1 Some main group elements are similar to transition elements as they are capable of showing different oxidation states.

(a) Fig. 1.1 shows a sketch of the nine successive ionisation energies of element **A**, a main group element.

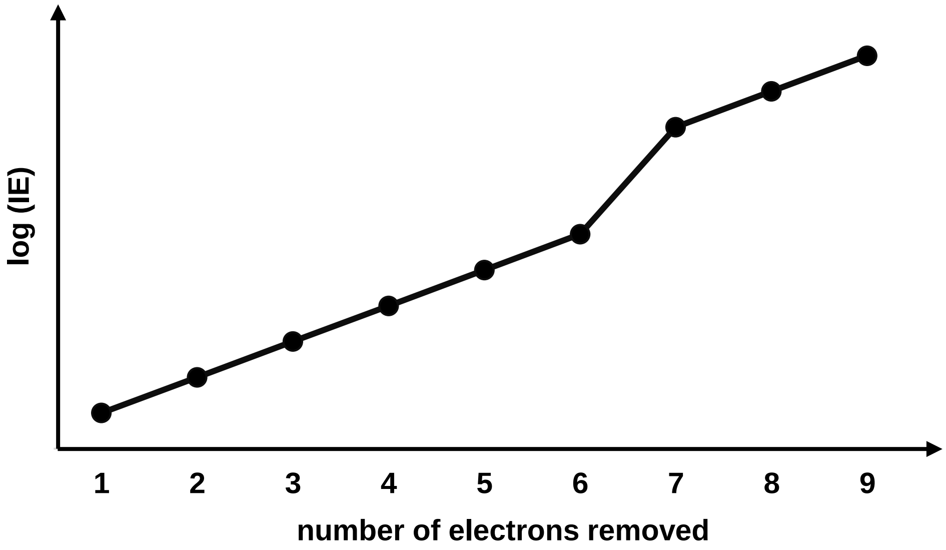


Fig. 1.1

(i) Write the equation for the third ionisation energy of element **A**.

A^{2+} (g) → A^{3+} (g) + e^- [1] for correct equation with state symbols [1]

Marker's Comments

- This question was generally well attempted, errors include balancing the electron wrongly, not remembering the definition of ionisation energy and not including the state symbols.

(ii) Explain the general trend in successive ionisation energy shown in the graph of Fig. 1.1.

There is a general increase in successive ionisation energy. This is due to **increasing amount of energy** required to remove successive electrons from an **increasingly positive ion** [1] due to an **increasing strength of electrostatic forces of attraction** between the **nucleus and valence electrons.** [1]

[2]

Marker's Comments

- Candidates need to understand the question was referring to the general trend of **successive** ionisation energies, not trend across the period.
- A significant number also tried to explain about the large increase between 6th and 7th IE, not realising that later part in (iii) was asking about similar concept.
- Some errors included not understanding that the nuclear charge did not increase (same number of protons) in A, and trying to explain with effective nuclear charge as an approach.
- Strong answers included the increasing positive ion that is formed and trying to remove an electron from this would require increasing energy.

(iii) Suggest, with reasoning, the group number of element **A** and state its identity, given that it belongs to Period 4.

The biggest increase between 6th and 7th ionisation energy is due to the fact the **6th electron** is **removed from the inner quantum shell** ✓ which is **closer to the nucleus.** Hence, there is **stronger electrostatic force of attraction** between **the 6th electron and nucleus** and **a lot more energy** ✓is required to remove it.

Element A belongs to Group 16 ✓ **and is selenium** ✓**.** [2]

4 ✓ [2]

2✓ [1]

Marker's Comments

- Common errors included not answering either the group number or identity of A. Candidates need to be more careful in their answering of questions and not miss out parts of the question requirements.
- Emphasis of this question was on the large increase between 6th and 7th IE which enable the determination of the group number.
- Candidates also need to be updated with writing down the correct Group Number of the Periodic Table, it is Group 16 and not Group 6.

Transition elements form complexes that are responsible for the colour of many gemstones such sapphires and rubies.

(b) Define the term *transition element*.

A transition element is a ***d*-block element that forms at least one stable ion with partially-filled *d* subshell.** **[1]** [1]

(c) In an isolated gas phase transition metal ion, the *d*-orbitals have the same energy. However, in the octahedral complex ion, $[Cr(H_2O)_6]^{3+}$, the d subshell is spilt into two energy levels.

(i) Complete the electronic configuration of Cr and Cr^{3+}.

Cr : $1s^2$ $2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Cr^{3+} : $1s^2$ $2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$ **[1] for both** [1]

Marker's Comments

- Candidates need to realise that there is additional stability for half-filled d-orbitals for Cr, hence electronic configuration should be $[Ar]3d^5 4s^1$ instead of $[Ar]3d^4 4s^2$.

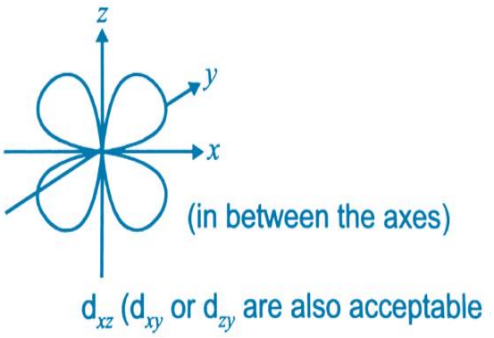
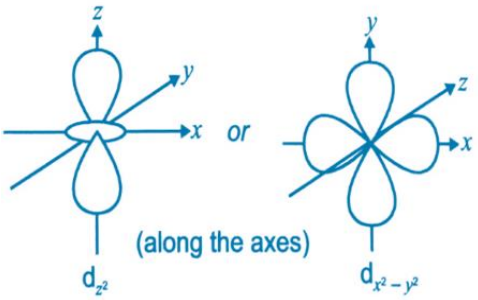
(ii) Explain why the splitting of *d*-orbitals occurs in the presence of ligands.

Electron pairs in *d* orbitals that are near / pointing towards lone pairs of the ligands are repelled to higher energy level. [1] OR different extent of repulsion towards the ligands OR words to that effect. [1]

Marker's Comments

- Emphasis of this question was about the different extent of repulsion between the electrons in d orbitals and lone pairs of electrons in ligands due to orientation of the ligands and orbitals.
- A significant number of candidates tried to answer the question by rephrasing the question without addressing the '**why**'.

(iii) Draw and name the shape of one of the *d* orbitals in the lower energy level and one of the *d* orbitals in the upper energy level for the octahedral complex ion. Indicate the axes labels clearly.

 ***lobes in between the axes***	 ***lobes along the axes***
Name of lower energy *d* orbital: **d_{xy}** **(d_{xz} OR d_{yz} are also acceptable)**	Name of upper energy *d* orbital: **d_{z^2} OR $d_{x^2-y^2}$** **correct shape + label [1]**

[2]

***correct shape + label* [1]**

Marker's Comments

- Quite a number of candidates did not obtain the marks for this bookwork question about the label and drawing of d orbitals. They need to realise the name of the d orbitals will need to be in sync with the axis's labels.

