2019 Y5 H2 Chemistry Promotion Exam – Suggested Solutions

Section A

Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Answer	D	C	A	B	B	C	C	B	A	D	D	A	A	C	B

MCQ worked solutions

1 (Ans: D)

A : Incorrect.

(A mole of substance is the amount of that substance which contains 6.02 × 10^{23} elementary entities of that substance.)

Since 1 mole of compound (e.g. CO_2) contains more than 1 mole of atoms (e.g. 1 mole of C and 2 moles of O atoms), it will not contain the same number of atoms as there are atoms in 12 g of carbon-12 (i.e. 1 mole of ^{12}C).

B : Incorrect.

$$\text{Relative molecular mass} = \frac{\text{(weighted) average mass of } \mathbf{1\ molecule} \text{ of the substance}}{\frac{1}{12} \times \text{mass of } \mathbf{1\ atom} \text{ of carbon-12}}$$

C : Incorrect.

$$\text{Relative isotopic mass} = \frac{\mathbf{\text{mass of 1 atom of the isotope}}}{\frac{1}{12} \times \text{mass of 1 atom of carbon-12}}$$

D : Correct.

$$\text{Relative atomic mass} = \frac{\text{(weighted) average mass of 1 atom of the element}}{\frac{1}{12} \times \text{mass of 1 atom of carbon-12}}$$

2 (Ans: C)

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

Mass of carbon dioxide and water vapour lost = 0.85 g

Let the amount of $NaHCO_3$ be x mol.

Amount of $CO_2(g)$ = amount of $H_2O(g)$ = (x/2) mol

$(x/2)(44) + (x/2)(18) = 0.85 \Rightarrow x = 0.02742$

% purity by mass = [(0.02742 x 84.0) / 3.50] x 100 = <u>65.8%</u>

Note: The sample of $NaHCO_3$ is impure. After decomposition, the mass of Na_2CO_3 in the remaining residue is NOT = (3.50 – 0.85) g due to the impurities present.

3 (Ans: A)

No of protons and neutrons in **X** = 289 + 3(1) – 244 = 48

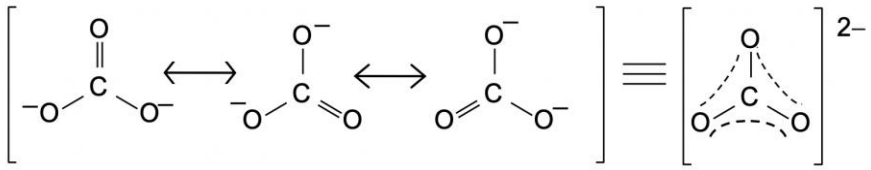
No of protons in **X** = 114 + 3(0) − 94 = <u>20</u>

No of neutrons in **X** = 48 − 20 = <u>28</u>

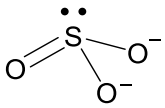
4 (Ans: B)

CO_3^{2-} ion exhibits resonance.

⇒ All C–O bonds present in the ion are of the same bond length.



CO_3^{2-} ion has 3 regions of electron density around the central C atom (sp^2 hybridisation). Since there are 3 bond pairs of electrons present, the CO_3^{2-} ion has a trigonal planar shape and a bond angle of 120^0.



SO_3^{2-} ion has 4 regions of electron density around the central S atom. Since there are 3 bond pairs and 1 lone pair of electrons present, the SO_3^{2-} ion has a trigonal pyramidal shape and a bond angle of approximately 107^0.

Hence, only options 1 and 2 are correct.

5 (Ans: B)

A: Correct

There are 2 π bonds in the C≡C triple bond in ethyne (H–C≡C–H).

There are 2 π bonds in the C≡N triple bond in butanenitrile ($CH_3CH_2CH_2C{\equiv}N$).

⇒ Both molecules have the same number of π bonds

B: Incorrect.

Since butanenitrile is polar (with a net overall dipole moment), the molecules are held together by permanent dipole-permanent dipole (pd-pd) interactions. On the other hand, ethyne is non-polar (with no net dipole moment) and the molecules are held together by the weaker instantaneous dipole–induced dipole (id-id) interactions.

In addition, since butanenitrile has a larger and more polarisable electron cloud than ethyne, its id-id interactions are stronger than that of ethyne.

⇒ Butanenitrile forms stronger intermolecular forces of attraction than ethyne.

C: Correct.

