# 2022 Y6 H2 Chemistry Preliminary Exam Paper 3 – Suggested Solutions

## Section A

**1(a)(i)**

$$[CO_3^{2-}] = \frac{0.010 \times \frac{20}{1000}}{\frac{20+20}{1000}} = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$$

As maximum amount of AgC*l* have been precipitated without precipitating $Ag_2CO_3$, the solution is saturated with $Ag_2CO_3$. Hence,

ionic product = $K_{sp}(Ag_2CO_3)$
$[Ag^+]^2(5.00 \times 10^{-3}) = 8.1 \times 10^{-12}$
$[Ag^+] = 4.025 \times 10^{-5}$ mol dm$^{-3}$

As the solution is also saturated with AgC*l*,
$[Ag^+][Cl^-]_{remaining} = (4.025 \times 10^{-5})[Cl^-]_{remaining} = 2.0 \times 10^{-10}$
$[Cl^-]_{remaining} = \underline{4.97 \times 10^{-6} \text{ mol dm}^{-3}}$

**Comments:**
- Instead of using the concentration of $CO_3^{2-}$, several students incorrectly substituted the amount/number of moles of $CO_3^{2-}$ into the $K_{sp}$ expression.
- A handful of students did not consider the dilution of $CO_3^{2-}$ upon the mixing of the two solution, KC*l*(aq) and $Na_2CO_3$(aq).
- Some students attempted to calculate the solubility of $Ag_2CO_3$ in water, without realising that there was already $CO_3^{2-}$ present before the addition of $AgNO_3$.

**1(a)(ii)**

$$\text{Initial } [Cl^-] \text{ in mixture} = \frac{0.010 \times \frac{20}{1000}}{\frac{20+20}{1000}} = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$$

Percentage of C*l*$^-$ precipitated

$$= \frac{(5.00 \times 10^{-3}) - (4.97 \times 10^{-6})}{5.00 \times 10^{-3}} \times 100\%$$

= <u>99.9%</u>

This is <u>an effective</u> method.

**Comments:**
- Several students erroneously subtracted the concentration of C*l*$^-$ remaining from the amount of C*l*$^-$ present initially.

**1(b)(i)** Co-ordination number is the number of nearest neighbouring ions that surrounds an ion of opposite charge.

**Comments:**

- Students are advised to read the question carefully. The question requires students to define the term co-ordination number when used to refer to a crystal lattice. For the crystal lattices given in this question, the bonds formed are ionic in nature (rather than dative covalent, which are present in transition metal complexes).
- Weaker responses referred to the number of ionic bonds that an ion forms with other oppositely charged ions. Students should note that ionic bonds are non-directional (i.e. ionic bonds can also be formed between oppositely charged ions that are not in close vicinity).

**1(b)(ii)** As the $Ba^{2+}$ ion is larger than the $Ca^{2+}$ ion, the $Ba^{2+}$ ion is able to accommodate a greater number of chloride ions surrounding it.

**Comments:**

- Several students have the misconception that the larger $Ba^{2+}$ ion is less sterically hindered.
- A handful of students wrongly concluded that the lower charge density of $Ba^{2+}$ allowed for a larger coordination number.

**1(b)(iii)** The ions in $CaCl_2$ are less tightly packed in the lattice structure. Hence, less energy is required to overcome the weaker electrostatic forces of attraction between $Ca^{2+}$ and $Cl^-$ ions.

OR

Due to its smaller size/radius, $Ca^{2+}$ has a higher charge density and polarising power than $Ba^{2+}$. As such, $CaCl_2$ has a greater covalent character than $BaCl_2$, resulting in an unexpectedly lower melting point than that of $BaCl_2$.

**Comments:**

- Many students focused on explaining why the lattice energy of $CaCl_2$ is expected to be more exothermic than that of $BaCl_2$, rather than why the melting point of $CaCl_2$ is lower.

**1(c)(i)** As the process occurs readily (or is spontaneous), $\Delta G$ is negative. Since there is a decrease in the number of ways the water particles can be arranged, $\Delta S$ is negative.

$\Delta G = \Delta H - T\Delta S.$ Since $-T\Delta S$ is positive, $\Delta H_1$ must be negative.

**Comments:**

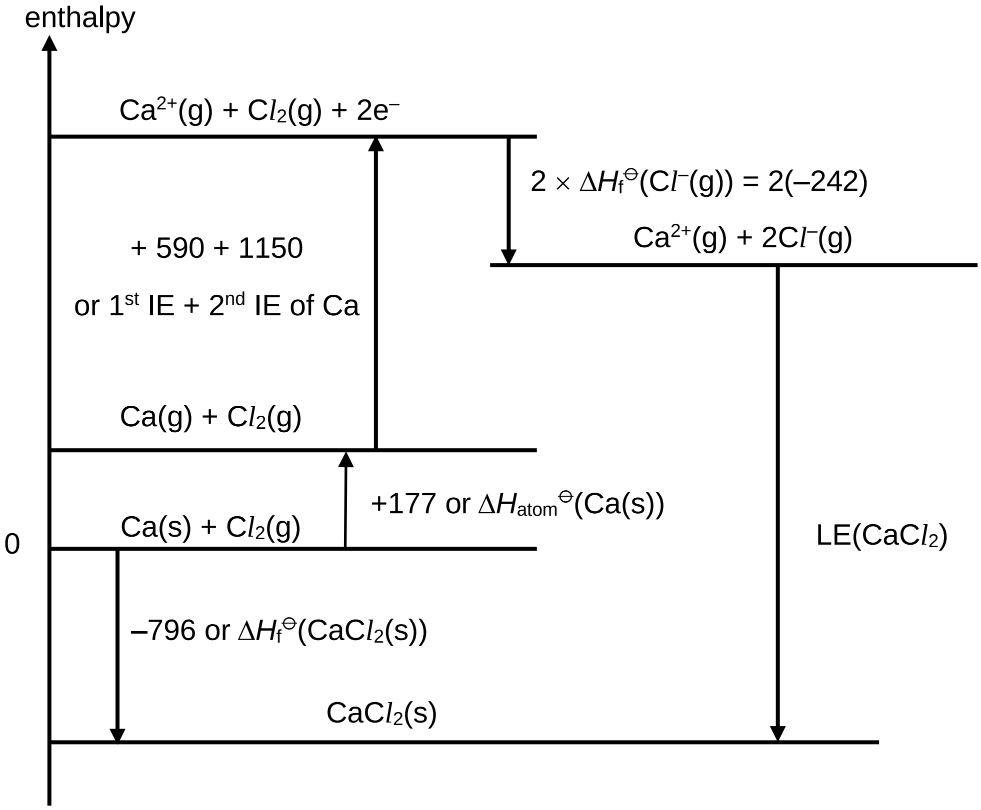
- Several students simply stated that $\Delta G$ is negative and $\Delta S$ is negative without any explanation of how they arrived that the conclusions.
- In their explanation of why $\Delta S$ is negative, students are expected to refer to the decrease in the number of liquid particles (or the number of ways the water particles can be arranged).