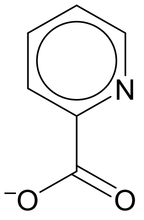
(iv) Cr^{3+} ions forms a complex that gives rise to the red colour of rubies. Explain how the colour arises.

When an electron in lower energy *d*-orbital moves to upper energy level, it absorbs light energy/ energy from visible spectrum/ a photon. [1] Since energy absorbed corresponds mainly to the green **region of the visible spectrum, the complex appears red (the complementary colour of the colour absorbed). [1]** [2]

Marker's Comments

- One major misconception is a significant portion of candidates mentioned that d-orbitals absorb energy and got promoted instead of electrons.

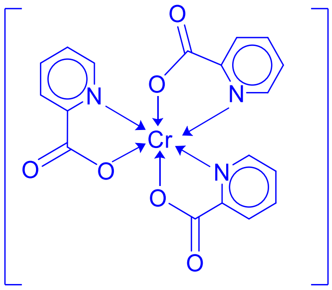
(d) Chromium(III) picolinate, $Cr(C_5H_4N(COO))_3$, another bright red complex, is used to treat Type 2 diabetes. Picolinate is bidentate and forms an octahedral complex ion with chromium(III). The nitrogen atom in the benzene ring of picolinate has a lone pair of electrons available for coordination.



picolinate ligand

Using the information provided, draw the octahedral structure of chromium(III) picolinate in the space below showing the coordinate bonds clearly.

[1]



[1]

[Total: 13]

Marker's Comments

- The lone pair of electrons on N (indicated in question stem) and the lone pair of electrons on the –O⁻ of the carboxylate anion are more available for coordination (dative bonding). Since picolinate ligand is bidentate, 3 moles of picolinate ligands are needed to form octahedral structure of chromium(III) picolinate.
- Candidates need to take note of the distribution of charges and be accurate in their presentation of their structures, showing the shape accurately.
- The coordinate bonds should also be reflected as arrows without the inclusion of the lone pair of electrons.

2(a) Magnesium oxide reacts reversibly with chlorine according to the following equation.

equation 2.1 $2MgO(s) + 2Cl_2(g) \rightleftharpoons 2MgCl_2(s) + O_2(g)$

Under certain conditions, a dynamic equilibrium is established.

(i) Explain what is meant by the term *dynamic equilibrium*.

Dynamic equilibrium is a state in a reversible reaction where the **rate of forward reaction** is **equal** to the **rate of reverse reaction**, with the **substances still reacting together** although the **concentrations of reactants and products remain constant / unchanged**. **[1]** [1]

Marker's Comments

- Candidates need to learn this standard definition well.
- Rate of forward reaction = rate of reverse reaction
- **Concentrations** of reactants and products remain **constant but may not be equal.**

(ii) At 1.00 × 10^5 Pa and 500 K, 70% of the initial amount of $Cl_2(g)$ has reacted with MgO.

Calculate the equilibrium constant, K_p for the reaction. [2]

$$K_p = \frac{\left(P_{O_2}\right)}{\left(P_{Cl_2}\right)^2}$$

Marker's Comments

- Candidates need to recognise for this question on K_p, only pressure of gases (O_2 and Cl_2) will be involved in the K_p expression.
- The total pressure at equilibrium is 1.00 × 10^5 Pa.

Let the initial amount of $Cl_2(g)$ be x mol.

	$2MgO(s)$ +	$2Cl_2(g)$ $\rightleftharpoons$	$2MgCl_2(s)$ +	$O_2(g)$
Initial amount / mol		x		0
Change in amount / mol		$-0.70x$		$+0.35x$
Equilibrium amount / mol		$0.30x$		$0.35x$
Mole fraction		$\frac{0.30x}{0.30x + 0.35x} = \frac{0.30}{0.65}$		$\frac{0.35x}{0.30x + 0.35x} = \frac{0.35}{0.65}$
Partial pressure / Pa		$\frac{0.30}{0.65} \times 1.00 \times 10^5$ **$= 4.615 \times 10^4$**		$\frac{0.35}{0.65} \times 1.00 \times 10^5$ **$= 5.385 \times 10^4$**

[1] for either mole fraction or partial pressure

$$K_p = \frac{\left(P_{O_2}\right)}{\left(P_{Cl_2}\right)^2} = \frac{\left(\frac{0.35}{0.65} \times 1.00 \times 10^5\right)}{\left(\frac{0.30}{0.65} \times 1.00 \times 10^5\right)^2}$$

= **2.53×10^{-5} Pa^{-1}** **[1] with units**

(iii) Predict and explain the effect of decreasing the volume of the system in equation 2.1 on the

- composition of reactants and products [2]

As pressure of system increases (due to decreasing volume), **equilibrium position of (1) shifts right to decrease number of moles of gas to decrease pressure.** **[1]** **The new equilibrium mixture contains more products and less reactants.** **[1]** **Amount of O_2 gas increases** while **amount of Cl_2 gas decreases.** The concentrations (i.e. density) of **solid MgO and $MgCl_2$** are essentially constant (and do not feature in the equilibrium constant).

Marker's Comments

- When pressure changes, candidates need to take note to relate their answers to no of mol of gases.
- When the equilibrium position shifts right leading to an increase in the amount of products and decrease in the amount of reactants, it does not necessarily mean that the amount of products will be more than the reactants and hence candidates should not be comparing the amount of products with the amount of reactants.

- equilibrium constant, K_p.

Volume changes (i.e. pressure change) has **no effect on K_p**. K_p is **only temperature dependent.** **[1]** [1]

Marker's Comments

- Question asks to predict and explain. Hence candidates need to provide a brief explanation that K_p is temperature dependent.

(b) Hard water is water that contains high concentrations of calcium and magnesium ions.

Temporary hard water consists of dissolved hydrogencarbonate (HCO_3^-) ions. Heating HCO_3^- causes it to decompose according to equation 2.2. The carbonate then forms an insoluble metal carbonate with one of the metal ions according to equation 2.3, which gives the characteristic white 'scales' found in kettles used to boil such water.

equation 2.2 $2HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + CO_2(g) + H_2O(l)$

equation 2.3 $M^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons MCO_3(s)$ where M = Ca or Mg

(i) With reference to the equations given above, explain why the hardness of temporary hard water can be reduced by boiling.

On heating HCO_3^-, CO_3^{2-} (aq) is formed as shown in equation 2.2. With an increase in $[CO_3^{2-}]$, the equilibrium position of equation 2.3 will shift right, which in turns decreases $[M^{2+}]$, and hence decreasing the hardness of water. **[1]**

Marker's Comments

- The hardness of water is dependent on the concentration of metal ions. Hence candidates need to make reference to the concentration of M^{2+} ions when they make use of the equations to answer.

The numerical value of the solubility products of some of the compounds involved in the processes in part **(b)** are shown in Table 2.1.

Table 2.1

Compound	Solubility product, K_{sp}, at 25 °C
$CaCO_3$	2.8×10^{-9}
$MgCO_3$	3.5×10^{-8}
$Ca(OH)_2$	5.5×10^{-6}
$Mg(OH)_2$	1.8×10^{-11}

(ii) Deduce whether calcium or magnesium ion is likely to be precipitated out first in equation 2.3.