Since the C atoms in ethyne are sp hybridised while the C atom bonded to H_a in butanenitrile is sp^3 hybridised, there is higher s-character in the hybrid orbitals of the C atoms in ethyne.

⇒ In ethyne, the less diffuse sp hybrid orbital of C overlap more effectively with the 1s orbital of H. Hence, C–H bond energy in ethyne is greater than that of C–H_a in butanenitrile.

6 (Ans: C)

$pV = nRT = \frac{m}{M}RT$

$pM = \frac{m}{V}RT = \rho RT$

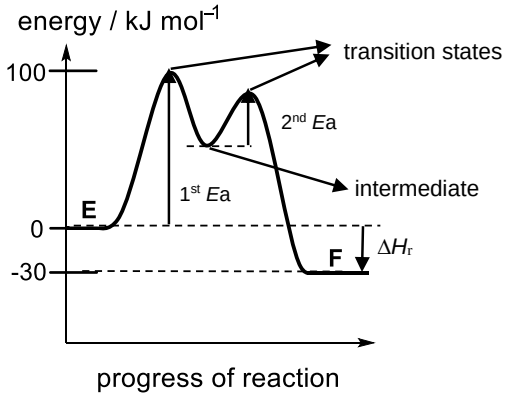
$p = \frac{\rho RT}{M}$

$\frac{\text{pressure of gas A}}{\text{pressure of gas B}} = (\frac{\text{density of A}}{\text{density of B}})(\frac{\text{temp of A in K}}{\text{temp of B in K}})(\frac{\text{relative molecular mass of B}}{\text{relative molecular mass of A}})$

$= (\frac{3}{1})(\frac{273+30}{273+20})(\frac{4}{1})$

$= \underline{12.4}$

7 (Ans: C)



A: Correct. The enthalpy change for the conversion of **E** to **F**, ΔH_r, is –30 kJ mol^{-1}.
B: Correct. The 1st E_a is 100 kJ mol^{-1}.
C: Incorrect. There are **two** transition states in the reaction.
D: Correct. Since 1st E_a is greater than 2nd E_a, the first step is the rate-determining step.

8 (Ans: B)

Statement 1 is correct. The degree of covalent character in an ionic compound depends on the polarising power of the cation and polarisability of the anion. Both **JY** and **LY** have the same anion, hence we compare the polarising power of **J**$^+$ and **L**$^+$. **J**$^+$ has a <u>higher polarising power</u> as **J**$^+$ has a higher charge density (same charge but smaller radius) than **L**$^+$. Hence, **JY** has higher covalent character than **LY**.

Statement 2 is correct.

$$|\text{LE}| \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

$$|\text{LE of } \mathbf{MZ}| \propto \left|\frac{2 \times 2}{0.18 + 0.14}\right| > |\text{LE of } \mathbf{JX}| \propto \left|\frac{1 \times 1}{0.08 + 0.12}\right|$$

Hence, the LE of **MZ** is <u>more exothermic</u> than that of **JX**.

(Recall: The lattice energy is always exothermic as it is the energy released when one mole of the solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 bar.)

Statement 3 is incorrect.

$$|\Delta H_{hyd}| \alpha \left|\frac{q}{r}\right|$$

Since **J**$^+$ has the same charge but smaller ionic radius than **L**$^+$, **J**$^+$ has a larger q/r value, and hence a <u>more exothermic hydration energy</u>.

(Recall: The hydration of gaseous ions by water molecules is an exothermic process due to the <u>formation of ion-dipole</u> interactions between the ions and water molecules.)

9 (Ans: A)

For a reaction which measures the time taken for a <u>coloured reactant</u> to disappear,
rate $\propto \frac{V_{I_2}}{t}$.

reaction mixture	volume of aqueous CH_3COCH_3 / cm^3	volume of aqueous I_2 / cm^3	volume of aqueous HC*l* / cm^3	volume of starch solution / cm^3	volume of water / cm^3	time taken for disappearance of deep blue colour / s	$\frac{V_{I_2}}{t}$ / $cm^3\ s^{-1}$
1	20	10	10	1	5	54	$\frac{10}{54}$
2	15	10	10	1	10	72	$\frac{10}{72}$
3	20	5	10	1	10	y	$\frac{5}{y}$
4	15	10	15	1	5	48	$\frac{10}{48}$

Statement 1 is correct.
Comparing reaction mixtures 1 and 3:
Since order of reaction with respect to I_2 is zero,
rate of reaction mixture 1 = rate of reaction mixture 3
$\Rightarrow \frac{10}{54} = \frac{5}{y}$. Solving, <u>y = 27</u>.