**1(c)(ii)** The lattice energy (LE) of calcium chloride is the energy released when 1 mole of solid $CaCl_2$ is formed from $Ca^{2+}(g)$ and $Cl^{-}(g)$ at 1 bar and 298 K.

**Comments:**

- Students are advised to learn the definitions well.

**1(c)(iii)**



$+177 + 590 + 1150 + 2(-242) + LE(CaCl_2) = -796$

$LE(CaCl_2) = \underline{-2230 \text{ kJ mol}^{-1}}$

**Comments:**

- A number of students erroneously included bond energy of Cl-Cl into the calculations, without realising that the enthalpy change of formation of $Cl^-(g)$ is not the same as the electron affinity of Cl(g).
- Some students drew the arrows in the wrong direction (e.g. upwards for exothermic reactions).

**1(d)** $AlCl_3$ exists as simple covalent molecules but dissolves in water to form $[Al(H_2O)_6]^{3+}$ ions.

$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

In $[Al(H_2O)_6]^{3+}$, the high charge density of $Al^{3+}$ polarises and weakens the O–H bond of the water molecules, allowing the complex ion to undergo hydrolysis to form $H_3O^+$. A weakly acidic solution of <u>pH 3</u> results.

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

$PCl_5$ exists as simple covalent molecules, which hydrolyses in water as the low-lying d-orbitals of the central P atom accepts a lone pair of electrons from $H_2O$. The reaction produces HC*l* as a product which dissolves in water to form a strongly acidic solution of <u>pH 2</u>.

$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$

**Comments:**
- Students are advised to learn the reactions well.
- A handful of students included the reactions with limited water, without realising that the term “resulting solutions” implies reaction with excess water.

**2(a)(i)** Cyclopentadienyl anion consists of a <u>ring</u> of five <u>$sp^2$ hybridised</u> carbon atoms. Each carbon atom has an unhybridised <u>p orbital that overlaps continuously</u>.

The C atom bearing the negative charge contains a <u>lone pair of electrons</u> in its unhybridised p orbital. Hence, together with the 4 $\pi$ electrons from the two C=C bonds, the cyclopentadienyl anion has a total of <u>6 delocalised $\pi$ electrons</u>.

**Comments:**
- Many students did not identify the hybridisation of the carbon atom bearing the negative charge while some identified it wrongly.
- Many students simply stated the number of delocalised $\pi$ electrons without any explanation.

**2(a)(ii)** When naphthalene undergoes substitution reaction, the product formed <u>retains its aromaticity (of the entire molecule) as there are 10 delocalised $\pi$ electrons in the continuously overlapping p orbitals</u>.

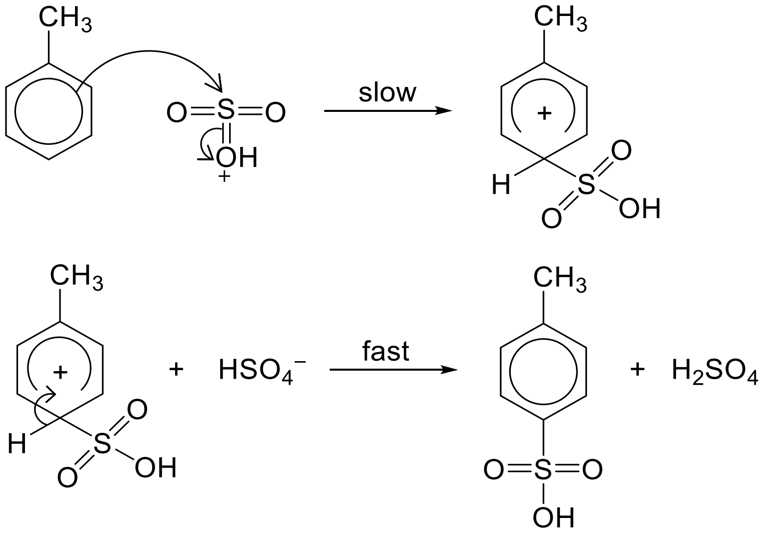
However, if naphthalene undergoes addition reaction, the product formed is <u>no longer aromatic (across the entire molecule) due to the absence of continuously overlapping p orbitals (or absence of 4n + 2 delocalised $\pi$ electrons)</u>.

**Comments:**
- Many students either did not mention that substitution allows the molecule to retain its aromaticity, or that addition causes the molecule to lose its aromaticity.

**2(b)(i)** $SO_3 + H_2SO_4 \rightleftharpoons HSO_3^+ + HSO_4^-$

**Comments:**
- $SO_3 + H^+ \rightleftharpoons HSO_3^+$ is not accepted because the question clearly stated that the formation of $HSO_3^+$ results from the protonation of $SO_3$ by $H_2SO_4$.

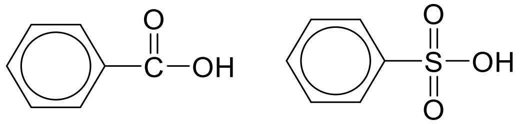
**2(b)(ii)** Electrophilic substitution



**Comments:**
- The curly arrow should start from <u>inside</u> (not outside) the benzene ring for the first step to show the movement of a pair of <u>delocalised electrons</u>. This arrow should be pointing towards the S atom (not O atom) as a C−S bond (not C-O bond) is formed (as shown in the product).
- Some students did not show the regeneration of $H_2SO_4$ catalyst in the second step.

**2(b)(iii)** concentrated $H_2SO_4$, concentrated $HNO_3$, heat (under reflux)

**Comments:**
- Both acids need to be <u>concentrated</u> for the reaction to work. Students should not use the state symbol, (aq), as it implies that the acid is diluted.
- Students should draw parallel from −COOH to deduce that $-SO_3H$ is an <u>electron-withdrawing / deactivating group</u>:
  - both C (in −COOH) and S (in $-SO_3H$) atoms do not contain any lone pair of electrons to delocalise into the benzene ring, hence there is no resonance electron-donating effect.
  - both −COOH and $-SO_3H$ have electronegative O atoms that results in inductive electron-withdrawing effect.



- Since compound **A** contains both mildly activating $-CH_3$ and deactivating $-SO_3H$, heat will be required for the reaction to occur.

**2(c)** Nitrogen is less electronegative than oxygen and its lone pair of electrons is more readily delocalised into the benzene ring. Hence, $-NH_2$ group is more activating than the -OH group and directs the electrophilic substitution to occur more at the 2-position relative to $-NH_2$.

**Comments:**

- Given that **B** is formed in a greater proportion compared to **C**, many students were able to deduce that $-NH_2$ group is more activating than the -OH group but majority were not able to link to the fact that N is less electronegative than O.

