

CBSE Class 12 Chemistry Question Paper 2011 with Solution PDF-Set 56/1 (Outside Delhi)

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 Hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains 30 questions. All questions are compulsory.
- (ii) There is no overall choice. An internal choice is provided in 5 questions (Q16, Q20, Q28, Q29, Q30); attempt only one of the alternatives in such questions.
- (iii) Marks for each question are indicated against it.

1. Define 'order of a reaction'.

[1 mark]

Solution:

Concept:

- For a rate law $r = k[A]^m[B]^n$, r is the reaction rate and k is the rate constant.
- The exponents in a rate law are found experimentally and need not equal the coefficients in the balanced equation.

Step 1: Write the experimental rate law Consider a reaction involving reactants A and B whose experimentally measured rate law is $r = k[A]^m[B]^n$. Here m and n are the individual orders with respect to A and B.

Step 2: Add the concentration exponents The overall order is $m + n$: only the powers of reactant concentrations appearing in the rate law are added. Order can be zero, integral or fractional, and is not generally inferred from the balanced equation.

Step 3: Conclusion The order of a reaction is the sum of the powers of the reactant concentrations in its experimentally determined rate law.

Quick Tip to Solve: Write the rate law first, then add its concentration exponents; do not add stoichiometric coefficients.

2. What is meant by 'shape-selective catalysis'?

[1 mark]

Solution:

Concept:

- Shape-selective catalysis depends on the pore or cavity dimensions of a catalyst and the molecular sizes and shapes of reactants and products.
- Zeolites are porous aluminosilicates with molecular-sized channels that can act as molecular sieves.

Step 1: Identify the geometrical selection In a porous catalyst, only molecules of suitable size and shape can enter its channels, reach active sites and undergo reaction. The available space can also favour formation or escape of particular products.

Step 2: Relate selection to catalysis Thus the catalyst selects among possible reactions through the fit between molecules and its pores. Zeolites are standard examples because their uniform channels impose this molecular-size restriction.

Step 3: Conclusion Shape-selective catalysis is catalysis in which the reaction selectivity depends on the pore size of the catalyst and the size and shape of the reactant and product molecules.

Quick Tip to Solve: Connect the word shape to molecular fit inside catalyst pores; zeolites are the standard example.

3. Differentiate between a mineral and an ore.

[1 mark]

Solution:

Concept:

- A mineral is a naturally occurring substance in the earth crust containing a metal or its compounds.
- An ore is a mineral from which the metal can be extracted conveniently and economically.

Step 1: State what qualifies as a mineral Minerals are naturally occurring metal-containing substances. The presence of a metal compound alone does not guarantee that a deposit can be used profitably to obtain the metal.

Step 2: Apply the extraction criterion An ore must contain the metal in a suitable form and sufficient concentration for convenient, economical extraction. Hence every ore is a mineral, whereas a mineral that cannot be economically processed is not an ore.

Step 3: Conclusion A mineral is a naturally occurring metal-containing substance; an ore is a mineral from which the metal can be extracted conveniently and economically.

Quick Tip to Solve: Use economic extractability as the deciding distinction: all ores are minerals, but the reverse is false.

4. What is meant by 'lanthanoid contraction'?

[1 mark]

Solution:

Concept:

- Across the lanthanoid series, increasing atomic number increases nuclear charge while electrons enter the $4f$ subshell.
- The $4f$ electrons shield the nuclear charge poorly, so effective nuclear attraction increases across the series.

Step 1: Identify the size trend On moving from lanthanum towards lutetium, the atomic radii and, especially, the radii of the corresponding trivalent ions show a gradual decrease with increasing atomic number.

Step 2: Explain the contraction The added $4f$ electrons do not completely shield the increased nuclear charge. The outer electrons therefore experience greater effective attraction, causing the gradual reduction in size known as lanthanoid contraction.

Step 3: Conclusion Lanthanoid contraction is the gradual decrease in atomic and ionic radii of lanthanoids with increasing atomic number, owing to poor shielding by $4f$ electrons.

Quick Tip to Solve: Mention both the gradual decrease in radii and the poor shielding of added nuclear charge by $4f$ electrons.

5. Write the IUPAC name of the following compound: $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br}$

[1 mark]

Solution:

Concept:

- The parent chain must contain the carbon-carbon double bond; a three-carbon alkene has the parent name propene.
- Number the chain to give the double bond the lowest locant before assigning the substituent locant.

Step 1: Choose and number the parent chain The structure is $\text{CH}_2 = \text{CH} - \text{CH}_2\text{Br}$. It contains three carbons, and numbering from the alkene end places the double bond between carbon 1 and carbon 2, giving prop-1-ene.

Step 2: Locate the bromo substituent With this numbering, bromine is attached to carbon 3. Numbering from the bromine end would give the double bond locant 2 and is therefore inappropriate. Prefix the parent name with 3-bromo.

Step 3: Conclusion The IUPAC name is 3-bromoprop-1-ene.

Quick Tip to Solve: Give the double bond the lower number before considering the locant of the bromo substituent.

6. Draw the structure of 4-chloropentan-2-one.

[1 mark]

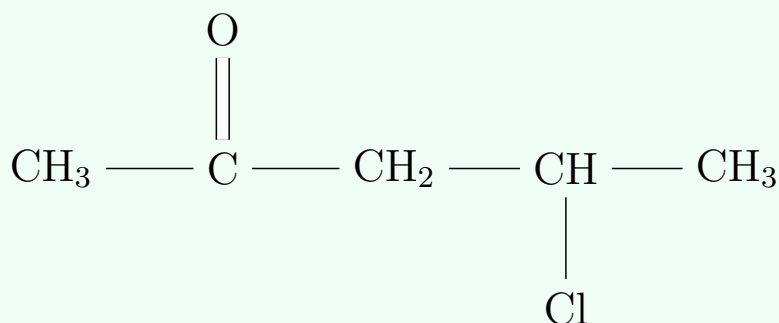
Solution:

Concept:

- Pentan-2-one has a five-carbon chain with a ketone carbonyl group at carbon 2.
- The prefix 4-chloro places a chlorine substituent on carbon 4 of that same numbered chain.

Step 1: Construct the ketone parent Write a chain of five carbon atoms numbered from the end nearer the carbonyl group. Carbon 2 is a carbonyl carbon, bonded to oxygen by a double bond; this gives the skeleton $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$.

Step 2: Add chlorine at carbon 4 Replace one hydrogen on carbon 4 by chlorine. Carbon 4 is then $\text{CH}(\text{Cl})$, while carbon 3 remains CH_2 . The ketone carbon remains bonded to carbons on both sides, as required by the suffix -one.



Structure of 4-chloropentan-2-one

Step 3: Conclusion The structure is $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_2 - \text{CH}(\text{Cl}) - \text{CH}_3$.

Quick Tip to Solve: Number from the carbonyl end: C=O must be at carbon 2, and chlorine must be at carbon 4.

7. How would you convert ethanol to ethene?

[1 mark]

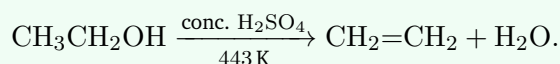
Solution:

Concept:

- Dehydration of an alcohol removes one molecule of water and forms a carbon-carbon double bond.
- Concentrated sulphuric acid acts as a dehydrating agent; the temperature controls the main product.

Step 1: Choose the reagent and conditions Heat ethanol with concentrated sulphuric acid at 443 K (about 170°C). These conditions favour elimination of water from ethanol.

Step 2: Write the conversion An OH group and a hydrogen atom on the adjacent carbon are eliminated as water:



The carbon skeleton remains unchanged; the two-carbon alcohol gives the two-carbon alkene.

Step 3: Conclusion Ethanol is converted to ethene by heating with concentrated H_2SO_4 at 443 K.

Quick Tip to Solve: Remember the higher temperature, 443 K, for ethene formation by dehydration of ethanol.

8. Rearrange the following compounds in increasing order of their basic strengths:

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

[1 mark]

Solution:

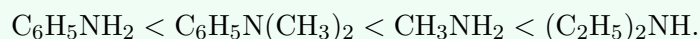
Concept:

- Basicity depends on the availability of the nitrogen lone pair for accepting a proton.
- Resonance reduces lone-pair availability in aromatic amines; alkyl groups increase electron density through their positive inductive effect.

Step 1: Compare aromatic and aliphatic amines In aniline and *N,N*-dimethylaniline the nitrogen lone pair is delocalised into the benzene ring. It is therefore less available for protonation than in methylamine and diethylamine.

Step 2: Compare the members of each pair The two methyl groups increase the basicity of *N,N*-dimethylaniline relative to aniline. Among the given aliphatic amines, diethylamine is more basic than methylamine because of the electron-releasing alkyl groups, with effective solvation of its conjugate acid in water.

Step 3: Conclusion The increasing order is



Quick Tip to Solve: First separate aromatic from aliphatic amines; then compare alkyl substitution within each pair.

9. Explain how you can determine the atomic mass of an unknown metal if you know its mass density and the dimensions of the unit cell of its crystal. [2 marks]

Solution:

Concept:

- Density is mass divided by volume: $\rho = m_{\text{cell}}/V_{\text{cell}}$.
- If a unit cell contains Z atoms, its mass is ZM/N_A , where M is molar mass and N_A is the Avogadro constant.