Ca^{2+} ions are likely to be precipitated out first as $CaCO_3$ due to its **lower K_{sp} value / solubility** ($K_{sp}(CaCO_3) < K_{sp}(MgCO_3)$) **[1]** [1]

Marker's Comments

- Question asks for deduce, hence candidates need to give some brief explanation based on the K_{sp} value of the carbonates to deduce which ion is likely to be precipitated out first.

Hard water can be softened by raising the pH of the water to precipitate out some metal ions.

A sample of hard water contained equal concentrations of calcium and magnesium ions at 8.00×10^{-3} mol dm^{-3} each. Its pH was raised to 10.0 at 25 °C.

(iii) By considering the relevant ionic product, deduce which metal ion will be precipitated out.

pOH = 14.0 – 10.0 = 4.0

$[OH^-] = 10^{-4.0} = 1.0 \times 10^{-4}$

Ionic product of $M(OH)_2$ $= [M^{2+}][OH^-]^2$

$= (8.00 \times 10^{-3})(1.0 \times 10^{-4})^2$

$= \mathbf{8.00 \times 10^{-11}}$ where M = Ca or Mg

[1] ignore units

Ionic product of $Ca(OH)_2$ < $K_{sp}(Ca(OH)_2)$ while **ionic product of $Mg(OH)_2$ > $K_{sp}(Mg(OH)_2)$**, hence only **Mg^{2+}** is precipitated out as $Mg(OH)_2$. **[1]**

Marker's Comments

- This question was rather poorly attempted.
- Candidates need to relate the pH to the concentration of OH^- and substitute into the ionic product expression to compare with the respective K_{sp} values of the metal hydroxide.

(c) Phosphates from fertilizers used in agriculture could enter the water supply and combine with calcium ions present to form the sparingly soluble salt calcium phosphate, $Ca_3(PO_4)_2$. The value of K_{sp} for calcium phosphate is 1.0×10^{-26}.

(i) Write the K_{sp} expression and calculate the solubility, in mol dm^{-3}, of calcium phosphate. [2]

Let s be the solubility of $Ca_3(PO_4)_2$.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$\qquad\qquad 3s \qquad\qquad 2s$$

K_{sp} $= \underline{\mathbf{[Ca^{2+}]^3[PO_4^{3-}]^2}}$ **[1]**

1.0×10^{-26} $= (3s)^3(2s)^2$

$= 108\ s^5$

$\Rightarrow s = \underline{\mathbf{2.47 \times 10^{-6}}}$ mol dm^{-3} **[1] ignore units**

Marker's Comments

- There are 2 parts to this question, asking for the K_{sp} expression and the solubility value. Candidates need to take care to answer both parts and be careful with the manipulation of the terms in the equation.

(ii) Suggest why calcium phosphate is expected to be less soluble in phosphoric acid than it is in water.

Due to presence of common ion PO_4^{3-} , $[PO_4^{3-}]$ increases in solution.

$$\mathbf{Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

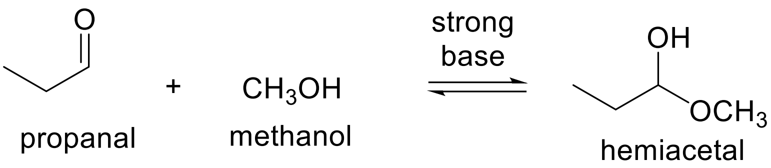
Equilibrium position shifts left to decrease $[PO_4^{3-}]$, hence **solubility of $Ca_3(PO_4)_2$ decreases.** **[1]** [1]

Marker's Comments

- This is a standard question on the decrease in solubility due to the presence of a common ion. Candidates need to write the equilibrium equation clearly when making reference to the shift in equilibrium position.

[Total: 13]

3(a) In the presence of a base catalyst, aldehyde can react with alcohol via nucleophilic addition to give hemiacetal. An example involving propanal and methanol is shown below.



This reaction occurs via a three-step mechanism.

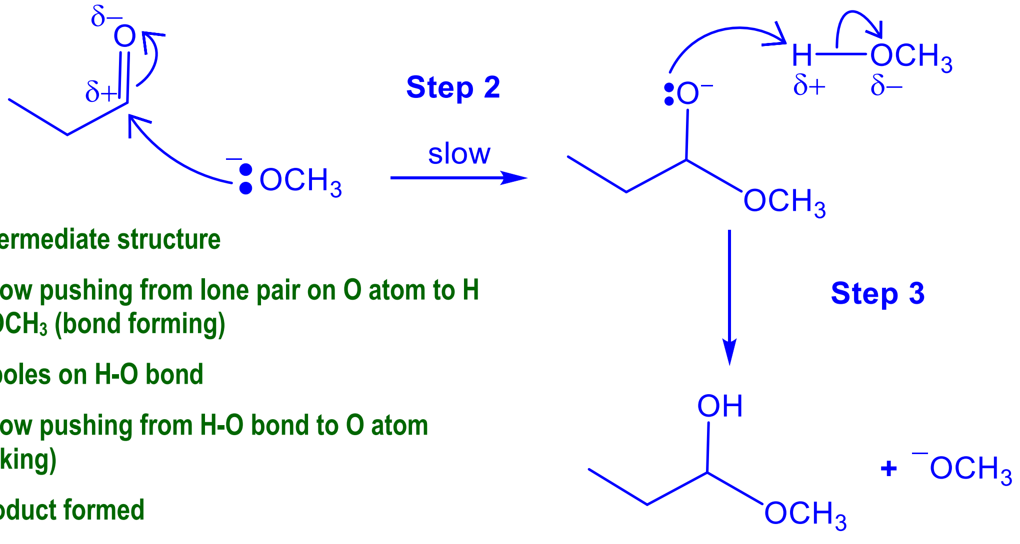
Step 1 The base removes a proton to form a methoxide anion, CH_3O^-.

Step 2 The methoxide anion undergoes nucleophilic addition with the carbonyl group generating an anionic intermediate, in a rate determining step.

Step 3 The anionic intermediate abstracts a proton from a CH_3OH molecule.

Draw the mechanism for steps 2 and 3 of the reaction between propanal and methanol. In your answer, you should show all relevant charges, dipoles, and lone pairs; and show the movement of electrons using curly arrows.

- ✓ Correct arrow pushing from lone pair on O atom of CH_3O^- to δ⁺ C atom (bond forming)
- ✓ Correct arrow pushing from bond to O atom (bond breaking)
- ✓ Correct dipoles on C=O bond
- ✓ Indicate slow step



- ✓ Correct intermediate structure
- ✓ Correct arrow pushing from lone pair on O atom to H atom of $HOCH_3$ (bond forming)
- ✓ Correct dipoles on H-O bond
- ✓ Correct arrow pushing from H-O bond to O atom (bond breaking)
- ✓ Correct product formed
- ✓ Balanced equation with CH_3O^-

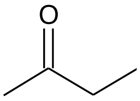
8 – 10 ✓ [3]
5 – 7 ✓ [2]
2 – 4 ✓ [1]

[3]

Marker's Comments

- Most candidates were able to interpret the information given and provided a good response to this question. Some candidates failed to account for the information of CH_3OH as the source of proton in Step 3.

