

CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/1 - Compartment



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) 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. Why are crystalline solids anisotropic?

[1 mark]

Solution:

Concept:

- Anisotropy means that a physical property has different values along different directions in a solid.
- A crystal has a regular, ordered arrangement of its constituent particles, but the arrangement need not be identical along different directions.

Step 1: Examine different directions In a crystalline solid, the spacing and arrangement of atoms, ions or molecules can differ along different crystallographic directions.

Step 2: Relate structure to properties Because the particle arrangement and interactions depend on direction, properties such as electrical conductivity and refractive index can have different values when measured in different directions.

Step 3: Conclusion Crystalline solids are anisotropic because their constituent particles have different arrangements along different directions, giving direction-dependent physical properties.

Quick Tip to Solve: Connect a direction-dependent property directly to the different particle arrangements along crystal directions.

2. What are emulsions? Name an emulsion in which water is a dispersed phase.

[1 mark]

Solution:

Concept:

- An emulsion is a colloidal dispersion of one liquid in another immiscible liquid.
- The dispersed phase forms small droplets, while the dispersion medium is the continuous liquid phase.

Step 1: Define an emulsion Two immiscible liquids can form a colloidal system when droplets of one liquid are dispersed throughout the other. Such a system is called an emulsion.

Step 2: Identify the required type When water is the dispersed phase and oil is the continuous medium, the system is a water-in-oil emulsion. Butter is a standard example: water droplets are dispersed in a continuous fat phase.

Step 3: Conclusion Emulsions are colloidal dispersions of one liquid in another immiscible liquid. Butter is an example in which water is the dispersed phase.

Quick Tip to Solve: For the requested example, check that water occurs as droplets rather than as the continuous medium.

3. What are the collectors used in froth floatation process? Name a substance that can be used as such. [1 mark]

Solution:

Concept:

- Froth floatation separates sulphide ore particles from gangue using their different wetting behaviour.
- Collectors increase the non-wettability of mineral particles by water, helping those particles attach to air bubbles.

Step 1: State the function of a collector A collector is a reagent added to make the surface of ore particles more water-repellent. The treated ore particles attach more readily to rising air bubbles and are carried into the froth.

Step 2: Name a suitable reagent A xanthate, such as sodium ethyl xanthate, is used as a collector. Its role is to improve the collection of sulphide mineral particles in the froth during separation from the gangue.

Step 3: Conclusion Collectors increase the non-wettability of ore particles in froth floatation; sodium ethyl xanthate is an example.

Quick Tip to Solve: Remember xanthates as collectors: their key role is making sulphide ore particles water-repellent.

4. Why is F_2 a stronger oxidising agent than Cl_2 ? [1 mark]

Solution:

Concept:

- An oxidising agent accepts electrons; the reduction is $X_2 + 2e^- \rightarrow 2X^-$.
- The aqueous oxidising power depends on bond dissociation, electron gain and hydration of the resulting halide ions.

Step 1: Compare bond breaking The $F - F$ bond is unusually weak because of repulsion between lone pairs on the small fluorine atoms. Less energy is required to dissociate F_2 than Cl_2 .

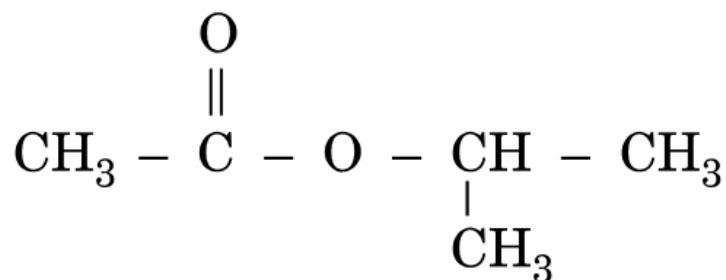
Step 2: Compare ion hydration The very small F^- ion has a much more negative hydration enthalpy than Cl^- . Together with the weak $F - F$ bond, this makes the overall reduction of fluorine in water more favourable, despite its less negative electron-gain enthalpy.

Step 3: Conclusion F_2 is a stronger oxidising agent than Cl_2 because of its low bond dissociation enthalpy and the very high hydration enthalpy (in magnitude) of F^- .

Quick Tip to Solve: Compare the whole aqueous reduction process; electron-gain enthalpy alone does not determine oxidising strength.

5. Name the alcohol that is used to make the following ester.

[1 mark]



Solution:

Concept:

- An ester has the general structure $RCOOR'$; the group OR' is derived from the alcohol.
- Replace the acyl group attached to the ester oxygen by hydrogen to identify the parent alcohol $R'OH$.

Step 1: Locate the alcohol-derived group The given ester is $\text{CH}_3\text{COOCH}(\text{CH}_3)\text{CH}_3$. The part on the alcohol side of the ester oxygen is $-\text{CH}(\text{CH}_3)\text{CH}_3$, an isopropyl group.

Step 2: Reconstruct and name the alcohol Attach OH to that group to obtain $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. The parent chain has three carbon atoms and the hydroxyl group is on carbon 2, so 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: Split an ester at the bond between its carbonyl carbon and oxygen; the oxygen-bearing fragment gives the alcohol.

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

[1 mark]

Solution:

Concept:

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

Step 1: Test propan-2-one Warm each sample separately with iodine and aqueous NaOH. Propan-2-one, CH_3COCH_3 , contains a methyl ketone group and gives a yellow precipitate of CHI_3 .

Step 2: Compare pentan-3-one Pentan-3-one is $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$. Its carbonyl carbon is bonded to ethyl groups on both sides, so it has no $\text{CH}_3\text{CO}-$ group and gives no yellow iodoform precipitate.

Step 3: Conclusion Use the iodoform test: propan-2-one gives a yellow precipitate, whereas pentan-3-one does not.

Quick Tip to Solve: Look for a methyl group directly attached to the carbonyl carbon before predicting an iodoform result.

7. How does a homopolymer differ from a copolymer?

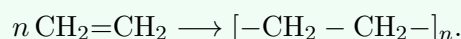
[1 mark]

Solution:

Concept:

- A monomer is a small molecule that joins repeatedly to form a polymer. Polymers are classified by the number of chemically distinct monomer species used.

Step 1: Homopolymer A homopolymer is formed from only one kind of monomer. For example, polyethene is obtained by polymerising ethene:



All the repeating units arise from the same monomer species.

Step 2: Copolymer A copolymer is formed from two or more different kinds of monomers. For example, Buna-S is made by copolymerising 1,3-butadiene and styrene. Its chain therefore contains units derived from both monomers.

Step 3: Conclusion A homopolymer uses one monomer species, whereas a copolymer uses two or more different monomer species.

Quick Tip to Solve: Count chemically different starting monomers, rather than the number of atoms in the repeating unit.

8. Define a 'Peptide linkage'.

[1 mark]

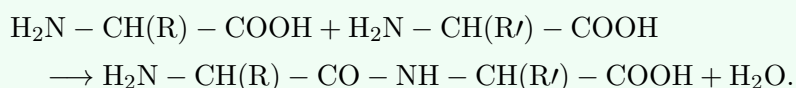
Solution:

Concept:

- Amino acids contain amino and carboxyl groups; condensation between these groups joins amino acids into peptides and proteins.

Step 1: Identify the bond A peptide linkage is the amide linkage $-\text{CO} - \text{NH}-$ formed between the carboxyl group of one amino acid and the amino group of another amino acid.

Step 2: Explain its formation The carboxyl group loses $-\text{OH}$ and the amino group loses one hydrogen atom, eliminating one water molecule:



The newly formed carbonyl-carbon-to-nitrogen bond is the peptide bond.

Step 3: Conclusion The $-\text{CO} - \text{NH}-$ linkage joining two amino-acid residues by loss of water is called a peptide linkage.

Quick Tip to Solve: Write the complete amide group, CO-NH , when defining a peptide linkage; an N-H bond alone is insufficient.

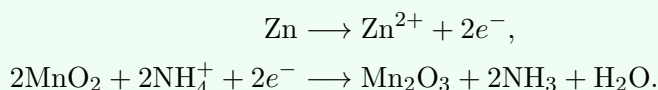
9. Set up Nernst equation for the standard dry cell. Using this equation show that the voltage of a dry cell has to decrease with use. [2 marks]

Solution:

Concept:

- The Nernst equation is $E = E^\circ - (RT/nF) \ln Q$, where Q is the reaction quotient, n the electrons transferred, R the gas constant and F the Faraday constant. Pure solid activities are unity.