Step 1: Find the mass and volume of one unit cell Calculate the unit-cell volume from its dimensions. For a cubic unit cell of edge a , $V_{\text{cell}} = a^3$. The mass of one cell is then $m_{\text{cell}} = \rho a^3$. Use consistent units: with density in g cm^{-3} , express the edge in cm.

Step 2: Use the number of atoms per cell Identify the lattice type to obtain Z : it is 1 for simple cubic, 2 for body-centred cubic and 4 for face-centred cubic. Since

$$\rho a^3 = \frac{ZM}{N_A}, \quad M = \frac{\rho a^3 N_A}{Z},$$

substitution gives the molar mass in g mol^{-1} . Its numerical value equals the atomic mass in u. Density and dimensions must be supplemented by knowledge of the number of atoms per cell; otherwise the atomic mass is not uniquely fixed.

Step 3: Conclusion The atomic mass is numerically $\rho V_{\text{cell}} N_A / Z$ when ρ is in g cm^{-3} and V_{cell} is in cm^3 ; for a cubic lattice, use $V_{\text{cell}} = a^3$.

Quick Tip to Solve: Convert the cell edge to cm before cubing it, and determine Z from the lattice type.

10. Calculate the packing efficiency of a metal crystal for a simple cubic lattice. [2 marks]

Solution:

Concept:

- Packing efficiency is the percentage of unit-cell volume actually occupied by the constituent hard-sphere atoms.
- A simple cubic cell has eight corner atoms, each contributing $1/8$, and neighbouring atoms touch along an edge.

Step 1: Relate atomic radius to edge length The effective number of atoms in one simple cubic unit

cell is

$$Z = 8 \times \frac{1}{8} = 1.$$

Atoms at adjacent corners touch along the cube edge. Therefore the edge length is $a = 2r$, where r is the atomic radius.

Step 2: Calculate the occupied fraction The volume occupied by the one effective atom is $4\pi r^3/3$. The cube volume is $a^3 = (2r)^3 = 8r^3$. Hence

$$\begin{aligned}\text{Packing efficiency} &= \frac{Z(4\pi r^3/3)}{a^3} \times 100 \\ &= \frac{4\pi r^3/3}{8r^3} \times 100 \\ &= \frac{\pi}{6} \times 100 \approx 52.36\%.\end{aligned}$$

The remaining approximately 47.64% is unoccupied space in the hard-sphere model; it is not included in the occupied volume.

Step 3: Conclusion The packing efficiency of a simple cubic metal crystal is approximately 52.4%.

Quick Tip to Solve: For simple cubic packing use $Z = 1$ and $a = 2r$; the radius then cancels out of the ratio.

11. State the following:

(i) Raoult's law in its general form in reference to solutions.

(ii) Henry's law about partial pressure of a gas in a mixture.

[2 marks]

Solution:

Concept:

- Partial vapour pressure is the contribution made by one component to the total vapour pressure above a solution.
- Mole fraction is dimensionless. The proportionality constants in Raoult's and Henry's laws refer to a fixed temperature.

Step 1: State Raoult's law For an ideal solution of volatile components at a given temperature, the partial vapour pressure of each component equals its mole fraction in the liquid solution multiplied by its vapour pressure in the pure state:

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

Here p_i is the partial vapour pressure, x_i the liquid-phase mole fraction and p_i° the vapour pressure of pure component i at that temperature. Thus the total pressure is $P = \sum_i x_i p_i^\circ$.

Step 2: State Henry's law At a constant temperature, the partial pressure of a gas above a solution is directly proportional to its mole fraction dissolved in the liquid:

$$p = K_H x.$$

Here p is the gas partial pressure, x its dissolved mole fraction and K_H Henry's law constant for that

gas-solvent pair at that temperature. In a gaseous mixture, use the partial pressure of the particular gas rather than the total mixture pressure.

Step 3: Conclusion Raoult's law: $p_i = x_i p_i^\circ$. Henry's law: $p = K_H x$, at fixed temperature.

Quick Tip to Solve: Use the pure liquid vapour pressure in Raoult's law and the gas-specific Henry constant in Henry's law.

12. What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are:

(i) $\text{L}^{-1} \text{mol s}^{-1}$

(ii) $\text{L mol}^{-1} \text{s}^{-1}$

[2 marks]

Solution:

Concept:

- The rate law relates the experimentally measured reaction rate to the concentrations of reactants at a fixed temperature.
- For an overall order n , $[k] = (\text{mol L}^{-1})^{1-n} \text{s}^{-1}$, since rate has units $\text{mol L}^{-1} \text{s}^{-1}$.

Step 1: Define rate law and rate constant For reactants A and B, the rate law is $r = k[A]^a[B]^b$, where a and b are experimentally determined partial orders and $a + b$ is the overall order. The rate constant k is the proportionality constant at a specified temperature; numerically, it equals the rate when each concentration appearing in the rate law is unity in the chosen units.

Step 2: Identify the orders from the units (i) $\text{L}^{-1} \text{mol s}^{-1} = \text{mol L}^{-1} \text{s}^{-1}$, the units of rate itself. Hence $1 - n = 1$, giving $n = 0$. (ii) $\text{L mol}^{-1} \text{s}^{-1} = (\text{mol L}^{-1})^{-1} \text{s}^{-1}$. Thus $1 - n = -1$, giving $n = 2$.

Step 3: Conclusion The rate law is the experimental concentration dependence of rate, and k is its proportionality constant. The orders are (i) zero and (ii) second.

Quick Tip to Solve: Write concentration as mol per litre first; the concentration exponent in the units of k is always 1 minus the order.

13. The thermal decomposition of HCO_2H is a first-order reaction with a rate constant of $2.4 \times 10^{-3} \text{s}^{-1}$ at a certain temperature. Calculate how long it will take for three-fourths of the initial quantity of HCO_2H to decompose. ($\log 0.25 = -0.6021$)

[2 marks]

Solution:

Concept:

- For a first-order reaction, $t = \frac{2.303}{k} \log_{10} \left(\frac{[A]_0}{[A]_t} \right)$, where $[A]_0$ and $[A]_t$ are the initial and remaining concentrations.
- Three-fourths decomposed means that one-fourth remains; the integrated law uses the amount remaining.

Step 1: Find the fraction remaining Let the initial amount of formic acid be a . When three-fourths has decomposed, the amount remaining is $a - 3a/4 = a/4$. At constant volume the concentration ratio is therefore $[A]_0/[A]_t = a/(a/4) = 4$. The initial amount cancels, as expected for a specified fractional conversion in a first-order reaction.

Step 2: Substitute into the integrated rate law Using $k = 2.4 \times 10^{-3} \text{ s}^{-1}$ and $\log_{10} 4 = -\log_{10} 0.25 = 0.6021$,

$$t = \frac{2.303 \times 0.6021}{2.4 \times 10^{-3}} = 577.8 \text{ s}.$$

This is approximately 9.63 min. The positive logarithm gives a positive time; using the decomposed fraction instead of the remaining fraction would give an incorrect result.

Step 3: Conclusion The required time is $5.78 \times 10^2 \text{ s} \approx 9.63 \text{ min}$.

Quick Tip to Solve: A remaining fraction of one-fourth corresponds to two half-lives, so check the result against twice 0.693 divided by k .

14. Describe the principle controlling each of the following processes:

(i) Vapour phase refining of titanium metal

(ii) Froth flotation method of concentration of a sulphide ore

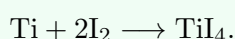
[2 marks]

Solution:

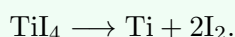
Concept:

- Vapour phase refining requires selective formation of a volatile metal compound followed by its decomposition to deposit pure metal.
- Froth flotation separates sulphide ore from gangue by their different wetting behaviour towards oil and water.

Step 1: Vapour phase refining of titanium In the van Arkel method, impure titanium is heated with iodine at about 523 K, forming volatile titanium tetraiodide:



The iodide vapour is separated from non-volatile impurities and passed over a hot tungsten filament at about 1700 K. It decomposes, depositing pure titanium and regenerating iodine:



Thus purification relies on volatility of the iodide and its thermal decomposition.

Step 2: Froth flotation of a sulphide ore The powdered ore is mixed with water and a collector such as a xanthate and a frother such as pine oil, and air is blown through the agitated mixture. Sulphide particles are preferentially wetted by oil and attach to air bubbles, while gangue is preferentially wetted by water and remains behind. The mineral-bearing froth rises to the surface, is skimmed off, and is then dried to recover the concentrated ore.

Step 3: Conclusion (i) Titanium is refined through volatile TiI_4 formation and subsequent decom-

position. (ii) Froth flotation works through preferential wetting of sulphide by oil and gangue by water.

Quick Tip to Solve: For titanium name the volatile iodide and hot-filament decomposition; for flotation explicitly state which material oil and water wet.

15. How would you account for the following:

(i) Cr^{2+} is reducing in nature while, with the same d-orbital configuration (d^4), Mn^{3+} is an oxidising agent.

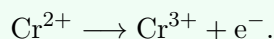
(ii) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series. [2 marks]

Solution:

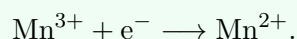
Concept:

- Redox behaviour depends on the relative stability of the oxidation states formed, rather than on the initial d-electron count alone.
- Transition metals have ns and (n-1)d orbitals of comparable energy; both sets of electrons can participate in bonding.