(b) Butanone undergoes the same nucleophilic addition reaction with methanol.



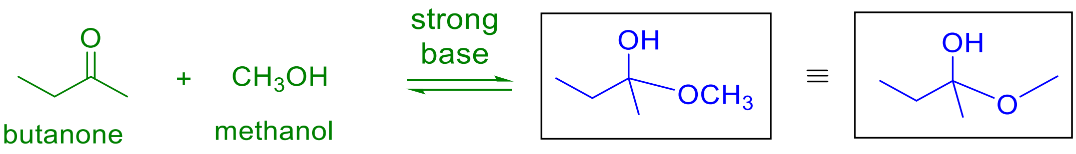
butanone

Observations were made about the reactions as shown in Table 3.1.

Table 3.1

	Reaction between propanal and methanol	Reaction between butanone and methanol
Relative rate of reaction	faster	slower
Optical activity of product	does not rotate plane polarised light	does not rotate plane polarised light

(i) Draw the structure of the product formed from the reaction between butanone and methanol.



[1] for correct structure

[1]

Marker's Comments

- Most candidates were able to apply the information given in the earlier part of question to deduce the structure of the product correctly. Some candidates omitted some H atoms in their responses especially for candidates who drew the displayed formula.

(ii) Explain the observations made about the two reactions in Table 3.1. Use the concepts of electronic and steric effects, and stereochemistry in your answer.

5 ✓ [3]
3 – 4 ✓ [2]
2 ✓ [1]

The ✓ **nucleophile** can **attack** the **trigonal planar** sp^2 hybridised electron-deficient **carbonyl carbon atom** of propanal and butanone ✓ **from top and bottom of the plane with equal probability.** This forms ✓ **equal amount of each (+) and (–) enantiomers** i.e. **a racemic mixture.**

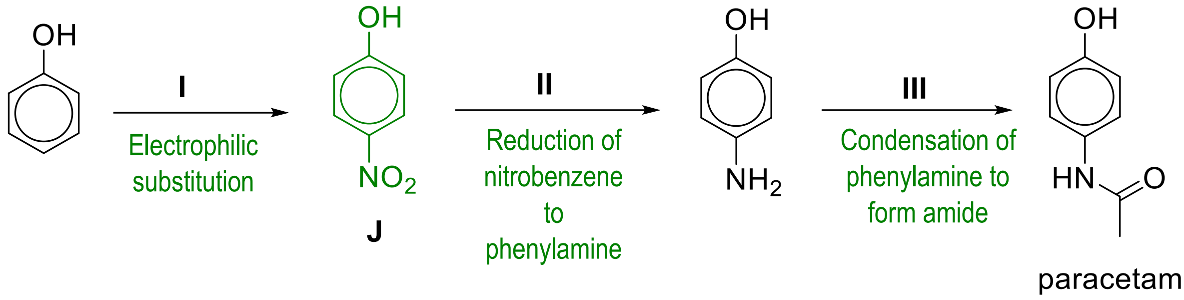
In **butanone**, the ✓ **two bulky R groups** provide **more steric hindrance** which makes it harder for the nucleophile to attack the carbonyl carbon atom.

In **butanone**, the ✓ **two electron-donating R groups** makes the **carbonyl carbon atom less electron deficient** and hence less susceptible to nucleophile attack. [3]

Marker's Comments

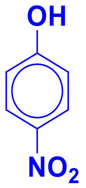
- Most candidates who did their bookwork well scored full credit for this question.
- Common mistakes:
  - Omitting the explanation for the electronic effect in their responses.
  - Some candidates had the misconception that the electronic effect is to account for the stability of the anionic intermediate.
  - Wrong "trigonal planar structure" identified – some candidates **wrongly** used "carbocation" or "sp^3 hybridised anionic intermediate"

(c) Paracetamol is an over-the-counter medication used to treat pain and fever. It can be prepared from phenol via a three-step synthesis as shown below.



(i) Suggest the structure of compound **J**. [1]

J:



(ii) Suggest the reagents and conditions for steps **II** and **III**.

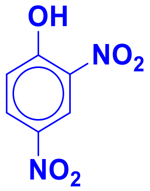
step **II**: **Sn,** excess **conc HC*l*, heat; followed by** controlled addition of **NaOH (aq)** [1]

step **III**: anhydrous **CH_3COCl**, (acyl chloride) r.t.p. [1] [2]

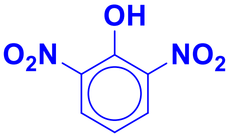
Marker's Comments

- This question was generally well attempted. Most candidates were able to get the correct structure of **J.**
- Common mistakes:
  - For **Step II** - Omitting heat in the conditions or getting the sequence of heating wrong. Writing conc HC*l* (aq) which is contradictory as aqueous acid is not concentrated.
  - For **Step III** - Using acyl chloride in the (aq) state or with (aq) reagents. Acyl chloride will hydrolyse in an aqueous medium. **OR** Using carboxylic acid will not work as phenylamine (amines in general will only react with acyl chloride to form an amide. Several candidates only stated "acyl chloride", which is a functional group and not a specific reactant.

(iii) Identify one possible organic side product with the molecular formula, $C_6H_4N_2O_5$, formed in step **I**. Suggest the reaction conditions to minimise its formation.



OR



[1]

Use excess phenol OR dilute HNO_3(aq) at low temperature / r.t.p, to minimise (multiple) di-substitution. [1] Reject conc. HNO_3 [2]

Marker's Comments

- This question was generally well attempted. Most candidates were able to get the correct structure of side product and proposed relevant ways to minimise the formation of the di-substituted product.

(d) Amino acids are soluble in both dilute acids and dilute alkalis due to the ability to exist as zwitterions.

(i) Explain what is meant by the term zwitterion.

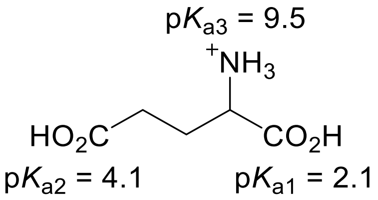
Zwitterion is an **electrically neutral dipolar ion.** **[1]**

[1]

Marker's Comments

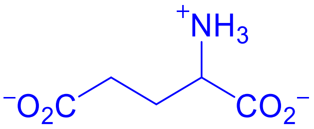
- This question was generally well attempted.
- Electrically neutral means no net charge.
- A dipolar ion means an ion that is both positively and negatively charged.

(ii) There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.



Use the given pK_a values to suggest

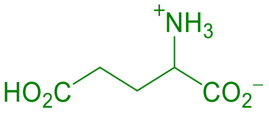
1. the structure of the major species present in a solution of glutamic acid at pH 6.0, and



[1]

2. a pH at which the predominant species of glutamic acid is a zwitterion.

pH = 3 (any pH value between pH 2.1 and 4.1) **[1]**

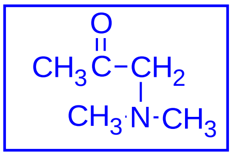


[2]

Marker's Comments

- This question was generally well attempted.