Statement 2 is correct.
Comparing reaction mixtures 1 and 2:
When $V_{CH3COCH3}$ is increased from 15 to 20 cm^3, i.e. $V_{CH3COCH3} \times \frac{4}{3}$, rate $\times \frac{4}{3}$
$\Rightarrow$ <u>order of reaction with respect to CH_3COCH_3 is 1</u>.

Statement 3 is incorrect.
Comparing reaction mixtures 2 and 4:
When V_{HCl} is increased from 10 to 15 cm^3, i.e. $V_{HCl} \times 1.5$, rate $\times$ 1.5
$\Rightarrow$ order of reaction with respect to H^+ is 1.

When HC*l* (monobasic acid) is replaced by H_2SO_4 (dibasic acid) of the same concentration,
$\Rightarrow [H^+] \times 2$ and rate $\times$ 2.
Hence time taken for the disappearance of deep blue colour should be <u>halved</u>.

10 (Ans: D)

Based on the mechanisms, the rate equations and overall equations are shown below.

	rate equation	overall equation for reaction
A	rate = $k[P]^2[Q_2]$	$P + Q_2 + R \rightarrow PQR + Q$
B	rate = $k[P]^2$	$2P + Q_2 + R \rightarrow P_2Q + QR$
C	rate = $k[P][Q_2]$	$2P + Q_2 + R \rightarrow P_2Q + QR$
D	rate = $k[P]^2[Q_2]$	$2P + Q_2 + R \rightarrow P_2Q + QR$

Only D has the correct rate equation and overall equation for the reaction.

11 (Ans: D)

A: Incorrect.
Water is a solvent and not a catalyst in this reaction. Also, a catalyst increases the rates of both the forward and backward reactions to the same extent.

B and C: Incorrect.
Even though H_2O is added and the number of moles/amount of H_2O increases, the $[H_2O]$ stays almost the same/does not change appreciably as H_2O is the solvent and is already present in large excess. Hence, the shift in position of equilibrium is not due to change in $[H_2O]$.

D: Correct.
Addition of water reduces the total ion concentration in the system. Hence the system tries to counteract this change by favouring the reaction that produces more ions (which is the forward reaction in this case), resulting in the solution turning pink.

12 (Ans: A)

Decreased proportion of products imply that the position of equilibrium shifted left after the following changes were introduced.

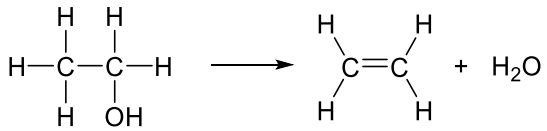
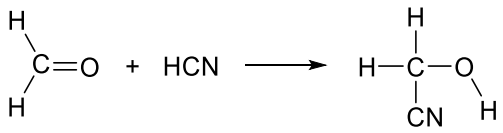
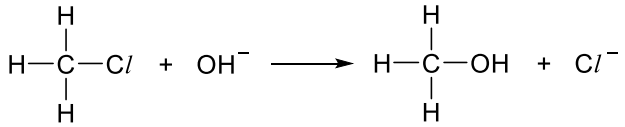
		P is increased at constant T *(reaction that produces fewer gas particles is favoured)*	T is decreased at constant P *(exothermic reaction is favoured)*
A	$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ ΔH = +57 kJ mol^{-1}	left	left
B	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ ΔH = +53 kJ mol^{-1}	no shift	left
C	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ΔH = –92 kJ mol^{-1}	right	right
D	$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ ΔH = –950 kJ mol^{-1}	left	right

13 (Ans: A)

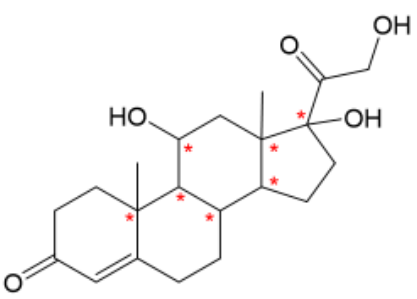
	V	W	Conclusion
A	Molecular formula: C_4H_{10} Empirical formula: C_2H_5 Branched isomer ⇒ smaller surface area for id-id interactions ⇒ weaker id-id interactions	Molecular formula: C_4H_{10} Empirical formula: C_2H_5 Straight-chain isomer ⇒ larger surface area for id-id interactions ⇒ stronger id-id interactions	Same empirical formula. V has a lower boiling point than W.
B	Molecular formula: C_3H_8 Empirical formula: C_3H_8 Smaller and less polarisable electron cloud ⇒ weaker id-id interactions	Molecular formula: C_6H_{14} Empirical formula: C_3H_7 Larger and more polarisable electron cloud ⇒ stronger id-id interactions	Different empirical formula. V has a lower boiling point than W.

