

CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/2 - Compartment



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 8 are very short-answer questions and carry 1 mark each.
- (iii) Questions number 9 to 18 are short-answer questions and carry 2 marks each.
- (iv) Questions number 19 to 27 are also short-answer questions and carry 3 marks each.
- (v) Questions number 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 is meant by 'antiferromagnetism'?

[1 mark]

Solution:

Concept:

- Magnetic behaviour depends on the arrangement of the magnetic moments of neighbouring ions.
- Equal moments aligned antiparallel cancel, giving zero resultant magnetic moment.

Step 1: Identify the arrangement In an antiferromagnetic substance, neighbouring magnetic moments are aligned in opposite directions in an ordered arrangement. Each moment is opposed by an equal moment.

Step 2: Find the resultant moment The oppositely directed equal moments cancel one another. Thus the substance has no net spontaneous magnetic moment; manganese(II) oxide, MnO , is a standard example.

Step 3: Conclusion Antiferromagnetism is the phenomenon in which equal magnetic moments align antiparallel and cancel, producing zero net magnetic moment.

Quick Tip to Solve: Remember antiferromagnetism by pairing equal arrows in opposite directions; their vector sum is zero.

2. Define dialysis.

[1 mark]

Solution:

Concept:

- Dialysis purifies a colloidal solution using a semipermeable membrane.
- Small dissolved ions and molecules can diffuse through the membrane, whereas colloidal particles are retained.

Step 1: Separate by particle size The impure colloidal solution is placed in a suitable semipermeable membrane and surrounded by pure water. Dissolved electrolytes and other small soluble impurities can pass through this membrane.

Step 2: Remove the impurities The impurities diffuse into the surrounding water, while the larger colloidal particles remain inside. Replacing the surrounding water maintains the concentration difference and continues purification.

Step 3: Conclusion Dialysis is the removal of dissolved small molecules or ions from a colloidal solution by diffusion through a suitable semipermeable membrane.

Quick Tip to Solve: In dialysis, identify what crosses the membrane: small impurities pass out, but colloidal particles remain.

3. What is the role of CO₂ in the extractive metallurgy of aluminium from its ore?

[1 mark]

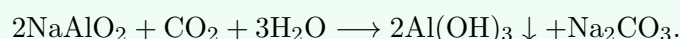
Solution:

Concept:

- Bauxite is purified by dissolving its alumina in concentrated sodium hydroxide to obtain sodium aluminate.
- Carbon dioxide neutralises the alkaline aluminate solution and precipitates hydrated alumina.

Step 1: Identify the purification stage During the extraction of aluminium, the solution obtained after leaching bauxite contains sodium aluminate. Carbon dioxide is passed through this solution to recover aluminium as aluminium hydroxide.

Step 2: Write the precipitation reaction Carbon dioxide causes the precipitation of hydrated alumina, represented as Al(OH)₃:



The precipitate yields pure alumina on heating.

Step 3: Conclusion CO₂ precipitates hydrated alumina (aluminium hydroxide) from sodium aluminate solution during the purification of bauxite.

Quick Tip to Solve: Associate carbon dioxide with precipitation of hydrated alumina from the alkaline leach solution.

4. Why is nitrogen gas very unreactive?

[1 mark]

Solution:

Concept:

- The nitrogen molecule contains a strong triple covalent bond, N $\equiv$ N.
- A large bond dissociation enthalpy makes bond breaking and hence reaction difficult under ordinary conditions.

Step 1: Examine the molecular bond Each nitrogen atom shares three electron pairs with the other atom in N₂. The resulting short triple bond has a very high bond dissociation enthalpy, approximately 941 kJ mol⁻¹.

Step 2: Connect bond strength with reactivity A substantial amount of energy is needed to break or sufficiently weaken this bond before new bonds can form. Consequently, many reactions of nitrogen have a large activation barrier and proceed very slowly at ordinary temperature.

Step 3: Conclusion Nitrogen gas is very unreactive because its strong N $\equiv$ N triple bond has a very high bond dissociation enthalpy.

Quick Tip to Solve: For low reactivity of nitrogen, cite the strong triple bond and the high energy needed to break it.

5. Give a test to distinguish between propan-2-one and pentan-3-one.

[1 mark]

Solution:

Concept:

- The iodoform test detects the methyl ketone group $\text{CH}_3\text{CO}-$.
- On warming with iodine and aqueous sodium hydroxide, methyl ketones give a yellow precipitate of iodoform, CHI_3 .

Step 1: Apply the test to propan-2-one Warm each sample separately with iodine and aqueous sodium hydroxide. Propan-2-one, CH_3COCH_3 , contains the methyl ketone group, so it gives a yellow precipitate of iodoform.

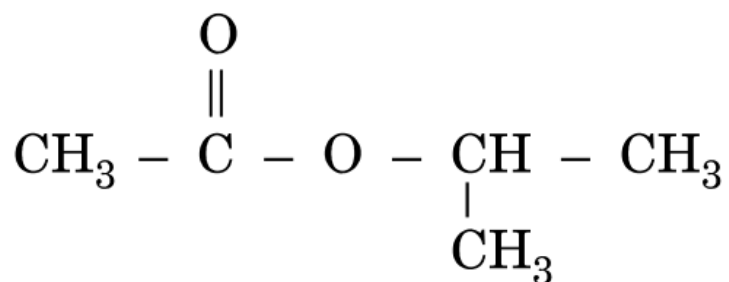
Step 2: Compare with pentan-3-one Pentan-3-one has the structure $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$. Neither group directly attached to its carbonyl carbon is a methyl group, so it does not give the iodoform precipitate under the same test conditions.

Step 3: Conclusion Use the iodoform test: propan-2-one gives a yellow precipitate of CHI_3 with I_2/NaOH , whereas pentan-3-one gives no such precipitate.

Quick Tip to Solve: Check the carbon directly next to the carbonyl: the required group is CH_3CO , not merely any CH_3 group.

6. Name the alcohol that is used to make the following ester:

[1 mark]



Solution:

Concept:

- An ester has the form RCOOR' ; the alcohol supplies the OR' portion.
- Replace the acyl group attached to the ester oxygen with hydrogen to recover the alcohol $\text{R}'\text{OH}$.

Step 1: Identify the alcohol-derived group The given ester is $\text{CH}_3\text{COOCH}(\text{CH}_3)_2$. The group bonded to the single-bonded ester oxygen is $\text{CH}(\text{CH}_3)_2$, so the alcohol-derived portion is isopropyl.

Step 2: Recover and name the alcohol Joining this group to OH gives $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. Its longest carbon chain has three carbon atoms, and the hydroxyl group is on carbon 2; its IUPAC name is propan-2-ol.

Step 3: Conclusion The alcohol is propan-2-ol (isopropyl alcohol), $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$.

Quick Tip to Solve: Trace the ester oxygen away from the carbonyl carbon; the group on that side identifies the alcohol.

7. Define a 'Peptide linkage'.

[1 mark]

Solution:

Concept:

- Amino acids contain an amino group and a carboxyl group; they can join by a condensation reaction.
- The amide group $-\text{CO} - \text{NH}-$ joining amino-acid residues is called a peptide linkage.

Step 1: Identify the reacting groups The carboxyl group $-\text{COOH}$ of one amino acid reacts with the amino group $-\text{NH}_2$ of another amino acid.

Step 2: Identify the bond formed Elimination of one molecule of water produces the covalent amide linkage $-\text{CO} - \text{NH}-$. Repeated formation of this linkage joins amino-acid residues into a polypeptide chain.

Step 3: Conclusion A peptide linkage is the $-\text{CO} - \text{NH}-$ linkage formed between two amino acids by loss of water from the carboxyl group of one and the amino group of the other.

Quick Tip to Solve: Remember peptide as the amide connection between two amino-acid residues.

8. How does a homopolymer differ from a copolymer?

[1 mark]

Solution:

Concept:

- Polymers are macromolecules formed by repeated joining of monomer molecules.
- The distinction between a homopolymer and a copolymer is the number of different monomer species used.

Step 1: Homopolymer A homopolymer is formed from only one kind of monomer. For example, ethene molecules polymerise to form polythene, whose repeating units originate from ethene alone.

Step 2: Copolymer A copolymer is formed from two or more different kinds of monomers. For example, Buna-S is formed by copolymerisation of 1,3-butadiene and styrene. Both monomer species contribute units to the polymer chain.

Step 3: Conclusion A homopolymer uses one kind of monomer, whereas a copolymer uses two or more different kinds; examples are polythene and Buna-S, respectively.

Quick Tip to Solve: Count distinct monomer species, rather than the total number of monomer molecules.

9. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with change in temperature. [2 marks]

Solution:

Concept:

- Conductivity κ is the reciprocal of resistivity: $\kappa = 1/\rho$. It describes the ability of an electrolyte solution to conduct electric current.
- Molar conductivity is $\Lambda_m = \kappa/c$, where c is the amount concentration in units consistent with those used for conductivity.
- Electrolytic conduction occurs through the motion of ions, whose mobility generally increases on heating.

Step 1: Define conductivity Conductivity is the conductance of a solution column of unit length and unit cross-sectional area. If G is conductance, l the electrode separation and A the cross-sectional area, then $\kappa = Gl/A$. Its SI unit is S m^{-1} .

Step 2: Define molar conductivity Molar conductivity is the conductance of the volume of solution containing one mole of electrolyte when placed between electrodes of unit separation. Thus $\Lambda_m = \kappa/c$ for c in mol m^{-3} , giving the SI unit $\text{S m}^2 \text{mol}^{-1}$. When κ is in S cm^{-1} and concentration C is in mol L^{-1} , use $\Lambda_m = 1000\kappa/C$.

Step 3: Explain the temperature effect For an electrolyte solution, both conductivity and molar conductivity generally increase with rise in temperature. Heating reduces the viscosity of the solvent and increases ionic mobility, so ions carry charge more readily. In weak electrolytes, increased ionisation may also contribute to the increase. On cooling, the reverse trend is observed.

Step 4: Conclusion Conductivity is conductance normalised for solution geometry; molar conductivity is conductivity divided by molar concentration. Both generally increase with temperature for an electrolyte solution.

Quick Tip to Solve: For temperature changes, connect the increase in conductance to easier ionic motion in a less viscous solvent.

10. Define each of the following:

(i) Specific rate of a reaction

(ii) Energy of activation of a reaction [2 marks]

Solution:

Concept:

- The rate law is $r = k[A]^m[B]^n$, where k is the rate constant and m, n are the experimentally determined partial orders.
- Activation energy E_a is the energy barrier separating reactants from the activated complex along the reaction pathway.

Step 1: (i) Specific rate of a reaction The specific rate of a reaction is its rate constant k . Numerically, it is the reaction rate when the concentration of each reactant appearing in the rate law is unity in the

chosen concentration units. For $r = k[A]^m[B]^n$, setting $[A] = [B] = 1$ gives the numerical equality $r = k$. At a specified temperature, k is characteristic of the reaction and does not depend on the reactant concentrations; its units depend on the overall reaction order.

Step 2: (ii) Energy of activation The activation energy is the minimum additional molar energy that reactants must acquire to reach the activated complex and undergo reaction. It is the difference between the molar energy of the activated complex and that of the reactants:

$$E_a = E_{\text{activated complex}} - E_{\text{reactants}}.$$

It is commonly expressed in kJ mol^{-1} . A collision must have sufficient energy as well as suitable orientation to be effective.

Step 3: Conclusion (i) Specific rate means the rate constant, numerically equal to the rate at unit concentrations of the reactants. (ii) Activation energy is the minimum additional energy required for reactants to reach the activated complex.

Quick Tip to Solve: Distinguish the threshold energy of the activated complex from the additional energy barrier called activation energy.

11(a). Describe the underlying principle of each of the following processes:

(i) Recovery of silver from the solution obtained by leaching silver ore with a solution of NaCN

(ii) Electrolytic refining of a crude metal

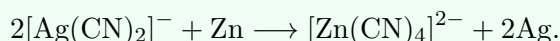
[2 marks]

Solution:

Concept:

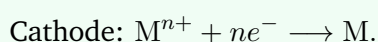
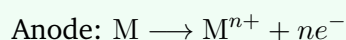
- Displacement uses a more electropositive metal to reduce the ions of a less electropositive metal.
- Electrolytic refining transfers a metal selectively from an impure anode to a pure cathode.

Step 1: Recover silver by zinc displacement The leach solution contains silver as the soluble dicyanoargentate(I) complex, $[\text{Ag}(\text{CN})_2]^-$. Zinc is more electropositive than silver, so it is oxidised while silver(I) is reduced to metallic silver. Adding zinc therefore precipitates silver:



This is a displacement or cementation reaction; cyanide keeps the zinc product in solution.

Step 2: Purify by selective electrolysis The crude metal is the anode, a thin sheet of pure metal is the cathode, and a solution of a suitable soluble salt of the same metal is the electrolyte. On passing current, the metal dissolves from the anode and deposits on the cathode:



Under suitable conditions, insoluble impurities collect as anode mud, while more readily oxidised impurities remain in solution rather than depositing with the pure metal.

Step 3: Conclusion (i) Silver is recovered by reduction of its cyanide complex with zinc. (ii) Electrolytic refining rests on selective anodic dissolution and cathodic deposition of the metal.

Quick Tip to Solve: For silver recovery, write zinc on the reactant side and remember that two silver complexes supply the two electrons accepted from one zinc atom.

OR

11(b). Describe the principle involved in each of the following processes:

(i) Zone refining of a metal

(ii) Vapour phase refining of metals

[2 marks]

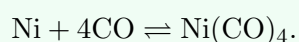
Solution:

Concept:

- Zone refining exploits the greater solubility of impurities in the molten metal than in the solid metal.
- Vapour phase refining separates a volatile metal compound and then decomposes it to obtain pure metal.

Step 1: Principle of zone refining A narrow region of an impure metal rod is melted with a moving heater. As the heater moves, the region behind it cools and crystallises. Since impurities are more soluble in the melt than in the solid, the crystallising metal is purer, while impurities concentrate in the moving molten zone. Repeated passes carry the impurities towards one end of the rod; the impure end is then removed. This method is useful for obtaining very pure semiconductors such as silicon and germanium.

Step 2: Principle of vapour phase refining The impure metal is treated with a reagent to form a volatile compound. This compound is separated from nonvolatile impurities and then decomposed under suitable conditions to give pure metal. Two conditions are essential: the metal must readily form a volatile compound, and that compound must be readily decomposable. For example, in the Mond process, nickel forms volatile nickel tetracarbonyl, which decomposes on stronger heating:

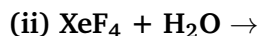
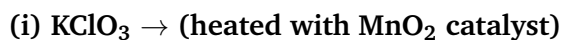


The forward formation and reverse decomposition are carried out at different suitable temperatures.

Step 3: Conclusion (i) Zone refining depends on preferential concentration of impurities in the molten zone. (ii) Vapour phase refining depends on formation, separation and decomposition of a volatile metal compound.

Quick Tip to Solve: For zone refining compare impurity solubility in liquid and solid; for vapour refining state both volatility and easy decomposition.

12. Complete the following chemical reaction equations:



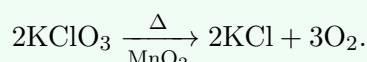
[2 marks]

Solution:

Concept:

- A catalyst changes the rate of a reaction without appearing in its overall stoichiometric balance.
- Complete hydrolysis of xenon tetrafluoride is accompanied by disproportionation of xenon in the +4 oxidation state.

Step 1: Complete the thermal decomposition On heating in the presence of manganese dioxide, potassium chlorate decomposes to potassium chloride and oxygen. Balance potassium and chlorine first, then oxygen:



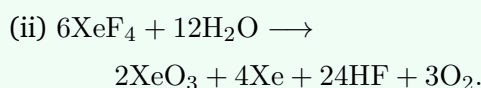
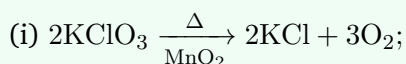
There are two potassium atoms, two chlorine atoms and six oxygen atoms on each side. Manganese dioxide is written over or under the arrow because it acts as the catalyst and is not consumed in the overall reaction.

Step 2: Complete hydrolysis of xenon tetrafluoride Xenon tetrafluoride reacts with water to give xenon trioxide, xenon, hydrogen fluoride and oxygen. The balanced equation is



The balance contains six xenon atoms, twenty-four fluorine atoms, twenty-four hydrogen atoms and twelve oxygen atoms on each side. Xenon is partly oxidised from +4 to +6 in the trioxide and partly reduced to elemental xenon; oxygen gas is also formed.

Step 3: Conclusion



Quick Tip to Solve: For xenon tetrafluoride hydrolysis, include both elemental xenon and oxygen before balancing; omitting either prevents the correct balance.

13. Assign reasons for the following:

(i) Copper(I) ion is not known to exist in aqueous solutions.

(ii) Both O₂ and F₂ stabilize high oxidation states of transition metals but the ability of oxygen to do so exceeds that of fluorine. [2 marks]

Solution:

Concept:

- Aqueous oxidation-state stability depends on the overall energetic balance, including hydration of the ions.
- Oxygen and fluorine stabilise high oxidation states through strong bonding; oxygen can also form multiple bonds to a metal.

