CBSE Class 12 Chemistry Question Paper 2009 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) **All** questions are compulsory.
(ii) Marks for each question are indicated against it.
(iii) Questions number **1** to **8** are very short-answer questions and carry **1** mark each.
(iv) Questions number **9** to **18** are short-answer questions and carry **2** marks each.
(v) Questions number **19** to **27** are also short-answer questions and carry **3** marks each.
(vi) Questions number **28** to **30** are long-answer questions and carry **5** marks each.
(vii) Use Log Tables, if necessary. Use of **calculators is not** allowed.

1. How do metallic and ionic substances differ in conducting electricity? [1 mark]

Solution:

Concept:

- Electrical conduction requires mobile charged particles.
- In metals the charge carriers are delocalised electrons; in ionic substances they are mobile ions.

Step 1: Identify metallic conduction A metal contains delocalised electrons that can move through its lattice under an applied potential difference. Hence metals conduct in the solid state and generally also when molten; the metal ions themselves need not migrate through the solid.

Step 2: Identify ionic conduction In a solid ionic substance the cations and anions are fixed at their lattice positions, so they cannot carry current through the solid. On melting, or on dissolution in water when the substance dissolves and produces ions, these ions become mobile and carry the current.

Step 3: Conclusion Metals conduct by movement of electrons, whereas ionic substances conduct by movement of ions in the molten state or aqueous solution, but not in the solid state.

Quick Tip to Solve: Always identify the mobile charge carrier first: electrons for metals and ions for ionic conductors.

2. What is the 'coagulation' process? [1 mark]

Solution:

Concept:

- Colloidal particles remain dispersed because their like charges prevent aggregation.
- Neutralising their charge can allow particles to aggregate into larger masses.

Step 1: Describe the change in the sol In a colloidal sol, dispersed particles are sufficiently small to remain distributed through the dispersion medium. If the stabilising charge on these particles is removed or neutralised, for example by adding a suitable electrolyte, the particles can approach one another.

Step 2: State what happens to the particles The colloidal particles then aggregate to form larger particles or flocs. These aggregates separate from the dispersion medium, often as a precipitate. The characteristic change is the aggregation and separation of the dispersed phase, rather than merely dissolving the solute.

Step 3: Conclusion Coagulation is the aggregation of colloidal particles into larger particles, leading to their separation or precipitation from the sol.

Quick Tip to Solve: Link coagulation with loss of colloidal stability: small dispersed particles aggregate and separate.

3. What is meant by the term 'pyrometallurgy'? [1 mark]

Solution:

Concept:

- Metallurgy concerns extraction of metals from their ores.
- Pyrometallurgical operations use high temperatures to bring about the necessary chemical changes.

Step 1: Identify the role of heat The prefix pyro refers to heat. In pyrometallurgy an ore or a suitable compound obtained from it is treated at high temperature so that chemical reactions needed for metal extraction can take place.

Step 2: Relate the term to extraction Such operations can include calcination, roasting and smelting or high-temperature reduction, depending on the ore and metal. The essential defining feature is the use of thermal processes to extract or recover the metal, rather than extraction chiefly through aqueous solutions or electrolysis.

Step 3: Conclusion Pyrometallurgy is the extraction of metals from their ores by chemical processes carried out at high temperatures.

Quick Tip to Solve: Remember pyro as heat, and include both metal extraction and high temperature in the definition.

4. Why is red phosphorus less reactive than white phosphorus? [1 mark]

Solution:

Concept:

- White phosphorus consists of discrete tetrahedral P_4 molecules with strained bonds.
- Red phosphorus has a polymeric network structure that is more stable.

Step 1: Examine white phosphorus In white phosphorus, four phosphorus atoms occupy the corners of a tetrahedron. Its P-P-P bond angles are about $60°$, much smaller than the preferred angles for phosphorus bonding. This produces considerable angular strain and makes the molecule relatively reactive.

Step 2: Compare red phosphorus Red phosphorus consists of a polymeric structure formed by linked phosphorus atoms. It does not retain the highly strained arrangement of isolated tetrahedral P_4 molecules to the same extent. Its more stable bonding arrangement therefore makes it less readily attacked by reagents.

Step 3: Conclusion Red phosphorus is less reactive because its polymeric structure is more stable and less strained than the tetrahedral P_4 structure of white phosphorus.

Quick Tip to Solve: Compare structural stability: white phosphorus has strained tetrahedral molecules, while red phosphorus is polymeric.

5. Give the IUPAC name of the following compound:

H_2C=CH-CH(OH)-CH_2-CH_2-CH_3 [1 mark]

Solution:

Concept:

- The alcohol group is the principal functional group and is denoted by the suffix -ol.
- Choose the longest chain containing both the hydroxyl group and the double bond, then number to give the hydroxyl group the lower locant.

Step 1: Choose and number the parent chain The structure has a continuous chain of six carbon atoms, including both the C=C bond and the carbon bearing OH. Numbering from the alkene end places OH at carbon 3, whereas numbering from the opposite end places it at carbon 4. The alcohol group controls this choice, so use the first numbering.

Step 2: Locate the unsaturation and form the name With this numbering, the double bond lies between carbon 1 and carbon 2, and the hydroxyl group is attached to carbon 3. The six-carbon parent therefore has the unsaturation descriptor hex-1-en and the alcohol suffix -3-ol. No additional substituent is present on the chain.

Step 3: Conclusion The IUPAC name is $\boxed{\text{hex-1-en-3-ol}}$.

Quick Tip to Solve: Number for the OH group before comparing double-bond locants; here OH gets 3 rather than 4.

6. Write the structural formula of 1-phenylpentan-1-one. [1 mark]

Solution:

Concept:

- In a ketone, the carbonyl carbon is bonded to carbon groups on both sides.
- The pentan-1-one chain has five carbons including the carbonyl carbon, with a phenyl group attached at carbon 1.

Step 1: Construct the five-carbon carbonyl chain Place the carbonyl group at carbon 1 of the pentane chain. Counting the carbonyl carbon as the first carbon leaves four carbons on its alkyl side, giving the fragment $-C(=O)-CH_2-CH_2-CH_2-CH_3$. The carbonyl carbon is part of the parent chain and must not be counted twice.

Step 2: Attach the phenyl group A phenyl group is C_6H_5-, obtained by removing one hydrogen from benzene. Attach this group directly to carbon 1, the carbonyl carbon. The carbonyl is then bonded to phenyl on one side and n-butyl on the other, as required for the named ketone.

Step 3: Conclusion The structural formula is

$$\boxed{C_6H_5-C(=O)-CH_2-CH_2-CH_2-CH_3}.$$

Quick Tip to Solve: Count the carbonyl carbon within pentanone: the chain beside it contains four, not five, carbon atoms.

7. Arrange the following compounds in an increasing order of basic strengths in their aqueous solutions:

NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ [1 mark]

Solution:

Concept:

- A base accepts a proton through the lone pair on nitrogen. In water, its strength depends on both electron donation by alkyl groups and hydration of the protonated amine.
- Methyl groups exert a positive inductive effect; hydration stabilises the conjugate acid and is less effective when the nitrogen is crowded.

Step 1: Compare with ammonia Methyl substitution increases electron density on nitrogen. Consequently, the three methylamines are stronger bases than NH_3 in aqueous solution.

Step 2: Compare the methylamines in water The secondary amine has a favourable combination of electron donation and hydration of its conjugate acid. The tertiary amine is less effectively hydrated because three methyl groups surround nitrogen. For these methylamines, this makes the secondary amine strongest, followed by the primary and then the tertiary amine.

Step 3: Conclusion Increasing basic strength in aqueous solution:

$$\boxed{NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH.}$$

Quick Tip to Solve: For methylamines in water, include hydration; counting methyl groups alone gives the wrong order.

8. What does '6,6' indicate in the name nylon-6,6? [1 mark]

Solution:

Concept:

- Nylon-6,6 is a condensation polyamide formed from a diamine and a dicarboxylic acid.
- The two numbers specify the carbon counts of the two separate monomers, including the carboxyl carbon atoms of the acid.

Step 1: Identify the diamine The diamine is hexamethylenediamine, $H_2N(CH_2)_6NH_2$. Its chain contains six carbon atoms, which accounts for the first 6.

Step 2: Identify the dicarboxylic acid The acid is adipic acid, $HOOC(CH_2)_4COOH$. It contains four methylene carbon atoms and two carboxyl carbon atoms, making six in all. This accounts for the second 6. The numbers count carbons in the monomers, rather than the number of repeating units in the polymer.

Step 3: Conclusion The two 6s indicate that the diamine and the dicarboxylic acid used to prepare nylon-6,6 each contain six carbon atoms.

Quick Tip to Solve: When counting carbons in adipic acid, include both carboxyl carbon atoms as well as the four methylene carbons.

9(a). What type of cell is a lead storage battery? Write the anode and the cathode reactions and the overall cell reaction occurring in the use of a lead storage battery. [2 marks]

Solution:

Concept:

- A secondary cell is rechargeable: an external current can reverse its discharge reaction.
- During discharge, oxidation occurs at the lead anode and reduction occurs at the lead dioxide cathode in sulphuric acid.