Step 1: Write the dry-cell reaction In the zinc-carbon dry cell, zinc is oxidised and manganese dioxide is reduced in the ammonium chloride paste. A conventional representation is



Thus the net reaction transfers $n = 2$ electrons. Ammonia can also form a complex with the zinc ions in the paste.

Step 2: Apply the Nernst equation and follow discharge Taking the activities of the solid phases and water as unity, the reaction quotient is

$$Q = \frac{a_{\text{Zn}^{2+}} a_{\text{NH}_3}^2}{a_{\text{NH}_4^+}^2}.$$

Hence

$$E = E^\circ - \frac{RT}{2F} \ln \left(\frac{a_{\text{Zn}^{2+}} a_{\text{NH}_3}^2}{a_{\text{NH}_4^+}^2} \right).$$

At 298 K, this becomes

$$E = E^\circ - \frac{0.0591}{2} \log \left(\frac{a_{\text{Zn}^{2+}} a_{\text{NH}_3}^2}{a_{\text{NH}_4^+}^2} \right) \text{ V}.$$

During use, reactants are consumed and products accumulate, so Q increases. The subtracted logarithmic term consequently increases.

Step 3: Conclusion The Nernst equation shows that as discharge increases the reaction quotient, the dry-cell voltage decreases.

Quick Tip to Solve: First write the balanced discharge reaction; products belong in the numerator of the Nernst quotient.

10. How does a change in temperature affect the rate of a reaction? How can this effect on the rate constant of a reaction be represented quantitatively? [2 marks]

Solution:

Concept:

- The rate law is $r = k[A]^m[B]^n$. At fixed reactant concentrations, a temperature-induced change in the rate constant k produces the corresponding change in reaction rate.

Step 1: Explain the effect of temperature For an ordinary reaction with positive activation energy, increasing temperature increases the rate. A larger fraction of molecules then has energy equal to or greater than the activation energy, so more collisions can lead to reaction. Many reactions show an approximate doubling of rate for a rise of 10 K, but this is an empirical tendency, not a universal law.

Step 2: Represent the change quantitatively The Arrhenius equation is

$$k = Ae^{-E_a/(RT)}, \quad \ln k = \ln A - \frac{E_a}{RT},$$

where A is the frequency factor, E_a the activation energy and T the absolute temperature. If A and E_a are approximately constant over the temperature interval,

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

For $T_2 > T_1$ and $E_a > 0$, the right side is positive; hence $k_2 > k_1$, explaining the increase in rate quantitatively.

Step 3: Conclusion Raising temperature generally increases reaction rate; the dependence of its rate constant on temperature is given by $k = Ae^{-E_a/(RT)}$.

Quick Tip to Solve: Use kelvin in the Arrhenius equation and keep the units of activation energy consistent with those of R .

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

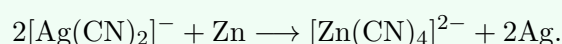
[2 marks]

Solution:

Concept:

- A more reactive metal can reduce a less reactive metal from its complex solution. Electrolytic refining uses selective anodic dissolution and cathodic deposition of the desired metal.

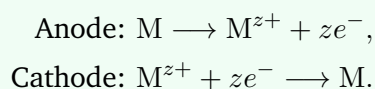
Step 1: Recover silver from the cyanide leach Silver present in the leach solution as soluble dicyanidoargentate(I), $[\text{Ag}(\text{CN})_2]^-$, is displaced by the more reactive metal zinc:



Zinc is oxidised from oxidation state zero to +2; silver(I) is reduced to metallic silver and precipitates.

This is a displacement or cementation reaction.

Step 2: Explain electrolytic refining The crude metal is made the anode, a thin sheet of pure metal the cathode, and a suitable soluble salt of the metal the electrolyte. On passing current, the desired metal dissolves from the anode as ions and deposits as pure metal at the cathode:



Insoluble noble impurities collect below the anode as anode mud; more reactive soluble impurities generally remain in solution under the operating conditions.

Step 3: Conclusion (i) Zinc reduces and displaces silver from its cyanide complex. (ii) Electrolysis transfers metal from the impure anode to the pure-metal cathode, separating impurities.

Quick Tip to Solve: For electrolytic refining, remember: impure anode dissolves, pure cathode gains metal, and insoluble impurities form anode mud.

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 uses the greater solubility of impurities in molten metal than in solid metal. The solid crystallising from a narrow molten zone is therefore purer.
- Vapour phase refining uses selective formation of a volatile metal compound, followed by its decomposition to deposit pure metal.

Step 1: Zone refining A moving heater produces a narrow molten zone in an impure metal rod. As the heater advances, pure metal crystallises behind it while impurities preferentially remain in the liquid zone. Repeated passes carry the impurities to one end, which is cut off. This method is used for highly pure silicon and germanium.

Step 2: Vapour phase refining The impure metal is converted into a volatile compound under suitable conditions. Nonvolatile impurities remain behind; the vapour is then decomposed under different conditions to recover pure metal. The compound must form readily and decompose easily. For example, nickel forms volatile Ni(CO)_4 , which decomposes on heating to give pure nickel and carbon monoxide.

Step 3: Conclusion Zone refining separates impurities by unequal solubility in solid and molten metal; vapour phase refining separates the metal through a volatile, readily decomposable compound.

Quick Tip to Solve: For zone refining, follow the impurities with the moving melt; for vapour refining, identify formation and decomposition of the volatile compound.

12. Complete the following chemical equations:



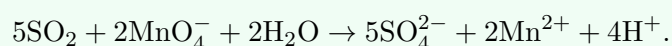
[2 marks]

Solution:

Concept:

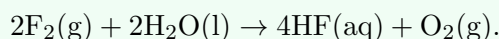
- Balance redox equations by conserving both atoms and total ionic charge. Sulfur in SO_2 is oxidised from +4 to +6.
- Fluorine is reduced from 0 to -1, while oxygen of water is oxidised from -2 to 0.

Step 1: Complete the sulfur dioxide reaction Permanganate oxidises sulfur dioxide to sulfate and is reduced to Mn^{2+} . Each sulfur atom loses two electrons, whereas each manganese atom gains five, giving a sulfur-to-manganese ratio of 5 : 2. The balanced equation is



There are five sulfur, two manganese, twenty oxygen and four hydrogen atoms on each side. Both sides have total charge -2.

Step 2: Complete the fluorine reaction Fluorine oxidises water to oxygen and forms hydrogen fluoride:



The four fluorine atoms gain four electrons in total; the two oxygen atoms lose four electrons. Hydrogen remains in oxidation state +1.

Step 3: Conclusion The products are (i) sulfate, manganese(II) and hydrogen ions, and (ii) hydrogen fluoride and oxygen, with the balanced coefficients shown above.

Quick Tip to Solve: For the first reaction, use the electron ratio 5 sulfur atoms to 2 manganese atoms, then check the total charge.

13. Assign reasons for the following:

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

(ii) Both O_2 and F_2 stabilize high oxidation states of transition metals but the ability of oxygen to do so exceeds that of fluorine.

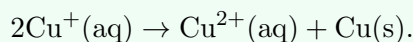
[2 marks]

Solution:

Concept:

- The stability of an aqueous ion depends on hydration enthalpy as well as ionisation enthalpy; strong hydration can stabilise a higher charge.
- High oxidation states are stabilised by strong bonds to electronegative elements; oxygen can also form multiple bonds with a transition metal.

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



The much more negative hydration enthalpy of Cu^{2+} , compared with Cu^+ , compensates for the energy needed to remove the second electron. Thus formation of hydrated copper(II) and copper metal is energetically favoured over retention of copper(I) in ordinary aqueous solution.

Step 2: Greater stabilising ability of oxygen Both oxygen and fluorine are strongly electronegative and form strong bonds with transition metals, stabilising positive oxidation states. Oxygen has the additional ability to form multiple bonds with metals, whereas fluorine forms single bonds. These strong metal-oxygen multiple bonds enable oxygen to stabilise especially high oxidation states. For example, manganese reaches +7 in Mn_2O_7 , whereas its highest fluoride is MnF_4 , containing manganese in +4.

Step 3: Conclusion Aqueous copper(I) disproportionates because copper(II) is strongly hydrated. Oxygen exceeds fluorine in stabilising high oxidation states because it can form strong multiple bonds with metals.