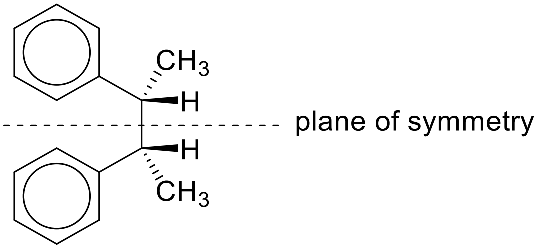
**2(d)(i)** (excess) benzene, $FeBr_3$ (or $AlBr_3$)

**Comments:**

- Some students did not recognise that step 2 involves the Friedel-Crafts alkylation of benzene via electrophilic substitution. Hence, benzene and a Lewis acid catalyst ($FeBr_3$ or $AlBr_3$) are required as reagents.

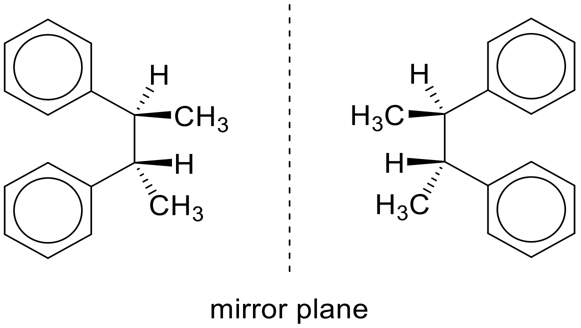
**2(d)(ii)**

Structure of **X**:



As **X** has a plane of symmetry / is a meso compound, **X** is optically inactive.

Structures of **Y** and **Z**:

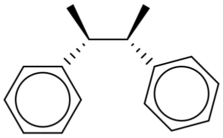


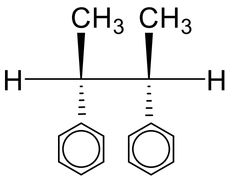
**Y** and **Z** are a pair of enantiomers and hence rotates plane-polarised light in equal but opposite directions.

**Comments:**

- Students should avoid drawing the following two structures as the orientation of the H atoms cannot be ascertained or the spatial arrangement of the atoms around the chiral carbons are poorly shown.

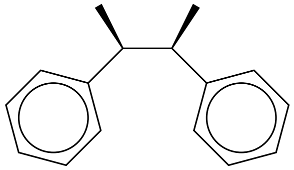
Avoid drawing these structures:



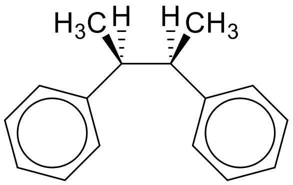


- The following structure is acceptable as the spatial orientation of the various groups around the chiral carbons can be ascertained.

Acceptable:

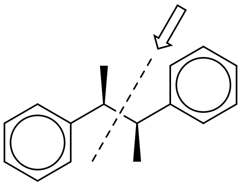


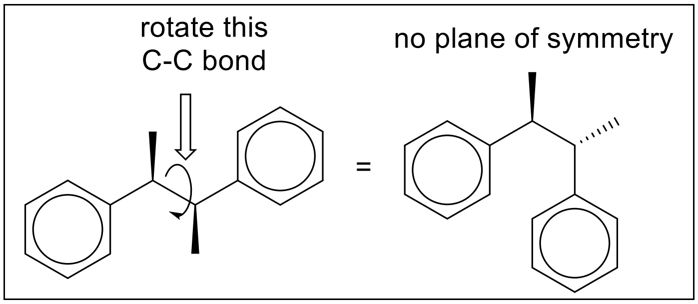
is equivalent to



- Some students drew the structure below and incorrectly concluded that there is a plane of symmetry. Note that when the C-C bond (shown below) is rotated, there is no plane of symmetry in the structure.

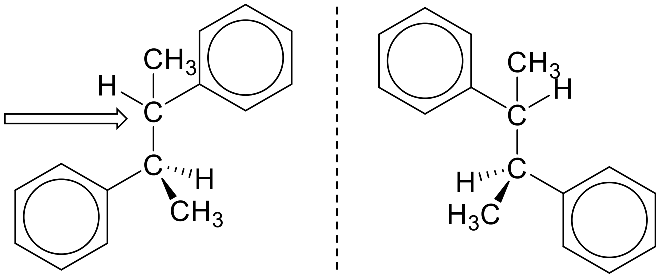
<u>NOT</u> a plane of symmetry





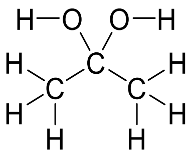
- Some students drew a pair of enantiomers, showing the spatial arrangement of atoms/groups around only one of the chiral carbons (an example is shown below). The spatial arrangement of atoms/groups around <u>both</u> chiral carbons must be shown in order to prove the absence of a plane of symmetry which is a criterion for a pair of enantiomers.

stereochemistry
of both chiral C
must be shown



- Some students did not understand that **X**, **Y** and **Z** are different stereoisomers (same structural formula but different spatial arrangements of atoms) of **W**. Hence, they erroneously proceeded to draw various constitutional/structural isomers of **W**.

**2(e)(i)**



**Comments:**

- Drawing the displayed formula means showing the full structural formula. Students need to ensure that <u>all bonds</u> (including O−H bonds) <u>and all atoms</u> are shown when drawing the displayed formula.

**2(e)(ii)** Let the molecular formula of **K** be $C_xH_yO_z$.

$$C_xH_yO_z + (x + \frac{y}{4} - \frac{z}{2})O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

$n(H_2O)$ collected = $\frac{0.090}{18.0}$ = <u>0.005 mol</u>

Vol of gases (after cooling) = V(unreacted $O_2$) + V($CO_2$) = 202 $cm^3$

V($CO_2$) = 144 $cm^3$

$n(CO_2)$ evolved = $\frac{144}{24000}$ = <u>0.006 mol</u>

V(unreacted $O_2$) = 202 − 144 = 58 $cm^3$

V(reacted $O_2$) = 250 − 58 = 192 $cm^3$

n(reacted $O_2$) = $\frac{192}{24000}$ = <u>0.008 mol</u>

| | $C_xH_yO_z$ | $O_2$ | $CO_2$ | $H_2O$ |
|---|---|---|---|---|
| amount / mol | 0.001 | 0.008 | 0.006 | 0.005 |
| mole ratio | 1 | 8 | 6 | 5 |

x = 6

$\frac{y}{2}$ = 5, hence y = 10

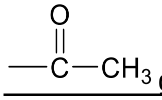
$x + \frac{y}{4} - \frac{z}{2} = 6 + 2.5 - \frac{z}{2} = 8$, hence z = 1

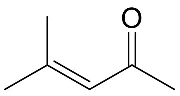
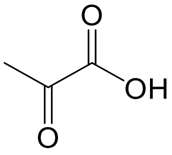
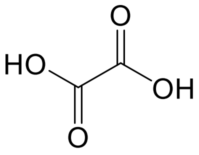
Molecular formula for **K** is $C_6H_{10}O$.

**Comments:**

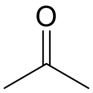
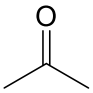
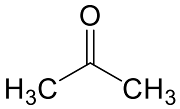
- Most students were able to find the amount of $H_2O$ and $CO_2$ formed but not the amount of $O_2$ reacted. Hence, they were not able to clearly prove that the molecular formula for **K** is $C_6H_{10}O$.
- Students who did not consider the amount of **K** in their calculation ended up deducing the empirical formula instead of the molecular formula of **K**.