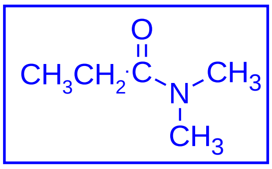
(e) Compound **K** and **L** are isomers.



$CH_3COCH_2N(CH_3)_2$

Compound **K**

$CH_3CH_2CON(CH_3)_2$



Compound **L**

Which of the isomers is a stronger base? Explain.

✓ **Compound K** *(tertiary amine)* is the stronger base.

In compound **K** *(tertiary amine)*, the ✓ **electron donating alkyl groups increases the electron density of the lone pair of electrons on N atom**.

Hence, the ✓ **lone pair of electrons on N atom is more available to accept a proton.**

In compound **L ,** *(amide)* the ✓ **lone pair of electrons on N atom** is **delocalised with adjacent C=O**, **decreasing the electron density of the lone pair on N atom,** making the ✓ **lone pair less available to accept a proton.** Hence, amide is neutral. [2]

4 – 5 ✓ [2]

2 – 3 ✓ [1]

Marker's Comments

- This question was generally well attempted.
- Some candidates failed to interpret the given structures correctly and did not identify that they were comparing between an amide and a tertiary amine.
- Some candidates did not explain the effect on the electron density on the N atom in their responses.

[Total: 17]

4 Two fatal explosions occurred at a hazardous chemical storage facility in Tianjin, China, almost a decade ago in August 2015. The chain of events which happened on that day is described below.

Stage 1: Fire

An overheated container of dry nitrocellulose was reported to cause the initial fire. Firefighters arrived at the scene to douse the flames with water.

Stage 2: Reaction between water and calcium carbide

Without prior knowledge of calcium carbide, $CaC_2(s)$, also being stored in the facility, the firefighters continued spraying water on the chemical which quickly fizzled and released an explosive gas, ethyne, $C_2H_2(g)$.

equation 4.1 $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

Stage 3: First explosion

After the ethyne had mixed sufficiently with the surrounding air, one part of this explosive gas mixture was ignited by the pre-existing flames, causing the first explosion.

equation 4.2 $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g)$

Stage 4: Second explosion

The heat from the first explosion initiated a runaway decomposition of about 800 tonnes (1 tonne = 1000 kg) of ammonium nitrate, $NH_4NO_3(s)$, which was stored nearby. This decomposition reaction produced a large quantity of gases under high temperatures and pressures. The rapid expansion of the gases outwards destroyed almost everything in their path.

equation 4.3 $4NH_4NO_3(s) \rightarrow 3N_2(g) + 2NO_2(g) + 8H_2O(g)$

The aftermath

This was one of the worst industrial disasters in China that caused many deaths and injuries due to improper storage of explosive chemicals.

(a) The carbon atoms in CaC_2 and C_2H_2 have similar hybridisation and hence they have similar bonding between the two carbon atoms.

(i) State the hybridisation of the carbon atoms in CaC_2 and C_2H_2.

sp **[1]** .... [1]

Marker's Comments

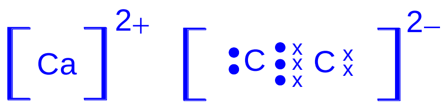
- Most candidates could recognise the C≡C triple bond in both structures.

(ii) Using structure and bonding, explain why CaC_2 is a solid at room temperature and pressure while C_2H_2 is a gas.

CaC_2 has a **giant ionic lattice structure**✓ where **strong ionic bonds between oppositely charged ions are broken**✓, while C_2H_2 has a **simple molecular structure**✓ where **weak intermolecular instantaneous dipole - induced dipole attractions are easily broken.**✓ **[2] for 4 ✓; [1] for 2–3 ✓** [2]

Marker's Comments
- This part was well answered.
- Common mistakes were missing structures, missing "between oppositely charged ions", etc.
- Major mistakes were NOT recognizing CaC_2 as giant ionic structure despite the question making mention of it.

(iii) The anion in calcium carbide has an approximate M_r of 24 and the cation has an approximate A_r of 40. Draw a dot-and-cross diagram to show the type of bonding present within a formula unit of calcium carbide. [1]



Marker's Comments
- Candidates should practice drawing dot-cross diagram with alternate dots and crosses.
- Despite very clear hints from the question, some candidates still drew carbide as C^- instead of C_2^{2-}

(b) The reaction of calcium carbide with water is exothermic and spontaneous.

(i) Using the data in Table 4.1, calculate the enthalpy change of reaction for equation 4.1. [2]

Table 4.1

	enthalpy change / kJ mol^{-1}
$\Delta H_f^\ominus$ (CaC_2(s))	–59.0
$\Delta H_f^\ominus$ (H_2O(l))	–285.8
$\Delta H_f^\ominus$ ($Ca(OH)_2$(s))	–985.2
$\Delta H_f^\ominus$ (C_2H_2(g))	+226.6

equation 4.1 $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

$\Delta H_r^\ominus$ (equation 4.1) $= \Sigma\Delta H_f^\ominus \text{ (products)} - \Sigma\Delta H_f^\ominus \text{ (reactants)}$

$= +226.6 - 985.2 - (-59.0 - 2 \times 285.8)$ **[1]**

$=$ **$\underline{-128 \text{ kJ mol}^{-1}}$** **[1]**

Marker's Comments
- This part was well answered by most candidates.
- Quite a few made computational mistakes (i.e. correct working, but wrong final answer) which was careless and unnecessary.

accept energy cycle method

(ii) Explain why the reaction in equation 4.1 is spontaneous at all temperatures.

ΔS is positive as the **number of moles of gases increases from 0 to 1.** ✓

$-T\Delta S$ is therefore **negative**.

Since **ΔH** and **$-T\Delta S$** are **negative** $\Rightarrow$ **$\Delta G < 0$ (–ve)** for **all temperatures.** ✓

The reaction is spontaneous at all temperatures. **2 ✓ for [1]** [1]

Marker's Comments

- This part was well answered.
- Those who did not score were those who did not explain why ΔS is positive using eqn. 4.1.

(c) The first explosion was due to the combustion of ethyne, which is given in equation 4.2.

equation 4.2 $$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g)$$

(i) Using bond energy values from the *Data Booklet*, show that the enthalpy change of combustion of ethyne is -1240 kJ mol^{-1}. [2]

equation 4.2 $$\mathbf{H{-}C{\equiv}C{-}H + \frac{5}{2}\,O{=}O \rightarrow 2\,O{=}C{=}O + H{-}O{-}H}$$

Bonds broken	**Bonds formed**
2 BE(C–H)	4 BE(C=O)
BE (C≡C)	2 BE(O–H)
$\frac{5}{2}$ BE(O=O)	

$$\Delta H_c^{\ominus} = [2\text{ BE(C–H)} + \text{BE (C≡C)} + \frac{5}{2}\text{ BE(O=O)}] - [4\text{ BE(C=O)} + 2\text{ BE(O–H)}]$$

$$\Delta H_c^{\ominus} = [2 \times (410) + (840) + \frac{5}{2} \times (496)]\ \textbf{[1]} - [4 \times (805) + 2 \times (460)]\ \textbf{[1]}$$

$$= -1240 \text{ kJ mol}^{-1}\ \textbf{(shown)}$$

Marker's Comments

- Many careless mistakes were made in this question, for e.g. not using the correct stoichiometry, using 740 kJ mol^{-1} instead of 805, which is for C=O bond CO_2.
- The more serious mistakes were those who did not use the relationship of BERP to calculate.