Quick Tip to Solve: For copper(I), write disproportionation first; for oxygen versus fluorine, identify the extra stabilisation from multiple bonding.

14. Write the IUPAC names of the following compounds:

(i) $\text{CH}_2=\text{CHCH}_2\text{Br}$

(ii) $(\text{CCl}_3)_3\text{CCl}$

[2 marks]

Solution:

Concept:

- Choose the longest suitable carbon chain. For an alkene, number it to give the carbon-carbon double bond the lowest locant.
- Halogen substituents are named with locants, and identical substituents use prefixes such as tri-, tetra- and hepta-.

Step 1: Name the unsaturated bromide The structure $\text{CH}_2=\text{CHCH}_2\text{Br}$ has a three-carbon chain containing the double bond. Numbering from the alkene end gives the double bond locant 1 and bromine locant 3. Numbering from the bromine end would give the double bond locant 2, so it is not selected. The parent is prop-1-ene and the substituent is 3-bromo; the name is **3-bromoprop-1-ene**.

Step 2: Name the chlorinated branched compound In $(\text{CCl}_3)_3\text{CCl}$, a central carbon is bonded to three trichloromethyl groups and one chlorine atom. The longest carbon chain passes through two outer carbons and the central carbon, giving a propane parent. Its terminal carbons carry three chlorine atoms each, while carbon 2 carries one chlorine and the remaining trichloromethyl group. Thus the chlorine locants on the parent are 1, 1, 1, 2, 3, 3, 3, and the name is **1,1,1,2,3,3,3-heptachloro-2-(trichloromethyl)propane**.

Step 3: Conclusion (i) 3-Bromoprop-1-ene. (ii) 1,1,1,2,3,3,3-Heptachloro-2-(trichloromethyl)propane.

Quick Tip to Solve: Expand the central carbon attachments before selecting the parent chain; three outer carbon groups do not form a four-carbon chain.

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

[2 marks]

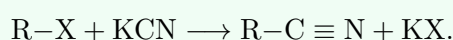
Solution:

Concept:

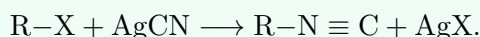
- A nucleophile donates an electron pair to an electron-deficient centre, usually the carbon bearing a leaving group.
- An ambident nucleophile has two alternative donor atoms. It can form a bond through either atom, but normally uses only one of them in a given substitution.

Step 1: Define ambident nucleophiles Ambident nucleophiles are nucleophiles possessing two different sites through which they can attack an electrophile. The two donor sites belong to the same ion; this does not mean that both sites must attack simultaneously.

Step 2: Explain using the cyanide ion The cyanide ion, CN^- , can attack through carbon or nitrogen. With potassium cyanide, carbon attack predominates and an alkyl halide gives an alkyl cyanide:



With silver cyanide, nitrogen attack predominates and an isocyanide is formed:



Thus the same cyanide group can give two different connectivities according to the atom involved in bond formation.

Step 3: Conclusion Ambident nucleophiles have two alternative attacking atoms; CN^- , which reacts through C or N to form cyanides or isocyanides, is an example.

Quick Tip to Solve: For an ambident ion, identify the atom bonded directly to R: R-CN is a cyanide, while R-NC is an isocyanide.

16. (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 pK_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]

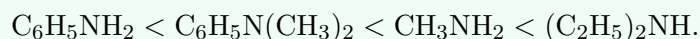
Solution:

Concept:

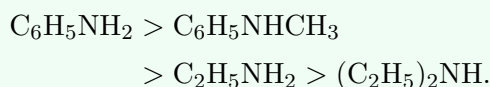
- Basicity depends on the availability of the nitrogen lone pair for protonation. Resonance with a benzene ring reduces that availability in aromatic amines.
- $pK_b = -\log K_b$: a stronger base has a larger K_b and a smaller pK_b . Alkyl groups increase electron density by their positive inductive effect; aqueous solvation also matters.

Step 1: (i) Arrange in increasing basic strength Aniline is weakest because its nitrogen lone pair is delocalised into the aromatic ring. The methyl groups of N,N-dimethylaniline increase electron density, so it is more basic than aniline, but both aromatic amines remain weaker than the given

aliphatic amines. In aqueous solution, diethylamine is stronger than methylamine. Therefore,



Step 2: (ii) Arrange in decreasing pK_b N-methylaniline is stronger than aniline due to the electron-releasing methyl group. Ethylamine is stronger than these aromatic amines, and diethylamine is stronger than ethylamine in aqueous solution. Since the weakest base has the largest pK_b , the required decreasing order is



The inequality here compares pK_b values, not base strengths.

Step 3: Conclusion (i) Increasing basicity: aniline < N,N-dimethylaniline < methylamine < diethylamine. (ii) Decreasing pK_b : aniline > N-methylaniline > ethylamine > diethylamine.

Quick Tip to Solve: Write the basic-strength order first; reverse it only when asked for increasing pK_b rather than increasing basicity.

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

(i) Ethylamine and Aniline

(ii) Aniline and Benzylamine

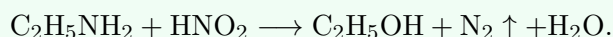
[2 marks]

Solution:

Concept:

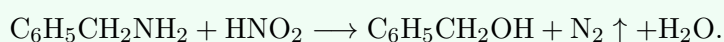
- Fresh nitrous acid is generated from NaNO_2 and dilute HCl . At 273–278 K, primary aromatic amines form diazonium salts.
- Primary aliphatic amines give unstable diazonium intermediates which decompose with nitrogen evolution; aniline gives a cold diazonium solution that couples to form an azo dye.

Step 1: (i) Ethylamine and aniline Treat separate cold samples with NaNO_2 and dilute HCl at 273–278 K. Ethylamine evolves nitrogen gas and forms ethanol:



Aniline forms benzenediazonium chloride without the corresponding brisk gas evolution at this temperature. Addition of alkaline beta-naphthol to its cold diazonium solution gives an orange-red azo dye; ethylamine does not give this dye.

Step 2: (ii) Aniline and benzylamine Apply the same cold nitrous-acid test, followed by coupling with alkaline beta-naphthol. Aniline forms a diazonium salt and gives the orange-red azo dye. Benzylamine is an aliphatic primary amine because the nitrogen is attached to a methylene group, not directly to the ring. It evolves nitrogen and forms benzyl alcohol:



It does not yield the aniline azo-dye test.

Step 3: Conclusion Cold nitrous acid followed by azo coupling distinguishes both pairs: aniline gives an orange-red azo dye, whereas ethylamine and benzylamine evolve nitrogen and do not give this dye.

Quick Tip to Solve: Check whether N is directly bonded to the benzene ring: benzylamine behaves as an aliphatic amine despite containing a phenyl group.

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

(i) Buna-S

(ii) Nylon-6, 6

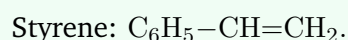
[2 marks]

Solution:

Concept:

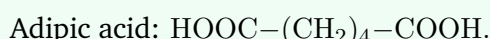
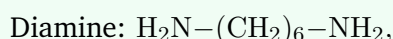
- Buna-S is an addition copolymer of a conjugated diene and styrene. Both monomers contain carbon-carbon double bonds.
- Nylon-6,6 is a condensation polymer of a diamine and a dicarboxylic acid. Each monomer has six carbon atoms, giving the designation 6,6.

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



The first monomer supplies the conjugated diene units, while styrene supplies phenyl-substituted units. Addition polymerisation of the two gives the synthetic rubber Buna-S.

Step 2: (ii) Nylon-6,6: names and structures The monomers are hexamethylenediamine (hexane-1,6-diamine) and adipic acid (hexanedioic acid):



The acid has four methylene carbon atoms plus two carboxyl carbon atoms, so it also contains six carbons. The amino and carboxyl groups condense with elimination of water to form the amide linkages of nylon-6,6.

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

Quick Tip to Solve: Count the carboxyl carbons in adipic acid: four CH₂ groups plus two COOH carbons give the six required for nylon-6,6.

19. 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 (bcc) cell contains eight corner atoms, each shared by eight cells, and one atom wholly inside the cell. Thus its effective number of atoms is $Z = 8(1/8) + 1 = 2$.
- The density relation is $\rho = ZM/(N_A a^3)$, where M is molar mass, a is edge length and N_A is Avogadro's constant.