**2(e)(iii)**

| Evidence / Information | Deduction / Explanation |
|---|---|
| **K** gives an orange ppt with 2,4-DNPH but does not form silver mirror with Tollens' reagent. | Condensation with 2,4-DNPH but no oxidation with Tollens' reagent.<br>**K** is a carbonyl compound but not an aldehyde.<br>**K** is a ketone. |
| When **K** is heated with acidified $KMnO_4$, **L** and propanone are formed. | Strong oxidation<br>**K** is an alkene that contains $=C(CH_3)_2$ group. |
| When **L** is heated with aqueous $I_2$ in dilute NaOH followed by acidification, **M** and a yellow ppt are formed. | Oxidation and acid-base reaction<br>**L** has 3 C atoms and contains<br> $-\overset{O}{\overset{\|}{C}}-CH_3$ group.<br>Yellow ppt is $CHI_3$.<br>**M** contains a –COOH group. |
| When **M** is heated with acidified $KMnO_4$, the only product form is a gas that gives a white precipitate with limewater. | Oxidation<br>Gas is $CO_2$. |

|  |  |  |
|---|---|---|
|  **K** |  **L** |  **M** |

**Comments:**

- Under deduction/explanation, students need to include the following:
  - type of reaction (e.g. oxidation),
  - functional group (e.g. **K** is an alkene) and
  - structure features (e.g. **L** contains $–COCH_3$ group).
- Students should avoid drawing skeletal structures to represent part of a full structure. Some drew  to denote the presence of a methyl ketone ($–COCH_3$) group. However,  is ambiguous as it can also represent the presence of a ketone or  $H_3C-\overset{O}{\overset{\|}{C}}-CH_3$.

**3(a)(i)** From the *Data Booklet*, $E^{\ominus}_{\text{cathode}}$ = +0.40 V and $E^{\ominus}_{\text{anode}}$ = 0.00 V.
Hence, $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}} = \underline{+0.40\text{ V}}$

**Comments:**
- This question is generally well done.

**3(a)(ii)** $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ (a)
$2H^+ + 2e^- \rightleftharpoons H_2$ (b)

At the cathode, $CO_2$ removes $OH^-$ formed, causing a decrease in $[OH^-]$. The position of equilibrium for reaction (a) shifts to the right and this causes $E_{\text{cathode}}$ to be more positive.

At the anode, the $CO_3^{2-}$ which migrates from the cathode removes $H^+$ formed, causing a decrease in $[H^+]$. The position of equilibrium for reaction (b) shifts to the left and this causes $E_{\text{anode}}$ to be more negative.

Hence, $E_{\text{cell}}$ of the EDCS is more positive than that of the hydrogen-fuel cell in **(a)**.

**Comments:**
- Many students had the misconception that $CO_2$ is reduced/oxidised to $CO_3^{2-}$ and vice versa. Reactions (2) and (4) are not reduction/oxidation reactions as there is no change in oxidation states of C, O or H.
- Many students did not realise that air is fed to the cathode and eventually $CO_2$ is removed from anode according to Fig. 3.1. Hence, it is incorrect to say that position of equilibrium (4) shifts left due to the increase in $[CO_2]$ in air at anode.
- Many students also used the wrong notations, such as $E^{\ominus}_{\text{cathode}}$ instead of $E_{\text{cathode}}$ since reactions are occurring under non-standard conditions. Another common mistake is to represent $E(H^+/H_2)$ as $E(H_2/H^+)$.
- Many students did not realise that shifting position of equilibrium (3) to the right will result in $E(H^+/H_2)$ or $E_{\text{anode}}$ becoming more negative instead of becoming more positive.

**3(a)(iii)** The higher the $CO_2$ concentration, the more positive the $E_{\text{cell}}$ and the current increases. Since $I = n_eF/t$, the amount of electrons transferred per second increases and hence increases the rate of removal of $CO_2$.

**Comments:**
- Students need to read the question carefully. Many did not consider their answer to 3(a)(ii) when answering this question.

**3(b)(i)** From the *Data Booklet*,

If a typical hydrogen-oxygen fuel cell operates under acidic conditions:
cathode reaction: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
anode reaction: $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

$E^\ominus_{cathode} = +1.23$ V and $E^\ominus_{anode} = 0.00$ V
Hence, $E^\ominus_{cell} = +1.23 - 0.00 = \underline{+1.23 \text{ V}}$

If a typical hydrogen-oxygen fuel cell operates under alkaline conditions:
cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
anode reaction: $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

$E^\ominus_{cathode} = +0.40$ V and $E^\ominus_{anode} = -0.83$ V
Hence, $E^\ominus_{cell} = +0.40 - (-0.83) = \underline{+1.23 \text{ V}}$

**Comments:**
- Many students struggled to come up with the correct anode reaction under alkaline conditions. Most used $E(H^+/H_2)$ instead of $E(H_2O/H_2)$ in the calculation of $E^\ominus_{cell}$ under alkaline conditions.

**3(b)(ii)** Under acidic conditions, there will not be any $OH^-$ ions at the cathode to react with and to convert atmospheric $CO_2$ to $CO_3^{2-}$. Hence, the $CO_2$ in air cannot be captured by the EDCS.

Under alkaline conditions, there will not be any $H^+$ ions at the anode to convert $CO_3^{2-}$ ions back to $CO_2$ to be removed into a separate storage.

Hence, a typical hydrogen-oxygen fuel cell cannot be used in the EDCS.

**Comments:**
- Most students merely mentioned that a typical hydrogen-oxygen fuel cell is either in acidic or alkaline conditions but did not elaborate on why it cannot be used in EDCS.
- Very few students were able to make reference to reactions (2) and (4), and explain how reactions (2) and (4) may not be able to work under acidic and alkaline conditions respectively.

**3(c)(i)** Volume of $CO_2$ removed per minute $= 0.99 \times 3000 \times \frac{400}{10^6} = 1.188 \text{ cm}^3$

Amount of $CO_2$ removed per second $= \frac{1.188}{24000} \div 60 = 8.25 \times 10^{-7}$ mol

From equations (1) – (4),
amount of electrons passed per second
$= 2 \times 8.25 \times 10^{-7}$
$= 1.65 \times 10^{-6}$ mol per second

Hence, current $= 1.65 \times 10^{-6} \times 96500 = \underline{0.159 \text{ A}}$

**Comments:**

- This question is generally well done. Common mistakes include:
    - not factoring in the 99% efficiency of EDCS
    - using the wrong molar ratio of $CO_2$ : $e^-$ in the calculation

**3(c)(ii)** The $CO_3^{2-}$ and electrons can diffuse more quickly across a larger surface area and hence increase the rate of $CO_2$ removal.

**Comments:**

- This question is generally well done.

**3(d)** Similar to graphite, CNTs have an **extended** delocalised $\pi$ electron cloud, which allows CNTs to conduct electricity.