(ii) Calculate the mass of ethyne needed to be completely burnt to raise the temperature of 1 kg of water from 30 °C to its boiling point, assuming 80% efficiency. [2]

M_r of ethyne (C_2H_2) = 26.0

Energy absorbed $= m \times c \times \Delta T$

$= 1000 \times 4.18 \times (100 - 30)$

$= \mathbf{292.6 \times 10^3\ J}$ **[1]**

$\Delta H_c^{\ominus} \times n\text{ (ethyne)} \times 80\% = 292.6 \times 10^3$

$$1240 \times 10^3 \times \frac{m}{26.0} \times \frac{80}{100} = 292.6 \times 10^3$$

m = **7.67 g** **[1]**

Marker's Comments

- Despite many practices, some candidates still made the mistakes of:
  - Mixing up **mass of water** with **mass of compound combusted**
  - Adding 273 K to ΔT
  - Not knowing how to apply the 80% efficiency
  - Wrong units conversion

(d) The second explosion caused by the decomposition of ammonium nitrate created an orange-brown fireball larger than the first one.

(i) Suggest a reason why this second explosion was more detrimental than the first.

- It produced **NO$_2$ which is a harmful gas.**
- The **expansion of gas was greater** as it **gave out more moles of gases**. [1]
- The **amount of heat produced was more exothermic**.

[1] any of the reasons

Marker's Comments

- Many reasonable answers were accepted except for the suggestion that 800 tonne of NH_4NO_3 was a lot, even though the amount of CaC_2 was not given. Hence there was no way to compare which compound were in greater quantity.

(ii) Calculate the total volume of gases produced, in m^3, when all the ammonium nitrate decomposed at 1000 °C and 1 atm. Hence, show that the diameter of the fireball is 186 m, assuming that the gases occupy a sphere. [3]

[Volume of sphere = $\frac{4}{3}\pi r^3$; where r = radius; diameter = 2r]

Amount of NH_4NO_3 $= \dfrac{800 \times 10^3 \times 10^3}{80} = 1.00 \times 10^7$ mol

equation 4.3 $4NH_4NO_3(s) \rightarrow 3N_2(g) + 2NO_2(g) + 8H_2O(g)$

$4NH_4NO_3 \equiv 13$ vol of gases

Total amount of gas produced $= \dfrac{13}{4} \times 1.00 \times 10^7 = \mathbf{3.25 \times 10^7}$ **mol [1]**

Using pV = nRT,

$$V = \frac{nRT}{P} = \frac{(3.25 \times 10^7) \times (8.31) \times (1000 + 273)}{101\,325} = \underline{\mathbf{3.39 \times 10^6\ m^3}}\ \textbf{[1]}$$

$$\text{Diameter of fireball} = \sqrt[3]{\frac{3.39 \times 10^6}{\frac{4}{3}\pi}} \times 2 = \underline{\mathbf{186\ m}}\ \textbf{[1]}$$

Marker's Comments

- This question was not well answered.
- Most common mistake was the failure to get the total amount of gases produced using the mole ratio $4NH_4NO_3 \equiv 13$ vol of gases.

(iii) The diameter of the fireball was measured to be about 180 m, which was smaller than the calculated value in **(d)(ii)**. Suggest a reason why this was so.

The calculation was made based on the **assumption that gases behaved ideally**. However, there is **significant intermolecular instantaneous dipole-induced dipole attraction** **[1]**, bringing the molecules closer together, making the volume smaller. [1]

[Total: 16]

Marker's Comments

- Only reasons pertaining to the ideal gas assumption were accepted as the discrepancy was a result of the calculation using PV=nRT.
- The volume of particles explanation was not accepted as it would have caused the actual volume to be larger than the calculated one.

5(a) The use of *Data Booklet* is relevant to this question.

The materials used for filling dental cavities have evolved significantly over the centuries. French dentists were among the first to innovate by mixing mercury with other metals to create a material that could be used to fill cavities effectively.

About a hundred years ago, a common filling material was copper amalgam, comprising roughly 30% copper and 70% mercury. However, this copper amalgam proved to be unstable and corroded over time. The copper in the amalgam oxidised while oxygen was reduced, leading to the generation of Cu^{2+} ions, which caused teeth to develop a stain.

(i) Construct the overall equation for the oxidation of copper by oxygen in the air in an acidic medium.

Oxidation: $Cu \rightarrow Cu^{2+} + 2e$ **Reduction:** $O_2 + 4H^+ + 4e \rightarrow 2H_2O$

Overall: $\underline{\mathbf{2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O}}$ **[1]** [1]

Marker's Comments

- Most candidates provided the correct equation, but some failed to note the acidic conditions given or did not know which equation to reference in the Data Booklet.

(ii) Calculate the standard cell potential, $E^{\ominus}_{cell}$, for this reaction. [1]

$Cu^{2+} + 2e \rightleftharpoons \boxed{Cu}$ $E^{\ominus} = +0.34\ V$ $E^{\ominus}_{oxid}$

$\boxed{O_2} + 4H^+ + 4e \rightleftharpoons 2H_2O$ $E^{\ominus} = +1.23\ V$ $E^{\ominus}_{red}$

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{oxid} = +1.23 - 0.34$$

$$= \underline{+0.89\ V}$$ **[1]**

Marker's Comments

- While most students arrived at the correct answer. However, many forgot to include the positive sign and units in their answers.

(iii) Given that $E^{\ominus}_{cell} = \frac{RT}{nF} \ln K_c$, determine the K_c value for the corrosion of the copper amalgam. [1]

$$E^{\ominus}_{cell} = \frac{RT}{nF} \ln K_c$$

$$\ln K_c = \frac{0.89 \times 4 \times 96500}{8.31 \times 298} = 138.7$$

$K_c = \underline{\mathbf{1.77 \times 10^{60}}}$ **[1]**

Marker's Comments

- Many candidates did not realise that the number of electrons involved depends on the equation they provided in part (i), and that the temperature for $E^{\ominus}$ is 298 K (this information is on page 2 of the Data Booklet).

In contrast, modern dental amalgams are composed of a mixture of silver, tin, and mercury. This amalgam contains three distinct solid layers: Ag_2Hg_3, Ag_3Sn, and Sn_8Hg.

Ag_3Sn, and Sn_8Hg layers each have their specific reduction potentials.

	$E^\ominus$
Sn^{2+} / Ag_3Sn	– 0.05 V
Sn^{2+}/ Sn_8Hg	– 0.13 V

(iv) Suggest and explain which of these layers is more likely to be corroded by oxygen.

Sn_8Hg phase as **$E^\ominus$ Sn^{2+}/ Sn_8Hg is the most negative** among the given phases, indicating **a higher tendency to be oxidised**. **[1]** [1]

Marker's Comments

- Although it was generally well attempted, it was surprising to see candidates using vague terms like "lower" or "smaller" to describe the $E^\ominus$ values. Candidates should also avoid using "it" as a vague reference and instead be specific in their explanations.