Step 1: Convert the cell edge and calculate its volume The given density is in g cm^{-3} , so express the edge in centimetres. Since $1 \text{ pm} = 10^{-10} \text{ cm}$, we obtain

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

The cell is cubic, hence

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

Step 2: Relate the cell mass to its two atoms One Fe atom has mass M/N_A ; therefore the mass of a bcc cell is $2M/N_A$. Dividing this mass by the cell volume gives $\rho = 2M/(N_A a^3)$. Rearranging before substitution,

$$N_A = \frac{2M}{\rho a^3} = \frac{2(55.84)}{7.874(2.8665 \times 10^{-8})^3} = 6.02177 \times 10^{23} \text{ mol}^{-1}.$$

The units are $(\text{g mol}^{-1})/[(\text{g cm}^{-3})(\text{cm}^3)] = \text{mol}^{-1}$, as required.

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

Quick Tip to Solve: For a bcc cell use $Z = 2$, and convert picometres to centimetres before cubing when density is in g cm^{-3} .

20. The resistance of 0.01 M NaCl solution at 25°C is 200Ω . 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 R is measured in ohms and G in siemens.
- 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: Calculate conductance and conductivity The measured resistance is $R = 200 \Omega$. Therefore

$$G = \frac{1}{200} = 5.00 \times 10^{-3} \Omega^{-1} = 5.00 \times 10^{-3} \text{ S}.$$

The cell constant is unity, i.e. $l/A = 1 \text{ cm}^{-1}$ in the conventional centimetre system. Thus

$$\kappa = G \frac{l}{A} = (5.00 \times 10^{-3})(1) = 5.00 \times 10^{-3} \text{ S cm}^{-1}.$$

Conductance refers to the given cell; multiplying by its cell constant yields the conductivity of the solution.

Step 2: Use the concentration to obtain molar conductivity The concentration is $C = 0.01 \text{ mol L}^{-1}$. One mole is therefore present in $1/0.01 = 100 \text{ L} = 100000 \text{ cm}^3$ of solution. Molar conductivity equals conductivity multiplied by this volume per mole:

$$\Lambda_m = \frac{1000\kappa}{C} = \frac{1000(5.00 \times 10^{-3})}{0.01} = 500 \text{ S cm}^2 \text{ mol}^{-1}.$$

The factor 1000 converts litres to cubic centimetres; omitting it would mix the concentration and conductivity units.

Step 3: Conclusion The molar conductivity at 25°C is $\Lambda_m = 500 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: Calculate $\kappa = (\text{cell constant})/R$ first, then use $1000\kappa/C$ with molarity in mol L^{-1} .

21. 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 K

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

Calculate the value of E_a for the reaction. ($\log 11.11 = 1.046$) ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) [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 two temperatures, assuming the Arrhenius parameters remain constant, $\log_{10}(k_2/k_1) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$. The rate constants must have identical units so their ratio is dimensionless.

Step 1: Form the rate constant ratio Here $T_1 = 650 \text{ K}$, $T_2 = 700 \text{ K}$, $k_1 = 2.15 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1}$, and $k_2 = 2.39 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$. Their ratio is

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

Using the supplied logarithm gives $\log_{10}(k_2/k_1) = 1.046$. The higher rate constant at the higher temperature is consistent with positive activation energy.

Step 2: Rearrange and substitute in the two-temperature equation The reciprocal-temperature difference is

$$\frac{1}{650} - \frac{1}{700} = \frac{700 - 650}{650 \times 700} = \frac{50}{455000} \text{ K}^{-1}.$$

Therefore

$$\begin{aligned} E_a &= 2.303R \log_{10} \left(\frac{k_2}{k_1} \right) \frac{T_1 T_2}{T_2 - T_1} \\ &= \frac{2.303(8.314)(1.046)(650)(700)}{50} \\ &= 1.82254 \times 10^5 \text{ J mol}^{-1}. \end{aligned}$$

Since R was used in joules, divide the result by 1000 to express it in kilojoules per mole.

Step 3: Conclusion The activation energy is $E_a \approx 1.82 \times 10^5 \text{ J mol}^{-1} = 182 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Pair k_2/k_1 with $(1/T_1 - 1/T_2)$; for $T_2 > T_1$ both are positive after taking the logarithm.

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 is adsorption through weak van der Waals forces; chemisorption involves formation of chemical bonds between the adsorbate and the adsorbent.
- Adsorption is generally exothermic. Its extent depends on temperature and the available surface, while the activation energy controls how readily adsorption begins.

Step 1: Effect of temperature Physisorption is favoured at low temperature. On heating, the weakly held molecules escape more readily, so the amount adsorbed decreases. For example, gases such as nitrogen are physically adsorbed on charcoal more strongly at low temperature. Chemisorption usually needs an initial rise in temperature to overcome its activation barrier; hence its extent initially increases with temperature. At sufficiently high temperature, desorption becomes important and the extent can decrease. Hydrogen adsorption on nickel illustrates chemisorption.

Step 2: Effect of surface area Both processes increase with the surface area of the adsorbent because a larger exposed surface provides more adsorption sites. Thus finely divided nickel adsorbs more hydrogen than a compact piece of nickel of the same mass. Porous, activated charcoal is an effective physical adsorbent because it exposes a very large internal surface to gas molecules.

Step 3: Effect of activation energy Physisorption requires little or practically no activation energy because no new chemical bond needs to form. It therefore occurs readily even at low temperature. Chemisorption generally requires appreciable activation energy for bond rearrangement and formation of surface bonds. For example, dissociative adsorption of hydrogen on nickel involves breaking the hydrogen molecule into surface-bound hydrogen atoms, so suitable heating helps initiate the process.

Step 4: Conclusion Low temperature favours physisorption; suitable initial heating favours activated chemisorption. Greater surface area favours both, while an appreciable activation barrier is characteristic of chemisorption.

Quick Tip to Solve: Compare the two processes under the same three headings: temperature, exposed surface area and bond-formation barrier.

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]

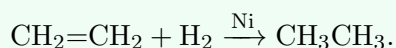
Solution:

Concept:

- Adsorption concentrates molecules at a solid or liquid surface. A porous solid has many accessible sites and can remove gases from the surrounding space.
- Selective adsorption can bring reactants together on a catalyst or change how mineral particles interact with water and air.

Step 1: (i) Production of vacuum After most of the air has been removed from a vessel by a vacuum pump, activated charcoal is placed in communication with the vessel. Its large porous surface adsorbs the residual gas molecules. Cooling the charcoal increases physical adsorption and improves gas removal. As the number of free gas molecules in the vessel falls, the pressure decreases and a high vacuum is obtained. The charcoal thus acts as an adsorbent for the traces of gas left behind.

Step 2: (ii) Heterogeneous catalysis In heterogeneous catalysis, gaseous or dissolved reactants are adsorbed on the solid catalyst surface. This increases their local concentration, places them in suitable orientations and may weaken their bonds. Reaction then proceeds along a surface pathway with lower activation energy. Products desorb, leaving active sites available again. For example, ethene and hydrogen adsorb on finely divided nickel and react to form ethane:



Step 3: (iii) Froth floatation Froth floatation concentrates sulphide ores by selective surface wetting. Collector molecules, such as xanthates, adsorb preferentially on sulphide mineral particles and make their surfaces water-repellent and oil-wettable. When air is blown through the aqueous slurry, these particles attach to air bubbles and rise with the froth, which is skimmed off. Gangue remains preferentially wetted by water and stays behind or settles. A frothing agent such as pine oil helps maintain the froth.

Step 4: Conclusion Adsorption produces vacuum by removing residual gases, promotes heterogeneous catalysis by binding reactants at active sites, and enables froth floatation through selective surface wetting of sulphide ore.

Quick Tip to Solve: For each application identify what is adsorbed and how the resulting surface change produces the useful effect.

23. Give reasons for the following:

(i) Transition metals exhibit a wide range of oxidation states.

(ii) Cobalt(II) is very stable in aqueous solutions but gets easily oxidised in the presence of strong ligands.

(iii) Actinoids exhibit a greater range of oxidation states than lanthanoids.

[3 marks]

Solution:

Concept:

- Electrons in subshells of similar energy can participate in bonding, producing several accessible oxidation states.
- Ligands alter the relative stability of metal oxidation states through crystal-field splitting and metal–ligand bonding; a strongly stabilised product is easier to form.