Step 1: Classify the cell and write the anode reaction A lead storage battery is a secondary cell (a rechargeable storage cell). During use, lead is oxidised from oxidation state 0 to +2 and forms insoluble lead sulphate:

$$\mathrm{Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-}.$$

The electrons leave the anode and flow through the external circuit.

Step 2: Write the cathode reaction Lead dioxide is reduced: lead changes from +4 to +2. In the acidic electrolyte the cathode reaction is

$$\mathrm{PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-}$$

$$\mathrm{\longrightarrow PbSO_4(s) + 2H_2O(l)}.$$

The two electrons consumed here equal the number released at the anode.

Step 3: Add the half-reactions Cancel the electrons and combine the hydrogen and sulphate ions as sulphuric acid. Both electrodes form lead sulphate, while sulphuric acid is consumed and water is produced. This accounts for the decrease in acid concentration during discharge.

Step 4: Conclusion The battery is a secondary cell. Its overall discharge reaction is

$$\boxed{\mathrm{Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)}}.$$

Quick Tip to Solve: During discharge both lead electrodes become lead sulphate; use this to check both half-reactions.

OR

9(b). Two half cell reactions of an electrochemical cell are given below:

$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$, $E^\circ = +1.51$ V

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ e^-$, $E^\circ = +0.15$ V

Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation. [2 marks]

Solution:

Concept:

- When combining redox half-reactions, the electrons gained and lost must cancel; electrode potentials are not multiplied by balancing factors.
- For the half-reactions in their printed directions, $E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} + E^\circ_{\text{oxidation}}$. A positive value gives $\Delta G^\circ = -nFE^\circ_{\text{cell}} < 0$.

Step 1: Balance the electron transfer The permanganate reduction consumes five electrons, whereas oxidation of one tin(II) ion releases two. The least common multiple is ten. Multiply the permanganate half-reaction by 2 and the tin half-reaction by 5, and then cancel the ten electrons.

Step 2: Construct the overall equation The balanced equation is

$$\begin{aligned} &2\mathrm{MnO_4^-(aq)} + 16\mathrm{H^+(aq)} + 5\mathrm{Sn^{2+}(aq)} \\ &\quad\longrightarrow 2\mathrm{Mn^{2+}(aq)} + 8\mathrm{H_2O(l)} + 5\mathrm{Sn^{4+}(aq)}. \end{aligned}$$

Each side has two manganese atoms, five tin atoms, eight oxygen atoms and sixteen hydrogen atoms. The net charge is $+24$ on each side.

Step 3: Use the potentials in the stated directions The paper gives $+1.51\,\mathrm{V}$ for permanganate reduction and $+0.15\,\mathrm{V}$ for tin oxidation as written. Thus

$$E^\circ_{\text{cell}} = 1.51 + 0.15 = +1.66\,\mathrm{V}.$$

With $n = 10$, the relation $\Delta G^\circ = -10FE^\circ_{\text{cell}}$ is negative; hence the forward reaction is thermodynamically favoured under standard conditions.

Step 4: Conclusion The balanced redox equation above favours formation of the products, since the cell potential calculated from the given directed half-reactions is positive.

Quick Tip to Solve: Check whether a quoted potential belongs to oxidation or reduction before adding it; never multiply a potential by a stoichiometric factor.

10. Define the following:

(i) Elementary step in a reaction

(ii) Rate of a reaction [2 marks]

Solution:

Concept:

- A reaction mechanism describes the sequence of individual molecular events by which reactants form products.
- Reaction rate measures concentration change with time; a positive rate is obtained by reversing the sign for a disappearing reactant.

Step 1: Define an elementary step An elementary step is a single reaction event that occurs in one stage, without proceeding through further intermediate steps. A complex reaction consists of a sequence of such steps. For an elementary step, the molecularity describes how many reacting species participate in that individual event; it is not read from the overall equation of a complex reaction.

Step 2: Define rate of reaction The rate of a reaction is the change in concentration of a reactant or product per unit time. For $\mathrm{A} \longrightarrow \mathrm{B}$, the average rate is

$$r_{\mathrm{av}} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = \frac{\Delta[\mathrm{B}]}{\Delta t}.$$

The instantaneous rate uses the corresponding derivatives. For a general reaction $a\mathrm{A} \longrightarrow b\mathrm{B}$, the normalised rate is

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = \frac{1}{b}\frac{d[\mathrm{B}]}{dt}.$$

Its usual concentration-based unit is $\mathrm{mol\,L^{-1}\,s^{-1}}$.

Step 3: Conclusion (i) An elementary step is a single-stage reaction event. (ii) Reaction rate is the change in reactant or product concentration per unit time, with sign and stoichiometric factors included as appropriate.

Quick Tip to Solve: Use a minus sign for reactant disappearance and a plus sign for product formation so that the reported reaction rate is positive.

11. Describe the underlying principle of each of the following metal refining methods:

(i) Electrolytic refining of metals

(ii) Vapour phase refining of metals [2 marks]

Solution:

Concept:

- Electrolytic refining uses selective dissolution of an impure metal and deposition of the pure metal under an applied potential.
- Vapour phase refining separates a metal through a volatile compound that can subsequently be decomposed to regenerate the metal.

Step 1: (i) Electrolytic refining The impure metal is made the anode, a thin sheet of pure metal the cathode, and a soluble salt of the same metal is used as electrolyte. On passing current, metal dissolves from the anode as ions and these ions are reduced at the cathode:

$$M \longrightarrow M^{n+} + ne^- \qquad M^{n+} + ne^- \longrightarrow M.$$

The potential is controlled so that pure metal deposits. Less reactive insoluble impurities collect as anode mud, while more reactive impurities can remain in solution.

Step 2: (ii) Vapour phase refining The crude metal is converted selectively into a volatile compound, leaving nonvolatile impurities behind. The purified vapour is then decomposed at a different temperature to obtain pure metal. The requirements are that the metal form a volatile compound with a suitable reagent and that this compound decompose readily to the metal. For example, nickel forms volatile nickel tetracarbonyl in the Mond process; heating this compound yields pure nickel and carbon monoxide.

Step 3: Conclusion Electrolytic refining relies on selective electrode dissolution and deposition; vapour phase refining relies on formation and decomposition of a volatile metal compound.

Quick Tip to Solve: For vapour refining, always state both requirements: volatility of the compound and its easy decomposition.

12. Complete the following chemical reaction equations:

(i) $XeF_2 + H_2O \longrightarrow$

(ii) $PH_3 + HgCl_2 \longrightarrow$ [2 marks]

Solution:

Concept:

- Xenon difluoride undergoes hydrolysis with water, producing xenon, hydrogen fluoride and oxygen.
- Phosphine reacts with mercuric chloride to form mercuric phosphide; balance phosphorus and mercury before hydrogen and chlorine.

Step 1: (i) Hydrolysis of xenon difluoride The printed fluoride is XeF_2. Its hydrolysis gives elemental xenon, hydrogen fluoride and oxygen. Balancing fluorine requires four HF for two molecules of the fluoride; two water molecules supply the hydrogen and oxygen:

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2.$$

The equation has two xenon atoms, four fluorine atoms, four hydrogen atoms and two oxygen atoms on each side.

Step 2: (ii) Reaction of phosphine with mercuric chloride The product is mercuric phosphide, Hg_3P_2, together with hydrogen chloride. Its formula requires three mercury atoms and two phosphorus atoms, so take three mercuric chloride molecules and two phosphine molecules:

$$2PH_3 + 3HgCl_2 \longrightarrow Hg_3P_2 + 6HCl.$$

The six hydrogen atoms from phosphine combine with the six chlorine atoms to form six HCl molecules. Mercuric phosphide is obtained as a black precipitate.

Step 3: Conclusion The completed equations are $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$ and $2PH_3 + 3HgCl_2 \rightarrow Hg_3P_2 + 6HCl$.

Quick Tip to Solve: Read the xenon fluoride subscript carefully: XeF2 hydrolysis gives Xe, HF and oxygen.

13. Complete the following chemical reaction equations:

(i) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \rightarrow$

(ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow$ [2 marks]

Solution:

Concept:

- In acidic medium, MnO_4^- is reduced to Mn^{2+}, whereas $Cr_2O_7^{2-}$ is reduced to Cr^{3+}.
- Balance redox equations by matching electrons, using water for oxygen and hydrogen ions for hydrogen; finally check net charge.

Step 1: (i) Oxidation of oxalate by permanganate The reduction half-reaction is

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O.$$

The oxidation half-reaction is $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$. Multiply the first by two and the second by five, then add and cancel the ten electrons:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O.$$

The net charge is $+4$ on both sides.

Step 2: (ii) Oxidation of iron(II) by dichromate The dichromate reduction half-reaction is

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O.$$

Each iron(II) ion loses one electron: $Fe^{2+} \rightarrow Fe^{3+} + e^-$. Hence six iron(II) ions supply the six electrons needed:

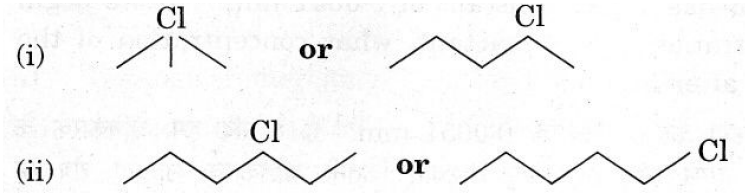
$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$$

The net charge is $+24$ on both sides, confirming the balance.