Step 1: Explain the opposite redox behaviour Cr^{2+} has a $3d^4$ configuration and readily loses an electron to form Cr^{3+} , which has the relatively stable $3d^3$ configuration (a half-filled t_{2g} set in an octahedral field):



It donates an electron and is therefore reducing. In contrast, Mn^{3+} , also $3d^4$, readily gains an electron to form Mn^{2+} with its especially stable half-filled $3d^5$ configuration:



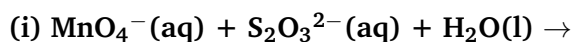
It accepts an electron and therefore acts as an oxidising agent.

Step 2: Explain the maximum number of oxidation states near the middle Near the middle of a transition series, the greatest number of unpaired d electrons is available together with the ns electrons for bonding, so several different numbers of electrons can participate. This produces the widest range of oxidation states; manganese, for example, commonly exhibits states from +2 to +7. Near the beginning there are fewer d electrons, while towards the end pairing and the reduced availability of d electrons restrict the range.

Step 3: Conclusion Cr^{2+} tends towards stable d^3 Cr^{3+} , whereas Mn^{3+} tends towards stable d^5 Mn^{2+} . The middle members have the most electrons available in varied bonding arrangements.

Quick Tip to Solve: Write the product ion and its d count first: electron loss by Cr(II) means reducing, and electron gain by Mn(III) means oxidising.

16(a). Complete the following chemical equations:



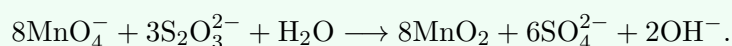
[2 marks]

Solution:

Concept:

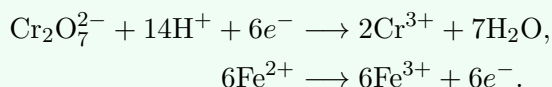
- Balance a redox reaction by equating electrons lost and gained; atoms and total ionic charge must both be conserved.
- In neutral or alkaline water, permanganate is reduced to MnO_2 . Acidified dichromate is reduced to Cr^{3+} .

Step 1: (i) Permanganate with thiosulphate The two sulphur atoms of $\text{S}_2\text{O}_3^{2-}$ have a combined oxidation number of +4; in two sulphate ions their combined oxidation number is +12. Thus one thiosulphate ion loses eight electrons. Each manganese atom changes from +7 to +4, gaining three electrons. Equating the transfer at 24 electrons gives eight permanganate ions for three thiosulphate ions. Balancing oxygen and hydrogen with water and hydroxide gives



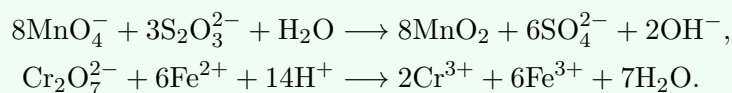
The charge is -14 on each side, and the brown manganese dioxide precipitate is the reduction product.

Step 2: (ii) Acidified dichromate with iron(II) Two chromium atoms each gain three electrons, whereas each iron(II) ion loses one electron:



Adding cancels the electrons and gives the balanced overall equation. Hydrogen ions supply the acidic medium; they must appear on the reactant side.

Step 3: Conclusion



Quick Tip to Solve: First identify the medium: water without acid gives MnO_2 , while dichromate with H^+ gives Cr^{3+} .

16(b). State reasons for the following:

(i) Cu^+ ion is not stable in an aqueous solution.

(ii) Unlike Cr^{3+} , Mn^{2+} , Fe^{3+} and the subsequent other M^{2+} ions of the 3d series of elements, the 4d and the 5d series metals generally do not form stable cationic species. [2 marks]

Solution:

Concept:

- Stability of an aqueous metal ion depends on the total energy change, including ionisation and hydration energies, rather than electronic configuration alone.
- More spatially extended 4d and 5d orbitals favour stronger covalent bonding and higher oxidation states.

Step 1: (i) Instability of aqueous copper(I) Although Cu^+ has a filled $3d^{10}$ configuration, it disproportionates in water:



One copper(I) ion is oxidised and the other reduced. The much more favourable hydration of the smaller, doubly charged Cu^{2+} ion compensates for the energy required to form it. Consequently, the overall disproportionation is favourable, and simple aqueous copper(I) is unstable.

Step 2: (ii) Cationic species of the heavier transition series The heavier transition metals generally have high enthalpies of atomisation and ionisation. Formation of simple aqueous cations is therefore energetically costly, and hydration does not generally compensate for this cost as effectively as for the familiar stable cations of the first series. The 4d and 5d orbitals are larger and more diffuse than 3d orbitals. Their electrons participate more extensively in covalent bonding, and the heavier transition elements favour higher oxidation states, often stabilised in covalent compounds, oxoanions or coordination complexes. They therefore show a much weaker general tendency to exist as simple, stable aqueous cations of the kind familiar for the 3d series. The statement is a general trend: it does not exclude stable complexes or every individual cation of a 4d or 5d metal.

Step 3: Conclusion Cu^+ disproportionates because hydration strongly stabilises Cu^{2+} . The heavier transition metals favour stronger covalent bonding and higher oxidation states, so simple cationic species are generally less characteristic.

Quick Tip to Solve: For aqueous copper(I), compare hydration and disproportionation; a filled d shell alone does not establish aqueous stability.

17. Explain what is meant by the following:

(i) Peptide linkage

(ii) Pyranose structure of glucose

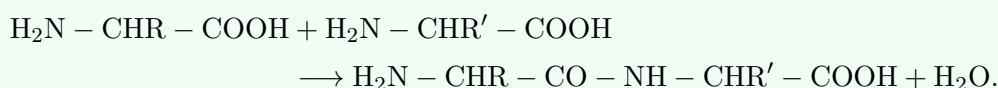
[2 marks]

Solution:

Concept:

- A peptide linkage is the amide bond formed by condensation of the carboxyl group of one amino acid with the amino group of another.
- A pyranose is a six-membered sugar ring containing five carbon atoms and one oxygen atom.

Step 1: (i) Peptide linkage The linkage $-\text{CO}-\text{NH}-$ joins amino-acid residues in peptides and proteins. It forms when the $-\text{COOH}$ group of one amino acid reacts with the $-\text{NH}_2$ group of another, eliminating one molecule of water:



The carbonyl carbon to nitrogen bond in the resulting amide group is the peptide bond; the side groups R and R' remain attached to their respective amino-acid carbon atoms.

Step 2: (ii) Pyranose structure of glucose Glucose predominantly exists as a cyclic hemiacetal with a six-membered ring resembling the ring skeleton of pyran. The hydroxyl group at carbon 5 reacts intramolecularly with the aldehyde group at carbon 1. Its oxygen becomes the ring oxygen, so the ring contains C1 through C5 and one oxygen atom. Carbon 6 remains outside the ring as a $-\text{CH}_2\text{OH}$ group. The newly formed hemiacetal carbon C1 is the anomeric carbon; its two possible hydroxyl orientations give α - and β -D-glucopyranose.

Step 3: Conclusion A peptide linkage is the $-\text{CO}-\text{NH}-$ amide linkage between amino-acid residues. The pyranose structure of glucose is its six-membered cyclic hemiacetal ring containing five carbon atoms and one oxygen atom.

Quick Tip to Solve: Count ring atoms, not all glucose carbons: a glucopyranose ring has five carbons plus one oxygen; C6 lies outside it.

18. Write the main structural difference between DNA and RNA. Of the four bases, name those which are common to both DNA and RNA.

[2 marks]

Solution:

Concept:

- DNA and RNA are polynucleotides, with sugar-phosphate backbones and nitrogenous bases attached to their sugars.
- The pentose sugar and the usual strand arrangement distinguish their structures; three nitrogenous bases occur in both.

Step 1: Compare their principal structural features DNA generally consists of two complementary polynucleotide strands coiled into a double helix, whereas RNA is generally a single polynucleotide

strand, which may fold upon itself. DNA contains 2-deoxy-D-ribose as its pentose sugar; RNA contains D-ribose. At the 2' carbon, RNA has an –OH group, while DNA has hydrogen instead. Thus both the usual strand arrangement and the sugar component distinguish the two nucleic acids. The word generally allows for particular biological exceptions to the typical strand arrangement.

Step 2: Identify the shared bases DNA contains adenine, guanine, cytosine and thymine. RNA contains adenine, guanine, cytosine and uracil. Comparing these two lists gives adenine (A), guanine (G) and cytosine (C) as the common bases. Adenine and guanine are purines, and cytosine is a pyrimidine. Thymine is characteristic of DNA in this comparison; RNA uses uracil in its place, so neither thymine nor uracil belongs in the requested common list.

Step 3: Conclusion DNA is usually double-stranded and contains 2-deoxyribose; RNA is usually single-stranded and contains ribose. The bases common to both are adenine, guanine and cytosine.

Quick Tip to Solve: Write the two base sets as A, G, C, T and A, G, C, U; their intersection immediately gives the three common bases.

19. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming that the gene fragment is a non-electrolyte, calculate its molar mass. [3 marks]

Solution:

Concept:

- For a dilute solution, osmotic pressure obeys $\pi V = nRT$, where V is solution volume, n is the amount of solute, R is the gas constant and T is absolute temperature.
- For a solute of mass w and molar mass M , $n = w/M$. Hence $M = wRT/(\pi V)$. The non-electrolyte does not dissociate, so its van't Hoff factor is $i = 1$.

Step 1: Convert all quantities to compatible units The given mass is $w = 8.95 \text{ mg} = 8.95 \times 10^{-3} \text{ g}$. Since the solution is dilute, take its volume as the stated water volume, $V = 35.0 \text{ mL} = 0.0350 \text{ L}$. The absolute temperature is $T = 25 + 273 = 298 \text{ K}$. Convert the pressure using $760 \text{ torr} = 1 \text{ atm}$:

$$\pi = \frac{0.335}{760} \text{ atm} = 4.408 \times 10^{-4} \text{ atm}.$$

We can now use $R = 0.0821 \text{ L atm mol}^{-1}\text{K}^{-1}$.

Step 2: Determine the molar mass Substituting $n = w/M$ in the osmotic-pressure equation and rearranging gives

$$M = \frac{wRT}{\pi V} = \frac{(8.95 \times 10^{-3})(0.0821)(298)}{(0.335/760)(0.0350)} \simeq 1.42 \times 10^4 \text{ g mol}^{-1}.$$

The pressure-volume units cancel those in the gas constant, leaving grams per mole. The very small osmotic pressure is consistent with relatively few molecules in a small mass of a large gene fragment. No extra ionic particle factor is required.

Step 3: Conclusion The molar mass of the gene fragment is $1.42 \times 10^4 \text{ g mol}^{-1}$, to three significant

figures.

Quick Tip to Solve: Convert torr to atm before using $R = 0.0821$; also convert milligrams to grams and millilitres to litres.

20(a). Classify colloids where the dispersion medium is water. State their characteristics and write an example of each of these classes. [3 marks]

Solution:

Concept:

- Colloids can be classified by the affinity between the dispersed phase and the dispersion medium. When the medium is water, the terms hydrophilic and hydrophobic replace lyophilic and lyophobic, respectively.
- Attraction to water gives a protective hydration layer around hydrophilic particles. Hydrophobic particles have little affinity for water; their stability largely depends on their electric charge.

Step 1: Hydrophilic colloids: water-loving sols These have a strong affinity between the dispersed substance and water. They form readily on mixing suitable substances with water and are extensively hydrated. Their sols are relatively stable and reversible: after removing water, the sol can generally be obtained again by adding water. They resist coagulation by small quantities of electrolyte because of the protective hydration layer. Examples are starch sol, gelatin sol and gum sol in water. Thus starch dispersed in water is a typical hydrophilic colloid.

Step 2: Hydrophobic colloids: water-hating sols These have little affinity between the dispersed phase and water. They usually require special preparation, such as chemical methods or dispersion methods, rather than simple mixing. Their sols are comparatively less stable and irreversible: a coagulated precipitate does not readily regenerate the sol merely by adding water. A small amount of a suitable electrolyte can neutralise the particle charge and cause coagulation. Examples are gold sol, arsenious sulphide sol and ferric hydroxide sol in water. Gold sol is a typical hydrophobic colloid.

Step 3: Conclusion With water as the dispersion medium, the two affinity classes are hydrophilic (for example, starch sol) and hydrophobic (for example, gold sol).

Quick Tip to Solve: Use the medium to choose the terminology: in water, lyophilic means hydrophilic and lyophobic means hydrophobic.

20(b). Explain what is observed when

(i) an electric current is passed through a colloidal solution

(ii) a beam of light is passed through a colloidal solution

(iii) an electrolyte (say NaCl) is added to ferric hydroxide sol

[3 marks]

Solution:

Concept:

- Colloidal particles generally carry an electric charge. Their directed movement in an electric field is called electrophoresis; they move towards the electrode carrying the opposite charge.
- Colloidal particles scatter light (the Tyndall effect). An electrolyte can reduce the stability of a sol by supplying counter-ions that neutralise particle charge, causing coagulation.

Step 1: Electric current through the sol Under the applied electric field, the charged colloidal particles migrate towards the oppositely charged electrode. This movement is observed as electrophoresis. A positively charged sol moves towards the cathode, whereas a negatively charged sol moves towards the anode. On reaching the electrode the particles may lose their charge and coagulate. The direction therefore depends on the sign of the charge of the particular sol.

Step 2: A beam of light through the sol The path of the light beam becomes visible when viewed from the side because colloidal particles scatter the incident light. This phenomenon is the Tyndall effect, and the illuminated region is called the Tyndall cone. It distinguishes a colloidal solution from a true solution under suitable conditions; the scattered beam reveals the particles collectively, without making individual particles visible to the unaided eye.

Step 3: Addition of sodium chloride to ferric hydroxide sol Ferric hydroxide sol has positively charged particles. The added sodium chloride provides Cl^- ions, which act as counter-ions and neutralise their positive charge. When sufficient electrolyte is added, the repulsion between the particles is reduced and they aggregate. Coagulation occurs, producing flocs or a precipitate of ferric hydroxide. The chloride ion, rather than the sodium ion, is responsible for destabilising this positive sol.

Step 4: Conclusion The observations are (i) electrophoretic migration, (ii) a visible light path due to the Tyndall effect, and (iii) coagulation of ferric hydroxide sol on adding sufficient NaCl.

Quick Tip to Solve: For coagulation, first identify the sol charge: positive ferric hydroxide particles are neutralised by chloride counter-ions.

21. How would you account for the following:

(i) H_2S is more acidic than H_2O .

(ii) The N–O bond in NO_2^- is shorter than the N–O bond in NO_3^- .

(iii) Both O_2 and F_2 stabilise high oxidation states, but the ability of oxygen to stabilise the higher oxidation state exceeds that of fluorine.

[3 marks]

Solution:

Concept:

- Acid strength of group 16 hydrides depends strongly on the ease of breaking the H–E bond; bond strength decreases down the group.
- Resonance distributes the double-bond character over equivalent bonds; a greater average bond order generally means a shorter bond.
- Oxygen can form multiple bonds with suitable central atoms, whereas fluorine normally forms only single bonds.

Step 1: Explain the acidity of the hydrides Sulphur is larger than oxygen, so the H–S bond is longer and weaker than the H–O bond. Consequently, removal of a proton from H_2S is easier than from H_2O . Thus, the decrease in bond strength down group 16 outweighs the decrease in electronegativity, and H_2S is the stronger acid.

Step 2: Compare the N–O bonds by resonance In NO_2^- , the two equivalent resonance structures distribute one double bond and one single bond over two N–O bonds. Their average bond order is $(2 + 1)/2 = 3/2$. In NO_3^- , three equivalent structures distribute one double bond and two single bonds over three N–O bonds, giving average bond order $(2 + 1 + 1)/3 = 4/3$. The higher bond order in nitrite makes its N–O bonds shorter.

Step 3: Explain the stabilisation of high oxidation states Both oxygen and fluorine are highly electronegative and therefore stabilise positive oxidation states of the elements bonded to them. Oxygen additionally forms strong multiple bonds with suitable elements; fluorine forms only single bonds. This additional bonding allows oxygen to stabilise still higher oxidation states. For example, manganese reaches +7 in Mn_2O_7 , whereas its highest fluoride, MnF_4 , contains manganese in +4.

Step 4: Conclusion H_2S is more acidic because H–S is weaker; nitrite has shorter N–O bonds because its bond order is $3/2 > 4/3$; oxygen stabilises higher oxidation states through strong multiple bonding.

Quick Tip to Solve: For hydride acidity compare bond strength; for resonance bond lengths first calculate the average bond order.

22. Explain the following terms, giving a suitable example in each case:

(i) Ambidentate ligand

(ii) Denticity of a ligand

(iii) Crystal field splitting in an octahedral field

[3 marks]

Solution:

Concept:

- A ligand donates an electron pair from a donor atom to a central metal atom or ion.
- Denticity counts donor atoms of one ligand attached simultaneously to the same central metal.
- An octahedral ligand field removes the degeneracy of the five metal d orbitals, producing two energy levels.

Step 1: Define an ambidentate ligand and give an example An ambidentate ligand has two different possible donor atoms, but coordinates through only one of them at a time. For example, NO_2^- can bind through nitrogen as a nitro ligand or through oxygen as a nitrito ligand. Thus $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ illustrate the two modes. Having two possible donor atoms does not mean that both bind simultaneously.

Step 2: Define denticity and give an example Denticity is the number of donor atoms of a single ligand that coordinate simultaneously to the same metal centre. Ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, written en, binds through both nitrogen atoms and is bidentate, with denticity 2. For comparison, ammonia binds through one nitrogen atom and is monodentate, with denticity 1.

Step 3: Explain octahedral crystal field splitting and give an example In an octahedral complex, six ligands approach along the Cartesian axes. The $d_{x^2-y^2}$ and d_{z^2} orbitals point towards the ligands, experience greater repulsion, and form the higher-energy e_g set. The d_{xy} , d_{xz} , d_{yz} orbitals lie between the axes and form the lower-energy t_{2g} set. The separation is Δ_o ; relative to the barycentre, t_{2g} is lowered by $0.4\Delta_o$ and e_g is raised by $0.6\Delta_o$. For example, in octahedral $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, the single d electron occupies t_{2g} , giving $t_{2g}^1 e_g^0$.

