen lone pair for protonation. $pK_b = -\log K_b$, so a weaker base has a larger pK_b .
- Aqueous amines generate hydroxide ions, and a nitrogen lone pair can also coordinate to a Lewis acid such as AlCl_3 .

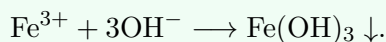
Step 1: (i) Comparing aniline and methylamine In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less available to accept a proton. In methylamine, the

electron-releasing inductive effect of the methyl group increases electron density on nitrogen and favours protonation. Consequently aniline is the weaker base: $K_b(\text{aniline}) < K_b(\text{methylamine})$, and hence its pK_b is larger.

Step 2: (ii) Formation of ferric hydroxide Methylamine acts as a base in water and produces hydroxide ions:

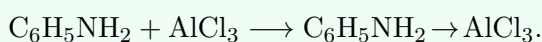


Ferric ions supplied by ferric chloride combine with these hydroxide ions to form insoluble reddish-brown ferric hydroxide:



Thus the precipitate results from the basic nature of the methylamine solution.

Step 3: (iii) Failure of the Friedel-Crafts reaction The Lewis-acid catalyst AlCl_3 accepts the nitrogen lone pair of aniline, forming a coordination complex:



Coordination removes the lone pair from donation into the ring and makes the nitrogen centre electron withdrawing. The ring is strongly deactivated towards electrophilic substitution, so aniline does not undergo the usual Friedel-Crafts alkylation or acylation.

Step 4: Conclusion The observations follow respectively from resonance weakening aniline as a base, hydroxide production by aqueous methylamine, and deactivation of aniline through complex formation with the Friedel-Crafts catalyst.

Quick Tip to Solve: For an amine, first ask whether its nitrogen lone pair is free, delocalised into a ring, or bound to a Lewis acid.

25. (a) What is a ligand? Give an example of a bidentate ligand.

(b) Explain as to how the two complexes of nickel, $[\text{Ni}(\text{CN})_4]^{2-}$ and $\text{Ni}(\text{CO})_4$, have different structures but do not differ in their magnetic behaviour. (Ni = 28) [3 marks]

Solution:

Concept:

- A ligand is an ion or molecule that donates one or more lone pairs to a central metal atom or ion, forming coordinate bonds. Denticity counts the donor atoms of one ligand that bind to the same metal.
- The oxidation state fixes the metal electron count. Hybridisation determines geometry, whereas unpaired electrons determine magnetic behaviour.

Step 1: (a) Define ligand and give a bidentate example A ligand acts as a Lewis base towards the metal centre, which accepts its lone pair. Ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, abbreviated en, is bidentate because both nitrogen atoms can donate a lone pair to the same metal ion. Thus one en molecule forms two coordinate bonds.

Step 2: (b) Analyse the cyanide complex Nickel has atomic number 28 and configuration $[\text{Ar}]3d^84s^2$.

In $[\text{Ni}(\text{CN})_4]^{2-}$, four cyanide ligands each carry charge -1 , so nickel is $+2$ and has configuration $3d^8$. The strong-field cyanide ligands pair the eight d electrons into four d orbitals. The vacant inner 3d orbital, one 4s and two 4p orbitals undergo dsp^2 hybridisation. The four bonds lie in one plane, giving a square-planar structure. All electrons are paired.

Step 3: (b) Analyse the carbonyl complex In $\text{Ni}(\text{CO})_4$, CO is neutral, so nickel has oxidation state zero. In the valence-bond description, its valence electrons become paired in a filled $3d^{10}$ subshell. The vacant 4s and three 4p orbitals form four sp^3 hybrids, directed tetrahedrally towards four CO ligands. There are no unpaired electrons in this complex either.

Step 4: Conclusion A ligand donates lone pairs; en is bidentate. $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar (dsp^2), whereas $\text{Ni}(\text{CO})_4$ is tetrahedral (sp^3). Both are diamagnetic because all their electrons are paired.

Quick Tip to Solve: First calculate the oxidation state of Ni: cyanide gives Ni(II), but neutral CO gives Ni(0).