Step 1: Explain the instability of aqueous copper(I) In aqueous solution, Cu⁺ undergoes disproportionation:



The much greater magnitude of the hydration enthalpy of Cu²⁺, compared with that of Cu⁺, compensates for the energy needed to form the higher-charge ion. The net process is therefore favourable. Consequently, ordinary aqueous copper(I) ions are unstable even though the isolated ion has a filled 3d¹⁰ configuration; electronic configuration alone does not determine stability in water.

Step 2: Compare oxygen and fluorine Both elements are highly electronegative and form strong bonds with transition metals, thereby stabilising their high oxidation states. Oxygen has the additional ability to form multiple bonds with the metal, whereas fluorine forms only single bonds. These strong metal-oxygen multiple bonds allow oxygen to stabilise still higher oxidation states. For example, manganese reaches +7 in Mn₂O₇, while its highest fluoride is MnF₄, with manganese in +4. Thus the bonding available to oxygen explains its greater ability.

Step 3: Conclusion (i) Aqueous Cu⁺ disproportionates because hydration strongly stabilises Cu²⁺. (ii) Oxygen exceeds fluorine because it can form strong multiple bonds with transition metals.

Quick Tip to Solve: Use hydration to explain aqueous copper(I), and explicitly mention metal-oxygen multiple bonding when comparing oxygen with fluorine.

14. Write the structures of the following organic halogen compounds:

(i) 4-tert-Butyl-3-iodoheptane

(ii) 4-Bromo-3-methylpent-2-ene [2 marks]

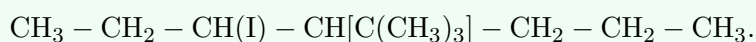
Solution:

Concept:

- The parent chain fixes the number of carbon atoms; locants specify the positions of substituents and multiple bonds.
- A tert-butyl substituent is –C(CH₃)₃, attached through its central carbon. Each carbon must have total valency four.

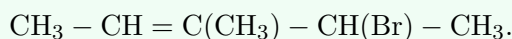
Step 1: (i) Construct the substituted heptane chain Heptane supplies a saturated seven-carbon chain.

Number it from the end giving iodine position 3 and tert-butyl position 4. Replace one hydrogen at carbon 3 by iodine and one at carbon 4 by $-\text{C}(\text{CH}_3)_3$. The condensed structure is



The tert-butyl attachment carbon has three methyl groups and its fourth bond joins the parent chain.

Step 2: (ii) Construct the substituted pentene chain Pent-2-ene has five carbons with a double bond between carbons 2 and 3. Attach methyl to carbon 3 and bromine to carbon 4, giving



Carbon 3 has no hydrogen because its double bond and two single bonds already satisfy its valency. No geometrical configuration is specified in the name.

Step 3: Conclusion (i) $\text{CH}_3\text{CH}_2\text{CH}(\text{I})\text{CH}[\text{C}(\text{CH}_3)_3]\text{CH}_2\text{CH}_2\text{CH}_3$.

(ii) $\text{CH}_3\text{CH} = \text{C}(\text{CH}_3)\text{CH}(\text{Br})\text{CH}_3$.

Quick Tip to Solve: Write and number the parent chain first, then replace its hydrogens at the stated locants.

15. (i) Arrange the following compounds in an increasing order of basic strength:

$\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2

(ii) Arrange the following compounds in a decreasing order of $\text{p}K_b$ values:

$\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}_2$

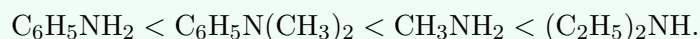
[2 marks]

Solution:

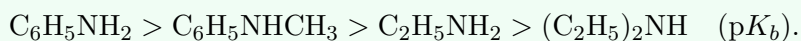
Concept:

- Basicity measures the availability of the nitrogen lone pair for accepting a proton. Delocalisation into a benzene ring lowers its availability.
- $\text{p}K_b = -\log K_b$: a stronger base has larger K_b and smaller $\text{p}K_b$. Alkyl groups donate electron density through their positive inductive effect.

Step 1: (i) Compare basic strengths In aniline and N,N-dimethylaniline the nitrogen lone pair is delocalised into the aromatic ring, so both are weaker bases than the aliphatic amines. The methyl groups increase electron density in N,N-dimethylaniline, making it stronger than aniline. Diethylamine is stronger than methylamine because the electron-donating alkyl groups favour proton acceptance, while its conjugate acid is effectively solvated. Thus the increasing order is



Step 2: (ii) Convert basic strength to the required $\text{p}K_b$ order Aniline is weaker than N-methylaniline because the methyl group donates electron density. Both aromatic amines are weaker than ethylamine; diethylamine is stronger than ethylamine. Since decreasing $\text{p}K_b$ means moving from weaker to stronger bases, the required order is



Step 3: Conclusion (i) $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 < \text{CH}_3\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$.
(ii) Decreasing pK_b : $\text{C}_6\text{H}_5\text{NH}_2 > \text{C}_6\text{H}_5\text{NHCH}_3 > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH}$.

Quick Tip to Solve: For decreasing pK_b , write the weakest base first and the strongest base last.

16. What are ambident nucleophiles? Explain with an example.

[2 marks]

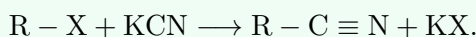
Solution:

Concept:

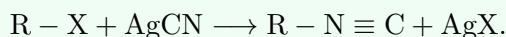
- A nucleophile donates an electron pair to an electron-deficient centre to form a covalent bond.
- An ambident nucleophile has two alternative donor atoms; bonding through either atom gives products with different atom connectivity.

Step 1: Define an ambident nucleophile Ambident nucleophiles are nucleophiles that can attack an electrophile through either of two different atoms. Only one of these sites normally forms the new bond in a particular substitution reaction. Thus the term refers to alternative sites of attack within the same nucleophile, rather than to simultaneous bonding through both sites.

Step 2: Explain using the cyanide ion The cyanide ion, CN^- , can form a new bond through carbon or through nitrogen. With an alkyl halide $\text{R} - \text{X}$, predominantly ionic KCN supplies cyanide that attacks through carbon to form an alkyl cyanide (nitrile):



With largely covalent AgCN, the carbon end is bound to silver, so alkylation occurs through nitrogen, forming an isocyanide:



These two connectivities illustrate the ambident character of cyanide.

Step 3: Conclusion Ambident nucleophiles have two alternative attacking atoms. For example, CN^- attacks through carbon to give $\text{R} - \text{CN}$, or through nitrogen to give $\text{R} - \text{NC}$.

Quick Tip to Solve: Identify the atom directly bonded to R: $\text{R} - \text{CN}$ is a nitrile, whereas $\text{R} - \text{NC}$ is an isocyanide.

17. Write the names and structures of monomers used for getting the following polymers:

(i) Buna-S

(ii) Nylon-6, 6

[2 marks]

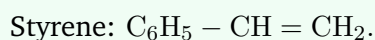
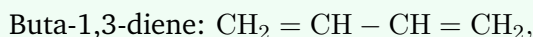
Solution:

Concept:

- A copolymer is prepared from two different monomers; Buna-S is an addition copolymer of a diene and an aromatic vinyl compound.
- Nylon-6,6 is a condensation polymer made from a diamine and a dicarboxylic acid. Each monomer

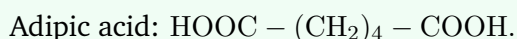
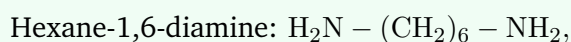
contains six carbon atoms.

Step 1: (i) Identify the monomers of Buna-S The two monomers are buta-1,3-diene (1,3-butadiene) and styrene (phenylethene). Their condensed structures are



Their carbon-carbon double bonds participate in addition copolymerisation. Styrene contributes the phenyl substituent to the resulting synthetic rubber.

Step 2: (ii) Identify the monomers of nylon-6,6 The monomers are hexane-1,6-diamine (hexamethylenediamine) and hexanedioic acid (adipic acid):



The amino and carboxyl groups condense to form amide linkages, $-\text{CO} - \text{NH}-$, with elimination of water. The acid has six carbons because its two carboxyl carbons count along with the four methylene carbons.

Step 3: Conclusion Buna-S: buta-1,3-diene and styrene. Nylon-6,6: hexane-1,6-diamine and adipic acid, with the structures shown above.

Quick Tip to Solve: Count the carboxyl carbons in adipic acid: four CH_2 carbons plus two COOH carbons give six.