C	Molecular formula: C_6H_{12} Empirical formula: CH_2 Larger and more polarisable electron cloud ⇒ stronger id-id interactions	Molecular formula: C_2H_4 Empirical formula: CH_2 Smaller and less polarisable electron cloud ⇒ weaker id-id interactions	Same empirical formula. W has a lower boiling point than V.
D	Molecular formula: $C_2H_2Br_2$ Empirical formula: CHBr Cis isomer with net dipole moment. ⇒ polar with stronger pd-pd interactions.	Molecular formula: $C_2H_2Br_2$ Empirical formula: CHBr Trans isomer with no net dipole moment. ⇒ non-polar with weaker id-id interactions.	Same empirical formula. W has a lower boiling point than V.

14 (Ans: C)

	reaction	type of reaction
1	 • involves the <u>removal of H_2O</u> from <u>adjacent</u> C atoms to form C=C bond • <u>degree of unsaturation increases</u>	elimination (not condensation)
2	 • 2 species react to give a single product • the C=O π bond is broken to form two new O–H and C–C σ bonds (<u>decrease in degree of unsaturation</u>) • the C–O σ bond remains unbroken	addition
3	 • C*l* in CH_3C*l* is replaced by OH. • 2 species react to give 2 products. • <u>degree of unsaturation remains unchanged</u>.	substitution

15 (Ans: B)



There are 7 chiral carbons in the molecule. Hence, the total number of stereoisomers is 2^7.

(Note: The C=C bond in the cyclic ring does not exhibit cis-trans isomerism as the trans isomer is too unstable to exist due to its highly strained structure.)

Section B

B1(a) Let the temperature decrease be 5 °C and volume of water used be 50 cm^3.

Heat change, $q = mc\Delta T = 50 \times 4.18 \times -5 = -1045$ J

Since ΔH_{soln} (NH_4NO_3) ≈ +23 kJ mol^{-1} and $\Delta H_{soln} = -\frac{q}{n(NH_4NO_3)}$,

amount of $NH_4NO_3 = -\frac{-1045}{23 \times 10^3} = 0.04543$ mol

mass of $NH_4NO_3 = 0.04543 \times 80.0 = 3.635$ g

Procedure

1 Place the Styrofoam cup in a 250 cm^3 beaker.
2 Using a 50.0 cm^3 measuring cylinder, transfer 50.0 cm^3 of water into the Styrofoam cup and put the lid on.
3 Using an analytical balance, weigh accurately about 3.6 g of NH_4NO_3 in a clean and dry weighing bottle. Record the total mass of NH_4NO_3 and weighing bottle.
4 Insert the thermometer through the lid and ensure that the bulb of the thermometer is in contact with the water.
5 Record the temperature at time = 0 min. Start timing using the stopwatch.
6 Record the temperature of the water at 1 min and at 2 min.
7 At exactly 3 min, open the lid of the cup and tip all the NH_4NO_3 carefully into the water. Replace the lid quickly.
8 Using the thermometer, stir the mixture gently.
9 Record the temperature of the mixture at every 0.5-min interval until there are 5 temperature readings after the lowest temperature recorded.
10 Reweigh the weighing bottle with any residual NH_4NO_3 and record this mass reading.
11 Rinse out the Styrofoam cup and the weighing bottle and dry them.
12 Repeat steps 1 to 10 to obtain an average value for the enthalpy change of solution.

(max 5 m)

[1] pre-calculations for mass of NH_4NO_3 to be weighed

[1] use of appropriate apparatus and capacity

[1] start stopwatch, at least 3 temperature data points before addition & specify time of addition of solid

[1] collect at least 5 temperature data points after minimum temperature at regular specified time intervals (max interval = 1 min)