26. Name the reagents which are used in the following conversions:

(i) A primary alcohol to an aldehyde

(ii) Butan-2-one to butan-2-ol

(iii) Phenol to 2, 4, 6-tribromophenol

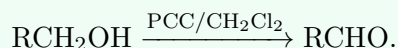
[3 marks]

Solution:

Concept:

- A primary alcohol undergoes controlled oxidation to an aldehyde; stronger aqueous oxidation may carry the reaction on to a carboxylic acid.
- A ketone is reduced to a secondary alcohol. The hydroxyl group in phenol strongly activates the ortho and para positions towards electrophilic substitution.

Step 1: (i) Primary alcohol to aldehyde Use pyridinium chlorochromate (PCC) in anhydrous dichloromethane. It oxidises the primary alcohol selectively to the aldehyde under these conditions:



Avoid an excess of an aqueous strong oxidising agent because the aldehyde can then be oxidised further to the corresponding acid.

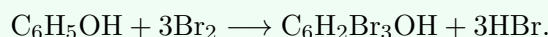
Step 2: (ii) Butan-2-one to butan-2-ol Use sodium borohydride, NaBH_4 , followed by hydrolysis or protonation. Hydride addition at the carbonyl carbon and subsequent protonation convert the carbonyl group into a secondary alcohol without changing the four-carbon skeleton:



Lithium aluminium hydride followed by hydrolysis is another suitable reducing reagent.

Step 3: (iii) Phenol to 2,4,6-tribromophenol Use excess bromine water, $\text{Br}_2(\text{aq})$. Phenol reacts readily without a Lewis-acid catalyst because the hydroxyl group activates the ring. Bromine replaces the

hydrogens at both ortho positions and the para position:



A white precipitate of 2,4,6-tribromophenol forms, and bromine water is decolourised.

Step 4: Conclusion The reagents are (i) PCC in anhydrous CH_2Cl_2 , (ii) NaBH_4 followed by hydrolysis, and (iii) excess bromine water.

Quick Tip to Solve: To stop a primary alcohol at the aldehyde stage, choose anhydrous PCC; bromine water gives all three ring substitutions in phenol.

27. Write chemical equations for the following processes:

(i) Chlorine reacts with a hot concentrated solution of sodium hydroxide

(ii) Orthophosphorous acid is heated

(iii) PtF_6 and xenon are mixed together

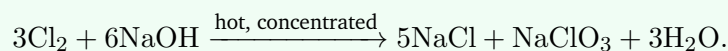
[3 marks]

Solution:

Concept:

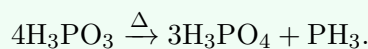
- Disproportionation occurs when one element in a reactant is simultaneously oxidised and reduced. Chlorine in hot concentrated alkali gives chloride and chlorate.
- Orthophosphorous acid, H_3PO_3 , disproportionates on heating. Xenon reacts with the strong oxidising agent PtF_6 to give xenon hexafluoridoplatinate.

Step 1: (i) Chlorine with hot concentrated sodium hydroxide The balanced equation is



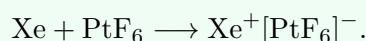
Chlorine changes from oxidation state 0 to -1 in chloride and $+5$ in chlorate. Five chlorine atoms gain one electron each while one loses five electrons. Hot concentrated alkali therefore gives chlorate; the hypochlorite reaction belongs to cold dilute alkali.

Step 2: (ii) Heating orthophosphorous acid Orthophosphorous acid decomposes by disproportionation:



Phosphorus initially has oxidation state $+3$. Three phosphorus atoms are oxidised to $+5$ in orthophosphoric acid, and one is reduced to -3 in phosphine. The six electrons lost and gained balance, as do all H and O atoms.

Step 3: (iii) Mixing xenon and platinum hexafluoride The conventional equation for the formation of xenon hexafluoridoplatinate is



The product is commonly written as XePtF_6 . This reaction demonstrated that xenon, despite its closed-shell configuration, can react with a sufficiently powerful oxidising agent such as platinum hexafluoride.