Step 3: Conclusion The balanced ionic equations have coefficient ratios $2 : 5 : 16 : 2 : 10 : 8$ in (i) and $1 : 6 : 14 : 2 : 6 : 7$ in (ii), in the order shown above.

Quick Tip to Solve: In acid, remember five electrons per permanganate ion and six per dichromate ion before balancing the reductant.

14. Which one in the following pairs undergoes S_N1 substitution reaction faster and why? [2 marks]



Solution:

Concept:

- An S_N1 reaction has slow ionisation of the carbon–halogen bond as its rate-determining step, forming a carbocation.
- For comparable alkyl chlorides, easier formation of a more stable carbocation gives a faster reaction: tertiary carbocation $>$ secondary $>$ primary.

Step 1: (i) Compare the first pair The left-hand compound is 2-chloro-2-methylpropane (tert-butyl chloride), whereas the right-hand compound is 2-chloropentane. On ionisation, the former gives the tertiary tert-butyl carbocation, $(CH_3)_3C^+$; the latter gives a secondary carbocation. Three alkyl groups stabilise the tertiary cation through their electron-releasing inductive effect and hyperconjugation. Consequently, the left-hand compound ionises more readily and undergoes S_N1 substitution faster.

Step 2: (ii) Compare the second pair The left-hand compound is 3-chlorohexane and the right-hand compound is 1-chloropentane. Loss of chloride from 3-chlorohexane gives a secondary carbocation, whereas loss from 1-chloropentane would give a much less stable primary carbocation. The secondary cation is better stabilised by neighbouring alkyl groups through the positive inductive effect and hyperconjugation. Thus 3-chlorohexane, the left-hand compound, has the faster S_N1 reaction.

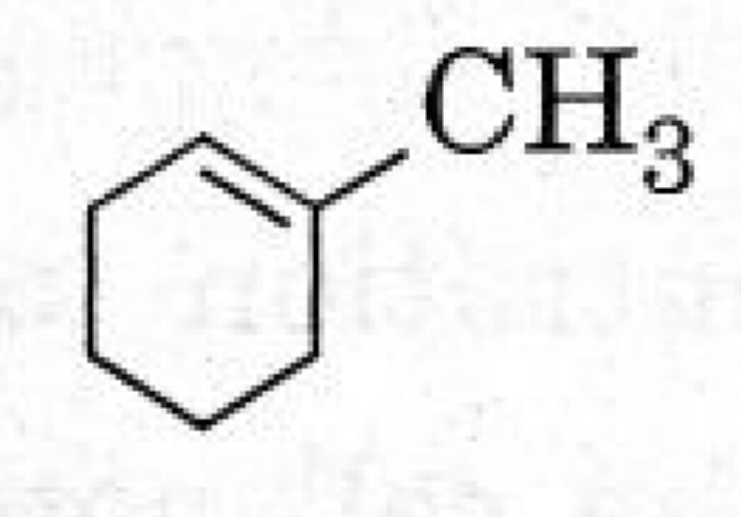
Step 3: Conclusion In both (i) and (ii), the left-hand compound reacts faster: tertiary over secondary in (i), and secondary over primary in (ii), because its carbocation is more stable.

Quick Tip to Solve: Count alkyl groups attached to the carbon bearing Cl; compare the resulting carbocations, not total chain length.

15. Complete the following reaction equations:

(i) 1-Methylcyclohexene (structure shown below) + $\mathrm{HI} \rightarrow$

(ii) $\mathrm{CH_3CH_2CH{=}CH_2} + \mathrm{HBr} \rightarrow$ [2 marks]



Solution:

Concept:

- An alkene undergoes electrophilic addition of a hydrogen halide across its carbon-carbon double bond.
- Markovnikov's rule: hydrogen attaches to the double-bonded carbon already bearing more hydrogen atoms; the halide attaches to the other carbon. The preferred intermediate is the more stable carbocation.

Step 1: Complete reaction (i) In 1-methylcyclohexene, the methyl-bearing double-bonded carbon has no hydrogen, while the adjacent double-bonded carbon has one. Addition of hydrogen to the latter gives a tertiary carbocation at the methyl-bearing carbon. Iodide then attacks this carbon. Thus,

$$\text{1-methylcyclohexene} + \mathrm{HI} \longrightarrow \text{1-iodo-1-methylcyclohexane}.$$

The ring remains intact and its double bond becomes a single bond.

Step 2: Complete reaction (ii) In but-1-ene the terminal carbon is $\mathrm{CH_2}$. Hydrogen adds to this terminal carbon, producing a secondary carbocation on the adjacent carbon rather than the less stable primary carbocation. Bromide attacks the secondary carbon:

$$\mathrm{CH_3CH_2CH{=}CH_2} + \mathrm{HBr} \longrightarrow \mathrm{CH_3CH_2CH(Br)CH_3}.$$

No peroxide is specified, so ordinary Markovnikov addition applies.

Step 3: Conclusion (i) 1-Iodo-1-methylcyclohexane; (ii) 2-bromobutane, $\mathrm{CH_3CH_2CH(Br)CH_3}$.

Quick Tip to Solve: For each alkene, place H on the carbon with more H atoms, then place I or Br on the other carbon.

16. Name the four bases present in DNA. Which one of these is not present in RNA? [2 marks]

Solution:

Concept:

- DNA and RNA are nucleic acids whose nucleotide units contain a nitrogenous base, a pentose sugar and phosphate.
- The bases are classified as purines (adenine and guanine) and pyrimidines. DNA has cytosine and thymine as its pyrimidines.

Step 1: List the bases of DNA The four nitrogenous bases present in deoxyribonucleic acid (DNA) are **adenine (A), guanine (G), cytosine (C) and thymine (T)**. Adenine and guanine are the two purine bases; cytosine and thymine are the two pyrimidine bases. In double-stranded DNA, adenine pairs with thymine and guanine pairs with cytosine.

Step 2: Identify the base absent from RNA Of these four DNA bases, **thymine is not present in RNA**. RNA contains uracil (U) in its place. Its four usual bases are therefore adenine, guanine, cytosine and uracil. The difference asked for concerns the nitrogenous base; the distinct sugars in DNA and RNA do not change this answer.

Step 3: Conclusion DNA contains adenine, guanine, cytosine and thymine. Thymine is absent from RNA, which contains uracil instead.

Quick Tip to Solve: Remember DNA as A, G, C, T; replace T by U to obtain the usual RNA bases.

17. Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet. [2 marks]

Solution:

Concept:

- Vitamins A, D, E and K are fat-soluble vitamins: they are absorbed along with dietary fats.
- A complete response should link each chosen vitamin with a source and its characteristic deficiency disease. Vitamins A and D provide two standard examples.

Step 1: Vitamin A: sources and deficiency **Vitamin A** is a fat-soluble vitamin found in fish liver oil, milk, butter and egg yolk. Carrots and green leafy vegetables supply carotene, which the body can convert into vitamin A. Its deficiency causes **night blindness**, in which vision in dim light becomes poor. Severe deficiency can also cause drying of the cornea (xerophthalmia).

Step 2: Vitamin D: sources and deficiency **Vitamin D** is another fat-soluble vitamin. Dietary sources include fish liver oil, egg yolk and butter; exposure of skin to sunlight also promotes vitamin D formation. Its deficiency causes **rickets in children**, with poor mineralisation of growing bones and possible bowing of the legs. In adults, deficiency can cause osteomalacia.

Step 3: Conclusion Vitamin A: fish liver oil or carrots; deficiency causes night blindness. Vitamin D: fish liver oil or egg yolk; deficiency causes rickets in children.

Quick Tip to Solve: Use the pairs A–night blindness and D–rickets, and name at least one dietary source for each.

18. Differentiate between molecular structures and behaviours of thermoplastic and thermosetting polymers. Give one example of each type. [2 marks]

Solution:

Concept:

- Polymer behaviour on heating depends on the arrangement of the chains and the extent of covalent cross-linking between them.
- Thermoplastics have linear or slightly branched chains; thermosetting polymers form highly cross-linked three-dimensional networks on curing.

Step 1: Thermoplastics: structure, behaviour and example Thermoplastic polymers consist of **linear or slightly branched chains**. The chains are held together mainly by intermolecular forces and can move relative to one another when heated. Consequently, these polymers **soften on heating and harden on cooling**; this can be repeated, allowing remoulding. **Polythene** is an example.

Step 2: Thermosetting polymers: structure, behaviour and example Thermosetting polymers form **highly cross-linked, three-dimensional networks** during curing. The covalent links restrict the motion of the chains and produce a rigid material. Once set, they **do not soften for remoulding on reheating**; strong heating eventually decomposes or chars them. Thus setting is essentially irreversible. **Bakelite** is an example.

Step 3: Conclusion Thermoplastics have linear/slightly branched chains and can be softened and remoulded (polythene). Thermosets have cross-linked networks and cannot be remoulded after setting (Bakelite).

Quick Tip to Solve: Link easy chain movement to remouldable polythene, and rigid covalent cross-links to Bakelite.