18. Give a chemical test to distinguish between each of the following pairs of compounds:

(i) Ethylamine and Aniline

(ii) Aniline and Benzylamine

[2 marks]

Solution:

Concept:

- Aromatic primary amines such as aniline react readily with bromine water to give a white precipitate of 2,4,6-tribromoaniline.
- The amino group directly attached to the benzene ring activates the two ortho positions and the para position towards bromination.

Step 1: (i) Ethylamine and aniline Add bromine water to separate samples. Aniline gives a white precipitate of 2,4,6-tribromoaniline:



Ethylamine does not give this characteristic precipitate. Thus the white solid identifies aniline in this pair.

Step 2: (ii) Aniline and benzylamine Add bromine water to separate samples. Aniline again produces

the white precipitate of 2,4,6-tribromoaniline, whereas benzylamine does not give this precipitate. In benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, the amino group is separated from the ring by a $-\text{CH}_2-$ group and cannot activate the ring by direct resonance donation in the way aniline does.

Step 3: Conclusion Bromine water distinguishes both pairs: aniline gives a white precipitate of 2,4,6-tribromoaniline; ethylamine and benzylamine do not give this precipitate.

Quick Tip to Solve: Use the white tribromoaniline precipitate as the distinguishing observation, rather than merely a change in bromine colour.

19. For a decomposition reaction, the values of k at two different temperatures are given below:

$$k_1 = 2.15 \times 10^{-8} \text{ L/(mol.s) at } 650 \text{ K}$$

$$k_2 = 2.39 \times 10^{-7} \text{ L/(mol.s) at } 700 \text{ K}$$

Calculate the value of E_a for the reaction.

$$(\text{Log } 11.11 = 1.046) \quad (R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

[3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, R is the gas constant and T is absolute temperature.
- For the same reaction at two temperatures, assuming the pre-exponential factor A is constant over this interval,

$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Step 1: Calculate the rate-constant ratio Take $T_1 = 650 \text{ K}$ and $T_2 = 700 \text{ K}$. Since the two rate constants have identical units, their ratio is dimensionless:

$$\frac{k_2}{k_1} = \frac{2.39 \times 10^{-7}}{2.15 \times 10^{-8}} = 11.116 \approx 11.11.$$

Using the logarithm supplied in the question gives $\log_{10}(k_2/k_1) = 1.046$.

Step 2: Substitute in the two-temperature equation Rearrange for activation energy and evaluate the reciprocal-temperature difference:

$$E_a = \frac{2.303R \log_{10}(k_2/k_1)}{(1/T_1) - (1/T_2)}, \quad \frac{1}{650} - \frac{1}{700} = \frac{50}{650 \times 700}.$$

Hence

$$\begin{aligned} E_a &= \frac{2.303 \times 8.314 \times 1.046 \times 650 \times 700}{50} \\ &= 1.82254 \times 10^5 \text{ J mol}^{-1}. \end{aligned}$$

The sign is positive: the rate constant increases with temperature, as expected for a positive activation barrier. Convert joules into kilojoules by dividing by 1000.

Step 3: Conclusion The activation energy is $E_a \approx 182.3 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Pair the larger rate constant with 700 K and use $1/650$ minus $1/700$ so that the calculated activation energy is positive.

20. Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3} . Use this information to calculate Avogadro's number (Gram atomic mass of Fe = 55.84 g mol⁻¹). [3 marks]

Solution:

Concept:

- A body centred cubic unit cell contains $z = 8(1/8) + 1 = 2$ atoms: eight corner contributions and one complete body-centre atom.
- The density relation is $\rho = zM/(N_A a^3)$, where M is molar mass, a is the cubic cell edge and N_A is the Avogadro constant.

Step 1: Convert the edge length and find cell volume The density is given in g cm⁻³, so use centimetres for the cell edge. Since 1 pm = 10⁻¹⁰ cm,

$$a = 286.65 \times 10^{-10} \text{ cm} = 2.8665 \times 10^{-8} \text{ cm}.$$

Therefore

$$a^3 = (2.8665 \times 10^{-8})^3 \text{ cm}^3 = 2.35535 \times 10^{-23} \text{ cm}^3.$$

The edge must be cubed after its unit conversion; the power of ten is cubed as well.

Step 2: Use mass per unit cell to obtain the Avogadro constant Two atoms of iron have mass $2M/N_A$. Equating that mass to the density times the unit-cell volume gives

$$\rho a^3 = \frac{2M}{N_A}, \quad N_A = \frac{2M}{\rho a^3}.$$

Substituting the given values,

$$\begin{aligned} N_A &= \frac{2 \times 55.84}{7.874 \times (2.8665 \times 10^{-8})^3} \\ &= 6.02177 \times 10^{23} \text{ mol}^{-1}. \end{aligned}$$

The units are (g mol⁻¹)/[(g cm⁻³)(cm³)] = mol⁻¹, consistent with the number of atoms per mole.

Step 3: Conclusion The calculated Avogadro constant is $N_A \approx 6.022 \times 10^{23} \text{ mol}^{-1}$.

Quick Tip to Solve: For a bcc cell use two atoms, and convert 286.65 pm to centimetres before cubing because the density uses cubic centimetres.

21. The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the solution. [3 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$, where G is in siemens (S) and R is in ohms.
- Conductivity is $\kappa = G(l/A)$, where l/A is the cell constant. For concentration C in mol L⁻¹, molar

conductivity is $\Lambda_m = 1000\kappa/C$ when κ is in S cm^{-1} .

Step 1: Find the conductance The measured resistance is $R = 200\ \Omega$ at 25°C . Thus the conductance of the solution between the electrodes is

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

Resistance and conductance are reciprocal quantities; the resistance itself must therefore not be substituted as conductivity.

Step 2: Use the cell constant to find conductivity The cell constant is unity, i.e. $l/A = 1\ \text{cm}^{-1}$ in the conventional centimetre-based units. Therefore

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

The conductance and conductivity have the same numerical value here only because the cell constant is unity; their units differ.

Step 3: Calculate the molar conductivity The concentration is $C = 0.01\ \text{mol L}^{-1}$. One mole is therefore contained in $1000/C = 100000\ \text{cm}^3$ of solution. Multiplying conductivity by this volume per mole gives

$$\Lambda_m = \frac{1000\kappa}{C} = \frac{1000(5.0 \times 10^{-3})}{0.01} = 500\ \text{S cm}^2\ \text{mol}^{-1}.$$

The factor 1000 converts litres to cubic centimetres and is essential when these units are used.

Step 4: Conclusion The molar conductivity at 25°C is $500\ \text{S cm}^2\ \text{mol}^{-1}$.

Quick Tip to Solve: With a unity cell constant, first take the reciprocal of resistance, then use $1000\kappa/C$.

22(a). Giving appropriate examples, explain how the two types of processes of adsorption (physisorption and chemisorption) are influenced by the prevailing temperature, the surface area of adsorbent and the activation energy of the process? [3 marks]

Solution:

Concept:

- Physisorption binds an adsorbate to a surface through weak van der Waals forces; chemisorption involves the formation of chemical bonds with surface sites.
- Both processes occur at the surface and are generally exothermic. Temperature changes must be considered together with the activation barrier for forming the adsorbed state.

Step 1: Effect of temperature Physisorption is favoured by low temperature. Since adsorption releases heat, increasing temperature favours desorption and decreases the extent of physical adsorption at a fixed gas pressure. For example, gases are readily physically adsorbed on charcoal at low temperature. Chemisorption often increases initially with temperature because molecules acquire the energy needed to form chemical bonds with the surface. At sufficiently high temperature, desorption becomes important and its extent decreases; hence it is favoured over an appropriate temperature range rather

than by unlimited heating.

Step 2: Effect of surface area For a given mass of adsorbent, increasing the exposed surface area increases adsorption in both processes because more surface sites become available. Finely divided or porous charcoal therefore physically adsorbs more gas than a compact piece of the same mass. Similarly, finely divided nickel exposes more active sites for chemisorption of hydrogen than a compact nickel surface. The relevant quantity is accessible surface area, since adsorption occurs at the surface rather than throughout the bulk.

Step 3: Effect of activation energy, with examples Physisorption has little or no appreciable activation-energy requirement: weak intermolecular attractions can hold gas molecules on charcoal without first breaking or substantially rearranging bonds. Chemisorption generally requires appreciable activation energy because chemical bonds form and existing bonds may need to be weakened or broken. For example, hydrogen can chemisorb on nickel by dissociating into adsorbed hydrogen atoms. Heating initially helps hydrogen molecules overcome this barrier. This explains why physisorption is effective at low temperature whereas activated chemisorption may require a higher temperature to proceed readily.

Step 4: Conclusion Low temperature favours physisorption; chemisorption commonly needs initial heating to overcome its activation barrier. Larger accessible surface area promotes both, while appreciable activation energy is characteristic of chemisorption.