Step 4: Conclusion The products are (i) NaCl, NaClO₃ and water, (ii) H₃PO₄ and PH₃, and (iii) xenon hexafluoridoplatinate, Xe⁺[PtF₆]⁻, with equations balanced above.

Quick Tip to Solve: For hot concentrated alkali remember the chlorine ratio: three chlorine molecules give five chlorides and one chlorate.

28(a). Assign reasons for the following:

- (i) The enthalpies of atomisation of transition elements are high.
 - (ii) The transition metals and many of their compounds act as good catalyst.
 - (iii) From element to element the actinoid contraction is greater than the lanthanoid contraction.
 - (iv) The E° value for the Mn³⁺/Mn²⁺ couple is much more positive than that for Cr³⁺/Cr²⁺.
 - (v) Scandium (Z = 21) does not exhibit variable oxidation states and yet it is regarded as a transition element.
- [5 marks]

Solution:

Concept:

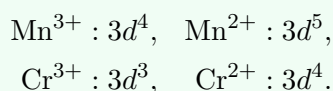
- Transition metals have partially filled d orbitals in their atoms or in at least one oxidation state; their d and s electrons influence metallic bonding and oxidation states.
- Half-filled d^5 and, in appropriate environments, d^3 configurations confer additional stability. A positive standard reduction potential favours reduction under standard conditions.
- Poor shielding by f electrons increases effective nuclear attraction across an f-block series, causing contraction.

Step 1: (i) High enthalpies of atomisation Atomisation separates the metal into individual gaseous atoms, so it requires metallic bonds to be broken. Transition elements generally have several unpaired d electrons, and both $(n - 1)d$ and ns electrons can participate in interatomic bonding. The resulting strong metallic bonding requires a large energy input for atomisation. Hence their enthalpies of atomisation are high.

Step 2: (ii) Catalytic activity Transition metals readily adopt different oxidation states because their d and s levels have comparable energies. They can therefore form intermediate compounds with reactants and subsequently regenerate the catalyst, providing a reaction path with a lower activation energy. Finely divided metals also adsorb reactants on their surfaces, bringing them together and weakening their bonds. These features explain the catalytic activity of the metals and many of their compounds.

Step 3: (iii) Greater actinoid contraction As atomic number increases, additional electrons enter the 5f subshell in the actinoids and the 4f subshell in the lanthanoids. The 5f electrons shield the increasing nuclear charge less effectively than the 4f electrons. The effective attraction experienced by the outer electrons consequently increases more strongly across the actinoids, producing a greater element-to-element decrease in size.

Step 4: (iv) Compare the reduction potentials The relevant configurations are



Reduction of Mn^{3+} produces the particularly stable half-filled $3d^5$ state of Mn^{2+} , so it is strongly favoured. In contrast, reduction of Cr^{3+} removes the comparatively stable $3d^3$ configuration to form $3d^4$. Thus the reduction potential of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that of $\text{Cr}^{3+}/\text{Cr}^{2+}$.

Step 5: (v) Scandium as a transition element The scandium atom has configuration $[\text{Ar}] 3d^1 4s^2$, so its d subshell is incomplete. It therefore satisfies the definition of a transition element through its atomic configuration. Loss of its three outer electrons gives the stable $[\text{Ar}]$ configuration of Sc^{3+} ; further ionisation would remove a core electron. This explains why its usual oxidation state is +3. Variable oxidation states are a common property of transition metals, but are not a necessary part of their definition.

Step 6: Conclusion The observations follow respectively from strong metallic bonding, variable oxidation states and adsorption, weaker shielding by 5f electrons, the relative stability of Mn^{2+} and Cr^{3+} , and scandium's incompletely filled atomic 3d subshell.

Quick Tip to Solve: For a reduction-potential comparison, write both ions' d configurations first and identify whether reduction gains or loses a particularly stable configuration.

OR

28(a). What may be the possible oxidation states of the transition metals with the following d electronic configurations in the ground state of their atoms:

$3d^3 4s^2$, $3d^5 4s^2$ and $3d^6 4s^2$. Indicate relative stability of oxidation states in each case.