Thus, it is likely that CNTs help conduct electricity across the membrane and increases the membrane's electrical conductivity.

**Comments:**

- Many students did not mention extended delocalised $\pi$ electron cloud or give an indication that there is continuous side-on overlap of the p orbitals in increasing the membrane's electrical conductivity.

**3(e)(i)** $Mg^{2+}$ has a smaller ionic radius than $Ca^{2+}$. Hence, with the same charge, $Mg^{2+}$ has a higher charge density and hence greater polarizing power than $Ca^{2+}$. As a result, $Mg^{2+}$ distorts the electron cloud of $R\text{-}COO^-$ to a greater extent. The covalent bonds within $R\text{-}COO^-$ are weakened to a greater extent as compared to that in $(R\text{-}COO^-)_2Ca^{2+}$. Therefore, less heat energy is needed to decompose $(R\text{-}COO^-)_2Mg^{2+}$. Hence $(R\text{-}COO^-)_2Mg^{2+}$ has lower thermal stability.

**Comments:**

- This question is generally well done. Some students had vague answers like "weakened the bonds in $(R\text{-}COO^-)_2Mg^{2+}$ or weakened ionic bonds in $(R\text{-}COO^-)_2Mg^{2+}$" which are not accepted.

**3(e)(ii)** $MgCO_3 \longrightarrow MgO + CO_2$

**Comments:**

- This question is generally well done.

**3(e)(iii)** $(CH_3\text{-}COO^-)_2Mg^{2+} \longrightarrow CH_3COCH_3 + CO_2 + MgO$

**Comments:**

- Most students did not manage to balance the equation, either missing out on $CO_2$ or coming up with a wrong structure instead of $CH_3COCH_3$.

## Section B

**4(a)** Nitrogen has a higher number of protons and hence higher nuclear charge than carbon. Although there is one more electron in nitrogen than carbon, this electron is added to the same outermost shell, and hence shielding effect remains approximately constant. Thus, nitrogen has a higher effective nuclear charge and stronger electrostatic attraction between the nucleus and the valence electrons than carbon, resulting in an increase in the amount of energy required to remove the valence electron from nitrogen. Hence, the first ionisation energy of nitrogen is higher than carbon.

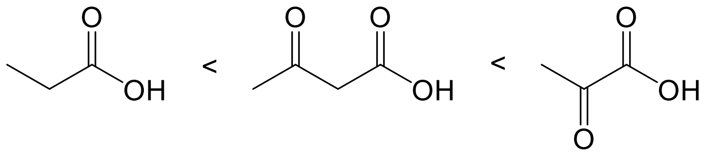
The first ionisation energy of oxygen is lower than that of nitrogen. This is because the 2p electron to be removed from oxygen is a paired electron while that to be removed from nitrogen is an unpaired electron. Due to inter–electronic repulsion between paired electrons in the same orbital, less energy is required to remove the paired 2p electron from oxygen.

**Comments:**

- Students should note that the question requires an explanation in terms of the three elements (C, N, O) and not a general trend across the period.
- Students should explain trends and variations in atomic/ionic radii, ionisation energies and electronegativities across a period in terms of shielding and nuclear charge (as required by the syllabus).
- Many students did not realise that the first ionisation energy of oxygen is lower than that of nitrogen and hence did not explain this variation.

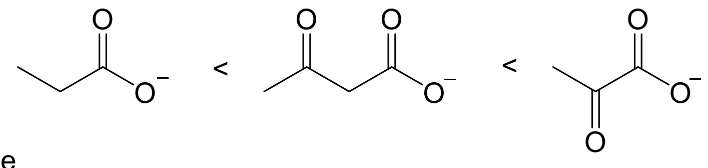
**4(b)** The stronger the acid, the lower the p$K_a$ value and the more stable the conjugate base.

Based on the given p$K_a$ values, acidity increases in the order:



**F** **D** **E**

and the stability of the conjugate base increases in the order:



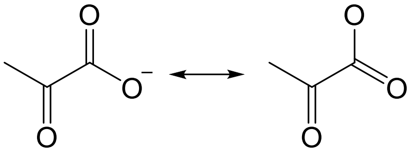
conjugate base of: **F** **D** **E**

Compared to the conjugate base of **F**, the conjugate bases of **D** and **E** are more stable due to the presence of the electron-withdrawing carbonyl group to disperse the negative charge and hence stabilising the anions.

The conjugate base of **E** is more stable than that of **D** as the electron-withdrawing carbonyl group is nearer to the $-COO^-$, and can better disperse the negative charge, thus stabilising the conjugate base of **E** to a greater extent.

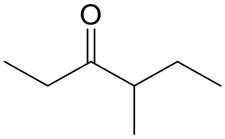
**Comments:**

- Students need to discuss the stability of the conjugate base of D/E/F (which has the negatively charged carboxylate group, $-COO^-$) and not centre their discussion on D/E/F.
- A significant number of students thought that the negative charge in conjugate base of E can be delocalised across all 3 oxygen atoms. This is incorrect despite the overlapping of the p orbitals as it would not be possible to have a resonance hybrid structure with the negative charge on the carbonyl oxygen. The ketone functional group is electron-withdrawing by inductive effect only.

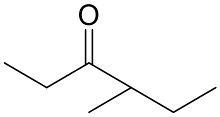


- For the conjugate bases of all three compounds, the negative charge of the carboxylate group is delocalised across 2 electronegative oxygen atoms.
- D and E each contains 1 carboxylic acid (-COOH) and 1 ketone (C=O) groups and their conjugate bases each contains 1 carboxylate ($-COO^-$) and 1 ketone (C=O) groups. It is incorrect to say that D/E has 2 C=O groups as the C=O in $COOH/COO^-$ should be considered collectively with the $OH/O^-$ respectively as they are part of the same functional group.
- A few students had the misconception that D and E are cis/trans isomers even though D and E are not isomers (different molecular formula) and do not have restricted rotations about the C-C single bonds.

**4(c)(i)**

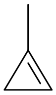


**Comments:**

- This question is generally well done except for some cases of missing or extra carbons.
- Students are reminded to show skeletal structures properly and avoid structures such as  .
- Students should note that $CO_2$ is not an organic compound and should not be included in the answer if the question is asking for only organic compounds.

**4(c)(ii)** step 1: ethanolic KOH, heat (under reflux)

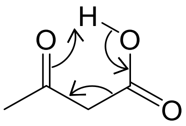
**I** :



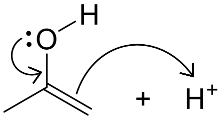
step 2: $KMnO_4$(aq), $H_2SO_4$(aq), heat (under reflux)

**Comments:**
- This question is generally well done.
- A few students left out “heat” as a condition for step 1 (elimination of HBr).
- Students are reminded to specify the identity of the acid used and not just write “acidified”.
- Students are also reminded to answer on the answer lines and not in any empty spaces in the question booklet.
- Students should only use “heat with immediate distillation” when trying to obtain aldehyde from primary alcohol as indiscriminate use of this condition may affect a reaction negatively.