Quick Tip to Solve: Explain the initial rise of chemisorption with temperature using activation energy, then mention desorption at high temperature.

OR

22(b). Explain clearly how the phenomenon of adsorption finds application in

- (i) production of vacuum in a vessel
- (ii) heterogeneous catalysis
- (iii) froth floatation process in metallurgy

[3 marks]

Solution:

Concept:

- Adsorption is the accumulation of molecules at a surface, giving a higher concentration there than in the surrounding bulk phase.
- Its applications depend on gas removal by a large surface, activation of reactants at catalyst sites, or preferential adsorption that changes surface wetting.

Step 1: Production of vacuum in a vessel After most of the gas has been pumped out of a vessel, activated charcoal is introduced or connected to the vessel and cooled. Its large porous surface adsorbs the residual gas molecules, reducing the number of molecules remaining in the gas phase. The gas pressure consequently falls and a higher vacuum is obtained. Low temperature favours this physical adsorption because adsorption is exothermic. Thus charcoal helps remove the small quantity of gas that ordinary pumping has left behind.

Step 2: Heterogeneous catalysis In heterogeneous catalysis, the catalyst and reactants are in different phases, commonly a solid catalyst and gaseous reactants. Reactant molecules adsorb on the active sites of the solid. Adsorption brings them close together and can weaken their bonds, providing a reaction pathway with lower activation energy. The products then desorb, leaving sites available for further reaction. For example, in hydrogenation of vegetable oils over finely divided nickel, hydrogen and the unsaturated reactant interact at the nickel surface; adsorbed hydrogen adds across carbon-carbon double bonds.

Step 3: Froth floatation in metallurgy Froth floatation concentrates sulphide ores using differences in surface wetting. A collector, such as a xanthate, is preferentially adsorbed on sulphide ore particles and makes their surfaces water-repellent and readily wetted by oil, while gangue remains preferentially wetted by water. When air is blown through the aqueous suspension, the treated ore particles attach to air bubbles and rise into the froth. Pine oil may be used as a frother to help produce the froth. The ore-rich froth is skimmed off, while the water-wetted gangue is left behind. Preferential surface adsorption thus enables the separation.

Step 4: Conclusion Adsorption removes residual gases to produce a high vacuum, activates reactants on a solid catalyst, and enables selective flotation of sulphide ore particles through preferential surface wetting.

Quick Tip to Solve: For each application, identify what is adsorbed, the surface involved, and how that surface effect produces the desired result.

23. Assign reasons for the following:

- (i) Cu(I) ion is not known to exist in aqueous solutions.
- (ii) Transition metals are much harder than the alkali metals.
- (iii) From element to element actinoid contraction is greater than the lanthanoid contraction.

[3 marks]

Solution:

Concept:

- Metal-ion stability in water depends on the total energy change, including hydration enthalpy, rather than on electronic configuration alone.
- Metallic bonding binds metal atoms together through delocalised valence electrons. Poor shielding by f electrons causes a progressive decrease in ionic radii across an f-block series.

Step 1: (i) Instability of Cu(I) in water In aqueous solution, Cu^+ undergoes disproportionation:



The hydration enthalpy of Cu^{2+} is much more negative than that of Cu^+ . This large hydration stabilisation makes the overall disproportionation favourable, despite the extra ionisation energy required to form Cu^{2+} . Thus the filled $3d^{10}$ configuration alone does not make free aqueous Cu(I) stable.

Step 2: (ii) Greater hardness of transition metals Transition metals have more valence electrons available for metallic bonding, involving both $(n-1)d$ and ns electrons. Their stronger metallic bonds and higher atomisation enthalpies hold the atoms more firmly in the crystal. Alkali metals contribute only one ns electron per atom and have weaker metallic bonding; they are consequently much softer.

Step 3: (iii) Greater actinoid contraction Across the actinoid series, added electrons enter the $5f$ subshell. These electrons shield the increasing nuclear charge less effectively than $4f$ electrons do in the lanthanoid series. The effective nuclear attraction therefore increases more strongly from element to element, giving the greater contraction in actinoid ionic radii.

Step 4: Conclusion The reasons are: favourable disproportionation of hydrated Cu^+ , stronger metallic bonding in transition metals, and poorer shielding by $5f$ electrons in actinoids.

Quick Tip to Solve: For Cu(I) , discuss hydration and disproportionation; for hardness, bonding; for contraction, shielding.

24. Giving one example in each of the following cases, discuss briefly the role of coordination compounds in

(i) extraction metallurgy of metals

(ii) analytical chemistry

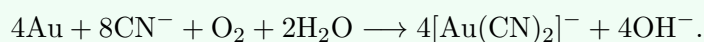
[3 marks]

Solution:

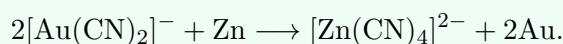
Concept:

- Complex formation can selectively dissolve a metal into a soluble coordination ion, allowing separation from insoluble ore material.
- In qualitative analysis, a characteristic coloured complex or insoluble coordination compound can identify a particular metal ion.

Step 1: (i) Role in extraction metallurgy In the cyanide process for extracting gold, finely divided gold in its ore dissolves in dilute cyanide solution in the presence of oxygen. It forms the soluble dicyanidoaurate(I) complex:

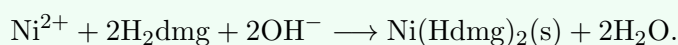


Complex formation brings gold into solution while much of the gangue remains insoluble and can be removed. Zinc then displaces gold from the complex:



Thus coordination chemistry assists both selective leaching and subsequent recovery of the metal.

Step 2: (ii) Role in analytical chemistry Nickel(II) ions are detected by adding dimethylglyoxime in ammoniacal medium. A characteristic bright red precipitate of bis(dimethylglyoximate)nickel(II) forms. If neutral dimethylglyoxime is denoted by H_2dmg , the reaction is



Each ligand loses one proton and coordinates through two nitrogen atoms, giving a chelate complex. Its distinctive colour and low solubility make the reaction useful for identification, separation and gravimetric estimation of nickel.

Step 3: Conclusion Coordination compounds enable extraction of gold through soluble cyanide complexes and identification of Ni^{2+} through its red dimethylglyoxime complex.

Quick Tip to Solve: Connect each named complex to its function: soluble cyanide complex for extraction, red nickel chelate for detection.

25. What are essential and non-essential amino acids? Give two examples of each.

[3 marks]

Solution:

Concept:

- Amino acids are building units of proteins. Their classification as essential or non-essential depends on whether the human body can synthesise enough of them.
- Both classes are required for normal protein synthesis; the distinction concerns their dietary supply, not their biological importance.

Step 1: Define essential amino acids and give examples Essential amino acids are those which the human body cannot synthesise, or cannot synthesise in sufficient amounts to meet its needs. They must therefore be obtained through the diet. Two examples are valine and leucine. These amino acids are incorporated into body proteins just like other amino acids, but their required supply must come from food proteins. A diet deficient in an essential amino acid can limit protein synthesis even when the other amino acids are available.

Step 2: Define non-essential amino acids and give examples Non-essential amino acids are those which the human body can synthesise in adequate amounts under normal conditions, so their obligatory supply through the diet is not required. Two examples are glycine and alanine. Their carbon skeletons can be produced in metabolism and converted into the corresponding amino acids. They remain necessary constituents of proteins and other biomolecules: the word non-essential does not mean that the body can function without them.

Step 3: Conclusion Essential amino acids must be supplied in the diet, e.g. valine and leucine. Non-essential amino acids can be synthesised by the body, e.g. glycine and alanine.

Quick Tip to Solve: Ask whether the body can make enough: valine and leucine require dietary supply; glycine and alanine can be synthesised.

26. Explain the following with an example for each:

(i) Kolbe's reaction

(ii) Reimer-Tiemann reaction

(iii) Williamson ether synthesis

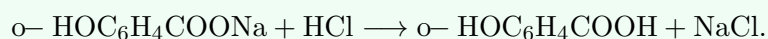
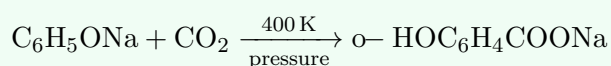
[3 marks]

Solution:

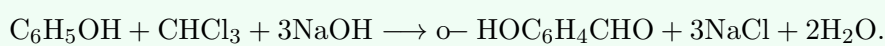
Concept:

- Phenoxide ion activates the aromatic ring towards electrophilic substitution, especially at the ortho and para positions.
- Williamson synthesis forms an ether by an S_N2 reaction of an alkoxide ion with a suitable alkyl halide.