[3 marks]

Solution:

Concept:

- In transition-metal ion formation the 4s electrons are removed before the 3d electrons. Comparable energies of these orbitals permit several oxidation states.
- A half-filled d^5 subshell provides additional stability. Relative stability also depends on the ligands and medium; high oxidation states are stabilised particularly by oxygen and fluorine.

Step 1: Analyse $3d^3 4s^2$: vanadium Removal of the two 4s electrons gives +2; successive removal of d electrons gives +3, +4 and +5. Their d configurations are respectively d^3 , d^2 , d^1 and d^0 . Thus the possible common oxidation states are +2, +3, +4, +5. The highest state, +5, uses all five valence electrons and is stable in oxo compounds; +4 is also stable, especially as the vanadyl ion VO^{2+} . The lower states +2 and +3 act as reducing agents and are readily oxidised in air. The d^3 configuration gives V^{2+} some electronic stability, but does not make it the most stable state in an oxidising medium.

Step 2: Analyse $3d^5 4s^2$: manganese The common oxidation states are +2, +3, +4, +6, +7; +5 is also possible but less common and less stable. Loss of only the two 4s electrons gives Mn^{2+} with the

especially stable half-filled $3d^5$ configuration. Hence +2 is particularly stable in aqueous solution, whereas Mn^{3+} , with $3d^4$, readily accepts an electron to become Mn^{2+} . The +4 state is stable in MnO_2 , while oxygen stabilises +6 in manganate and +7 in permanganate. These higher states commonly show oxidising behaviour; their stability must therefore be specified with the medium.

Step 3: Analyse $3d^6 4s^2$: iron The common oxidation states are +2 and +3. The +2 ion is $[Ar] 3d^6$, while loss of one further electron yields Fe^{3+} , $[Ar] 3d^5$. The half-filled configuration gives the +3 state additional stability, so Fe^{2+} is readily oxidised to Fe^{3+} in air. Both states form many stable compounds. A higher +6 state occurs in ferrate, FeO_4^{2-} , under strongly alkaline conditions, but is much less common and strongly oxidising.

Step 4: Conclusion Vanadium commonly shows +2, +3, +4, +5, with +5 stable in oxo compounds; manganese shows +2, +3, +4, +6, +7, with +2 particularly stable because it is d^5 ; iron chiefly shows +2, +3, with the d^5 +3 state having added electronic stability.

Quick Tip to Solve: Remove the two 4s electrons first, then count d electrons: Mn(II) and Fe(III) both leave a half-filled d5 subshell.

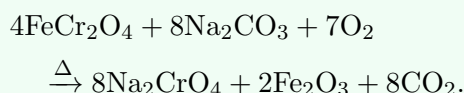
28(b). Write steps involved in the preparation of (i) Na_2CrO_4 from chromite ore and (ii) K_2MnO_4 from pyrolusite ore. [2 marks]

Solution:

Concept:

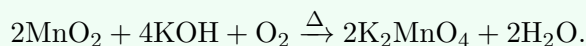
- Oxidative roasting or fusion in an alkaline medium converts the metal in its ore into the soluble oxoanion salt. Oxygen in air acts as the oxidising agent.
- Chromite is $FeCr_2O_4$, with chromium in the +3 state; pyrolusite is MnO_2 , with manganese in the +4 state. Both are oxidised to the +6 state in the requested products.

Step 1: (i) Prepare sodium chromate from chromite Finely powder chromite ore and roast it strongly with sodium carbonate in an excess of air. Chromium is oxidised to chromate, while iron forms insoluble iron(III) oxide:



Leach the roasted mass with water. Sodium chromate dissolves, giving a yellow solution; filter off the insoluble iron oxide and other residue. Concentrate the filtrate to obtain sodium chromate.

Step 2: (ii) Prepare potassium manganate from pyrolusite Fuse finely powdered pyrolusite with potassium hydroxide in the presence of air or oxygen. The alkaline oxidation produces green potassium manganate:



Extract the fused mass with water to obtain a green manganate solution. Keep the solution alkaline to stabilise manganate; concentration yields the required salt. This preparation stops at manganate and does not require its further oxidation to permanganate.