Step 4: Conclusion Ambidentate ligands have alternative donor atoms; denticity counts simultaneous donor attachments; an octahedral field splits d orbitals into lower t_{2g} and upper e_g levels separated by Δ_o .

Quick Tip to Solve: Distinguish two possible donor sites (ambidentate) from two sites bound at once (bidentate).

23. Rearrange the compounds of each of the following sets in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane

[3 marks]

Solution:

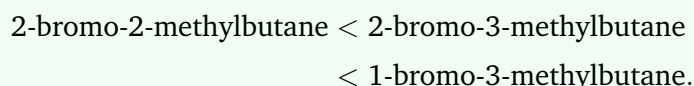
Concept:

- An S_N2 reaction proceeds by a single concerted backside attack of the nucleophile on the carbon bearing the leaving group.
- For the same leaving group and reaction conditions, steric hindrance usually gives primary > secondary > tertiary reactivity.
- Branching on the adjacent carbon can strongly hinder backside approach even to a primary carbon, as in neopentyl bromide.

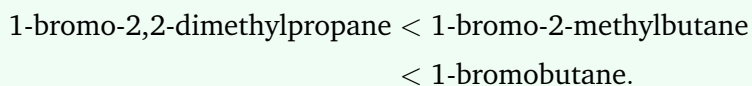
Step 1: Order set (i) All three compounds contain the same leaving group, bromide, so compare crowding around the carbon bonded to bromine. In 1-bromopentane this carbon is primary, in 2-bromopentane it is secondary, and in 2-bromo-2-methylbutane it is tertiary. Increasing substitution obstructs the nucleophile's backside approach. Hence the increasing order is:



Step 2: Order set (ii) 1-Bromo-3-methylbutane is primary, with its branch farther from the reacting carbon. 2-Bromo-3-methylbutane is secondary and more hindered, while 2-bromo-2-methylbutane is tertiary and is least favourable for concerted displacement. Thus the increasing order is:



Step 3: Order set (iii) All three bromides have a primary carbon bearing bromine, so the primary/secondary classification alone cannot distinguish them. 1-Bromobutane has no adjacent branching and is most accessible. 1-Bromo-2-methylbutane has one branch at the adjacent carbon and reacts more slowly. In 1-bromo-2,2-dimethylpropane (neopentyl bromide), the adjacent carbon is bonded to three methyl groups, creating severe steric hindrance to the transition state. Hence the increasing order is:



Step 4: Conclusion In increasing reactivity, each set follows the orders given above: the least hindered reacting carbon gives the fastest S_N2 displacement, including the effect of adjacent branching in set (iii).

Quick Tip to Solve: After counting substituents on the C-Br carbon, inspect the next carbon for neopentyl-type crowding.

24. How would you obtain the following:

(i) Benzoquinone from phenol

(ii) 2-Methylpropan-2-ol from methylmagnesium bromide

(iii) Propan-2-ol from propene

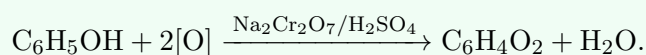
[3 marks]

Solution:

Concept:

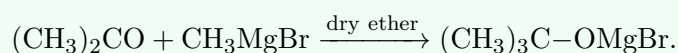
- Oxidation of phenol with acidified dichromate converts the phenolic ring into a quinone containing two carbonyl groups.
- A Grignard reagent adds its alkyl group to a carbonyl carbon. Hydrolysis of the magnesium alkoxide then gives an alcohol.
- Acid-catalysed hydration of an unsymmetrical alkene follows Markovnikov addition: the hydroxyl group reaches the more substituted carbon.

Step 1: Part (i): Oxidise phenol Treat phenol with sodium dichromate and dilute sulphuric acid. Oxidation produces para-benzoquinone (1,4-benzoquinone):

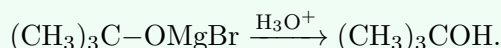


The product has carbonyl groups at the 1 and 4 positions of the six-membered ring.

Step 2: Part (ii): Add methylmagnesium bromide to propanone Use propanone (acetone), since its carbonyl carbon already bears two methyl groups. Addition of the methyl group from the Grignard reagent gives a tertiary alkoxide:

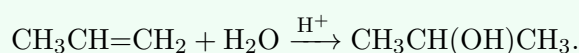


Hydrolyse this intermediate with dilute acid:



Moisture must be excluded until the addition is complete because water destroys the Grignard reagent.

Step 3: Part (iii): Hydrate propene Pass propene into water in the presence of dilute sulphuric acid:



Protonation forms the more stable secondary carbocation; water attacks this carbon, followed by loss of a proton. Thus the hydroxyl group attaches to the middle carbon.

Step 4: Conclusion The required routes are (i) phenol $\xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4}$ para-benzoquinone; (ii) methylmagnesium bromide + propanone, then acidic hydrolysis, giving 2-methylpropan-2-ol; (iii) acid-catalysed hydration of propene, giving propan-2-ol.

Quick Tip to Solve: For the tertiary alcohol, count its three methyl groups: acetone supplies two and methylmagnesium bromide supplies the third.

25. State reasons for the following:

- (i) pK_b value for aniline is more than that for methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not soluble in water.
(iii) Primary amines have higher boiling points than tertiary amines.

[3 marks]

Solution:

Concept:

- For a base B , $K_b = [BH^+][OH^-]/[B]$ and $pK_b = -\log K_b$. A larger pK_b therefore indicates a weaker base.
- Water solubility reflects both hydrogen bonding with water and the size of the nonpolar hydrocarbon part.
- Intermolecular hydrogen bonding raises boiling points when amines of comparable molar mass are compared.

Step 1: Part (i): Compare the availability of the nitrogen lone pair In aniline, the lone pair on nitrogen is delocalised into the benzene ring by resonance. It is therefore less available to accept a proton. In methylamine, the methyl group exerts a positive inductive effect, increasing electron density on nitrogen and favouring proton acceptance. Consequently aniline is the weaker base:

$$K_b(\text{aniline}) < K_b(\text{methylamine}), \quad pK_b(\text{aniline}) > pK_b(\text{methylamine}).$$

Step 2: Part (ii): Compare hydration and the hydrocarbon portions Ethylamine forms hydrogen bonds with water through its nitrogen lone pair and its N–H bonds. Its small ethyl group offers relatively little nonpolar surface, so hydration is sufficient for good solubility. Aniline can also hydrogen-bond with water, but its large hydrophobic phenyl group opposes dissolution. Thus aniline is only sparingly soluble in water and is described here as insoluble; the distinction is not an absence of all hydrogen bonding in aniline.

Step 3: Part (iii): Compare association between amine molecules A primary amine, RNH_2 , contains N–H bonds and a nitrogen lone pair, so its molecules form intermolecular $N-H \cdots N$ hydrogen bonds. A tertiary amine, R_3N , has no N–H bond and cannot form these hydrogen bonds with other tertiary-amine molecules. For comparable molar masses, stronger association in a primary amine requires more energy to separate molecules into the vapour, giving the higher boiling point.

Step 4: Conclusion Aniline has the higher pK_b because resonance reduces lone-pair availability; ethylamine is more water-soluble because its nonpolar group is smaller; primary amines have higher boiling points than comparable tertiary amines because primary amines self-associate through hydrogen bonds.

Quick Tip to Solve: Distinguish hydrogen bonding with water from self-association: tertiary amines can accept hydrogen bonds from water but cannot donate them to one another.

26. Draw the structures of the monomers of the following polymers:

(i) Polythene

(ii) PVC

(iii) Teflon

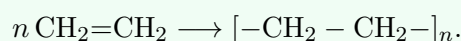
[3 marks]

Solution:

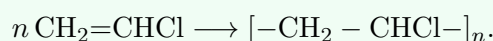
Concept:

- An addition polymer forms when the carbon-carbon double bonds of its monomers open and join into a long carbon backbone.
- To recover an alkene monomer, select the two-carbon repeat unit, restore a double bond between those carbons, and retain all substituents.

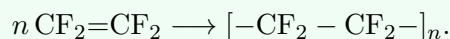
Step 1: Part (i): Polythene The repeat unit of polythene is $-\text{CH}_2 - \text{CH}_2-$. Restoring the double bond gives ethene, $\text{CH}_2=\text{CH}_2$. Its two carbon atoms each carry two hydrogen atoms, so the monomer contains only carbon and hydrogen. The polymerisation can be represented as



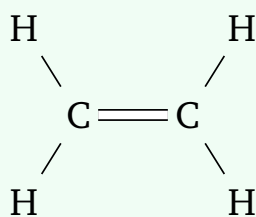
Step 2: Part (ii): PVC PVC is polyvinyl chloride. Its repeat unit is $-\text{CH}_2 - \text{CHCl}-$, so its monomer is vinyl chloride, also called chloroethene, $\text{CH}_2=\text{CHCl}$. One hydrogen of ethene is replaced by chlorine; chlorine remains attached to the same carbon during polymerisation:



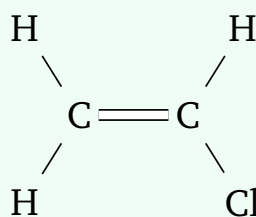
Step 3: Part (iii): Teflon Teflon is polytetrafluoroethene. Its repeat unit is $-\text{CF}_2 - \text{CF}_2-$, so the monomer is tetrafluoroethene, $\text{CF}_2=\text{CF}_2$. All four hydrogen positions of ethene are occupied by fluorine:



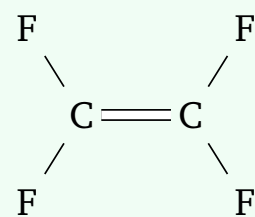
Each monomer carbon has four bonds overall: two in the double bond and two to its hydrogen, chlorine or fluorine substituents. The structural formulae below show these substituents explicitly.