Step 1: (i) Variable oxidation states of transition metals The energies of the outer ns and inner $(n - 1)d$ orbitals in transition metals are relatively close. Consequently, varying numbers of both ns and $(n - 1)d$ electrons can participate in bond formation or be removed. This gives a wide range of oxidation states rather than a single fixed state. For example, manganese exhibits oxidation states from +2 to +7 in its compounds. The availability of partly filled d orbitals is central to this variability.

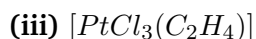
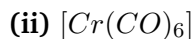
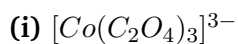
Step 2: (ii) Stability and oxidation of cobalt(II) In aqueous solution, Co^{2+} is relatively stable, whereas Co^{3+} is a strong oxidising species and readily tends to return to Co^{2+} . Strong-field ligands, however, stabilise cobalt(III) much more effectively. The d^6 configuration of Co^{3+} in a strong octahedral field becomes low-spin $t_{2g}^6 e_g^0$, with large crystal-field stabilisation. This stabilisation of the cobalt(III) complex makes oxidation of cobalt(II) easier in the presence of suitable strong ligands, such as cyanide.

Step 3: (iii) Greater range for actinoids In actinoids the $5f$, $6d$ and $7s$ subshells have comparable energies. Different numbers of electrons from these subshells can therefore participate in bonding, allowing many oxidation states. For example, uranium exhibits +3, +4, +5 and +6. In lanthanoids, the $4f$ electrons are more deeply buried and less readily involved in bonding; +3 is consequently the predominant oxidation state, with only a limited number of +2 and +4 exceptions.

Step 4: Conclusion The reasons are comparable ns and $(n - 1)d$ energies in transition metals, strong-ligand stabilisation of low-spin cobalt(III), and comparable $5f$, $6d$ and $7s$ energies in actinoids.

Quick Tip to Solve: For oxidation-state questions, identify the accessible subshells; for cobalt, compare the ligand stabilisation of the two oxidation states.

24. Write the IUPAC name and draw the structure of each of the following complex entities:



(At. nos. Cr = 25, Co = 27, Pt = 78)

[3 marks]

Solution:

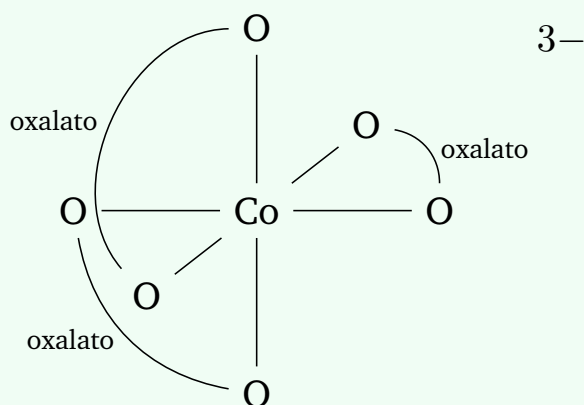
Concept:

- Find the oxidation state from $x + \sum q_{\text{ligands}} = q_{\text{complex}}$. Oxalato is a bidentate ligand of charge -2 ; carbonyl and ethene are neutral, whereas chlorido has charge -1 .
- An anionic coordination entity uses the metal name ending in -ate. Oxidation states are written as Roman numerals, and each oxalato ligand supplies two oxygen donor atoms.

Step 1: Tris(oxalato)cobaltate(III) For $[Co(C_2O_4)_3]^{3-}$,

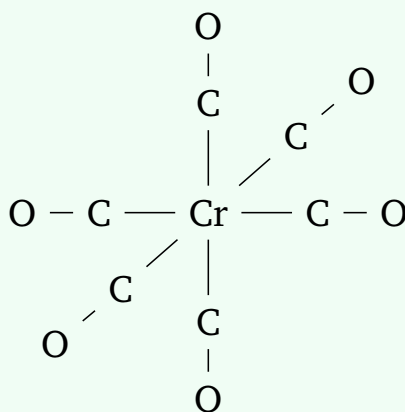
$$x + 3(-2) = -3 \Rightarrow x = +3.$$

The name is **tris(oxalato)cobaltate(III)**. Three bidentate oxalato ligands supply six oxygen donor atoms, so the coordination number is six and the structure is octahedral. In the schematic below, each curved connection joins the two oxygen donors belonging to one oxalato ligand; each such pair is linked through $-C(=O)-C(=O)-$.



Octahedral cobalt complex: paired O donors belong to one oxalato ligand.

Step 2: Hexacarbonylchromium(0) Carbonyl is neutral and the complex is uncharged, so $x + 6(0) = 0$, giving chromium in oxidation state zero. The name is **hexacarbonylchromium(0)**. Six carbonyl ligands coordinate through their carbon atoms and occupy the six vertices of an octahedron. The printed atomic number beside Cr does not enter this charge calculation.

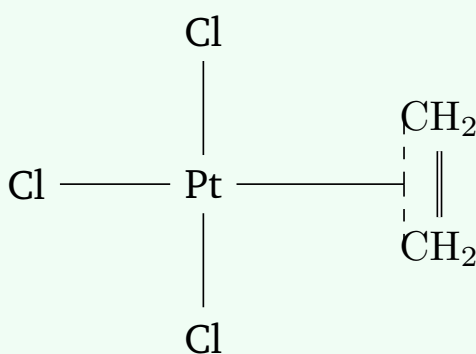


Octahedral hexacarbonylchromium(0); each ligand binds through carbon.

Step 3: Trichlorido(ethene)platinum(III) The printed formula $[PtCl_3(C_2H_4)]$ has no overall charge. Thus

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

Its literal name is **trichlorido(ethene)platinum(III)**; ethene binds side-on through its π bond. The drawing shows the four ligand sites and the side-on ethene attachment. A square-planar arrangement is the conventional structural sketch of this ligand framework. The familiar square-planar Zeise ion is instead $[PtCl_3(C_2H_4)]^-$, with Pt(II); that charge is absent in the printed entity. The neutral Pt(III) formula by itself does not establish a unique molecular geometry, so the schematic must not be taken as a derivation of a Pt(II), d^8 configuration.



Ligand connectivity of the printed platinum entity; ethene binds side-on.

Step 4: Conclusion (i) Tris(oxalato)cobaltate(III), octahedral; (ii) hexacarbonylchromium(0), octahedral; (iii) trichlorido(ethene)platinum(III) for the neutral formula as printed, with side-on ethene coordination.

Quick Tip to Solve: Count donor atoms separately from ligands: three oxalato ligands supply six donors. Check the printed overall charge before naming platinum.

25. Explain the following with an example for each:

(i) Kolbe's reaction

(ii) Reimer-Tiemann reaction

(iii) Williamson ether synthesis

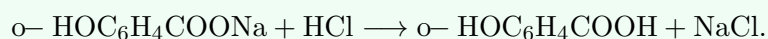
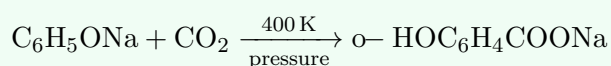
[3 marks]

Solution:

Concept:

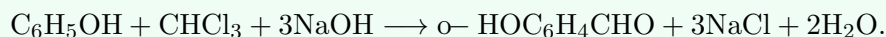
- Phenoxide ion activates the benzene ring towards electrophilic substitution, especially at the ortho and para positions.
- Williamson synthesis forms an ether by nucleophilic substitution: an alkoxide ion attacks an alkyl halide, preferably a primary one.

Step 1: Kolbe reaction Sodium phenoxide reacts with carbon dioxide under pressure at about 400 K. Electrophilic substitution occurs mainly at the ortho position, forming sodium salicylate. Acidification gives salicylic acid (2-hydroxybenzoic acid):



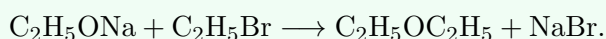
Here Kolbe reaction means carboxylation of phenoxide, as used in the chemistry of phenols.

Step 2: Reimer-Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide; subsequent acidification produces mainly salicylaldehyde (2-hydroxybenzaldehyde). The formyl group enters predominantly ortho to the hydroxyl group. Dichlorocarbene, :CCl₂, is the electrophile generated in the alkaline medium. The overall transformation is



The alkaline reaction mixture is acidified during work-up to obtain the free phenolic product.