The electrochemical properties of dental amalgams can cause discomfort in some unexpected situations. For instance, if a person accidentally bites down on a piece of aluminum foil used in candy wrappers and it comes into contact with a dental filling, an electrochemical cell is created in the mouth. This "cell" generates a small electric current that can result in a sharp, sudden pain. In this electrochemical reaction, the Sn^{2+} ions formed from the amalgam reacts with the aluminum and this leads to the formation of tin metal.

(v) Write the overall equation for the electrochemical reaction between the Sn^{2+} ions in the amalgam and aluminium.

$2Al + 3Sn^{2+} \rightarrow 2Al^{3+} + 3Sn$ **[1]** [1]

Small pieces of gold leaf can be used to decorate luxurious desserts. Unlike aluminium, gold does not induce pain when bitten.

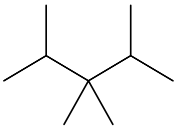
(vi) Suggest why biting on a piece of gold metal does not cause the pain that aluminium foil does.

Gold is an inert / noble metal **OR** **has a very positive $E^\ominus$ value**; **resistant to oxidation** **OR** **Overall $E^\ominus_{cell}$ is negative** and hence it is not a spontaneous reaction, so there is no current flow. **[1]** [1]

Marker's Comments

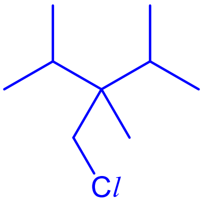
- Some candidates incorrectly stated that gold is Ag when it is Au, and they should be aware that gold is a good conductor of electricity.

(b) Scientists are studying 2,3,3,4-tetramethylpentane, which has a molecular formula of C_9H_{20}. During the investigation, they study the free radical substitution chlorination of this alkane to understand the distribution of chlorinated products.

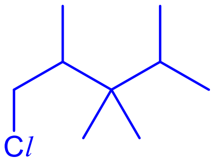


2,3,3,4-tetramethylpentane

(i) Draw the structures for all possible monochlorinated isomers of 2,3,3,4-tetramethylpentane. [2]



A



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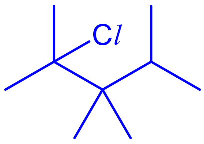


C

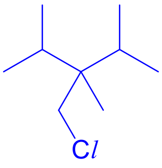
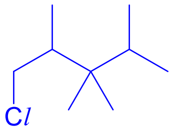
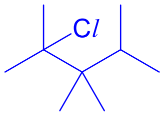
Any 2 correct structures for **[1]**

All 3 correct structures for **[2]**

(ii) It is found by experiment that during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates as shown in Table 5.1.

Reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	4
$R_3CH \rightarrow R_3CCl$	5

Calculate the expected relative ratio of the monochlorinated isomers produced from the chlorination of 2,3,3,4-tetramethylpentane, using the information in Table 5.1 and the number of hydrogen atoms of each (primary, secondary or tertiary) within the molecule. [1]

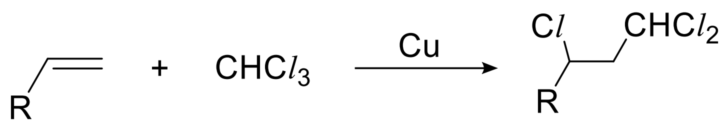
	 C*l* **A**	 C*l* **B**	 C*l* **C**
Type and number of H atoms	primary , 6H	primary, 12H	tertiary, 2H
Ratio	6 x 1 = 6	12 x 1 = 12	2 x 5 = 10

Simplest ratio = **3 : 6 : 5** **[1]**

Marker's Comments

- Many candidates did not recognise that the molecule provided was symmetrical, with three possible positions for mono-chlorinated substitution (two primary and one tertiary). Some also missed the fact that the middle carbon atom lacks hydrogen. The relative ratio in the substitution reaction depends on two factors: the number of available hydrogen atoms in the compound and the relative rate of reaction.
- Some candidates are unfamiliar with skeletal structures and consequently drew erroneous molecules.

(c) The Kharasch addition is a copper-catalysed free radical addition reaction where compounds such as excess $CHCl_3$ are added to terminal alkenes.

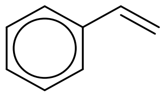


The reaction proceeds via the following steps.

- The initiation step involves the formation of a dichloromethyl free radical (•$CHCl_2$) from $CHCl_3$ by the abstraction of the chlorine atom.
- The first propagation step involves •$CHCl_2$ adding to a terminal alkene molecule to form a free radical intermediate. The relative stabilities of free radical intermediates are similar to the relative stabilities of carbocations.
- In the second propagation step, the free radical intermediate formed in the step 2 reacts with **excess** $CHCl_3$ to form the final product and regenerate •$CHCl_2$.

(i) Write equations for the first and second propagation steps in this reaction between •$CHCl_2$ and styrene. (curly arrows are not required) In your answer, show clearly the structure of the free radical intermediate that is formed in the first propagation step. [2]

You can represent styrene as Ph–CH=CH_2 in your drawing.



= $PhCH=CH_2$

stryene

First propagation step:

Ph–CH=CH_2 + **•$CHCl_2$** → Ph–CH•CH_2**$CHCl_2$** (free radical intermediate) **[1]**

Second propagation:

Ph–CH•CH_2**$CHCl_2$** + **$CHCl_3$** → Ph–CH(**Cl**)CH_2**$CHCl_2$** + **•$CHCl_2$** **[1]**

In the above reaction, more than one possible free radical intermediate can be generated. Explain why one free radical intermediate is likely to be formed in greater proportion. [1]

The likely free radical intermediate formed is a **secondary radical which is more stable than a primary radical due to two electron–donating alkyl groups** adjacent to the carbon atom carrying the radical. **[1]** **OR** **the lone electron can delocalise into the benzene ring**, **stabilising** **[1]** the free radical intermediate.

Marker's Comments

- Overall, this question was poorly answered, with many candidates relied on their knowledge of free radical substitution, even though the mechanism is free radical addition (this is the Kharasch Addition, not substitution).

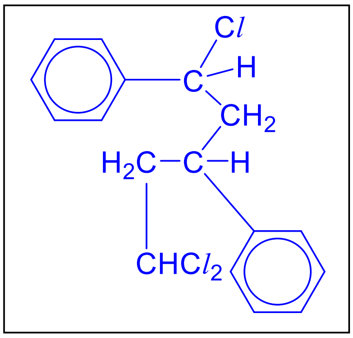
- Despite the clue provided, candidates failed to appreciate that the stability of the radical formed is similar to that of carbocations. The preferred explanation involves delocalisation of the electron (not a lone pair, as there is only one electron) into the adjacent benzene ring, increasing the stability of the secondary radical. Candidates should also note that alkyl (R) groups are electron-donating, which further stabilises the radical. Some candidates wrongly referred to charges being dispersed when the radical is charge-neutral.

- Candidates struggled with understanding the requirements of the question. They are reminded to label their molecules clearly, so the examiners know which structures they are referring to.