Step 3: Conclusion Roast chromite with Na_2CO_3 in air and leach to obtain yellow Na_2CrO_4 . Fuse

pyrolusite with KOH in air to obtain green K_2MnO_4 .

Quick Tip to Solve: Pair chromite with sodium carbonate and pyrolusite with potassium hydroxide; both preparations need an oxidising alkaline medium.

29(a). Derive the general form of the expression for the half-life of a first order reaction.

(b) The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$? [5 marks]

Solution:

Concept:

- For a first order reaction, $-d[A]/dt = k[A]$, where $[A]$ is reactant concentration and k is its rate constant. The half-life $t_{1/2}$ is the time for concentration to fall to half its initial value.
- For a zero order decomposition, the rate of disappearance of the reactant is independent of its concentration: $-d[A]/dt = k$. Rates of formation of products follow the balanced chemical equation.

Step 1: (a) Integrate the first order rate equation Let the initial concentration be $[A]_0$, and let the concentration after time t be $[A]_t$. Separate the variables in the differential rate law and integrate between these limits:

$$\begin{aligned}\frac{d[A]}{[A]} &= -k dt, \\ \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} &= -k \int_0^t dt, \\ \ln \frac{[A]_t}{[A]_0} &= -kt.\end{aligned}$$

Thus the integrated first order rate equation is

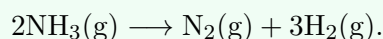
$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t} = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}.$$

Step 2: Substitute the half-life condition At $t = t_{1/2}$, the reactant concentration is $[A]_t = [A]_0/2$. Substitution cancels the initial concentration:

$$t_{1/2} = \frac{1}{k} \ln \frac{[A]_0}{[A]_0/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

Therefore a first order half-life is independent of initial concentration. If k is measured in s^{-1} , the half-life is in seconds. The derivation applies for constant k at a fixed temperature.

Step 3: (b) Relate the ammonia decomposition rate to product formation The balanced reaction on the platinum surface is



For zero order decomposition, $-d[\text{NH}_3]/dt = k = 2.5 \times 10^{-4}$. The printed unit $\text{mol}^{-1} \text{ L s}^{-1}$ is dimensionally inconsistent with a zero order rate constant; the required rate unit is $\text{mol L}^{-1} \text{ s}^{-1}$. Use

the stated numerical value as the ammonia disappearance rate in these units. From the stoichiometric coefficients,

$$-\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}.$$

Step 4: Calculate the two rates of production One mole of nitrogen is formed for every two moles of ammonia consumed, whereas three moles of hydrogen are formed:

$$\begin{aligned} \frac{d[\text{N}_2]}{dt} &= \frac{k}{2} = 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}, \\ \frac{d[\text{H}_2]}{dt} &= \frac{3k}{2} = 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

Both production rates are positive, and their ratio is 1 : 3, as required by the balanced equation.

Step 5: Conclusion (a) $t_{1/2} = 0.693/k$, independent of initial concentration. (b) The production rates of N_2 and H_2 are respectively 1.25×10^{-4} and $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$.

Quick Tip to Solve: First set the reactant concentration to half its initial value; for the gas rates, divide ammonia disappearance by 2 before applying product coefficients.

OR

29(b). (a) List the factors that affect the rate of a chemical reaction.

(b) The half-life of radioactive decay of ^{14}C is 5730 years. An archaeological artefact containing wood had only 80% of ^{14}C activity found in living tree. Estimate the age of the artefact. [5 marks]

Solution:

Concept:

- Reaction rate depends on the frequency of effective collisions. Reactant nature, concentration, temperature, catalysts, exposed surface area and, for suitable reactions, light can alter the rate.
- Radioactive decay follows first-order kinetics: $N = N_0 e^{-kt}$, where N_0 and N are the original and remaining numbers of radioactive nuclei, k is the decay constant and t is elapsed time.
- Activity is $A = kN$, so $A/A_0 = N/N_0$. For first-order decay, $k = \ln 2/t_{1/2}$.