**4(c)(iii)** step 1:



step 2:



**Comments:**
- Students should note that curly arrows represent the movement of electron pairs and these arrows should account for the formation and breaking of bonds involved in the mechanism.
- Lone pair of electrons should be clearly shown when they are involved in the mechanism and curly arrows should begin and end at the correct positions.

**4(d)(i)** Acidic hydrolysis and oxidation

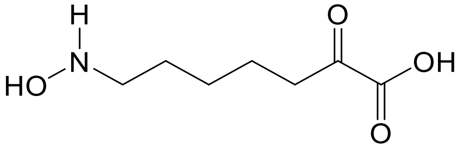
**Comments:**
- This question is generally well done.

**4(d)(ii)** $KMnO_4$(aq), $H_2SO_4$(aq), heat OR $K_2Cr_2O_7$(aq), $H_2SO_4$(aq), heat

**Comments:**
- This question is generally well done.
- A small number of students wrote two sets of reagents and conditions (one for acidic hydrolysis and another for oxidation) without realising that the acidic hydrolysis conditions are already present in that for oxidation.

**4(e)(i)**

**J**:



**Comments:**

- This question is generally well done except for some cases of missing or extra carbon.
- Student should note that the H atom that is bonded to the N atom should be shown in the structure.

**4(e)(ii)** High dilution or low concentration of reactant

**Comments:**

- Many students suggested using "limited J" to minimise polymerisation. The KAHA ligation of J is an intramolecular reaction involving only one reactant, hence "limiting" and "excess" have no meaning in this context.
- In order for polymerisation to occur, molecules of J must collide with each other and a low concentration of J will reduce the probability of these collisions, thus minimising polymerisation.

**4(f)(i)** A catalytic amount of $H^+$ is not sufficient as $H^+$ is consumed stoichiometrically in step 6 to protonate the $NH_3$ hydrolysis product.

**Comments:**

- Students are required to show understanding that the $H^+$ undergoes further reaction with $NH_3$ and hence would not be able to catalyse the reaction if only a small amount of $H^+$ were added.

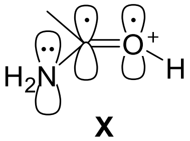
**4(f)(ii)** In conjugate acid **X**, the lone pair of electrons on the N atom interacts with the $\pi$ electron cloud of the adjacent C=O bond and is delocalised, hence dispersing the positive charge on the O atom and stabilising **X**.

In conjugate acid **Y**, there is no continuous side-on overlap of p orbitals and hence **Y** is not resonance stabilised.

**Comments:**

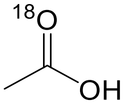
- Students need to be clear about which compound they are referring to in their explanations. Often, it is difficult to know if students are referring to the reactant (ethanamide) or conjugate acid X/Y or which lone pair of electrons is being discussed.
- A significant number of students mistook conjugate acid X as "conjugate acid **of** X" and explained in terms of the basicity of X/Y.
- The question required students to consider the structures of the conjugate acids X and Y, hence discussions involving the reactant (ethanamide) were not given credit.
- Some students incorrectly used prepared explanations involving resonance like "p orbital of positively charged O atom overlaps with the $\pi$ electron cloud of C=O" which is not relevant here since the p orbital of O and that of C are already overlapping due to the $\pi$ bond in C=O.

- Only a few students managed to recognise that the positive charge on O in X can be delocalised due to the interaction of the lone pair of electrons on the N atom with the π electron cloud of the adjacent C=O bond.

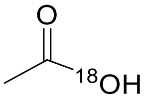


**X**

**4(f)(iii)**

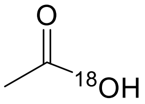


and

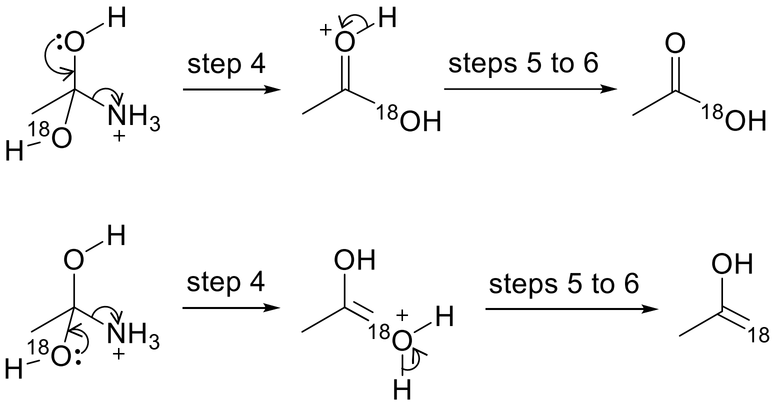


**Comments:**

- Students are reminded that the relative isotopic mass should be shown on the "top left hand" relative to the element (i.e. $^{18}O$) as shown in the question.
- By following the mechanism in Fig. 4.7, many students were able to obtain



. To obtain the other product, students will need to realise that in step 4, the -OH involved need not necessarily be the one that is derived from water since both -OH groups are the same.



- Students should note that $NH_4^+$ is not an organic compound and should not be included in the answer if the question is asking for only organic compounds.

**5(a)(i)** Cyclohexanone and compound **P** are constitutional (or structural) isomers.

**Comments:**

- This question is generally well done.
- Although cyclohexanone and P have the same molecular formula, they have different structural formula. Hence, these two compounds are not stereoisomers. (Recall: Stereoisomers are compounds with the same molecular formula and structural formula but differ in their spatial arrangement of atoms.)

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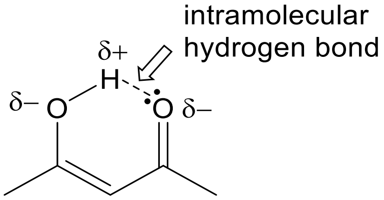
**5(a)(ii)** Compound **Q** is more stable than pentane-2,4-dione because:

- the H atom of the –OH group can form intramolecular hydrogen bond with the O atom of the nearby carbonyl group.
- there is resonance stabilisation / delocalisation of lone pair of electrons on the O atom of -OH group with the π electron cloud of the C=C and C=O groups.

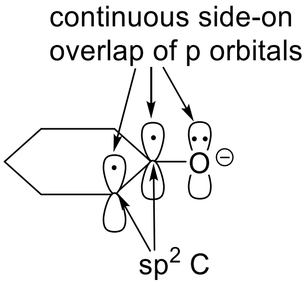
**Comments:**

- Students need to refer to the differences between the structures of cyclohexanone vs P and pentane-2,4-dione vs Q, and suggest how the additional C=O group in pentane-2,4-dione and Q results in Q being more stable.
- Only a handful of students identified the intramolecular hydrogen bond in Q. Responses need to state clearly that the hydrogen bond is formed within the molecule of Q.



- Students who identified the continuous side-on overlapping of p orbitals between O, C=C and C=O should also include the delocalisation of electrons that results in the resonance stabilisation.