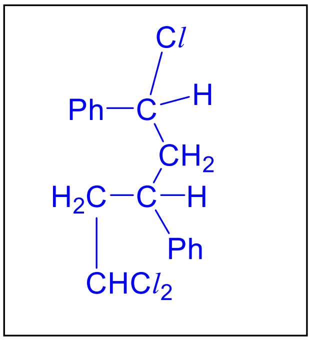
If excess styrene is used, the free radical intermediate formed in the first propagation step will react with styrene to generate another radical of larger molecular mass.

(ii) Compound **B** with a molecular formula of $C_{17}H_{17}Cl_3$ is formed in a reaction that involves excess styrene reacting with $CHCl_3$ in 2:1 mole ratio.

Suggest the structure of compound **B**. [1]



OR



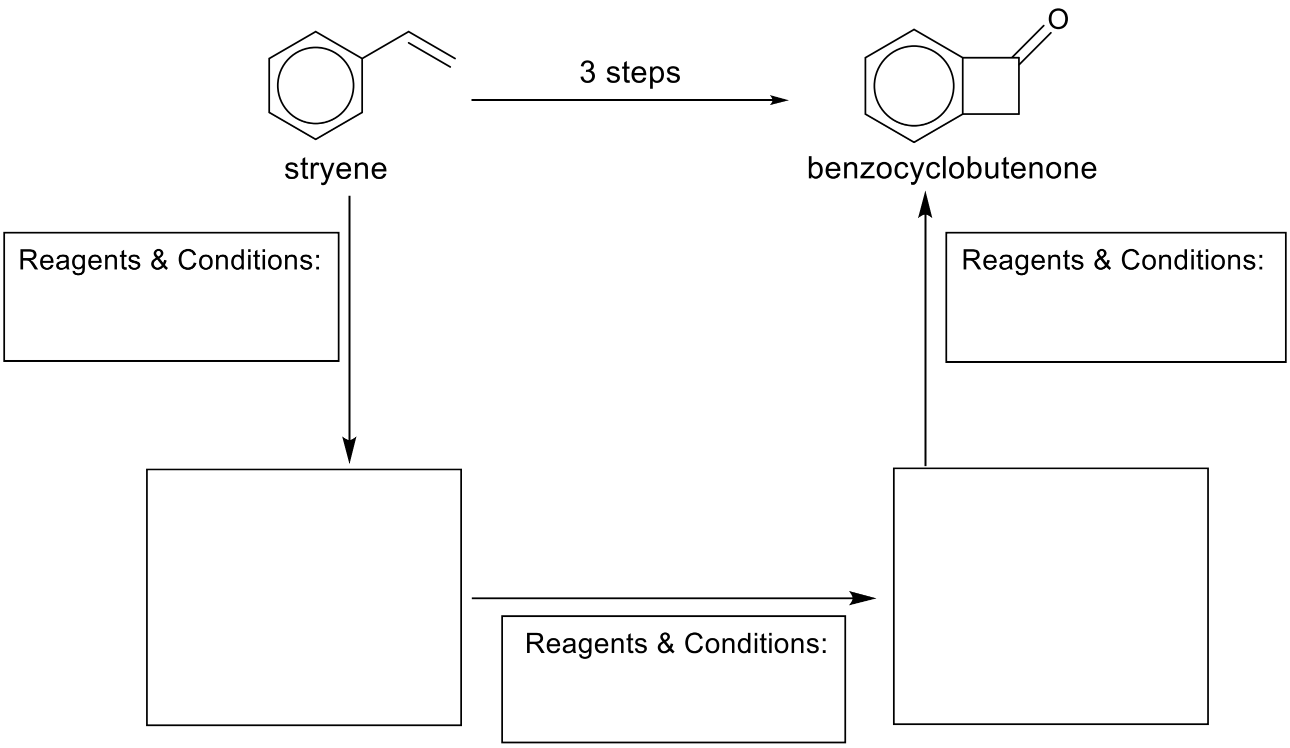
[1]

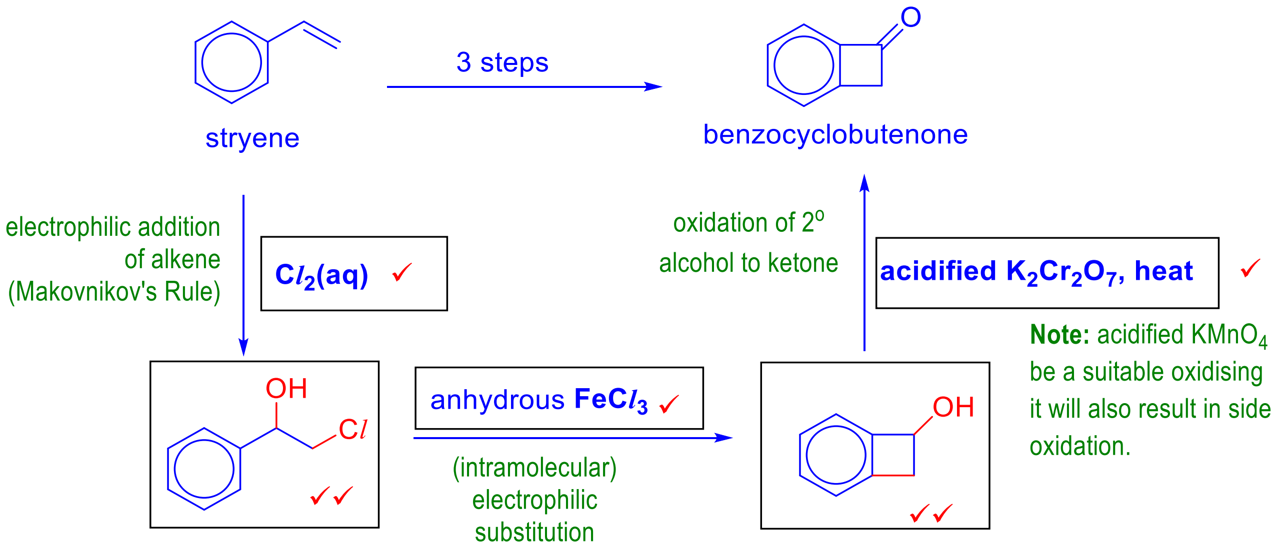
Marker's Comments

- Many candidates did not use the information provided to answer the question correctly. The question requires candidates to recognise that the more stable radical attacks another molecule of styrene to form a larger radical, and that the preferred attack position depends on the stability of the resulting radical.

(d) Benzocyclobutenone can be synthesised from styrene in three steps.

Suggest reagents and conditions for each step. Draw the structures of the intermediate compounds. [3]





Note: acidified $KMnO_4$ will not be a suitable oxidising agent as it will also result in side-chain oxidation.

Steps 2 & 3 are interchangeable.

[3] for 5 – 7 ✓
[2] for 3 – 4 ✓
[1] for 1 – 2 ✓

[Total: 16]

Marker's Comments

To approach this question correctly, students should:

- Recognise that the number of carbon atoms remains constant throughout the reaction.
- Work backward from the product to identify the starting material.
- Consider the possible reactions of alkenes (EA) and benzene (ES).
- Be mindful of the choice of oxidising agent – for example, acidified $KMnO_4$ should not be used, as it may trigger side-chain oxidation.