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19. A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of the reactant, what concentration of the reactant will be left after 3 hours? [3 marks]

Solution:

Concept:

- For a first order reaction, the rate is proportional to the instantaneous reactant concentration: $-d[A]/dt = k[A]$. Here k is the rate constant, $[A]_0$ the initial concentration and $[A]_t$ the concentration after time t.
- The integrated rate equation is $\ln([A]_0/[A]_t) = kt$, or $[A]_t = [A]_0 e^{-kt}$. The time unit must match the inverse time unit of the rate constant.

Step 1: Put all data in consistent units The given rate constant is $k = 0.0051\,\text{min}^{-1}$, and the initial concentration is $[A]_0 = 0.10\,\text{mol L}^{-1}$. Since k is expressed per minute, convert the elapsed time before substitution:

$$t = 3 \times 60 = 180\,\text{min}.$$

Thus the dimensionless product is $kt = 0.0051 \times 180 = 0.918$.

Step 2: Calculate the concentration remaining Using the integrated first order rate equation,

$$\begin{aligned}[A]_t &= [A]_0 e^{-kt} \\ &= 0.10 e^{-0.918} \\ &= 0.10 \times 0.3993 \\ &= 0.03993\,\text{mol L}^{-1}.\end{aligned}$$

Equivalently, the common logarithm form gives $\log([A]_0/[A]_t) = kt/2.303 = 0.3986$. The remaining fraction is about 0.399, so the result is smaller than the initial concentration, as expected for consumption of the reactant.

Step 3: Conclusion The reactant concentration after 3 hours is $\boxed{[A]_t \approx 0.040\,\text{M}}$.

Quick Tip to Solve: Convert 3 hours to 180 minutes before multiplying by k; then use the exponential to obtain the fraction remaining.

20. Silver crystallises with face-centred cubic unit cells. Each side of the unit cell has a length of 409 pm. What is the radius of an atom of silver? (Assume that each face atom is touching the four corner atoms.) [3 marks]

Solution:

Concept:

- In a face-centred cubic (fcc) unit cell, atoms touch along a face diagonal. A corner atom, the face-centred atom and the opposite corner atom have their centres on this diagonal.
- For a square face with edge length a, the face diagonal is $\sqrt{a^2 + a^2} = a\sqrt{2}$. If the atomic radius is r, contact along this diagonal gives $4r = a\sqrt{2}$.

Step 1: Relate the face diagonal to the atomic radius Consider one square face of the silver unit cell. Moving along its diagonal from one corner centre to the opposite corner centre passes through the centre of the atom at the face centre. The first corner atom touches the face atom, and the face atom touches the opposite corner atom. Each distance between two touching atom centres is $2r$; hence the full face diagonal has length $2r + 2r = 4r$. Combining this with the square-face geometry,

$$4r = a\sqrt{2}, \qquad r = \frac{a\sqrt{2}}{4} = \frac{a}{2\sqrt{2}}.$$

Step 2: Substitute the edge length of silver The edge length is $a = 409\,\text{pm}$. Therefore,

$$\begin{aligned}r &= \frac{409}{2\sqrt{2}}\,\text{pm} \\ &= \frac{409}{2.8284}\,\text{pm} \\ &= 144.6\,\text{pm}.\end{aligned}$$

The radius is about $0.354a$, which is consistent with contact along the face diagonal of an fcc cell.

The edge itself is not a line of contact between nearest neighbours, so setting $a = 2r$ would give an incorrect result.

Step 3: Conclusion The radius of a silver atom is $\boxed{r \approx 145\,\text{pm}}$ (about 1.45×10^{-10} m).

Quick Tip to Solve: For fcc, first identify the face diagonal as the contact line: its length is four radii, so divide the edge by 2 sqrt(2).

21. A copper-silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential measured 0.422 V. Determine the concentration of silver ion in the cell.

Given: $E^\circ_{Ag^+/Ag}$ = +0.80 V, $E^\circ_{Cu^{2+}/Cu}$ = +0.34 V. [3 marks]

Solution:

Concept:

- The electrode with the larger standard reduction potential is reduced at the cathode. The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solid metal activities are unity.

Step 1: Write the spontaneous cell reaction Since $E^\circ_{Ag^+/Ag} = +0.80\,\text{V}$ exceeds $E^\circ_{Cu^{2+}/Cu} = +0.34\,\text{V}$, silver ions are reduced and copper is oxidised:

$$\begin{aligned} \text{Cu(s)} &\longrightarrow \text{Cu}^{2+}\text{(aq)} + 2e^- \\ 2\text{Ag}^+\text{(aq)} + 2e^- &\longrightarrow 2\text{Ag(s)}. \end{aligned}$$

Thus $n = 2$, and the overall reaction is $\text{Cu(s)} + 2\text{Ag}^+\text{(aq)} \longrightarrow \text{Cu}^{2+}\text{(aq)} + 2\text{Ag(s)}$. The standard cell potential is $0.80 - 0.34 = 0.46\,\text{V}$.

Step 2: Apply the Nernst equation and find silver ion concentration Using the usual room-temperature value 298 K, the reaction quotient is $Q = [\text{Cu}^{2+}]/[\text{Ag}^+]^2$, with concentrations referred to 1 M. Substitution gives

$$\begin{aligned} 0.422 &= 0.460 - \frac{0.0591}{2}\log\frac{0.10}{[\text{Ag}^+]^2}, \\ \log\frac{0.10}{[\text{Ag}^+]^2} &= \frac{2(0.460 - 0.422)}{0.0591} = 1.286, \\ \frac{0.10}{[\text{Ag}^+]^2} &= 10^{1.286} \approx 19.32, \\ [\text{Ag}^+] &= \sqrt{\frac{0.10}{19.32}} \approx 0.0719\,\text{M}. \end{aligned}$$

Taking the positive square root is required because concentration cannot be negative. The quotient is greater than unity, consistently lowering the potential below its standard value.

Step 3: Conclusion The silver ion concentration is $\boxed{[\text{Ag}^+] \approx 7.2 \times 10^{-2}\,\text{M}}$.

Quick Tip to Solve: Balance the electron transfer first: two silver ions are reduced per copper atom, so square the silver ion concentration in Q.

22. What happens in the following activities and why?

(i) An electrolyte is added to a hydrated ferric oxide sol in water.

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

(iii) An electric current is passed through a colloidal solution. [3 marks]

Solution:

Concept:

- Colloidal particles carry like charges; electrostatic repulsion helps prevent their aggregation. Counter-ions can neutralise this charge and cause coagulation.
- The Tyndall effect is the scattering of light by colloidal particles. Electrophoresis is their directed motion in an applied electric field.

Step 1: Addition of an electrolyte Hydrated ferric oxide sol is positively charged. On adding a sufficient amount of an electrolyte, its anions (the oppositely charged ions) neutralise the positive charge on the sol particles. The repulsion between particles decreases, so they aggregate into larger particles and settle as a precipitate. This destabilisation of the sol is called coagulation or flocculation.

Step 2: Passage of a beam of light The path of the beam becomes visible as a luminous cone when viewed from a direction different from that of the incident beam. The colloidal particles scatter the incident light in different directions because their size is suitable for appreciable light scattering. This phenomenon is the Tyndall effect; it does not require the particles to settle.

Step 3: Passage of electric current Under the applied electric field, charged colloidal particles move towards the oppositely charged electrode. Positively charged particles migrate towards the cathode, whereas negatively charged particles migrate towards the anode. This movement is called electrophoresis. On reaching the electrode, particles may lose their charge and coagulate.

Step 4: Conclusion The observations are (i) coagulation by charge neutralisation, (ii) the Tyndall effect due to scattering, and (iii) electrophoresis due to migration of charged particles.

Quick Tip to Solve: Remember the three causes separately: counter-ions remove charge, light is scattered, and an electric field moves charged particles.

23(a). Giving a suitable example for each, explain the following:

(i) Crystal field splitting

(ii) Linkage isomerism

(iii) Ambidentate ligand [3 marks]

Solution:

Concept:

- Ligands interact differently with metal orbitals of different orientations; this removes the equal energies (degeneracy) of the five metal d orbitals.
- An ambidentate ligand has two alternative donor atoms but uses only one at a time. Different donor-atom attachment can produce linkage isomerism.

Step 1: Crystal field splitting with an example Crystal field splitting is the separation of the five initially degenerate metal d orbitals into groups of different energies in the electric field of surrounding ligands. For example, in the octahedral complex $[Ti(H_2O)_6]^{3+}$, ligands approach along the coordinate axes. The orbitals d_{xy}, d_{yz}, d_{xz} form the lower-energy t_{2g} set, while $d_{x^2-y^2}, d_{z^2}$ form the higher-energy e_g set. Their energy separation is the octahedral splitting energy, Δ_o.

Step 2: Linkage isomerism with an example Linkage isomerism occurs when coordination compounds have the same composition but differ in the donor atom through which an ambidentate ligand binds to the metal. For example, $[Co(NH_3)_5(NO_2)]Cl_2$ has an N-bonded nitro ligand, whereas $[Co(NH_3)_5(ONO)]Cl_2$ has an O-bonded nitrito ligand. The change is in the metal–ligand linkage, not in the composition.

Step 3: Ambidentate ligand with an example An ambidentate ligand can coordinate through either of two different donor atoms, with only one donor atom attached in a given linkage. For example, NO_2^- can bind through nitrogen (nitro) or oxygen (nitrito). Similarly, SCN^- can bind through sulfur or nitrogen. This is different from a chelating bidentate ligand, which attaches through two donor atoms simultaneously.