Step 3: Williamson ether synthesis An alkoxide reacts with a primary alkyl halide through the S_N2 mechanism, replacing halide by the alkoxy group. For example, sodium ethoxide and bromoethane give ethoxyethane:



A primary halide favours substitution; a tertiary halide instead readily undergoes elimination with the basic alkoxide.

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

Quick Tip to Solve: Remember the new group on phenol: Kolbe adds COOH, whereas Reimer-Tiemann adds CHO, mainly ortho to OH.

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

[3 marks]

Solution:

Concept:

- Amino acids are the building units of proteins; their nutritional classification depends on whether the human body can synthesise enough of them.
- Essential and non-essential describe dietary requirements, not whether an amino acid is important for normal functioning.

Step 1: Essential amino acids Essential amino acids are those which the human body cannot synthesise, or cannot synthesise in sufficient quantities to meet its requirements. Therefore, they must be supplied through the diet, particularly through dietary proteins. Two examples are valine and leucine. Both participate in protein formation, but the body relies on an external supply of them.

Step 2: Non-essential amino acids Non-essential amino acids are those which the human body can synthesise in adequate amounts under normal conditions. Hence, their direct supply through the diet is not ordinarily essential. Two examples are glycine and alanine. They are still necessary for making proteins and carrying out body functions; the word non-essential refers only to their dietary supply.

Step 3: Conclusion Essential amino acids: valine and leucine; these must be obtained from the diet. Non-essential amino acids: glycine and alanine; these can be synthesised by the body.

Quick Tip to Solve: Classify by the ability of the body to synthesise the amino acid, not by its importance in proteins.

27. What is meant by the following terms? Explain with an example for each.

(i) Target molecules as used in medicinal chemistry

(ii) Food preservatives

(iii) Non-ionic detergents

[3 marks]

Solution:

Concept:

- Medicinal drugs act through interactions with biological target molecules, often proteins such as enzymes or receptors.
- Food preservatives prevent spoilage, whereas detergents remove dirt using a water-attracting part and an oil-attracting part.

Step 1: (i) Target molecules Target molecules are biological macromolecules with which a drug interacts to produce its therapeutic effect. They include enzymes, receptors and nucleic acids. For example, cyclooxygenase is an enzyme target of aspirin. Inhibition of this enzyme reduces the formation of prostaglandins involved in pain and inflammation. Thus the enzyme is the target molecule, while aspirin is the drug acting on it.

Step 2: (ii) Food preservatives Food preservatives are substances added to food to prevent spoilage and increase its storage life, for example by checking the growth of microorganisms. Sodium benzoate is a common example used to preserve foods such as fruit juices and squashes. It suppresses microbial

growth and thereby helps the food remain usable for longer.

Step 3: (iii) Non-ionic detergents Non-ionic detergents are cleansing agents whose molecules do not contain an ionic group and do not produce ions in aqueous solution. Their polar, uncharged part interacts with water while their hydrocarbon part interacts with grease. An example is the detergent obtained by reacting stearic acid with polyethylene glycol. This ester has an oil-attracting long hydrocarbon chain and a water-attracting polyethylene glycol portion.

Step 4: Conclusion Examples: target molecule—cyclooxygenase acted upon by aspirin; food preservative—sodium benzoate; non-ionic detergent—the ester of stearic acid with polyethylene glycol.

Quick Tip to Solve: For a target molecule, name the biological molecule acted upon; do not give only the name of the drug.

28(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:

- The van't Hoff factor i measures the change in the effective number of solute particles caused by dissociation or association.
- Colligative properties depend on the number of solute particles, so $i = P_{\text{obs}}/P_{\text{calc}}$, where P_{obs} is the observed colligative property and P_{calc} is its calculated value for unchanged solute particles.

Step 1: Define van't Hoff factor The van't Hoff factor is the ratio of the actual number of solute particles in solution to the number expected from the amount of solute dissolved if it remained unassociated and undissociated. Equivalently,

$$i = \frac{\text{normal molar mass}}{\text{apparent molar mass}}$$

The reference value is $i = 1$ when the particle number does not change.

Step 2: (i) Dissociation Dissociation splits a solute particle into two or more particles, increasing the particle count. Hence $i > 1$. For example, complete dissociation of NaCl gives Na^+ and Cl^- , ideally yielding $i = 2$.

Step 3: (ii) Association Association combines two or more solute particles into a larger particle, reducing the particle count. Hence $0 < i < 1$. For example, complete dimerisation combines two molecules into one dimer, so $i = \frac{1}{2}$.

Step 4: Conclusion Van't Hoff factor is the actual-to-expected particle-number ratio: $i > 1$ for dissociation and $0 < i < 1$ for association.

Quick Tip to Solve: Count particles after dissolution: splitting raises the factor above one; joining lowers it below one.

28(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: $\text{Na}_2\text{CO}_3 = 106 \text{ g}$, $\text{NaHCO}_3 = 84 \text{ g}$) [3 marks]

Solution:

Concept:

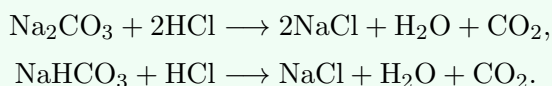
- Equimolar means equal numbers of moles, not equal masses. For a substance, $n = m/M$, where m is its mass and M its molar mass.
- Complete neutralisation consumes two moles of HCl per mole of carbonate and one mole of HCl per mole of hydrogen carbonate. Molarity obeys $c = n/V$, with V in litres.

Step 1: Determine the amount of each salt Let the amount of each salt in the mixture be $x \text{ mol}$. Their masses are then $106x \text{ g}$ and $84x \text{ g}$. The total mass gives

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

Equal amounts of the two salts therefore do not mean that each has a mass of 0.5 g.

Step 2: Use the balanced reactions The reactions for complete neutralisation are



Thus, the total amount of HCl required is

$$n(\text{HCl}) = 2x + x = \frac{3}{190} \text{ mol.}$$

The factor of two for carbonate is essential: its conversion to carbon dioxide requires two hydrogen ions per carbonate ion.

Step 3: Convert the amount of acid to volume For the given acid concentration, $c = 0.1 \text{ mol L}^{-1}$,

$$V = \frac{n}{c} = \frac{3/190}{0.1} \text{ L} = 0.157895 \text{ L} = 157.895 \text{ mL.}$$

This volume provides enough acid to react with both components completely.

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

Quick Tip to Solve: For an equimolar carbonate–hydrogen carbonate mixture, a pair of moles has mass $106 + 84 \text{ g}$ and consumes three moles of HCl.

28(a). Define**(i) Mole fraction****(ii) Molality****(iii) Raoult's law**

[3 marks]

Solution:**Concept:**

- Solution composition can be expressed using amounts in moles or mass of solvent. The choice of denominator distinguishes mole fraction from molality.
- Raoult's law relates the vapour pressure contributed by a volatile component to its mole fraction in the liquid solution at a fixed temperature.

Step 1: Define mole fraction The mole fraction of a component is the ratio of the number of moles of that component to the total number of moles of all components in the solution. For component i ,

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

Here n_i is the amount of component i , and the denominator includes solute and solvent. Mole fraction is dimensionless; the mole fractions of all components add up to unity.

Step 2: Define molality Molality is the number of moles of solute dissolved per kilogram of solvent:

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

Its unit is mol kg^{-1} . The mass in the denominator is the mass of solvent, not the total mass of solution. Since a change of temperature does not change these masses or amounts, molality is independent of temperature.

Step 3: State Raoult's law At a given temperature, the partial vapour pressure of each volatile component of an ideal solution equals the product of its mole fraction in the liquid and the vapour pressure of the pure component at that temperature:

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

Here p_i is its partial pressure and p_i° its pure-liquid vapour pressure. For a solution with a non-volatile solute, this relation applies to the solvent; its vapour pressure is lower because its mole fraction is below unity.

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

Quick Tip to Solve: Check the denominator: mole fraction uses total moles, while molality uses kilograms of solvent.

28(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 $\Delta T_f = iK_fm$, where i is the van't Hoff factor and m is the molality of solute.
- Water of crystallisation becomes part of the solvent when a hydrated salt dissolves. Complete dissociation of Na_2SO_4 gives three ions per formula unit, so $i = 3$.