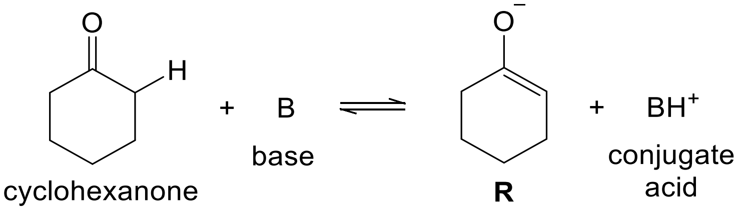
**5(b)(i)** The carbon atoms in the C=C bond are $sp^2$ hybridised, each with an unhybridised p orbital containing one electron. The p orbital of the adjacent O atom can overlap continuously side-on with the p orbitals of the $sp^2$ carbon atoms, resulting in delocalisation of the negative charge on the O atom into the C=C bond. Hence, **R** is resonance stabilised.



**Comments:**

- Most students discussed the delocalisation of negative charge or lone pair on the O atom, but some missed stating the hybridisation of the carbon atoms in the C=C bond, as required by the question.
- As the question requires student to draw a 'labelled diagram showing orbital overlap', students should show clearly the side-on overlapping of p orbitals between C=C and O atom, as well as label the orbitals and $sp^2$ C atoms accordingly.

**5(b)(ii)**



Unlike conjugate acids of **I** and **II**, the p$K_a$ of the conjugate acids of **III** and **IV** are higher than the p$K_a$ of cyclohexanone. This means that the conjugate acids of **III** and **IV** are weaker acids than cyclohexanone. Hence, the equilibrium position of the acid-base reaction of **III** and **IV** with cyclohexanone lie further right compared to that of **I** and **II** with cyclohexanone.

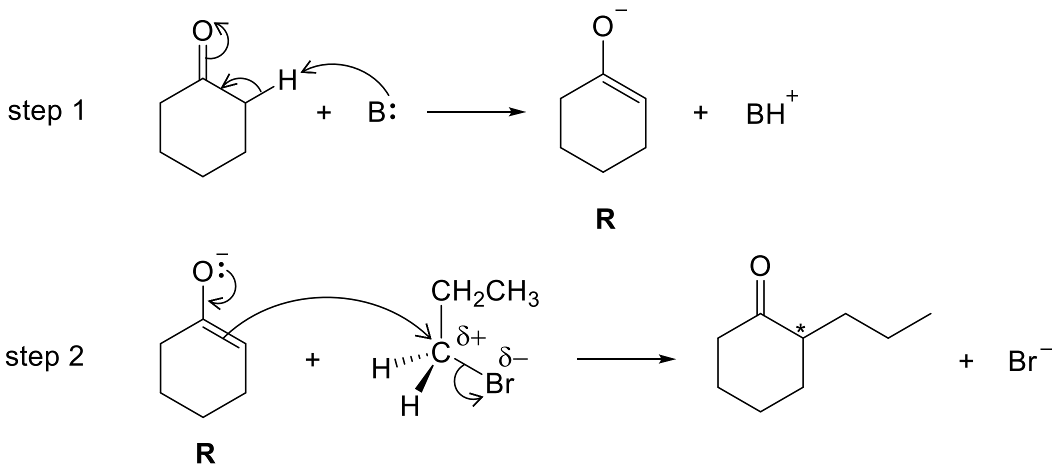
Compared to **IV**, **III** is more suitable as the presence of bulky alkyl groups in **III** prevents it from acting as a nucleophile to react with the carbonyl group in cyclohexanone, resulting in the formation of side/addition product.

Hence, **III** is the most suitable base to deprotonate cyclohexanone to form **R**.

**Comments:**

- For the equilibrium position of the acid-base reaction to lie right, the conjugate acid, $BH^+$, must be a weaker acid with a higher p$K_a$ value than cyclohexanone. Instead of simply citing conjugate acid of **III** having a high p$K_a$, students should refer to Table 5.1 and compare the p$K_a$ of the conjugate acids of the bases (**I**, **II**, **III** and **IV**) with that of cyclohexanone.
- Note that p$K_a$ measures the strength of an acid while p$K_b$ measures the strength of a base. Hence it is incorrect to state that conjugate base **III** has a p$K_a$ of 36. Additionally, students should avoid using ‘it’ in their responses and should clearly state if they are referring to the conjugate acid or the base itself.
- The given p$K_a$ values already show that the corresponding base **III** is a weaker base than **IV**. Hence, students should explain why despite being a weaker base than **IV**, **III** is the most suitable base to deprotonate cyclohexanone. A handful of students missed this and incorrectly focused their answers on the electron-donating effect of the alkyl groups instead of discussing about the steric hindrance posed by these bulky alkyl groups.

**5(c)(i)**

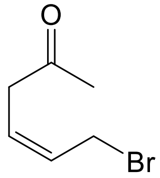


**Comments:**
- For mechanism drawing, the curly arrow shows the movement of electron pairs.
- Based on the given structures of the reactants and products for each step, students need to identify the bonds formed and broken in order to work out the movement of electron pairs and draw the corresponding curly arrows. Students need to show clearly where their curly arrows start and end.
- As step 2 is an $S_N2$ reaction, students need to show the partial charges on C and Br, as well as the backside attack of the nucleophile.

**5(c)(ii)** In step 2, the $S_N2$ reaction can occur with 1-bromopropane on <u>either side of the trigonal planar carbon</u> of C=C in **R** with <u>equal probability</u>, hence forming a <u>racemic mixture / equal amounts of a pair of enantiomers</u> which does not rotate the plane of polarised light.

**Comments:**
- Most students correctly deduced that a racemic mixture is produced. However, a handful regurgitated the explanation given in the notes and tutorial without referring to the species involved in step 2 – the trigonal planar carbon is present in R (nucleophile) and 1-bromopropane (electrophile) can approach this carbon from either side of the plane. Several students incorrectly wrote that the nucleophile attacks the trigonal planar carbon without realising that the planar carbon is on the nucleophile.
- Some students did not identify the presence of a chiral carbon in the product formed (refer to carbon marked with * in 5(c)(i)) and mistakenly thought that the product does not show optical activity as it is achiral.

**5(c)(iii)**



**S**

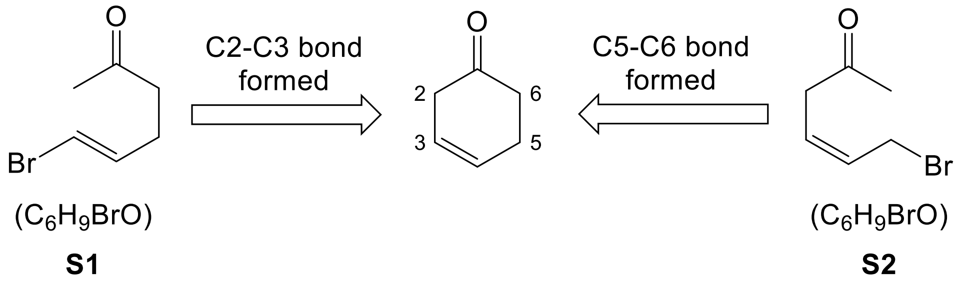
$C_6H_9BrO$

**Comments:**

- The following deductions can be made based on the information given in the question:
    - S decolourises $Br_2$ at r.t. in the dark ⇒ S undergoes electrophilic addition. S has alkene group.
    - S forms orange ppt with 2,4-DNPH ⇒ S undergoes condensation. S has the carbonyl group.
    - S gives yellow crystals with alkaline aqueous $I_2$ ⇒ S undergoes oxidation (positive iodoform). S contains the $-COCH_3$ group.