Ethene



Chloroethene



Tetrafluoroethene

Structures of the three alkene monomers

Step 4: Conclusion The monomers are (i) ethene, $\text{CH}_2=\text{CH}_2$; (ii) chloroethene (vinyl chloride), $\text{CH}_2=\text{CHCl}$; (iii) tetrafluoroethene, $\text{CF}_2=\text{CF}_2$.

Quick Tip to Solve: Restore one $\text{C}=\text{C}$ bond in each two-carbon repeat unit; keep every H, Cl and F substituent in its original position.

27. What are the following substances? Give one example of each.

(i) Food preservatives

(ii) Synthetic detergents

(iii) Antacids

[3 marks]

Solution:

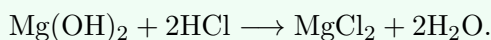
Concept:

- Food preservatives inhibit spoilage, synthetic detergents clean surfaces, and antacids neutralise excess stomach acid.
- A detergent has a hydrophobic hydrocarbon chain and a hydrophilic ionic head; an antacid acts as a mild base.

Step 1: (i) Food preservatives Food preservatives are substances added to food to prevent or retard spoilage, particularly that caused by microorganisms, and thus increase its shelf life. One example is sodium benzoate, $\text{C}_6\text{H}_5\text{COONa}$, which is used in acidic foods such as fruit juices and squashes. Its role is to inhibit microbial growth and keep the food fit for use for longer. A substance added merely to improve flavour or colour is not, on that basis alone, a food preservative.

Step 2: (ii) Synthetic detergents Synthetic detergents are manufactured cleansing agents that remove dirt and grease through surface activity and micelle formation. One example is sodium dodecylbenzene sulphonate, $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$. The hydrocarbon part associates with oily dirt, whereas the sulphonate head interacts with water. The resulting micelles keep grease dispersed so that it can be washed away. Such detergents can also clean in hard water because they do not form the insoluble calcium and magnesium salts characteristic of ordinary soaps.

Step 3: (iii) Antacids Antacids are substances used to neutralise excess hydrochloric acid in the stomach and relieve acidity. One example is magnesium hydroxide, $\text{Mg}(\text{OH})_2$, supplied as milk of magnesia. Its neutralisation reaction is



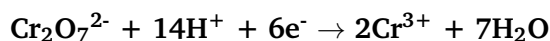
The mild base consumes excess acid. Its function differs from that of an antibiotic, which acts against microorganisms, or a digestive enzyme, which helps break down food.

Step 4: Conclusion (i) Food preservatives prevent spoilage: sodium benzoate. (ii) Synthetic detergents are manufactured cleansing agents: sodium dodecylbenzene sulphonate. (iii) Antacids neutralise excess stomach acid: magnesium hydroxide.

Quick Tip to Solve: Match each substance to its function: preserve food, remove grease, or neutralise stomach acid.

28(a). What type of battery is a lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(b) Calculate the potential for a half-cell containing 0.10 M $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, 0.20 M $\text{Cr}^{3+}(\text{aq})$ and 1.0×10^{-4} M $\text{H}^+(\text{aq})$. The half-cell reaction is



and the standard electrode potential is given as $E^\circ = 1.33$ V.

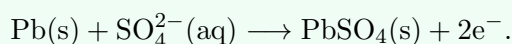
[5 marks]

Solution:

Concept:

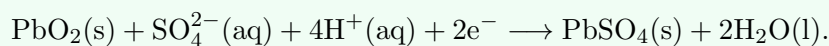
- A secondary battery is rechargeable: an external current reverses the chemical reaction that occurs during discharge.
- Oxidation occurs at the anode and reduction at the cathode. On adding the balanced half-reactions, electrons cancel.
- At 298 K, the Nernst equation is $E = E^\circ - (0.0591/n) \log_{10} Q$, where n is the electron number and Q is the reaction quotient. Pure solids and liquid water have unit activity.

Step 1: (a) Identify the battery and its anode reaction A lead storage battery is a secondary, or rechargeable, battery. During discharge it supplies electrical energy by a spontaneous redox reaction in sulphuric acid. The lead electrode is the anode, where lead is oxidised from oxidation state zero to +2:

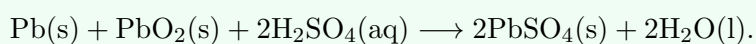


Thus, lead sulphate forms on the anode and two electrons enter the external circuit for each lead atom oxidised.

Step 2: Write the cathode and overall discharge reactions At the lead dioxide cathode, lead in oxidation state +4 is reduced to +2:

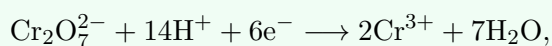


Adding the two half-reactions cancels the two electrons. Expressing the hydrogen and sulphate ions as sulphuric acid gives the overall cell reaction:



Sulphuric acid is consumed and both electrodes acquire lead sulphate during discharge. On charging, an external source drives the reverse reaction, regenerating lead, lead dioxide and sulphuric acid. This reversibility explains the classification as a secondary battery.

Step 3: (b) Construct the reaction quotient For the given reduction reaction,



the electron number is $n = 6$. Taking the stated molar concentrations as activities relative to the

standard concentration, and omitting liquid water,

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}} = \frac{(0.20)^2}{0.10(1.0 \times 10^{-4})^{14}} = 4.0 \times 10^{55}.$$

The dichromate concentration is 0.10 M, since each formula unit of potassium dichromate supplies one dichromate ion. Electrons are excluded from the quotient.

Step 4: Apply the Nernst equation Using the usual Nernst coefficient at 298 K,

$$\begin{aligned} E &= 1.33 - \frac{0.0591}{6} \log_{10}(4.0 \times 10^{55}) \\ &= 1.33 - \frac{0.0591}{6} (55.60206) \\ &= 1.33 - 0.54768 \\ &= 0.78232 \text{ V.} \end{aligned}$$

The very low hydrogen-ion concentration makes the reduction less favourable than under standard conditions, so the calculated potential is below 1.33 V, consistent with the sign of the correction.

Step 5: Conclusion The lead storage battery is a rechargeable secondary battery, with discharge reactions given above. The dichromate half-cell reduction potential is $E \approx 0.782 \text{ V}$ at 298 K.

Quick Tip to Solve: In this dichromate quotient, retain the fourteenth power of hydrogen-ion concentration and divide the Nernst correction by six.

OR

28(b). (a) How many moles of mercury will be produced by electrolysing 1.0 M $\text{Hg}(\text{NO}_3)_2$ solution with a current of 2.00 A for 3 hours? [$\text{Hg}(\text{NO}_3)_2 = 200.6 \text{ g mol}^{-1}$]

(b) A voltaic cell is set up at 25°C with the following half-cells: Al^{3+} (0.001 M) and Ni^{2+} (0.50 M). Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential. [5 marks]

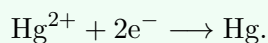
Solution:

Concept:

- Faraday's law relates the amount deposited to charge: $n(\text{metal}) = It/(zF)$, where I is current, t is time in seconds, z is the number of electrons required per metal atom, and $F = 96485 \text{ C mol}^{-1}$.
- A spontaneous galvanic cell oxidises the metal with the more negative standard reduction potential. Standard values used here are $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$ and $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$.
- At 25°C, the Nernst equation is $E = E^\circ - (0.0591/n_e) \log_{10} Q$, where n_e is the number of electrons in the balanced cell reaction and Q is its reaction quotient. Pure solid metals have unit activity; dilute ionic activities are approximated by their molar concentrations.

Step 1: (a) Determine the charge passed and the mercury reduction Mercury(II) nitrate supplies

Hg²⁺ ions. At the cathode,



Thus each mole of mercury needs two moles of electrons. Convert hours into seconds before applying Faraday's law:

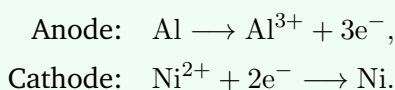
$$t = 3 \times 3600 = 10800 \text{ s}, \quad q = It = 2.00 \times 10800 = 21600 \text{ C}.$$

The electron amount is $21600/96485 = 0.2239 \text{ mol}$. The amount of mercury is therefore

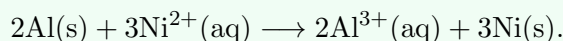
$$n(\text{Hg}) = \frac{21600}{2 \times 96485} = 0.1119 \text{ mol}.$$

This assumes that the current deposits mercury with complete current efficiency and sufficient solution is present. The stated molar-mass datum is unnecessary because the question asks for moles, not mass. Similarly, the concentration does not change the amount deposited by a specified charge under these conditions.