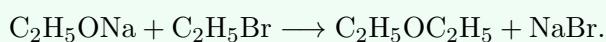
Step 1: (i) Kolbe reaction Sodium phenoxide reacts with carbon dioxide under pressure at about 400 K to form sodium salicylate. Acidification gives salicylic acid (2-hydroxybenzoic acid), with the carboxyl group ortho to the hydroxyl group. For example,



Step 2: (ii) Reimer-Tiemann reaction Phenol is treated with chloroform and aqueous sodium hydroxide on heating, followed by acidification. A formyl group is introduced mainly at the ortho position, giving salicylaldehyde (2-hydroxybenzaldehyde). The overall reaction after work-up is



Step 3: (iii) Williamson ether synthesis An alkoxide reacts with an alkyl halide to form an ether and a metal halide. For example, sodium ethoxide reacts with bromoethane to form ethoxyethane:



A primary alkyl halide is preferred because it favours substitution rather than elimination.

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

Quick Tip to Solve: Remember the introduced group: Kolbe adds $-\text{COOH}$, whereas Reimer-Tiemann adds $-\text{CHO}$.

27. Answer the following questions:

(i) Why should medicines not be taken without consulting a doctor?

(ii) What is meant by 'broad spectrum antibiotics'?

(iii) What are the main constituents of Dettol?

[3 marks]

Solution:

Concept:

- A medicine produces a desired therapeutic effect only when its identity, dose and duration suit the patient and the disease.
- Antibiotics act against susceptible bacteria; antiseptics are used to control microorganisms on living tissues.

Step 1: (i) Need for medical consultation Medicines should not be taken without consulting a doctor because an incorrect medicine or an unsuitable dose may be harmful or toxic. Drugs can cause side effects, allergic reactions or interactions with other medicines. A doctor selects the appropriate drug, dose and duration after diagnosing the illness and considering the patient's condition. Thus, a drug useful for one disease or person is not automatically suitable for another.

Step 2: (ii) Broad spectrum antibiotics Broad spectrum antibiotics are antibiotics effective against a wide range of bacteria, including both Gram-positive and Gram-negative bacteria. Chloramphenicol is a standard example. The word spectrum refers to the range of susceptible bacteria; it does not mean that these drugs cure every infection or act against viruses.

Step 3: (iii) Constituents of Dettol The main constituents of Dettol are chloroxylenol and terpineol. Chloroxylenol provides antiseptic action, and terpineol is an associated constituent of the antiseptic preparation. These are the two names required for the standard textbook composition of Dettol.

Step 4: Conclusion Medicines require a doctor's advice because inappropriate use may be harmful. Broad spectrum antibiotics act against both Gram-positive and Gram-negative bacteria. Dettol mainly contains chloroxylenol and terpineol.

Quick Tip to Solve: For broad spectrum, state both bacterial groups; for Dettol, recall the pair chloroxylenol and terpineol.

28(a). Write the IUPAC names of the following compounds:

(i) $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$

(ii) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CHO}$

[2 marks]

Solution:

Concept:

- The parent chain must contain the principal carbonyl group and is numbered to give that group the lowest possible locant.
- An aldehyde carbon is numbered 1; in an unsaturated aldehyde, specify the double-bond locant and any phenyl substituent.

Step 1: (i) Name the ketone Expand the chain as $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$. It contains seven carbon atoms, including the carbonyl carbon, so the parent hydrocarbon is heptane. Numbering from the end nearest the carbonyl group places the ketone at carbon 2 rather than carbon 6. Replacing the terminal e of heptane by the ketone suffix gives **heptan-2-one**.

Step 2: (ii) Name the unsaturated aldehyde In $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CHO}$, choose the three-carbon chain containing the aldehyde group as the parent. Starting at $-\text{CHO}$, the double bond is between carbons 2 and 3, and the phenyl group is attached at carbon 3. The parent is prop-2-enal, giving **3-phenylprop-2-enal**. No E or Z descriptor is assigned because the displayed condensed formula does not specify the double-bond geometry.

Step 3: Conclusion (i) Heptan-2-one.
(ii) 3-Phenylprop-2-enal.

Quick Tip to Solve: Count the carbonyl carbon in the parent chain, and always begin aldehyde numbering at the CHO carbon.

28(b). Describe the following conversions in not more than two steps:

(i) Ethanol to 3-Hydroxybutanal

(ii) Benzoic acid to m-Nitrobenzyl alcohol

(iii) Propanone to Propene

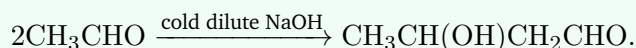
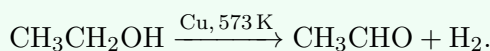
[3 marks]

Solution:

Concept:

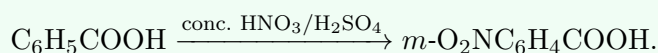
- Controlled dehydrogenation converts ethanol into ethanal. An aldehyde containing an alpha hydrogen undergoes aldol addition in cold dilute base.
- The $-\text{COOH}$ group directs electrophilic nitration to the meta position. BH_3 reduces the carboxylic acid group to $-\text{CH}_2\text{OH}$.
- A ketone is reduced to a secondary alcohol; heating the alcohol with concentrated sulphuric acid eliminates water to give an alkene.

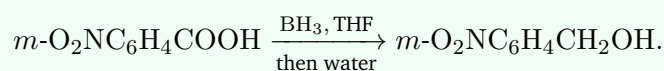
Step 1: Ethanol to 3-hydroxybutanal Pass ethanol vapour over heated copper at 573 K, then treat the ethanal with cold dilute sodium hydroxide:



Numbering from the aldehyde carbon places the hydroxyl group at carbon 3. Keep the aldol mixture cold: heating would dehydrate the required hydroxy aldehyde.

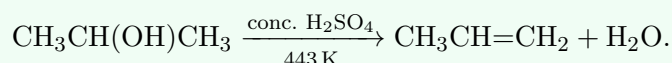
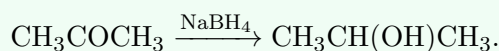
Step 2: Benzoic acid to m-nitrobenzyl alcohol First nitrate benzoic acid with concentrated nitric acid and concentrated sulphuric acid. Then reduce the acid group selectively using BH_3 in THF followed by hydrolysis:





Nitration must precede conversion of the acid group to the alcohol, because the carboxyl group supplies the required meta orientation. Borane selectively reduces the carboxylic acid group while retaining the nitro group.

Step 3: Propanone to propene Reduce the carbonyl group with sodium borohydride to obtain propan-2-ol, and dehydrate the alcohol by heating with concentrated sulphuric acid:



The carbon skeleton remains unchanged throughout the conversion.

Step 4: Conclusion The required sequences are ethanol → ethanal → 3-hydroxybutanal; benzoic acid → m-nitrobenzoic acid → m-nitrobenzyl alcohol; and propanone → propan-2-ol → propene.

Quick Tip to Solve: For the meta nitro product, nitrate while the meta-directing COOH group is still present; for the aldol product, avoid heating.

OR

28(a). Draw the structures of the following compounds:

(i) 4-Chloropentan-2-one

(ii) p-Nitropropiophenone

[2 marks]

Solution:

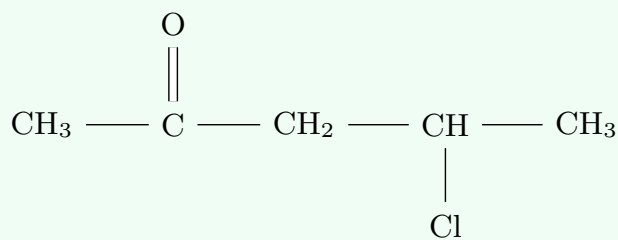
Concept:

- In an aliphatic ketone name, the parent chain contains the carbonyl carbon and is numbered to give the carbonyl group the lowest locant.
- Propiophenone has the structure $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$. The prefix para (p-) places the second ring substituent opposite the carbonyl-bearing carbon.

Step 1: Place the ketone and chlorine on the five-carbon chain Pentan-2-one has a five-carbon backbone with $\text{C}=\text{O}$ at carbon 2. Replace one hydrogen at carbon 4 by chlorine:

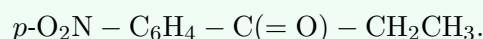


The terminal methyl group nearest the ketone is carbon 1; the chlorine-bearing carbon is therefore carbon 4.