Step 4: Conclusion Crystal field splitting concerns orbital energies; linkage isomerism concerns alternative metal–donor bonds; an ambidentate ligand provides the alternative donor atoms.

Quick Tip to Solve: Use the nitro/nitrito pair for both linkage isomerism and ambidentate ligands, and explicitly identify N-bonding versus O-bonding.

OR

23(b). Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units:

$[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $Ni(CO)_4$

(At. Nos.: Co = 27, Cr = 24, Ni = 28) [3 marks]

Solution:

Concept:

- Find the oxidation state first: both NH_3 and CO are neutral. The metal electron count and ligand-induced pairing then determine available hybrid orbitals.
- In valence bond theory, six d^2sp^3 hybrid orbitals give an octahedral structure; four sp^3 hybrid orbitals give a tetrahedral structure. Unpaired electrons produce paramagnetism.

Step 1: Hexaamminecobalt(III) In $[Co(NH_3)_6]^{3+}$, cobalt has oxidation state $+3$. Starting from Co, $[Ar]3d^74s^2$, the ion Co^{3+} has configuration $3d^6$. In this Co(III) complex, the ligand field produces pairing of the six d electrons, giving $t_{2g}^6e_g^0$. Thus two inner $3d$ orbitals become vacant and combine with one $4s$ and three $4p$ orbitals to give d^2sp^3 hybridisation. The complex is octahedral and diamagnetic, with no unpaired electrons.

Step 2: Hexaamminechromium(III) In $[Cr(NH_3)_6]^{3+}$, chromium is also in oxidation state $+3$. The neutral atom is $[Ar]3d^54s^1$, so Cr^{3+} is $3d^3$. The three electrons occupy separate lower-energy t_{2g}

orbitals, giving $t_{2g}^3 e_g^0$. Two inner $3d$ orbitals are already available, so the hybridisation is d^2sp^3 and the geometry is octahedral. Its three unpaired electrons make it paramagnetic; no pairing is needed to supply the vacant orbitals.

Step 3: Tetracarbonylnickel(0) In $Ni(CO)_4$, nickel has oxidation state zero because CO is neutral. Under the influence of CO, the valence electrons form the paired $3d^{10}$ arrangement, leaving the $4s$ and three $4p$ orbitals available. These combine into four sp^3 hybrid orbitals directed tetrahedrally. All electrons are paired, so the complex is diamagnetic. Four ligands here therefore give tetrahedral geometry, not a square-planar arrangement.

Step 4: Conclusion $[Co(NH_3)_6]^{3+}$: octahedral, diamagnetic, d^2sp^3. $[Cr(NH_3)_6]^{3+}$: octahedral, paramagnetic (three unpaired electrons), d^2sp^3. $Ni(CO)_4$: tetrahedral, diamagnetic, sp^3.

Quick Tip to Solve: Do not assign nickel a $+2$ state here: neutral CO makes Ni zero-valent, leading to the paired d-ten configuration and tetrahedral sp-three bonding.

24. Explain the following observations:

(i) The boiling point of ethanol is higher than that of methoxymethane.

(ii) Phenol is more acidic than ethanol.

(iii) o- and p-nitrophenols are more acidic than phenol. [3 marks]

Solution:

Concept:

- Boiling point depends on the strength of intermolecular attractions; hydrogen bonding requires hydrogen bonded directly to an electronegative atom.
- An acid is stronger when its conjugate base is more stable. Resonance and electron-withdrawing groups can stabilise a negative charge.

Step 1: (i) Compare intermolecular forces Ethanol, CH_3CH_2OH, contains an $O-H$ bond and forms intermolecular hydrogen bonds. Methoxymethane, CH_3OCH_3, has no hydrogen attached to oxygen and cannot form such bonds between its own molecules. Although the compounds have the same molecular formula and molar mass, more energy is needed to separate ethanol molecules into the vapour phase.

Step 2: (ii) Compare the conjugate bases Phenol loses H^+ to form phenoxide, $C_6H_5O^-$, in which the negative charge is delocalised over oxygen and the aromatic ring by resonance. Ethanol forms ethoxide, $C_2H_5O^-$, whose negative charge remains localised on oxygen. The electron-releasing $+I$ effect of the ethyl group further destabilises this negative charge. The greater relative stabilisation of phenoxide favours ionisation of phenol.

Step 3: (iii) Account for the nitro substituent The $-NO_2$ group withdraws electrons by both the inductive $(-I)$ and resonance $(-R)$ effects. At the ortho and para positions it allows further delocalisation of the negative charge of the corresponding nitrophenoxide ion towards the nitro group. This makes these conjugate bases more stable than phenoxide and favours release of H^+.

Step 4: Conclusion Ethanol has the higher boiling point because of intermolecular hydrogen bonding.

Phenol is more acidic than ethanol, and both o- and p-nitrophenol are more acidic than phenol because their conjugate bases have greater stabilisation.

Quick Tip to Solve: For acidity, compare the conjugate bases first; at ortho and para positions, include the nitro group resonance effect.

25. How would you account for the following:

(i) Many of the transition elements and their compounds can act as good catalysts.

(ii) The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.

(iii) There is a greater range of oxidation states among the actinoids than among the lanthanoids.

[3 marks]

Solution:

Concept:

- Transition metals often have variable oxidation states and available orbitals, allowing intermediate formation during catalysis.
- Poor shielding by $4f$ electrons produces lanthanoid contraction; the relative energies of valence subshells determine accessible oxidation states.

Step 1: (i) Catalytic activity of transition elements Transition elements and their compounds can adopt different oxidation states and form intermediate complexes with reactants. They can therefore participate in electron transfer or provide an alternative reaction pathway of lower activation energy, and are regenerated at the end of the catalytic cycle. Finely divided transition metals also adsorb reactants on their surfaces, bringing them together and weakening bonds before reaction. Thus both variable oxidation states and surface adsorption help account for their catalytic action.

Step 2: (ii) Similarity of corresponding 4d and 5d radii The $5d$ transition series follows the lanthanoids, across which electrons enter the $4f$ subshell. These electrons shield the increasing nuclear charge poorly. The effective nuclear attraction therefore increases and contracts the electron cloud: this is lanthanoid contraction. This contraction largely offsets the size increase expected from the additional shell in the $5d$ series, so corresponding $4d$ and $5d$ metals have almost equal metallic radii, for example zirconium and hafnium.

Step 3: (iii) Wider oxidation-state range of actinoids In actinoids the energies of the $5f$, $6d$ and $7s$ subshells are relatively close, so varying numbers of electrons from these subshells can participate in bonding. Their $5f$ electrons are also less deeply buried than the $4f$ electrons of lanthanoids. In lanthanoids the $4f$ electrons are more core-like and less readily involved in bonding, making $+3$ the predominant oxidation state. Actinoids consequently show a wider range of oxidation states.

Step 4: Conclusion The observations follow from variable oxidation states and adsorption in catalysis, lanthanoid contraction in the $5d$ series, and the comparable energies of $5f$, $6d$ and $7s$ subshells in actinoids.

Quick Tip to Solve: For the nearly equal sizes of 4d and 5d partners, always name lanthanoid contraction and the poor shielding by 4f electrons.

26. Complete the following reaction equations:

(i) $\mathrm{RCONH_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{LiAlH_4}}$

(ii) $\mathrm{C_6H_5N_2Cl + H_3PO_2 + H_2O} \longrightarrow$

(iii) $\mathrm{C_6H_5NH_2 + Br_2(aq)} \longrightarrow$ [3 marks]

Solution:

Concept:

- Lithium aluminium hydride reduces a primary amide, $\mathrm{RCONH_2}$, to the primary amine $\mathrm{RCH_2NH_2}$; the carbonyl carbon is retained.
- Hypophosphorous acid replaces an aryl diazonium group by hydrogen. The amino group activates aniline towards electrophilic bromination at both ortho positions and the para position.

Step 1: (i) Reduction of the amide The carbonyl group of the primary amide is reduced to a methylene group by $\mathrm{LiAlH_4}$, followed by hydrolysis. The completed transformation is

$$\mathrm{RCONH_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{LiAlH_4}} \mathrm{RCH_2NH_2}.$$

The product is a primary amine containing the same number of carbon atoms as the starting amide. It is not $\mathrm{RNH_2}$, which would have one fewer carbon atom.

Step 2: (ii) Replacement of the diazonium group by hydrogen Hypophosphorous acid reduces benzenediazonium chloride to benzene, while nitrogen is evolved. The balanced equation is

$$\mathrm{C_6H_5N_2Cl + H_3PO_2 + H_2O} \longrightarrow \mathrm{C_6H_6 + N_2 + H_3PO_3 + HCl}.$$

Thus the group $-\mathrm{N_2^+}$ is replaced by hydrogen, and $\mathrm{H_3PO_2}$ is oxidised to $\mathrm{H_3PO_3}$.

Step 3: (iii) Reaction of aniline with bromine water The strongly activating $-\mathrm{NH_2}$ group directs bromine substitution to positions 2, 4 and 6. With bromine water, substitution proceeds at all three positions without a Lewis-acid catalyst:

$$\mathrm{C_6H_5NH_2 + 3Br_2(aq)} \longrightarrow 2,4,6\text{-}\mathrm{C_6H_2Br_3NH_2 + 3HBr}.$$

The organic product, 2,4,6-tribromoaniline, separates as a white precipitate. Three molecules of bromine replace three ring hydrogens.