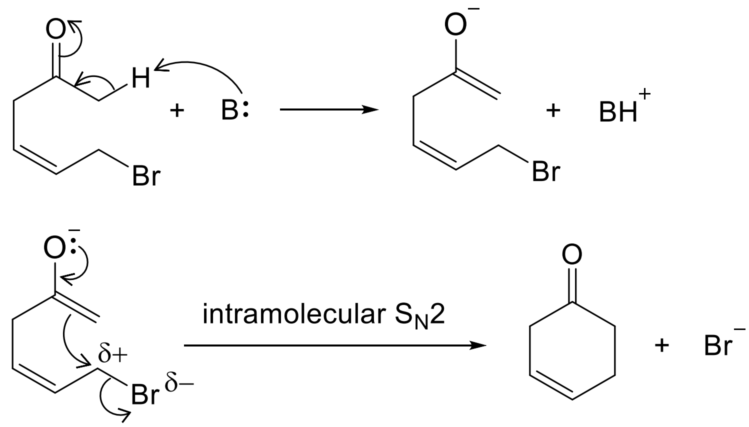
  Since the product also contains the alkene and carbonyl groups, students should deduce that the reaction does not involve these two groups. (Note: Both the C=C in S and the product are in the *cis* configuration.)

  Additionally, given that S is a non-cyclic compound whereas the product formed is cyclic, students should deduce that one of the C-C bonds in the cyclic ring must have been formed in step 1. Since S contains the $-COCH_3$ group, the C-C bond formed in step 1 must be either C2-C3 or C5-C6.



- As step 1 involves a base as the reagent and the Br atom is lost in the product, students need to recognise these similarities with the reaction scheme shown in Fig. 5.3 and use the information to work out the structure of S. Applying information from Fig. 5.3, S1 cannot be possible as it cannot undergo $S_N2$ reaction because its C-Br bond has partial double bond character and is difficult to break. Hence, S2 is the correct structure.

- The mechanism of step 1 is shown below.



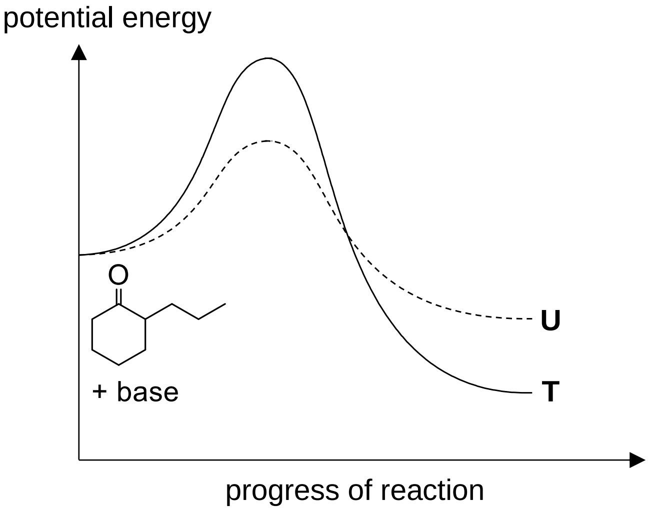
**5(c)(iv)** step 2: $H_2$, Ni, heat

step 3: $KMnO_4$(aq), $H_2SO_4$(aq), heat (under reflux)
OR
$K_2Cr_2O_7$(aq), $H_2SO_4$(aq), heat (under reflux)

**Comments:**

- In step 2, both the alkene (C=C) and ketone (C=O) groups are reduced. Hence, reducing agents such as $LiAlH_4$ and $NaBH_4$ cannot be used as these will only reduce the ketone group and not the alkene.
- The reagents and conditions for step 3 is generally well done. Note that the identity of the acid used need to be stated. Hence, answers such as 'acidified $KMnO_4$, heat' is not given any credits.

**5(d)**



**Comments:**

- A significant number of students confused 'reaction pathway diagram' with 'reaction mechanism'. Note that reaction pathway diagram refers to energy profile diagram.
- For a reaction pathway or energy profile diagram, students need to:
  - Label the axes
  - Label the reactants, intermediates (if any) and products
  - Show the relative energy levels of the reactants, transition states, intermediates (if any) and products
- Based on the given information in the question,
  - compound T is more stable than compound U ⇒ T is at a <u>lower energy</u> than U
  - compound T is formed more slowly than compound U ⇒ <u>$E_a$</u> for the formation of T is <u>greater</u> than that for U.

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**5(e)(i)** Step 1 is a condensation reaction.

**Comments:**

- This question is generally well done.
- The reaction of cyclohexanone with $NH_2OH$ produced compound V and $H_2O$ (by mass balance). Since two molecules react together to form one larger molecule with the elimination of a small molecule of $H_2O$, and the degree of unsaturation remains unchanged, the reaction is therefore a condensation reaction.
- Note that for elimination reaction, the degree of unsaturation increases.

**5(e)(ii)** Compound **V** does not exhibit cis-trans isomerism. Although there is restricted rotation about the C=N bond, the C atom in the C=N bond has two identical groups bonded to it.

**Comments:**

- In order for a compound to exhibit cis-trans isomerism, there must first be restricted rotation about a bond, either by the presence of a double bond (e.g. C=C, C=N, N=N) or a ring structure. In compound V, there is restricted rotation about the C=N bond and the 6-membered ring. Since all the carbons (except for the doubly bonded carbon) on the ring have two identical groups (i.e. H atoms) attached to them, students should focus their answers on explaining whether the C=N bond in V can exhibit cis-trans isomerism.
- In order for the C=N group to exhibit cis-trans isomerism, each of the C and N atoms in the C=N bond must have two different groups attached to them. Note that the lone pair of electrons and -OH group on N are counted as two different groups. Since the ring is symmetrical about the C in C=N, the two groups are considered identical.
- Some students mistakenly thought that compound V does not exhibit cis-trans isomerism due to the absence of C=C bond or absence of two different groups on the N atom (as N has only one -OH group).
- Please revise Section 5.2.1 of the 'Introduction to Organic Chemistry' notes.

**5(e)(iii)** $H_2SO_4$(aq) / HC*l*(aq) / $HNO_3$(aq), heat
OR
NaOH(aq), heat

**Comments:**

- This question is generally well done, with many students giving the correct reagents and conditions for the acidic or basic hydrolysis of the amide group in compound W.
- Students need to state the identity of the acid or base used, instead of simply stating $H^+$ or $OH^-$.