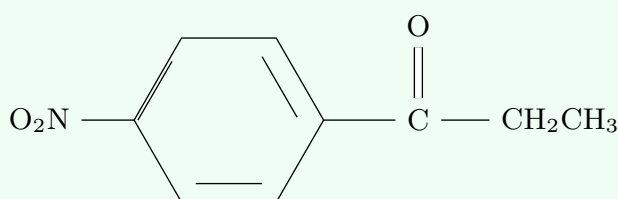


4-Chloropentan-2-one

Step 2: Place the nitro group para to the propionyl group In propiophenone the ring is bonded directly to the carbonyl carbon of $-\text{COCH}_2\text{CH}_3$, not to its terminal methyl carbon. Put $-\text{NO}_2$ at the opposite ring carbon:



Thus the two ring attachments have a 1,4 relationship.



p-Nitropropiophenone: para ring substitution

Step 3: Conclusion (i) $\text{CH}_3\text{COCH}_2\text{CH}(\text{Cl})\text{CH}_3$. (ii) $p\text{-O}_2\text{NC}_6\text{H}_4\text{COCH}_2\text{CH}_3$, with the nitro and propionyl groups para to one another.

Quick Tip to Solve: For propiophenone, attach the ring directly to COCH_2CH_3 ; para means the second substituent is on the opposite ring carbon.

28(b). Give tests to distinguish between the following pairs of compounds:

(i) Ethanal and Propanal

(ii) Phenol and Benzoic acid

(iii) Benzaldehyde and Acetophenone

[3 marks]

Solution:

Concept:

- A distinguishing test must give different visible observations for the two compounds under the same conditions.
- The iodoform test detects the $\text{CH}_3\text{CO}-$ group (and ethanal); carboxylic acids liberate CO_2 from bicarbonate; aldehydes reduce Tollens' reagent.

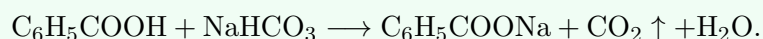
Step 1: Distinguish ethanal and propanal Warm separate samples with iodine solution and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3 , whereas propanal gives no

yellow precipitate. Ethanal contains the required $\text{CH}_3\text{CO}-$ unit, while propanal does not:



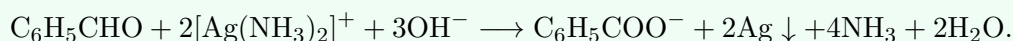
Both substances are aldehydes, so a general aldehyde test alone would not distinguish this pair.

Step 2: Distinguish phenol and benzoic acid Add aqueous sodium bicarbonate to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide, but phenol gives no effervescence:



Benzoic acid is sufficiently acidic to displace carbonic acid from bicarbonate. Phenol is weaker than carbonic acid and therefore does not liberate this gas under these conditions.

Step 3: Distinguish benzaldehyde and acetophenone Warm separate samples gently with freshly prepared Tollens' reagent. Benzaldehyde produces a silver mirror because its aldehyde group reduces the silver complex to metallic silver. Acetophenone is a ketone and gives no silver mirror:



Thus the observation identifies benzaldehyde directly; the unchanged sample is acetophenone.

Step 4: Conclusion The distinguishing tests are: (i) iodoform test: ethanal positive, propanal negative; (ii) bicarbonate test: benzoic acid effervesces, phenol does not; (iii) Tollens' test: benzaldehyde gives a silver mirror, acetophenone does not.

Quick Tip to Solve: Choose a test for which the two samples give opposite observations; both ethanal and propanal pass general aldehyde tests.

29(a). What is van't Hoff factor? What types of values can it have if in forming the solution the solute molecules undergo

(i) Dissociation?

(ii) Association?

[2 marks]

Solution:

Concept:

- Colligative properties depend on the number of dissolved solute particles rather than their chemical identity.
- The van't Hoff factor i corrects the calculated colligative property for association or dissociation of the solute.

Step 1: Define the factor The van't Hoff factor is the ratio of the observed colligative property to the value calculated by assuming that the solute neither associates nor dissociates:

$$i = \frac{\text{observed colligative property}}{\text{calculated colligative property}}.$$

Equivalently, it is the ratio of the actual number of solute particles present in solution to the number of formula units initially dissolved. It is dimensionless. If the solute undergoes neither process, $i = 1$.

Step 2: State the value for dissociation Dissociation produces more particles than the number of formula units dissolved. Hence $i > 1$. If a fraction α dissociates and each dissociated formula unit produces ν particles, then $i = 1 + \alpha(\nu - 1)$. For complete dissociation into two ions, for example, the ideal value is $i = 2$.

Step 3: State the value for association Association joins two or more solute molecules into a single larger particle, decreasing the number of independent particles. Thus $0 < i < 1$. If molecules associate in groups of n and the fraction associated is α , then $i = 1 - \alpha + \alpha/n$; complete association gives $i = 1/n$.

Step 4: Conclusion The van't Hoff factor is observed/calculated colligative property; dissociation gives $i > 1$, whereas association gives $i < 1$ (and positive).

Quick Tip to Solve: Count particles after dissolution: more particles raise i above one; joining particles lowers it below one.

29(b). How many mL of a 0.1 M HCl solution are required to react completely with 1 g of a mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of both? (Molar mass: $\text{Na}_2\text{CO}_3 = 106$ g, $\text{NaHCO}_3 = 84$ g) [3 marks]

Solution:

Concept:

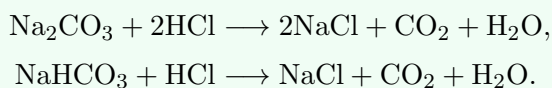
- Molarity is $M = n/V$, with n the amount in moles and V the solution volume in litres.
- Complete neutralisation consumes two moles of HCl per mole of Na_2CO_3 , but one mole per mole of NaHCO_3 .

Step 1: Calculate the equimolar amounts Let the amount of each component in the mixture be x mol. Equimolar means equal numbers of moles, rather than equal masses. Using the supplied molar masses, the total mass is

$$106x + 84x = 1.00, \quad 190x = 1.00, \quad x = \frac{1}{190} \text{ mol.}$$

The individual masses are therefore $106/190$ g and $84/190$ g, which add to the specified 1 g.

Step 2: Find the HCl required for complete reaction The balanced reactions are



Thus the carbonate consumes $2x$ mol of HCl and the bicarbonate consumes x mol. The total acid amount is

$$n(\text{HCl}) = 3x = \frac{3}{190} \text{ mol.}$$

The factor of two for carbonate is essential because neutralisation must proceed completely to carbon dioxide and water.

Step 3: Convert the acid amount into volume The HCl concentration is 0.1 mol L^{-1} . Therefore

$$V = \frac{n}{M} = \frac{3/190}{0.1} \text{ L} = 0.1578947 \text{ L} = 157.8947 \text{ mL}.$$

As a check, this volume of the acid contains $0.1 \times 0.1578947 = 0.01578947 \text{ mol HCl}$, exactly the amount required by both components together.

Step 4: Conclusion The required volume of 0.1 M HCl is 157.9 mL, approximately 158 mL.

Quick Tip to Solve: For an equimolar carbonate-bicarbonate mixture, one mole of each weighs 190 g and consumes three moles of HCl.

OR

29(a). Define

(i) Mole fraction

(ii) Molality

(iii) Raoult's law

[3 marks]

Solution:

Concept:

- Composition of a solution can be expressed as a ratio of mole amounts or as moles of solute per unit mass of solvent.
- Raoult's law relates the partial vapour pressure of a volatile component of an ideal solution to its mole fraction in the liquid.

Step 1: (i) Mole fraction The mole fraction of a component is the ratio of its number of moles to the total number of moles of all components of the solution. Thus, for component i ,

$$x_i = \frac{n_i}{\sum_j n_j}.$$

Here n_i is the amount of component i , in moles. Mole fraction has no unit and the sum of the mole fractions of all components is unity. For a binary solution, $x_1 = n_1/(n_1 + n_2)$ and $x_2 = n_2/(n_1 + n_2)$.

Step 2: (ii) Molality Molality is the number of moles of solute dissolved in one kilogram of solvent:

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

Its unit is mol kg^{-1} . The denominator is the mass of solvent, rather than the mass of the entire solution. Because masses do not change with temperature, molality is independent of temperature.

Step 3: (iii) Raoult's law At a fixed temperature, the partial vapour pressure of each volatile component of an ideal solution equals the product of its mole fraction in the solution and its vapour pressure in the pure state:

$$p_i = x_i p_i^\circ.$$

Here p_i° is the vapour pressure of pure component i at the same temperature. For a binary volatile solution, the total pressure is $p = x_1p_1^\circ + x_2p_2^\circ$.

Step 4: Conclusion Mole fraction is $n_i / \sum_j n_j$, molality is moles of solute per kilogram of solvent, and Raoult's law is $p_i = x_i p_i^\circ$.

Quick Tip to Solve: In molality use kilograms of solvent; in mole fraction count moles of every component in the denominator.