Step 4: Conclusion The products are (i) $\mathrm{RCH_2NH_2}$; (ii) benzene, with $\mathrm{N_2}$, $\mathrm{H_3PO_3}$ and HCl; and (iii) white 2,4,6-tribromoaniline, with HBr.

Quick Tip to Solve: Keep the amide carbon in the reduced amine; for aniline with bromine water, fill both ortho sites and the para site.

27. Describe the following substances with one suitable example of each type:

(i) Non-ionic detergents

(ii) Food preservatives

(iii) Disinfectants [3 marks]

Solution:

Concept:

- A detergent has a hydrophobic portion that associates with grease and a hydrophilic portion that interacts with water.
- Food preservatives inhibit food spoilage, whereas disinfectants destroy harmful microorganisms on non-living surfaces.

Step 1: (i) Non-ionic detergents Non-ionic detergents are cleansing agents whose molecules do not contain an ionic group and do not form ions in water. Their long hydrocarbon portion is hydrophobic, while oxygen-containing groups form the hydrophilic part. They remove grease by bringing it into an aqueous dispersion. A suitable example is polyethylene glycol stearate, obtained by the reaction of stearic acid with polyethylene glycol. Its polar polyethylene glycol portion makes it interact with water without an ionic head group.

Step 2: (ii) Food preservatives Food preservatives are substances added to food to prevent or retard spoilage, particularly deterioration caused by the growth of microorganisms. By delaying such changes, they help extend the period for which food remains suitable for use. Sodium benzoate is a suitable example; it is commonly used to preserve acidic foods such as fruit juices and squashes.

Step 3: (iii) Disinfectants Disinfectants are chemical substances used to kill microorganisms on non-living objects and surfaces, such as floors, drains and instruments. They are generally unsuitable for direct application to living tissues at the concentrations used for disinfection. A suitable example is a 1% phenol solution, used as a disinfectant.

Step 4: Conclusion Suitable examples are: (i) polyethylene glycol stearate, a non-ionic detergent; (ii) sodium benzoate, a food preservative; and (iii) 1% phenol solution, a disinfectant.

Quick Tip to Solve: Pair each definition with its use: non-ionic means no ionic head group, preservatives protect food, and disinfectants act on non-living surfaces.

28(a). Define the following terms:

(i) Mole fraction

(ii) Van't Hoff factor

(b) 100 mg of a protein is dissolved in enough water to make 10.0 mL of a solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of protein?

(R = 0.0821 L atm mol^{-1} K^{-1} and 760 mm Hg = 1 atm.) [5 marks]

Solution:

Concept:

- The mole fraction of a component is its amount in moles divided by the total amount in moles of all components in the solution.
- The van't Hoff factor i accounts for association or dissociation of solute particles in a colligative-property measurement.
- For a dilute solution, osmotic pressure is $\pi V = nRT = (w/M)RT$, where w is solute mass, M its molar mass, V solution volume and T absolute temperature.

Step 1: (a)(i) Define mole fraction The mole fraction of component j, denoted by x_j, is the ratio of the number of moles of that component to the total number of moles of all components in the solution:

$$x_j = \frac{n_j}{\sum_k n_k}.$$

For a binary solution containing components A and B, $x_{\mathrm{A}} = n_{\mathrm{A}}/(n_{\mathrm{A}} + n_{\mathrm{B}})$. Mole fraction is dimensionless, and the mole fractions of all components add to unity.

Step 2: (a)(ii) Define the van't Hoff factor The van't Hoff factor is the ratio of the observed colligative property to the value calculated for the same concentration assuming that the solute neither associates nor dissociates:

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

Equivalently, it is the normal molar mass divided by the molar mass inferred from the observed colligative property. Dissociation increases the number of solute particles, giving $i > 1$; association decreases it, giving $i < 1$. For a solute that does neither, $i = 1$.

Step 3: (b) Convert the experimental quantities to compatible units The supplied gas constant uses litres, atmospheres and kelvin. Hence,

$$\begin{aligned} w &= 100\,\text{mg} = 0.100\,\text{g}, \\ V &= 10.0\,\text{mL} = 0.0100\,\text{L}, \\ T &= 25 + 273 = 298\,\text{K}, \\ \pi &= \frac{13.3}{760}\,\text{atm} = 0.0175\,\text{atm}. \end{aligned}$$

The volume here is the final volume of the solution, as required by the osmotic-pressure equation.

Step 4: Calculate the protein's molar mass Treating the dissolved protein as a non-dissociating solute,

use $\pi V = (w/M)RT$ and rearrange:

$$\begin{aligned} M &= \frac{wRT}{\pi V} \\ &= \frac{0.100 \times 0.0821 \times 298}{0.0175 \times 0.0100} \\ &= 1.398 \times 10^4 \text{ g mol}^{-1}. \end{aligned}$$

The units reduce to grams per mole because the litre-atmosphere factors cancel. The large molar mass is consistent with a protein, for which a small mass contains relatively few solute particles and therefore produces a small osmotic pressure.

Step 5: Conclusion Mole fraction is $x_j = n_j / \sum_k n_k$, and the van't Hoff factor is the observed-to-calculated colligative-property ratio. The molar mass of the protein is approximately $\boxed{1.40 \times 10^4 \text{ g mol}^{-1}}$.

Quick Tip to Solve: Before using the given gas constant, convert milligrams to grams, millilitres to litres and mm Hg to atmospheres; retain the final solution volume.

OR

28(b). (a) What is meant by:

(i) Colligative properties

(ii) Molality of a solution

(b) What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air of 0.78. [K_H for nitrogen = 8.42×10^{-7} M/mm Hg] [5 marks]

Solution:

Concept:

- Colligative properties depend on the number of dissolved solute particles relative to the solvent, rather than on their chemical identity, for dilute solutions.
- Molality is $m = n_{\text{solute}}/w_{\text{solvent}}$, where n is in moles and w is the mass of solvent in kilograms.
- Dalton's law gives the partial pressure of nitrogen as $p_{N_2} = y_{N_2} P$. For the Henry constant expressed in M/mm Hg, Henry's law takes the form $c = K_H p_{N_2}$.

Step 1: (a)(i) Define colligative properties Colligative properties are those properties of dilute solutions that depend only on the number of solute particles present relative to the amount of solvent and not on the nature of the solute. They include relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. Thus, solutions with the same effective particle concentration show the same colligative effect under comparable conditions; dissociation or association changes that particle concentration.

Step 2: (a)(ii) Define molality Molality of a solution is the number of moles of solute dissolved in

one kilogram of solvent:

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

Its unit is mol kg^{-1}. The denominator is the mass of the solvent, rather than the mass or volume of the solution. Since masses do not change on heating, molality does not depend on temperature.

Step 3: (b) Calculate the nitrogen partial pressure The gas dissolves according to its own partial pressure. At the stated total pressure and nitrogen mole fraction,

$$p_{N_2} = 0.78 \times 1 = 0.78\,\text{atm} = 0.78 \times 760 = 592.8\,\text{mm Hg}.$$

The total atmospheric pressure cannot be used directly because only the nitrogen component determines the equilibrium concentration of dissolved nitrogen.

Step 4: Apply Henry's law at the stated temperature The units of the supplied constant specify the concentration form of Henry's law. Hence, at 25°C,

$$\begin{aligned} c_{N_2} &= K_H p_{N_2} \\ &= (8.42 \times 10^{-7}\,\text{mol L}^{-1}/\text{mm Hg})(592.8\,\text{mm Hg}) \\ &= 4.991376 \times 10^{-4}\,\text{mol L}^{-1}. \end{aligned}$$

The pressure units cancel, leaving molarity. The given temperature selects the supplied Henry constant; no ideal-gas conversion or water volume is required to find a concentration.

Step 5: Conclusion Colligative properties depend on solute particle number relative to solvent; molality is moles of solute per kilogram of solvent. The dissolved nitrogen concentration is $\boxed{c_{N_2} \approx 4.99 \times 10^{-4}\,\text{M}}$ at 25°C.

Quick Tip to Solve: Read the Henry constant's units first: M/mm Hg requires multiplying by the nitrogen partial pressure in mm Hg, after multiplying the total pressure by 0.78.

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

(i) $H_2S_2O_8$

(ii) $HClO_4$

(b) How would you account for the following:

(i) NH_3 is a stronger base than PH_3.