Step 1: (a) List the factors affecting rate The principal factors are the nature of the reactants; their concentrations (or partial pressures for gaseous reactants); temperature; the presence of a catalyst; and the surface area of a solid reactant in a heterogeneous reaction. Light intensity also affects photochemical reactions. Increasing concentration generally increases collision frequency, while increasing temperature increases the fraction of collisions with sufficient activation energy. A catalyst provides an alternative pathway with lower activation energy. Finely divided solids expose more surface for contact with the other reactant. These factors describe how the number of effective collisions can change; their precise influence depends on the reaction's rate law.

Step 2: (b) Convert the activity percentage into the remaining fraction Let A_0 be the activity of the same quantity of carbon in living wood and A the present activity in the artefact. When the tree dies, exchange of carbon with the surroundings stops and its radioactive carbon decays. Since activity is

proportional to the number of undecayed nuclei,

$$\frac{N}{N_0} = \frac{A}{A_0} = \frac{80}{100} = 0.80, \quad \frac{N_0}{N} = 1.25.$$

The given percentage is the fraction remaining, rather than the fraction that has decayed.

Step 3: Calculate the decay constant and age Using the half-life $t_{1/2} = 5730$ years,

$$k = \frac{\ln 2}{5730} = 1.2097 \times 10^{-4} \text{ year}^{-1}.$$

The integrated first-order law then gives

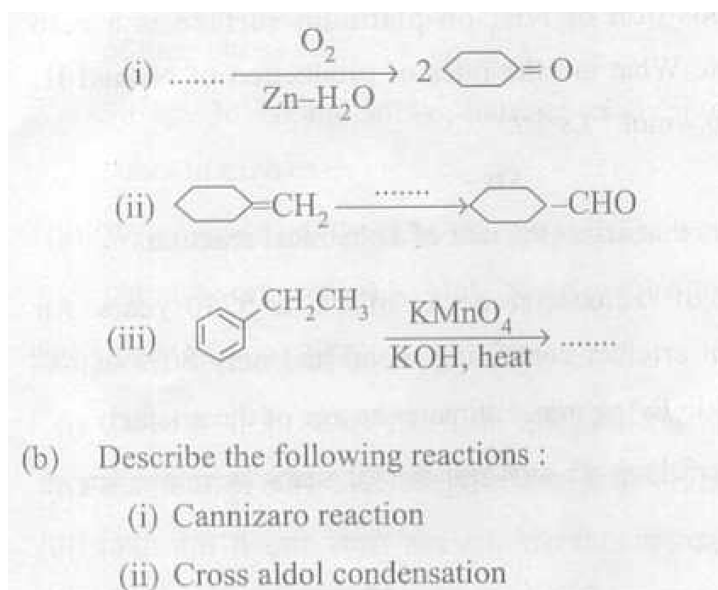
$$\begin{aligned} t &= \frac{1}{k} \ln \frac{N_0}{N} \\ &= \frac{5730}{\ln 2} \ln(1.25) \\ &= \frac{5730 \times 0.22314}{0.69315} \\ &\approx 1845 \text{ years.} \end{aligned}$$

The result is smaller than one half-life, consistent with more than half the original activity remaining.

Step 4: Conclusion (a) Rate is affected by reactant nature, concentration or gaseous pressure, temperature, catalysts, solid surface area and light in photochemical reactions. (b) The artefact is approximately 1.85×10^3 years old.

Quick Tip to Solve: For radiocarbon dating, put the fraction of activity remaining directly into $t = (t_{1/2} / \ln 2) \ln(1/f)$; here use $f = 0.80$, not 0.20.

30(a). Complete the following reaction statements by giving the missing starting material, reagent or product as required: [5 marks]



Solution:

Concept:

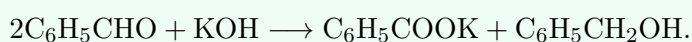
- Reductive ozonolysis cleaves an alkene at its double bond; each doubly bonded carbon becomes a carbonyl carbon.
- Hydroboration followed by oxidation gives the anti-Markovnikov alcohol. Hot alkaline permanganate oxidises a benzylic side chain to a carboxylate.
- An aldehyde without an alpha hydrogen undergoes Cannizzaro disproportionation; carbonyl compounds with alpha hydrogens can undergo aldol condensation.