Step 2: (b) Identify the electrodes and balance the cell reaction Nickel has the more positive reduction potential, so nickel ions are reduced at the cathode and aluminium is oxidised at the anode:



Multiply the aluminium equation by two and the nickel equation by three. Adding cancels six electrons and gives



Thus $n_e = 6$. Electrode potentials are intensive quantities, so their values are not multiplied by these balancing coefficients.

Step 3: (b) Calculate the cell potential at the specified concentrations The standard cell potential is

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.25 - (-1.66) = 1.41 \text{ V}.$$

Using the stoichiometric powers from the balanced reaction,

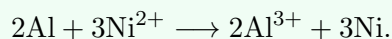
$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \frac{(0.001)^2}{(0.50)^3} = 8.0 \times 10^{-6}.$$

Substitution in the Nernst equation gives

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6} \log_{10}(8.0 \times 10^{-6}) \\ &= 1.41 - \frac{0.0591}{6}(-5.0969) \\ &= 1.4602 \text{ V} \simeq 1.46 \text{ V}. \end{aligned}$$

Since $Q < 1$, the logarithm is negative and the potential exceeds its standard value. Its positive sign confirms that the balanced reaction proceeds in the stated direction when the cell supplies current.

Step 4: Conclusion (a) The mercury deposited is 0.112 mol . (b) The balanced cell reaction is



Its potential at 25°C is 1.46 V , using the standard reduction potentials stated above.

Quick Tip to Solve: For mercury use two electrons per atom; for the Al/Ni cell balance six electrons first, then use the ionic coefficients as the powers in the reaction quotient.

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

(i) $(\text{HPO}_3)_3$

(ii) BrF_3

(b) Complete the following chemical equations:

(i) $\text{HgCl}_2 + \text{PH}_3 \rightarrow$

(ii) $\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow$

(iii) $\text{XeF}_4 + \text{H}_2\text{O} \rightarrow$

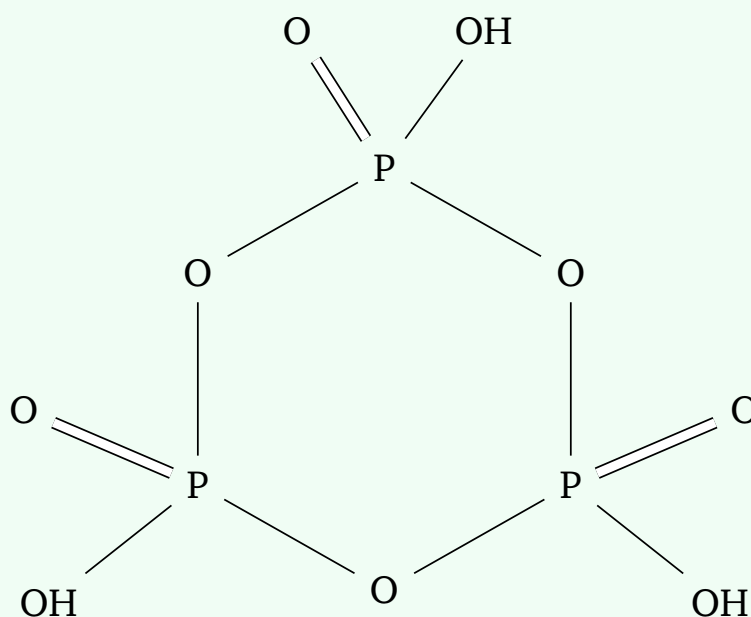
[5 marks]

Solution:

Concept:

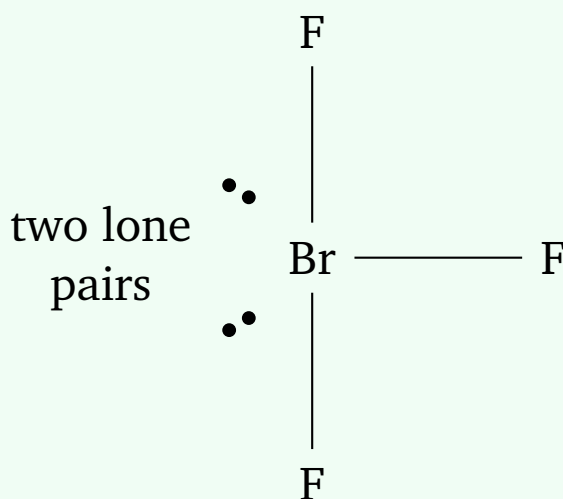
- Cyclic trimetaphosphoric acid, $(\text{HPO}_3)_3$, contains an alternating six-membered P – O ring. Each phosphorus also bears one terminal P = O bond and one P – OH group.
- In BrF_3 , five electron pairs surround bromine: three bonding pairs and two lone pairs. Their trigonal-bipyramidal arrangement gives a T-shaped molecule when the two lone pairs occupy equatorial positions.
- Chemical equations must conserve each element. Phosphine forms a metal phosphide with mercuric chloride; sulphur trioxide combines with sulphuric acid; xenon tetrafluoride undergoes hydrolysis accompanied by redox change.

Step 1: (a)(i) Structure of cyclic trimetaphosphoric acid Three PO_4 units share oxygen atoms to form a closed ring with the sequence P – O – P – O – P – O. Every phosphorus has two single bonds to bridging ring oxygens, a double bond to a terminal oxygen and a single bond to an OH group. Thus the molecule contains three phosphorus atoms, nine oxygen atoms and three hydrogen atoms, consistent with $\text{H}_3\text{P}_3\text{O}_9$. The diagram explicitly shows the ring connectivity and the terminal groups; its planar placement is a structural representation, not a statement that each phosphorus is planar.



Cyclic trimetaphosphoric acid: every P has one terminal O and one OH group.

Step 2: (a)(ii) Structure of bromine trifluoride Bromine has seven valence electrons. Formation of three Br – F bonds leaves two lone pairs on the central atom, so the VSEPR type is AX_3E_2 . Both lone pairs occupy equatorial sites to reduce repulsions involving 90° neighbours. The fluorine atoms then occupy two axial sites and one equatorial site, giving the T shape shown. Lone-pair repulsions make the axial-equatorial bond angles slightly smaller than the ideal 90° .



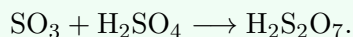
T-shaped BrF_3 ; the two dot pairs represent equatorial lone pairs on Br.

Step 3: (b)(i) Reaction of mercuric chloride with phosphine Phosphine reacts with mercuric chloride to produce mercuric phosphide and hydrogen chloride:



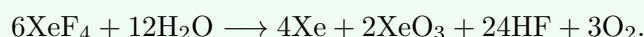
Three mercury atoms and two phosphorus atoms enter the phosphide, while the six chlorine atoms combine with the six hydrogen atoms to form hydrogen chloride. This checks every coefficient independently.

Step 4: (b)(ii) Formation of oleum Sulphur trioxide is absorbed by sulphuric acid to form disulphuric acid, a constituent of oleum:



The product contains two hydrogen atoms, two sulphur atoms and seven oxygen atoms, exactly as supplied by one molecule of each reactant.

Step 5: (b)(iii) Hydrolysis of xenon tetrafluoride Complete hydrolysis produces xenon, xenon trioxide, hydrogen fluoride and oxygen:



Xenon in oxidation state +4 forms both elemental xenon and xenon in oxidation state +6; oxygen is also released. The balanced equation has six Xe atoms, twenty-four F atoms, twenty-four H atoms and twelve O atoms on each side. In particular, the oxygen atoms on the right are divided equally between xenon trioxide and oxygen gas.

Step 6: Conclusion $(\text{HPO}_3)_3$ has the cyclic structure shown, and BrF_3 is T-shaped with two equatorial lone pairs. The completed reactions give $\text{Hg}_3\text{P}_2 + 6\text{HCl}$, $\text{H}_2\text{S}_2\text{O}_7$, and $4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$, respectively, with the reactant coefficients shown above.

Quick Tip to Solve: In metaphosphoric acid draw alternating P and O atoms in the ring, then add one double-bonded O and one OH to every P; for XeF_4 hydrolysis, balance fluorine into HF first.

OR

29(b). (a) What happens when

(i) chlorine gas is passed through a hot concentrated solution of NaOH?

(ii) sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt?

(b) Answer the following:

(i) What is the basicity of H_3PO_3 and why?

(ii) Why does fluorine not play the role of a central atom in interhalogen compounds?

(iii) Why do noble gases have very low boiling points?

[5 marks]

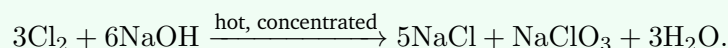
Solution:

Concept:

- Disproportionation is simultaneous oxidation and reduction of the same element. Hot concentrated alkali converts chlorine into chloride and chlorate.
- Sulphur dioxide acts as a reducing agent: sulphur changes from oxidation state +4 to +6, while iron(III) is reduced to iron(II).
- The basicity of an oxyacid is the number of ionisable hydrogen atoms bonded to oxygen. Noble-gas

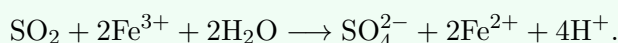
boiling points depend on weak London dispersion forces between their atoms.