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

(iii) F_2 is a stronger oxidising agent than Cl_2. [5 marks]

Solution:

Concept:

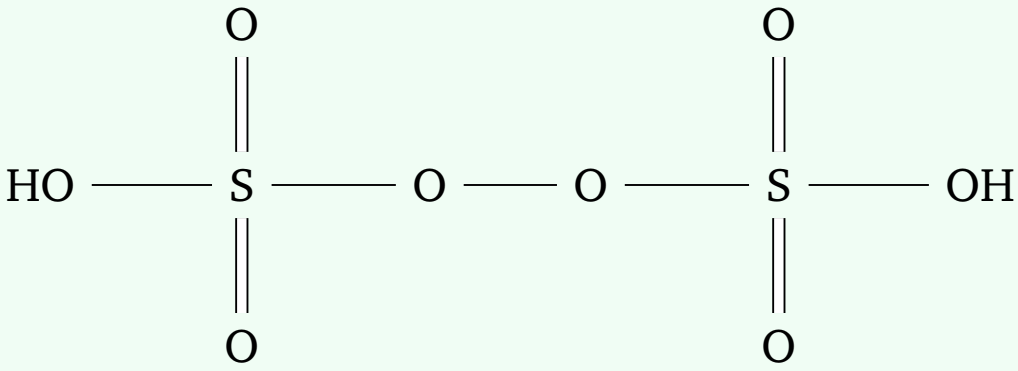
- Oxoacid structures must show the correct connectivity. Peroxodisulphuric acid contains an O – O peroxide linkage, while perchloric acid contains one hydroxyl group bonded to chlorine.
- Basicity depends on the availability of a lone pair for proton acceptance; catenation depends on

the stability of bonds between atoms of the same element.
- Oxidising power in aqueous solution is governed by the overall energetics of $X_2 + 2e^- \rightarrow 2X^-$, including bond dissociation, electron gain and hydration.

Step 1: (a)(i) Structure of peroxodisulphuric acid The structure of $H_2S_2O_8$ is drawn below. Its condensed structural formula is

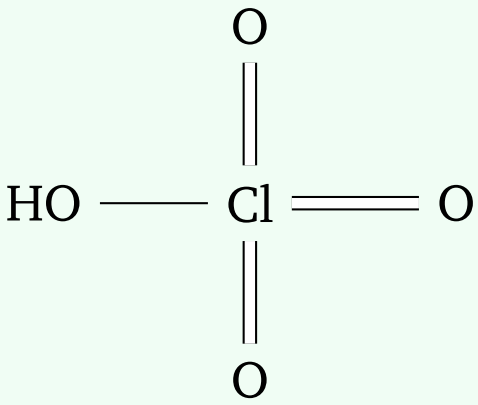
$$HO - S(=O)_2 - O - O - S(=O)_2 - OH.$$

Each sulphur is attached to two terminal oxygens by double bonds, one hydroxyl oxygen by a single bond and one peroxide oxygen by a single bond. The two sulphur-containing units are joined through $-O-O-$, not through a direct sulphur-sulphur bond. Counting the atoms gives two hydrogens, two sulphurs and eight oxygens.



Peroxodisulphuric acid: the central single bond joins two oxygen atoms.

Step 2: (a)(ii) Structure of perchloric acid The structure of $HClO_4$ is $HO - Cl(=O)_3$, as drawn below. Chlorine is the central atom and is surrounded approximately tetrahedrally by four oxygen atoms. One oxygen bears hydrogen and forms the $-OH$ group; the other three are shown as terminal doubly bonded oxygens in the conventional oxoacid structure.



Conventional structural formula of perchloric acid.

Step 3: (b)(i) Compare the basicities of ammonia and phosphine A base accepts a proton by donating its lone pair. Nitrogen is smaller than phosphorus, so its lone pair is concentrated in a smaller region

and is more readily available for bond formation with H^+. In phosphine the phosphorus lone pair has predominantly $3s$ character and is less readily donated. Consequently, ammonia accepts a proton more readily than phosphine and is the stronger base.

Step 4: (b)(ii) Explain the greater catenation of sulphur Catenation requires stable bonds between identical atoms. The small oxygen atoms bring nonbonding electron pairs very close together in an $O-O$ single bond, producing strong lone-pair repulsions that weaken that bond. Sulphur atoms are larger, so these repulsions are smaller and the $S-S$ single bond is stronger than the $O-O$ single bond. Sulphur therefore forms stable chains and rings more readily than oxygen.

Step 5: (b)(iii) Compare the oxidising powers of fluorine and chlorine The aqueous reduction $F_2 + 2e^- \rightarrow 2F^-$ is more favourable than the corresponding reduction of chlorine. Fluorine has a relatively weak $F-F$ bond because of strong lone-pair repulsions between the small fluorine atoms, so less energy is required to dissociate its molecule. Furthermore, the very small fluoride ion has a much more negative hydration enthalpy than chloride. These favourable contributions outweigh the less negative electron-gain enthalpy of fluorine atoms relative to chlorine atoms. Thus the overall reduction potential of fluorine is higher and it is the stronger oxidising agent.

Step 6: Conclusion The structures are $HO-S(=O)_2-O-O-S(=O)_2-OH$ and $HO-Cl(=O)_3$. Ammonia has the more available lone pair, sulphur forms stronger element-element single bonds, and fluorine has the more favourable overall aqueous reduction energetics.

Quick Tip to Solve: Distinguish the peroxide bridge in peroxodisulphuric acid from a single oxygen bridge, and compare halogen oxidising power using all three energetic contributions.

OR

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

(i) $H_2S_2O_7$

(ii) $HClO_3$

(b) Explain the following observations:

(i) In the structure of HNO_3, the N–O bond (121 pm) is shorter than the N–OH bond (140 pm).

(ii) All the P–Cl bonds in PCl_5 are not equivalent.

(iii) ICl is more reactive than I_2. [5 marks]

Solution:

Concept:

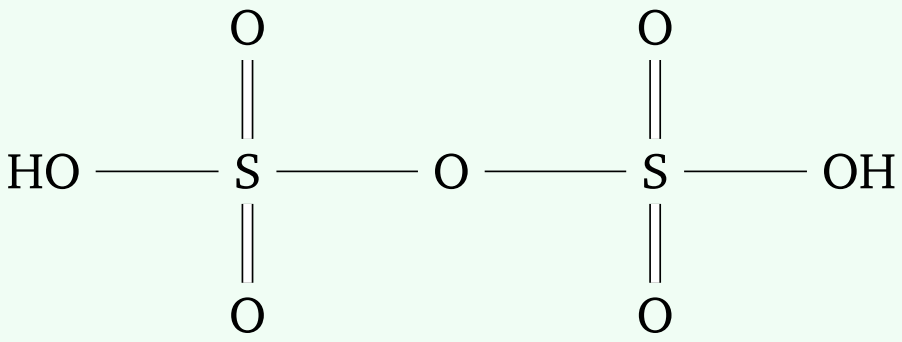
- Oxoacid structures distinguish terminal $S=O$ or $Cl=O$ bonds from hydroxyl groups and bridging oxygen atoms.
- Resonance gives equivalent bonds intermediate bond order; increasing bond order generally decreases bond length.
- Molecular geometry determines bond-pair repulsions, while bond polarity helps explain the reactivity of interhalogens.

Step 1: (a)(i) Structure of disulphuric acid Disulphuric acid, $H_2S_2O_7$, contains two sulphur centres

joined through one bridging oxygen. Each sulphur has two terminal doubly bonded oxygen atoms, one hydroxyl group and the bridging oxygen attached to it. Its connectivity is

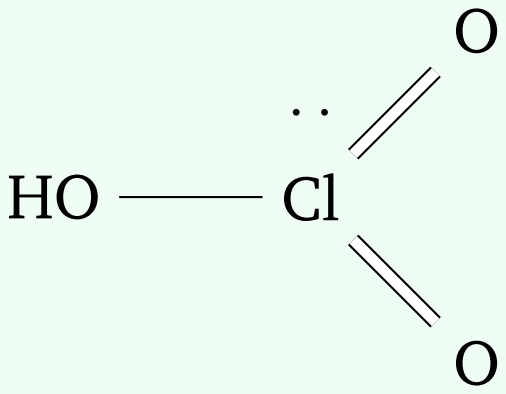
$$\mathrm{HO-S(=O)_2-O-S(=O)_2-OH.}$$

Thus, there are two $\mathrm{O-H}$ bonds and an $\mathrm{S-O-S}$ bridge; there is no peroxide $\mathrm{O-O}$ bond. Each sulphur is surrounded approximately tetrahedrally by four oxygen atoms.



Disulphuric acid: two sulphur centres linked by oxygen

Step 2: (a)(ii) Structure of chloric acid In $\mathrm{HClO_3}$, chlorine is bonded to one hydroxyl oxygen and to two terminal oxygen atoms represented by double bonds. Chlorine also has one lone pair. The structural formula is $\mathrm{HO-Cl(=O)_2}$. The three oxygen atoms and the lone pair give approximately tetrahedral electron-pair arrangement and a pyramidal arrangement of the oxygen atoms about chlorine.



Chloric acid: one hydroxyl group, two oxo groups and one lone pair

Step 3: (b)(i) Unequal bond lengths in nitric acid In nitric acid the two non-hydroxyl oxygen atoms participate in resonance:

$$\mathrm{HO-N^+(=O)-O^-} \longleftrightarrow \mathrm{HO-N^+(-O^-)=O.}$$

Consequently, the two non-hydroxyl $\mathrm{N-O}$ bonds have partial double-bond character and are equivalent in the resonance hybrid. Their bond length is therefore shorter, $121\,\mathrm{pm}$. The $\mathrm{N-OH}$ bond is predominantly a single bond and is longer, $140\,\mathrm{pm}$. The shorter bonds must not be interpreted as two

simultaneous localized double bonds on nitrogen, which would exceed its octet.