29(b). Assuming complete dissociation, calculate the expected freezing point of a solution prepared by dissolving 6.00 g of Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in 0.100 kg of water. (K_f for water = $1.86 \text{ K kg mol}^{-1}$, Atomic masses: Na = 23, S = 32, O = 16, H = 1) [2 marks]

Solution:

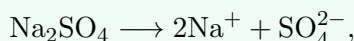
Concept:

- Freezing-point depression is $\Delta T_f = iK_f m$, where i counts the particles produced per formula unit and m is molality.
- On dissolving a hydrated salt, its water of crystallisation joins the solvent and must be included in the solvent mass.

Step 1: Calculate moles and the dissociation factor The molar mass of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is

$$M = 2(23) + 32 + 4(16) + 10(18) = 322 \text{ g mol}^{-1}.$$

Thus the amount of salt is $n = 6.00/322 = 0.01863 \text{ mol}$. Complete dissociation gives



so the van't Hoff factor is $i = 3$.

Step 2: Include crystal water and calculate the freezing point The crystal water contributes $(6.00/322)(180) = 3.354 \text{ g}$ of water. The total solvent mass after dissolution is therefore $0.100 + 0.003354 = 0.103354 \text{ kg}$, giving

$$m = \frac{0.01863}{0.103354} = 0.18029 \text{ mol kg}^{-1}.$$

Hence

$$\Delta T_f = 3(1.86)(0.18029) = 1.006 \text{ K}.$$

Subtracting this depression from the freezing point of pure water gives $T_f = 273.15 - 1.006 = 272.144 \text{ K}$. If crystal water is neglected in the solvent mass, the usual dilute-solution approximation gives $\Delta T_f = 1.040 \text{ K}$, or -1.04°C .

Step 3: Conclusion Including the water of crystallisation, the expected freezing point is approximately -1.01°C (272.14 K); neglecting that small solvent-mass correction gives -1.04°C .

Quick Tip to Solve: Use 322 g per mole of the hydrate, take three ions per formula unit, and add released crystal water to the solvent.

30(a). Write the formula and describe the structure of a noble gas species which is isostructural with

(i) IBr_2^-

(ii) BrO_3^-

[2 marks]

Solution:

Concept:

- VSEPR theory determines molecular shape from bonding domains and lone pairs around the central atom; a multiple bond counts as one domain.
- Isostructural species have the same molecular geometry, even when their constituent elements differ.

Step 1: (i) Species isostructural with dibromiodate(I) In IBr_2^- , iodine has two bonding domains and three lone pairs, giving the arrangement AX_2E_3 . Its five electron domains have a trigonal-bipyramidal arrangement. The three lone pairs occupy the equatorial sites, leaving the two bromine atoms at the axial sites. The corresponding noble-gas species is XeF_2 . Xenon likewise has two bond pairs and three lone pairs. It is linear, with $\angle \text{F} - \text{Xe} - \text{F} = 180^\circ$.

Step 2: (ii) Species isostructural with bromate In BrO_3^- , the central bromine has three bonding domains and one lone pair. The four electron domains have a tetrahedral arrangement, but the positions of the three oxygen atoms give a trigonal-pyramidal molecular shape, AX_3E . The noble-gas species with this structure is XeO_3 . Xenon has three Xe–O bonding domains and one lone pair; consequently, the oxygen atoms form a triangular base with xenon above that plane. Its molecular shape is trigonal pyramidal, rather than trigonal planar.

Step 3: Conclusion (i) $\boxed{\text{XeF}_2}$: linear, isostructural with IBr_2^- . (ii) $\boxed{\text{XeO}_3}$: trigonal pyramidal, isostructural with BrO_3^- .

Quick Tip to Solve: Match bonding domains and lone pairs: two plus three gives linear; three plus one gives trigonal pyramidal.

30(b). Assign reasons for the following:

(i) SF_6 is kinetically inert.

(ii) NF_3 is an exothermic compound whereas NCl_3 is not.

(iii) HCl is a stronger acid than HF though fluorine is more electronegative than chlorine. [3 marks]

Solution:

Concept:

- Strong bonds and a high activation-energy barrier can make a molecule kinetically inert even when a reaction is thermodynamically possible.
- Acid strength in water depends on the ease of breaking the hydrogen-halogen bond as well as on bond polarity.

Step 1: Explain the kinetic inertness of SF_6 In SF_6 , six fluorine atoms surround the sulphur atom in an octahedral arrangement. The strong S – F bonds are difficult to break, while the surrounding fluorine atoms shield sulphur and hinder attack by reagents such as water. A reaction therefore

requires a high activation energy and proceeds extremely slowly under ordinary conditions. This resistance to reaction is kinetic inertness.

Step 2: Compare formation of NF_3 and NCl_3 The formation of NF_3 releases energy because the strong N – F bonds formed provide sufficient stabilisation to compensate for the energy needed to break bonds in the elemental reactants. The much weaker N – Cl bonds do not provide the same compensation. Thus NF_3 has a negative enthalpy of formation and is exothermic, whereas NCl_3 is endothermic.

Step 3: Compare HCl and HF as acids Although fluorine makes the H – F bond more polar, this bond is exceptionally strong because the atoms are small. The H – Cl bond is longer and weaker and breaks more readily during ionisation in water. Consequently, HCl ionises essentially completely, whereas HF ionises only partially. The greater ease of bond cleavage makes hydrochloric acid stronger.

Step 4: Conclusion SF_6 is protected by strong bonds and steric shielding; strong N – F bonds favour exothermic formation of NF_3 ; and the weaker H – Cl bond makes HCl more acidic than HF.

Quick Tip to Solve: For hydrogen halides, compare bond strength before using electronegativity to predict acidity.

OR

30(a). How is ammonia prepared on a large scale? Name the process and mention the optimum conditions for the production of ammonia by this process. [2 marks]

Solution:

Concept:

- Le Chatelier's principle: high pressure favours the side with fewer moles of gaseous species.
- A catalyst increases the rate of attaining equilibrium without changing the equilibrium composition.

Step 1: State the process and reaction Ammonia is manufactured on a large scale by the Haber process. Purified nitrogen and hydrogen are mixed in the molar ratio 1 : 3 and reacted reversibly:



The reaction is exothermic and reduces the number of gaseous moles from four to two.

Step 2: Give and explain the optimum conditions The mixture is passed over finely divided iron catalyst, usually with a promoter such as molybdenum, at about 700 K and 200 atm. High pressure increases the equilibrium yield of ammonia. A moderately high temperature is a practical compromise: a lower temperature favours the exothermic forward reaction but makes its rate too slow. The iron catalyst supplies an alternative pathway with lower activation energy. Ammonia is condensed on cooling, and unreacted nitrogen and hydrogen are recycled.

Step 3: Conclusion The Haber process uses $\text{N}_2 : \text{H}_2 = 1 : 3$, approximately 700 K, about 200 atm, and finely divided iron catalyst.

Quick Tip to Solve: Remember the compromise: high pressure improves yield, while moderate temperature and iron provide a useful rate.

30(b). Assign reasons for the following:

(i) H_2S is more acidic than H_2O .

(ii) NH_3 is more basic than PH_3 .

(iii) Sulphur has a greater tendency for catenation than oxygen.

[3 marks]

Solution:

Concept:

- For hydrides down a group, increasing atomic size generally weakens the bond to hydrogen and facilitates proton release.
- Basicity involves availability of a lone pair for donation; catenation depends on the strength of bonds between like atoms.

Step 1: Compare the acidity of H_2S and H_2O Sulphur is larger than oxygen, so the S – H bond is longer and weaker than the O – H bond. Consequently, H_2S releases a proton more readily than H_2O . This bond-strength effect outweighs the higher electronegativity of oxygen, making hydrogen sulphide the stronger acid.

Step 2: Compare the basicity of NH_3 and PH_3 The nitrogen atom in NH_3 is smaller than the phosphorus atom in PH_3 . The lone pair on nitrogen is concentrated in a smaller region and is more readily donated to a proton. In phosphine, the lone pair is more diffuse and has greater s character, so it is less available for bonding. Hence NH_3 accepts a proton more readily and is more basic than PH_3 .

Step 3: Explain the greater catenation of sulphur Catenation is the formation of chains or rings through bonds between atoms of the same element. Oxygen atoms are small, so lone pairs on adjacent oxygen atoms repel one another strongly and weaken an O – O single bond. Larger sulphur atoms have less lone-pair repulsion, and the S – S single bond is stronger than the O – O single bond. Sulphur therefore forms stable extended chains and rings more readily.

Step 4: Conclusion H_2S is more acidic because its S-H bonds are weaker; NH_3 is more basic because its lone pair is more available; and stronger S – S bonds give sulphur greater catenation.

Quick Tip to Solve: Separate the three comparisons: H-X bond strength for acidity, lone-pair availability for basicity, and X-X bond strength for catenation.