Step 1: Calculate the amount of salt and the solvent mass The molar mass of Glauber's salt is

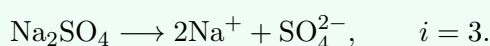
$$M = 2(23) + 32 + 4(16) + 10(18) = 322 \text{ g mol}^{-1}.$$

Hence $n = 6.00/322 = 0.0186335 \text{ mol}$. The hydrate releases 10 moles of water per mole of salt, giving

$$m_{\text{crystal water}} = \frac{6.00}{322} \times 180 = 3.354 \text{ g}.$$

The total mass of water after dissolution is therefore $100 + 3.354 = 103.354 \text{ g} = 0.103354 \text{ kg}$.

Step 2: Apply the freezing-point-depression equation The dissociation is



The molality of salt formula units is

$$m = \frac{0.0186335}{0.103354} = 0.18029 \text{ mol kg}^{-1}.$$

Consequently,

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

Subtract this depression from the freezing point of pure water, 0°C . A temperature difference has the same numerical value in kelvin and degrees Celsius.

Step 3: Conclusion The expected freezing point is -1.01°C , approximately 272.14 K .

Quick Tip to Solve: For hydrated salts, add the released crystal water to the solvent mass before calculating molality.

29(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 the number of bonding regions and lone pairs on the central atom; a multiple bond counts as one region.
- Isostructural species have the same arrangement of bonded atoms, even when the identities of the central and surrounding atoms differ.

Step 1: (i) Species isostructural with IBr_2^- Iodine has seven valence electrons and the negative charge adds one electron. With two I–Br bonds, the central iodine has three lone pairs. Thus it is an AX_2E_3 species. Its five electron-pair regions have a trigonal-bipyramidal arrangement, with the three lone pairs in equatorial positions. The two Br atoms occupy axial positions, giving a linear molecule with a bond angle of 180° . The noble gas compound XeF_2 also has two bond pairs and three lone pairs on Xe, so its structure is linear, $\text{F} - \text{Xe} - \text{F}$.

Step 2: (ii) Species isostructural with BrO_3^- The central bromine in BrO_3^- has three bonding regions and one lone pair. It therefore has an AX_3E arrangement: four electron-pair regions are arranged tetrahedrally, while the three oxygen atoms form a trigonal pyramid. The noble gas compound XeO_3 likewise has three Xe–O bonding regions and one lone pair on Xe. Its molecular shape is therefore trigonal pyramidal.

Step 3: Conclusion XeF_2 is linear and isostructural with IBr_2^- ; XeO_3 is trigonal pyramidal and isostructural with BrO_3^- .

Quick Tip to Solve: Count bonding regions and central lone pairs; do not confuse electron-pair geometry with molecular shape.

29(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:

- Kinetic inertness refers to a slow reaction rate caused by a large activation barrier; strong bonds and shielding of the reacting centre can produce it.
- The enthalpy of formation depends on the energy required to break reactant bonds compared with the energy released on forming product bonds.
- For hydrogen halides in water, ease of H–X bond cleavage is crucial: the much stronger H–F bond makes HF less acidic than HCl.

Step 1: (i) Kinetic inertness of SF_6 In SF_6 , six fluorine atoms surround sulphur in a compact

octahedral arrangement. The S–F bonds are very strong, and the surrounding fluorine atoms sterically shield the sulphur atom from attack by reagents such as water. Breaking these bonds and reaching the sulphur centre requires a high activation energy. Consequently, reactions such as hydrolysis are extremely slow and SF_6 is kinetically inert.

Step 2: (ii) Formation of NF_3 and NCl_3 The N–F bonds are much stronger than N–Cl bonds. Formation of the strong N–F bonds releases enough energy to outweigh the energy used in breaking the reactant bonds, so formation of NF_3 from its elements is exothermic. The weaker N–Cl bonds do not release sufficient energy to compensate for breaking the strong nitrogen-nitrogen triple bond and the chlorine-chlorine bonds; therefore NCl_3 is not an exothermic compound. Bond-energy balance, rather than electronegativity alone, explains this difference.

Step 3: (iii) Relative acid strengths of HCl and HF Although fluorine is more electronegative and the H–F bond is more polar, the H–F bond is exceptionally strong because of the small size of fluorine. The H–Cl bond is weaker and dissociates more readily in water to give hydronium ions. Hence HCl ionises essentially completely whereas HF ionises only partially. The greater ease of H–Cl bond cleavage outweighs the greater polarity of H–F.

Step 4: Conclusion SF_6 is inert because its strong bonds and octahedral shielding create a large kinetic barrier; strong N–F bonds make NF_3 formation exothermic; and the weaker H–Cl bond makes HCl more acidic than HF.

Quick Tip to Solve: For these three comparisons, identify the controlling factor: shielding, bond-energy balance, and H–X bond strength, respectively.

OR

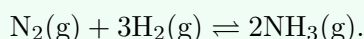
29(a). How is ammonia prepared on a large scale? Name the process and mention the optimum conditions for the production of ammonia by this process. [2 marks]

Solution:

Concept:

- Ammonia is manufactured by the Haber process: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, with $\Delta H^\circ \approx -92.4 \text{ kJ mol}^{-1}$ for the reaction as written.
- Le Chatelier's principle favours ammonia formation at high pressure and low temperature; an industrial compromise is needed because low temperature slows the reaction.

Step 1: Process and feed gases In the Haber process, purified nitrogen and hydrogen are mixed in the molar ratio 1 : 3, compressed and passed over a finely divided iron catalyst. They react reversibly to form ammonia:



The gases must be purified to prevent poisoning of the catalyst.

Step 2: Optimum operating conditions A temperature of about 700 K and a pressure of about 200 atm are used. Finely divided iron acts as catalyst, with small quantities of oxides such as K_2O and Al_2O_3 as promoters. High pressure favours the side with fewer gas molecules: two molecules of ammonia

replace four reactant molecules. A moderately high temperature gives a satisfactory rate while retaining a useful equilibrium yield, since excessive temperature opposes this exothermic reaction. The catalyst accelerates attainment of equilibrium without changing its position.

Step 3: Recovery and recycling The exiting gas mixture is cooled so that ammonia liquefies and can be removed. Unreacted nitrogen and hydrogen are recycled through the converter. Removal of ammonia also favours further product formation.

Step 4: Conclusion Ammonia is produced industrially by the Haber process using $N_2 : H_2 = 1 : 3$, about 700 K, about 200 atm, and promoted finely divided iron catalyst.

Quick Tip to Solve: Remember the Haber compromise: high pressure improves yield, moderate temperature maintains rate, and iron speeds equilibrium.

29(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.

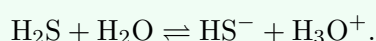
[3 marks]

Solution:

Concept:

- Acid strength of group 16 hydrides depends strongly on the strength of the element–hydrogen bond: a weaker bond allows easier proton release.
- Basicity is the tendency to donate a lone pair to a proton. Catenation is the ability of an element to form chains through bonds between its own atoms.

Step 1: Compare the acidity of hydrogen sulphide and water The sulphur atom is larger than the oxygen atom. Consequently, the S – H bond is longer and weaker than the O – H bond. Hydrogen sulphide therefore releases a proton more readily in aqueous solution:



Thus, although oxygen is more electronegative, the decrease in bond strength down the group controls this comparison, making H_2S more acidic.

Step 2: Compare the basicity of ammonia and phosphine The lone pair on the smaller nitrogen atom is concentrated in a smaller region and is more readily available for donation to a proton. The lone pair on phosphorus is less available for such donation. Thus ammonia accepts a proton more readily, forming NH_4^+ , whereas phosphine is a much weaker base. Hence NH_3 is more basic than PH_3 .

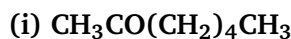
Step 3: Compare catenation in sulphur and oxygen Oxygen has a very small atomic size. When two oxygen atoms form an O – O single bond, repulsion between their nonbonding electron pairs is strong and weakens this bond. Sulphur atoms are larger, so such repulsions are smaller; the S – S single bond is stronger than the O – O single bond. Sulphur can therefore form more stable chains and rings, and has a greater tendency for catenation.

Step 4: Conclusion H_2S is more acidic because its S – H bond is weaker; NH_3 is more basic because

its lone pair is more available; sulphur catenates more because S – S bonds are stronger than O – O bonds.

Quick Tip to Solve: For these comparisons, distinguish bond strength (acidity and catenation) from lone-pair availability (basicity).