Step 4: (b)(ii) Axial and equatorial bonds in phosphorus pentachloride PCl_5 has a trigonal bipyramidal molecular geometry: three equatorial bonds lie in one plane at 120°, and two axial bonds are perpendicular to that plane. Each axial bond pair experiences three 90° interactions with the equatorial bond pairs. Each equatorial bond pair experiences only two such interactions with the axial bond pairs. Greater repulsion makes the axial $P-Cl$ bonds longer and weaker than the equatorial bonds. Hence the five bonds are not equivalent.

Step 5: (b)(iii) Greater reactivity of iodine monochloride Chlorine is more electronegative than iodine, so ICl has a polar $I^{\delta+}-Cl^{\delta-}$ bond. In I_2, the identical atoms share electrons equally and the bond is nonpolar. The polar interhalogen bond is more readily attacked and broken during reactions; interhalogen compounds such as ICl are therefore more reactive than the corresponding halogen I_2.

Step 6: Conclusion The structures are $HO-S(=O)_2-O-S(=O)_2-OH$ and $HO-Cl(=O)_2$. Resonance shortens the non-hydroxyl $N-O$ bonds; greater axial repulsion makes the bonds of PCl_5 unequal; and the polarity of ICl accounts for its greater reactivity.

Quick Tip to Solve: Count the hydroxyl groups first: disulphuric acid has an S-O-S bridge, whereas chloric acid has one OH group and a lone pair on chlorine.

30(a). Write chemical equations to illustrate the following name bearing reactions:

(i) Cannizzaro's reaction

(ii) Hell-Volhard-Zelinsky reaction

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

(i) Propanal and Propanone

(ii) Acetophenone and Benzophenone

(iii) Phenol and Benzoic acid [5 marks]

Solution:

Concept:

- Cannizzaro's reaction is the disproportionation of an aldehyde having no alpha-hydrogen in concentrated alkali: one molecule is oxidised to a carboxylate and another is reduced to an alcohol.
- The Hell-Volhard-Zelinsky (HVZ) reaction replaces an alpha-hydrogen of a carboxylic acid by chlorine or bromine, using the halogen and red phosphorus followed by hydrolysis.
- Tollens' reagent distinguishes an aldehyde from an ordinary ketone. The iodoform test detects the methyl ketone group CH_3CO-, while sodium hydrogencarbonate detects a sufficiently strong acid by evolution of carbon dioxide.

Step 1: (a)(i) Cannizzaro's reaction Benzaldehyde has no alpha-hydrogen and undergoes self-oxidation and reduction with concentrated sodium hydroxide:

$$2C_6H_5CHO + NaOH \xrightarrow{\text{concentrated}} C_6H_5COONa + C_6H_5CH_2OH.$$

The products are sodium benzoate and benzyl alcohol. The salt is formed because the reaction

medium is alkaline; acidification would give benzoic acid.

Step 2: (a)(ii) Hell-Volhard-Zelinsky reaction Propanoic acid, which contains alpha-hydrogen atoms, gives 2-bromopropanoic acid:

$$CH_3CH_2COOH + Br_2 \xrightarrow[\text{then water}]{\text{red P}} CH_3CHBrCOOH + HBr.$$

Bromination occurs at the carbon adjacent to the carboxyl group, rather than at the terminal methyl group.

Step 3: (b)(i) Propanal and propanone: Tollens' test Warm separate samples gently with freshly prepared Tollens' reagent. Propanal produces a silver mirror because its aldehyde group is oxidised to propanoate:

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O.$$

Propanone, a ketone, gives no silver mirror under these conditions. Thus the positive silver-mirror sample is propanal.

Step 4: (b)(ii) Acetophenone and benzophenone: iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Acetophenone contains $C_6H_5COCH_3$, so it gives a yellow precipitate of iodoform:

$$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3\downarrow + 3NaI + 3H_2O.$$

Benzophenone, $C_6H_5COC_6H_5$, has no methyl ketone group and gives no yellow iodoform precipitate.

Step 5: (b)(iii) Phenol and benzoic acid: hydrogencarbonate test Add aqueous sodium hydrogencarbonate to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide:

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O.$$

Phenol gives no effervescence because it is weaker than carbonic acid and cannot liberate carbon dioxide from sodium hydrogencarbonate. Sodium hydroxide is unsuitable for this distinction because both compounds react with it.

Step 6: Conclusion Cannizzaro's reaction gives an alcohol and a carboxylate; HVZ gives an alpha-halocarboxylic acid. The distinguishing observations are: propanal gives a silver mirror, acetophenone gives yellow iodoform, and benzoic acid gives carbon dioxide with $NaHCO_3$; their respective partners give negative results.

Quick Tip to Solve: For these pairs, select the functional-group-specific reagent: Tollens' for aldehyde, iodine/alkali for a methyl ketone, and hydrogencarbonate for a carboxylic acid.

OR

30(b). (a) How will you bring about the following conversions:

(i) Ethanol to 3-hydroxybutanal

(ii) Benzaldehyde to Benzophenone

(b) An organic compound A has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration reaction gives but-1-ene. Write equations for the reactions involved.

[5 marks]

Solution:

Concept:

- Controlled oxidation of a primary alcohol gives an aldehyde. Ethanal has alpha-hydrogen atoms and undergoes aldol addition in cold dilute alkali to give a beta-hydroxy aldehyde.
- A Grignard reagent adds its organic group to an aldehyde carbonyl. Acidic hydrolysis gives a secondary alcohol, whose oxidation produces a ketone.
- Acid-catalysed hydrolysis of an ester gives its constituent carboxylic acid and alcohol. Oxidation of a primary alcohol preserves its carbon skeleton and forms the corresponding carboxylic acid.

Step 1: (a)(i) Convert ethanol into ethanal, then perform aldol addition Pass ethanol vapour over heated copper at $573\,\text{K}$ to obtain ethanal by dehydrogenation:

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[573\,\text{K}]{\text{Cu}} \text{CH}_3\text{CHO} + \text{H}_2.$$

Treat ethanal with cold dilute sodium hydroxide. Two molecules combine, with the carbonyl group of one accepting attack from the alpha-carbon of the other:

$$2\text{CH}_3\text{CHO} \xrightarrow{\text{dil. NaOH, cold}} \text{CH}_3\text{CH(OH)CH}_2\text{CHO}.$$

The product is 3-hydroxybutanal: number from the aldehyde carbon, so the hydroxyl group is on carbon 3. Avoid heating the aldol product, since dehydration would give but-2-enal instead of the required hydroxy aldehyde.

Step 2: (a)(ii) Introduce a phenyl group and oxidise the secondary alcohol React benzaldehyde with phenylmagnesium bromide in dry ether, followed by acidic hydrolysis:

$$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{MgBr} \xrightarrow{\text{dry ether}} (\text{C}_6\text{H}_5)_2\text{CHOMgBr},$$

$$(\text{C}_6\text{H}_5)_2\text{CHOMgBr} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} (\text{C}_6\text{H}_5)_2\text{CHOH} + \text{Mg(OH)Br}.$$

The resulting diphenylmethanol is a secondary alcohol. Oxidise it with acidified potassium dichromate:

$$(\text{C}_6\text{H}_5)_2\text{CHOH} + [\text{O}] \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} (\text{C}_6\text{H}_5)_2\text{CO} + \text{H}_2\text{O}.$$

This forms benzophenone. Dry ether is essential during Grignard addition because water destroys the Grignard reagent.

Step 3: (b) Identify the alcohol, acid and ester Since alcohol C gives but-1-ene on dehydration and is oxidised to a carboxylic acid, it is the four-carbon primary alcohol butan-1-ol, $CH_3CH_2CH_2CH_2OH$. A secondary alcohol would yield a ketone on ordinary chromic acid oxidation, so butan-2-ol does not satisfy the oxidation clue. Oxidation of butan-1-ol gives butanoic acid B, $CH_3CH_2CH_2COOH$. A therefore consists of the butanoate group joined to an n-butyl group: it is butyl butanoate, $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$. Its formula is $C_8H_{16}O_2$, consistent with the given formula and ester hydrolysis.

Step 4: (b) Write the three identifying reactions Hydrolysis with dilute sulphuric acid, on heating, gives B and C:

$$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O \xrightarrow{\text{dil. } H_2SO_4,\ \text{heat}} CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH.$$

Chromic acid oxidises C to B:

$$CH_3CH_2CH_2CH_2OH + 2[O] \xrightarrow{H_2CrO_4} CH_3CH_2CH_2COOH + H_2O.$$

Dehydration of C gives the stated but-1-ene:

$$CH_3CH_2CH_2CH_2OH \xrightarrow[443\,K]{\text{conc. } H_2SO_4} CH_3CH_2CH{=}CH_2 + H_2O.$$

The carbon balance in hydrolysis is four carbons in each product, accounting for all eight carbons in A.

Step 5: Conclusion Ethanol gives 3-hydroxybutanal through ethanal and cold dilute-alkali aldol addition. Benzaldehyde gives benzophenone through phenylmagnesium bromide addition, hydrolysis and oxidation. In (b), A is butyl butanoate, B is butanoic acid and C is butan-1-ol.

Quick Tip to Solve: Use the oxidation clue before the ester formula: an alcohol that gives a carboxylic acid must be primary; combine the resulting acid and alcohol fragments to identify the ester.