Step 1: Identify the starting alkene in (a)(i) The missing compound is cyclohexylidenecyclohexane: two cyclohexane rings joined through an exocyclic $C = C$ bond between their ring carbons. Cleavage of that bond gives two molecules of cyclohexanone. Reversing the cleavage, remove the two carbonyl oxygens and join the two carbonyl carbons by a double bond. The printed reagent is O_2 ; the standard reagent for this reductive cleavage is ozone, O_3 , followed by Zn/H_2O . Molecular oxygen with zinc/water is not the usual ozonolysis sequence.

Step 2: Supply the reagents in (a)(ii) First convert methylenecyclohexane into cyclohexylmethanol by hydroboration and oxidation: (1) $BH_3 \cdot THF$, then (2) H_2O_2/OH^- . The hydroxyl group goes to the terminal carbon, giving $C_6H_{11}CH_2OH$. Then oxidise this primary alcohol with PCC in dry CH_2Cl_2 to $C_6H_{11}CHO$, cyclohexanecarbaldehyde. PCC stops at the aldehyde; a strong aqueous oxidant could give the acid.

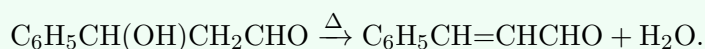
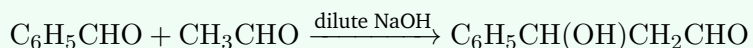
Step 3: Identify the product in (a)(iii) Ethylbenzene has benzylic hydrogens, so hot alkaline $KMnO_4$ oxidises its side chain to C_6H_5COOK , potassium benzoate. The carbon directly attached to the ring becomes the carboxyl carbon; the remaining side-chain carbon is oxidised further. Since the stated medium is KOH and no acidification is specified, the immediate organic product is the potassium salt. Acidification would give benzoic acid, C_6H_5COOH .

Step 4: Describe Cannizzaro reaction in (b)(i) An aldehyde having no alpha hydrogen undergoes self oxidation and reduction in concentrated alkali: one molecule gives a carboxylate and another gives a primary alcohol. For example, benzaldehyde reacts as follows:



Thus benzaldehyde is both oxidised and reduced in the same reaction.

Step 5: Describe cross aldol condensation in (b)(ii) Aldol condensation involving two different aldehydes or ketones is called cross aldol condensation. At least one partner must have an alpha hydrogen to form the enolate. The initial beta-hydroxy carbonyl compound loses water on heating. A selective example uses benzaldehyde (without alpha hydrogen) and ethanal:



The condensation product is cinnamaldehyde. When both partners have alpha hydrogens, self and cross products can form a mixture.

Step 6: Conclusion (a) (i) Cyclohexylidenecyclohexane; (ii) hydroboration–oxidation, then PCC; (iii) potassium benzoate. (b) Cannizzaro is aldehyde disproportionation in concentrated alkali; cross aldol condensation joins two different carbonyl partners and may eliminate water.

Quick Tip to Solve: For reverse ozonolysis, remove the two carbonyl oxygens and join their carbon atoms by a double bond; retain carboxylates in alkaline media.

OR

30(a). How would you account for the following:

- (i) Aldehydes are more reactive than ketones towards nucleophiles.
- (ii) The boiling points of aldehydes and ketones are lower than of the corresponding acids.
- (iii) The aldehydes and ketones undergo a number of addition reactions.

[3 marks]

Solution:

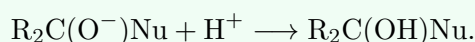
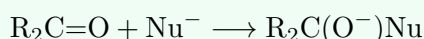
Concept:

- The carbonyl bond is polar: $C^{\delta+} = O^{\delta-}$. Nucleophiles attack its electrophilic carbon.
- Alkyl groups decrease carbonyl electrophilicity through their electron-releasing inductive effect and can obstruct an approaching reagent.
- Boiling point depends on intermolecular forces; carboxylic acids form strong intermolecular hydrogen bonds.