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



[2 marks]

Solution:

Concept:

- The parent chain must contain the carbonyl carbon. Number it to give the principal carbonyl functional group the lowest possible locant.
- An aldehyde carbon is numbered 1. A phenyl group, C_6H_5- , is named as a substituent when the aldehyde-containing chain is the parent.

Step 1: Name the ketone Expand the first formula as $\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$. The longest chain contains seven carbon atoms, including the carbonyl carbon, so the parent is heptane. Numbering from the end nearer the carbonyl group places the ketone at carbon 2; numbering from the other end would give 6. Replacing the terminal *-e* of heptane by *-2-one* gives **heptan-2-one**.

Step 2: Name the unsaturated aldehyde The printed abbreviation Ph denotes the phenyl group. Write the compound as $\text{CHO} - \text{CH} = \text{CH} - \text{C}_6\text{H}_5$ and number from the aldehyde carbon. The three-carbon parent has its double bond between carbons 2 and 3, and its phenyl substituent at carbon 3. The aldehyde suffix is *-al*, giving **3-phenylprop-2-enal**. The formula does not specify alkene stereochemistry, so an *E* or *Z* prefix is not assigned.

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 start aldehyde numbering at the CHO carbon.

30(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:

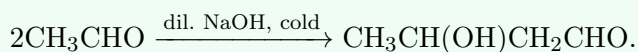
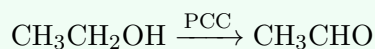
Concept:

- Controlled oxidation of a primary alcohol gives an aldehyde; aldehydes with an alpha hydrogen undergo aldol addition in cold dilute alkali.
- The carboxyl group directs electrophilic nitration to the meta position. Selective reduction must

preserve the nitro group.

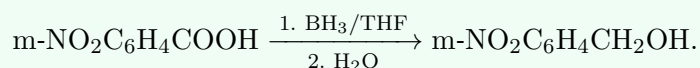
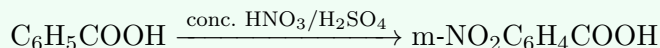
- Reduction of a ketone gives a secondary alcohol, which can be dehydrated to an alkene.

Step 1: Convert ethanol into 3-hydroxybutanal First oxidise ethanol to ethanal with pyridinium chlorochromate (PCC). Then carry out aldol addition using cold dilute sodium hydroxide:



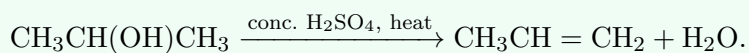
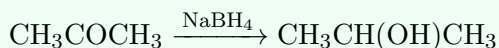
The product is 3-hydroxybutanal, numbering from the aldehyde carbon. Avoid heating during the second step, since heating favours dehydration of the aldol product.

Step 2: Convert benzoic acid into m-nitrobenzyl alcohol Nitrate benzoic acid first using concentrated nitric and sulphuric acids. The electron-withdrawing carboxyl group is meta directing, so the desired product is 3-nitrobenzoic acid. Then selectively reduce its carboxyl group using borane in tetrahydrofuran, followed by aqueous work-up:



Borane selectively reduces the carboxylic acid while retaining the nitro group. This selectivity is essential; a reagent that also reduces the nitro group would not give the required product.

Step 3: Convert propanone into propene Reduce propanone with sodium borohydride, followed by work-up, to obtain propan-2-ol. Dehydrate this secondary alcohol by heating with concentrated sulphuric acid:



Reduction converts the carbonyl group to an alcohol; elimination of water then forms the carbon-carbon double bond without changing the carbon skeleton.

Step 4: Conclusion (i) Ethanol → ethanal → 3-hydroxybutanal; (ii) benzoic acid → 3-nitrobenzoic acid → 3-nitrobenzyl alcohol; (iii) propanone → propan-2-ol → propene.

Quick Tip to Solve: Nitrate before reducing benzoic acid, and use a selective carboxyl reduction that leaves the nitro group intact.

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

(i) 4-Chloropentan-2-one

(ii) p-Nitropropiophenone

[2 marks]

Solution:

Concept:

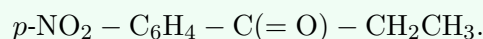
- A ketone has a carbonyl group, $>C=O$, bonded to two carbon atoms. The suffix and locant specify its position in the parent chain.
- In an aromatic compound, *p*- (para) means that the two ring substituents occupy positions 1 and 4. Propiophenone has the group $-COCH_2CH_3$ attached directly to a phenyl ring.

Step 1: (i) Construct 4-chloropentan-2-one Choose a five-carbon chain and number it so that the ketone carbonyl receives locant 2. Put chlorine on carbon 4. The resulting connectivity is

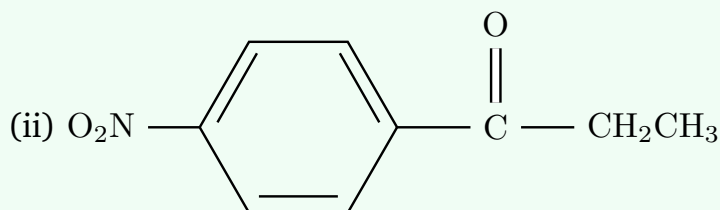
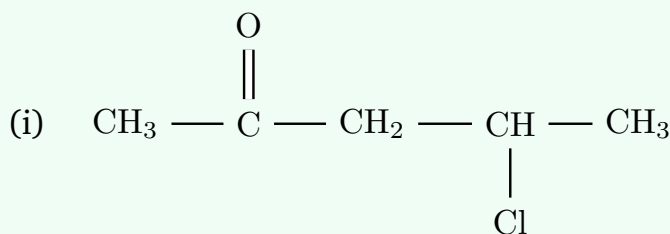


The carbonyl carbon is included among the five parent-chain carbons; chlorine replaces one hydrogen on the fourth carbon.

Step 2: (ii) Construct p-nitropropiophenone Attach the carbonyl carbon of $-COCH_2CH_3$ directly to benzene, then place $-NO_2$ on the opposite ring carbon. Thus the nitro group and propionyl group are para to each other:



The ethyl group lies on the other side of the carbonyl; it is not attached separately to the ring.



Structures of (i) 4-chloropentan-2-one and (ii) p-nitropropiophenone

Step 3: Conclusion The two labelled structures above show the required five-carbon ketone and para-substituted aromatic ketone.

Quick Tip to Solve: Build the ketone carbon skeleton first, then place substituents using their locants; para always means opposite positions on benzene.

30(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:

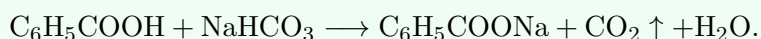
- A distinguishing test must give different observable results for the two members of a pair under the same conditions.
- The iodoform test detects a methyl ketone or ethanal; carboxylic acids release CO_2 from bicarbonate; aldehydes reduce Tollens' reagent to metallic silver.

Step 1: (i) Ethanal and propanal: iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3 ; propanal gives no yellow precipitate because it lacks the required $\text{CH}_3\text{CO}-$ unit (ethanal is the aldehyde that responds).



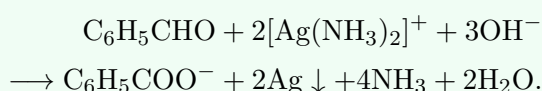
Thus a yellow precipitate identifies ethanal.

Step 2: (ii) Phenol and benzoic acid: bicarbonate test Add aqueous sodium hydrogen carbonate to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide; phenol gives no effervescence. Benzoic acid is sufficiently acidic to displace carbonic acid from bicarbonate, whereas phenol is not.



Passing the evolved gas into limewater turns it milky and confirms carbon dioxide.

Step 3: (iii) Benzaldehyde and acetophenone: Tollens test Warm each sample gently with freshly prepared Tollens' reagent in a clean test tube. Benzaldehyde produces a silver mirror (or a deposit of metallic silver), whereas acetophenone gives no silver mirror. Benzaldehyde is oxidised to benzoate while silver(I) is reduced:



Acetophenone is a ketone and does not undergo this mild aldehyde oxidation.

Step 4: Conclusion Use the iodoform test for ethanal/propanal, sodium bicarbonate for phenol/benzoic acid, and Tollens' reagent for benzaldehyde/acetophenone. The positive results identify ethanal, benzoic acid and benzaldehyde, respectively.

Quick Tip to Solve: Choose a test selective for a difference: ethanal gives iodoform, carboxylic acids fizz with bicarbonate, and aldehydes give a silver mirror.