Step 1: (a)(i) Chlorine with hot concentrated sodium hydroxide Chlorine disproportionates to sodium chloride and sodium chlorate. The balanced equation is



Chlorine has oxidation state 0 in Cl_2 , -1 in chloride and $+5$ in chlorate. Thus five chlorine atoms are reduced for each chlorine atom oxidised. The stated hot concentrated conditions are essential for chlorate formation.

Step 2: (a)(ii) Sulphur dioxide with an iron(III) salt Sulphur dioxide reduces iron(III) ions to iron(II) ions and is itself oxidised to sulphate in the aqueous medium:



Each iron(III) ion gains one electron; sulphur loses two electrons on changing from $+4$ to $+6$. Hence one mole of sulphur dioxide reduces two moles of iron(III) ions. The equation balances both atoms and total charge.

Step 3: (b)(i) Basicity of phosphorous acid Phosphorous acid has the structure $\text{H}-\text{P}(=\text{O})(\text{OH})_2$. Only its two hydrogen atoms attached to oxygen can ionise as protons in water. The remaining hydrogen is directly bonded to phosphorus and is not ionisable in the acid-base sense. Consequently H_3PO_3 is dibasic, with basicity 2, despite containing three hydrogen atoms in its molecular formula.

Step 4: (b)(ii) Fluorine in interhalogen compounds The central halogen in an interhalogen is normally larger and less electronegative than the surrounding halogen atoms. Fluorine is the smallest and most electronegative halogen, so it occupies terminal positions. Its valence shell cannot expand beyond an octet, and it forms only one bond in these compounds; it therefore cannot act as the central atom bonded to several halogen atoms.

Step 5: (b)(iii) Low boiling points of noble gases Noble gases exist as individual, nonpolar atoms with closed electron shells. There are no permanent dipole attractions between their atoms. The only interatomic attractions are weak London dispersion forces arising from instantaneous and induced dipoles. Little thermal energy is required to overcome these forces and separate the atoms, giving the noble gases very low boiling points. Dispersion forces generally increase down the group as atomic polarisability increases.

Step 6: Conclusion Hot concentrated NaOH gives NaCl and NaClO_3 ; SO_2 reduces Fe^{3+} to Fe^{2+} . The basicity of H_3PO_3 is 2. Fluorine is terminal because of its small size, high electronegativity and restricted valence shell; noble gases boil at low temperatures because their dispersion forces are weak.

Quick Tip to Solve: For oxyacid basicity, count O-H bonds rather than all hydrogen atoms; for chlorine with alkali, check whether the solution is cold dilute or hot concentrated before choosing the product.

30(a). Illustrate the following name reactions:

(i) Cannizzaro's reaction

(ii) Clemmensen reduction

(b) How would you obtain the following:

(i) But-2-enal from ethanal

(ii) Butanoic acid from butan-1-ol

(iii) Benzoic acid from ethylbenzene

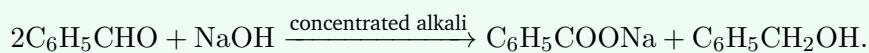
[5 marks]

Solution:

Concept:

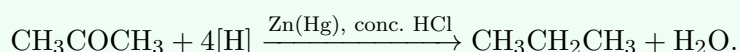
- Cannizzaro's reaction is the disproportionation of an aldehyde having no α hydrogen in concentrated alkali: one molecule is oxidised to a carboxylate and another is reduced to an alcohol.
- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- Aldehydes containing α hydrogen undergo aldol addition in dilute alkali; heating the β -hydroxy product gives an α,β -unsaturated aldehyde by dehydration.
- Primary alcohols are oxidised to carboxylic acids. An alkylbenzene having a benzylic hydrogen undergoes side-chain oxidation to benzoic acid with hot alkaline permanganate followed by acidification.

Step 1: (a)(i) Illustrate Cannizzaro's reaction Benzaldehyde has no α hydrogen and therefore undergoes Cannizzaro's reaction with concentrated sodium hydroxide:



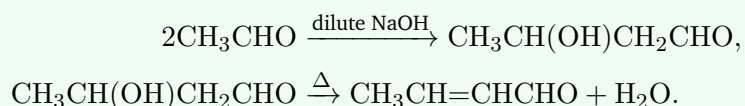
Thus, one benzaldehyde molecule is oxidised to sodium benzoate while the other is reduced to benzyl alcohol. Acidification of the benzoate gives benzoic acid. The reaction is a self-oxidation and self-reduction, with no external oxidising or reducing agent.

Step 2: (a)(ii) Illustrate Clemmensen reduction In Clemmensen reduction, an aldehyde or ketone is heated with zinc amalgam, Zn(Hg) , and concentrated HCl . For example, propanone gives propane:



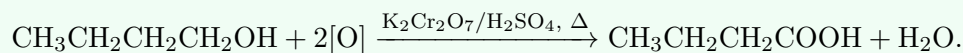
The carbonyl oxygen is removed and the carbonyl carbon becomes a saturated carbon without changing the carbon skeleton.

Step 3: (b)(i) Obtain but-2-enal from ethanal Treat ethanal with dilute sodium hydroxide to form the aldol, 3-hydroxybutanal. Heat this product to eliminate water:



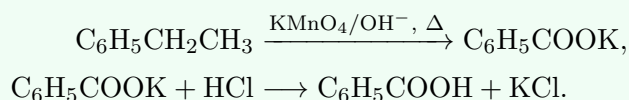
Ethanal has α hydrogens, so it undergoes aldol condensation. Numbering from the aldehyde carbon places the new double bond between carbon atoms 2 and 3, giving but-2-enal.

Step 4: (b)(ii) Obtain butanoic acid from butan-1-ol Heat butan-1-ol under reflux with excess acidified potassium dichromate. The primary alcohol is oxidised through butanal to the carboxylic acid:



Reflux and excess oxidant ensure that oxidation proceeds beyond the aldehyde stage. All four carbon atoms are retained.

Step 5: (b)(iii) Obtain benzoic acid from ethylbenzene Heat ethylbenzene with excess alkaline potassium permanganate, then acidify the resulting potassium benzoate:



Ethylbenzene contains benzylic hydrogen, so the side chain is oxidised to a carboxyl group attached directly to the ring. The extra side-chain carbon is oxidatively removed; the aromatic ring is retained.

Step 6: Conclusion Cannizzaro's reaction gives an alcohol and a carboxylate from a non-enolisable aldehyde; Clemmensen reduction replaces carbonyl oxygen by hydrogen. The required preparations use ethanal aldol condensation followed by dehydration, complete oxidation of butan-1-ol, and hot alkaline permanganate oxidation of ethylbenzene followed by acidification, respectively.

Quick Tip to Solve: Check alpha hydrogen before choosing Cannizzaro or aldol; for an alkylbenzene, check benzylic hydrogen before side-chain oxidation.

OR

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

(i) Benzoic acid and ethyl benzoate

(ii) Benzaldehyde and acetophenone

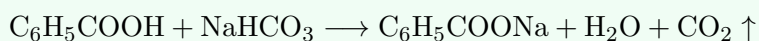
[5 marks]

Solution:

Concept:

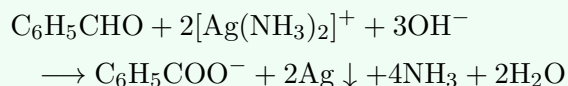
- A carboxylic acid reacts with aqueous sodium hydrogen carbonate to release carbon dioxide; a neutral ester does not give this immediate effervescence.
- Tollens' reagent is ammoniacal silver nitrate. An aldehyde reduces it to metallic silver while being oxidised to a carboxylate ion; an ordinary ketone does not.
- The iodoform test detects the methyl ketone group, $-\text{COCH}_3$, through formation of yellow CHI_3 with iodine and alkali.

Step 1: (i) Distinguish benzoic acid from ethyl benzoate Take small portions of the two compounds in separate test tubes and add aqueous sodium hydrogen carbonate, NaHCO_3 . Benzoic acid gives brisk effervescence of carbon dioxide, whereas ethyl benzoate gives no such effervescence under these test conditions.



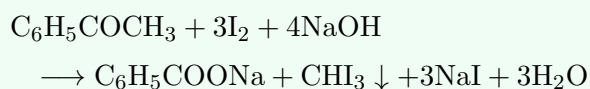
The evolved gas turns limewater milky. The acid supplies the proton needed to decompose hydrogen carbonate; the ester has no carboxylic acid proton.

Step 2: (ii) Distinguish benzaldehyde from acetophenone Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Benzaldehyde produces a silver mirror (or a deposit of silver), while acetophenone gives no silver mirror.



Benzaldehyde is an aldehyde and is oxidised to benzoate in this alkaline reagent. Acetophenone is a ketone and does not reduce Tollens' reagent.

Step 3: Confirm the second pair with the iodoform test As an alternative distinguishing test, warm fresh portions with iodine and aqueous sodium hydroxide. Acetophenone gives a yellow precipitate of iodoform because it contains $-\text{COCH}_3$; benzaldehyde gives no yellow iodoform precipitate.



Step 4: Conclusion (i) With aqueous NaHCO_3 , benzoic acid releases CO_2 ; ethyl benzoate does not. (ii) With Tollens' reagent, benzaldehyde gives a silver mirror; acetophenone does not.

Quick Tip to Solve: For this pair, link COOH to hydrogen carbonate effervescence, CHO to a silver mirror, and COCH_3 to yellow iodoform.