Step 1: Explain the higher reactivity of aldehydes in (i) In an aldehyde, the carbonyl carbon has one alkyl group and one hydrogen (two hydrogens in methanal), whereas a ketone has two alkyl groups. The additional alkyl group in a ketone donates electron density by the $+I$ effect, reducing the positive character of the carbonyl carbon and hence its attraction for a nucleophile. Two alkyl groups also cause greater steric hindrance to the approaching nucleophile. Aldehydes therefore generally react faster than ketones in nucleophilic addition.

Step 2: Compare the boiling points in (ii) Carboxylic acids contain an O – H group and a carbonyl oxygen, so their molecules form strong intermolecular hydrogen bonds and commonly associate as dimers. Aldehydes and ketones have a carbonyl oxygen but lack an O – H group; hence they do not form such hydrogen bonds between their own molecules. Their dipole–dipole attractions are weaker than the strong association in corresponding acids. Less energy is required to separate their molecules on boiling, so their boiling points are lower.

Step 3: Explain addition at the carbonyl group in (iii) The electronegative oxygen withdraws electron density from the carbonyl carbon, making it electrophilic. A nucleophile attacks this carbon, and the relatively weaker pi bond opens as its electron pair moves to oxygen. The strong carbon–oxygen sigma bond remains intact. The resulting alkoxide is protonated to form an addition product:



Thus the polar, unsaturated carbonyl group provides a favourable site for a variety of nucleophilic addition reactions.

Step 4: Conclusion (i) Aldehydes have less electron donation and steric hindrance. (ii) Acids have stronger intermolecular hydrogen bonding. (iii) The polar carbonyl pi bond opens during nucleophilic addition.

Quick Tip to Solve: For carbonyl reactivity, compare both steric and electronic effects; for boiling points, compare hydrogen bonding between the pure molecules.

30(b). Give chemical tests to distinguish between:

(i) Acetaldehyde and benzaldehyde

(ii) Propanone and propanol

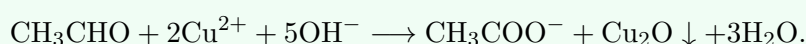
[2 marks]

Solution:

Concept:

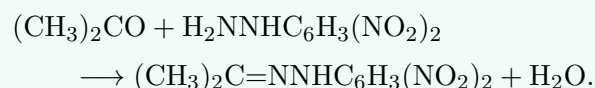
- A distinguishing test must give different visible results with the two compounds under the same conditions. Acetaldehyde is an aliphatic aldehyde, while benzaldehyde is an aromatic aldehyde.
- The reagent 2,4-dinitrophenylhydrazine (2,4-DNP) detects an aldehyde or ketone carbonyl group by forming a coloured, insoluble hydrazone; an alcohol does not give this reaction.

Step 1: (i) Acetaldehyde and benzaldehyde: Fehling's test Warm separate samples with freshly prepared Fehling's solution. Acetaldehyde reduces the alkaline copper(II) complex to a brick-red precipitate of copper(I) oxide, whereas benzaldehyde does not give this precipitate. The acetaldehyde is oxidised to acetate:



Thus the sample giving the brick-red precipitate is acetaldehyde. Tollens' reagent would not distinguish this pair because both are aldehydes and give a silver mirror.

Step 2: (ii) Propanone and propanol: 2,4-DNP test Add 2,4-DNP reagent to separate samples. Propanone gives a yellow to orange precipitate of its 2,4-dinitrophenylhydrazone; propanol gives no precipitate because it has no carbonyl group. The condensation is:



This test distinguishes propanone from either propan-1-ol or propan-2-ol, so the unspecified position of the hydroxyl group does not affect the result.

Step 3: Conclusion (i) Fehling's solution: acetaldehyde gives a brick-red precipitate; benzaldehyde does not. (ii) 2,4-DNP: propanone gives a yellow-orange precipitate; propanol does not.

Quick Tip to Solve: Use 2,4-DNP for propanone versus an unspecified propanol: propan-2-ol can also give the iodoform test.