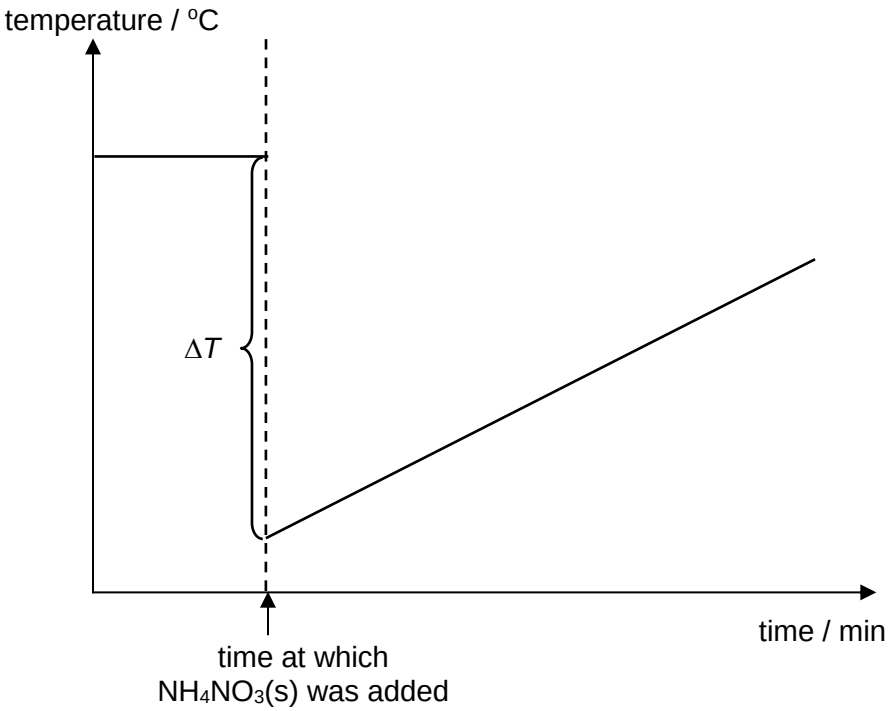
[1] stirring & repeating the experiment (award mark even if not enough solid to repeat the expt. Do not double penalise)

[1] determine mass of NH_4NO_3 used; weighing by difference

Comments:

- Students need to show the pre-calculations required to determine the mass of NH_4NO_3(s) needed to result in a decrease of about 5 ^oC in 50 cm^3 of water, using the assumptions given in the question.
- Apparatus used and its capacity need to be stated in the procedure.
- Students need to state that the stopwatch is started right after taking the temperature at time = 0 min.
- To determine the maximum temperature change, ΔT, two straight lines of best fit are required - one for the temperature of water before addition of NH_4NO_3(s) and the other for the **warming** of the solution once the dissolution is **completed**. Hence, students need to state the collection of at least 5 temperature data points **after** the **minimum/lowest** temperature is reached and NOT simply 5 temperature data points after the addition of NH_4NO_3(s). Students need to be aware that the temperature data point taken immediately after the addition of NH_4NO_3(s) may not be used for the best fit line to account for the heat gain from the surroundings, as the dissolution may not have been completed.

B1(b)(i)



[1] correct temperature profile (down then up)

- data points not required
- if exothermic (do not award)
- warming curve after mixing

[1] show how to obtain ΔT

- three construction lines shown
- only award if done using extrapolation
- vertical line must be at time of addition of solid

Comments:

- As the dissolution of NH_4NO_3(s) is an endothermic process, the temperature drops after the addition of NH_4NO_3(s) to water until the dissolution is completed. This is followed by an increase in temperature due to the heat gain from the surroundings.
- Students need to draw the extrapolation lines to the time of addition of NH_4NO_3(s) to account for the heat gain from the surroundings and to show clearly how ΔT is determined from the graph.

B1(b)(ii) Heat change, $q = mc\Delta T = (V \times 4.18 \times -5.0)$ J **[1]**

$n(NH_4NO_3) = \frac{y}{80.0}$ mol

$\Delta H_{soln} = -\frac{q}{n(NH_4NO_3)}$

$= -\frac{(V \times 4.18 \times -5.0) \times 80.0}{y}$ J mol^{-1} OR $-\frac{(V \times 4.18 \times -5.0) \times 80.0}{1000\,y}$ kJ mol^{-1}

[1] ignore missing unit ; [0] missing / wrong sign

Comments:
- Students are required to include the '–' sign in ΔT (= $T_{final} - T_{initial}$) as the dissolution process involves a decrease in temperature. Since $q = mc\Delta T$, q would be a negative value as well.
- Students are reminded that $\Delta H_{soln} = -\frac{q}{n(NH_4NO_3)}$.

B1(b)(iii) The heat gained from the surroundings will be accounted for via extrapolation of the graph to the point of addition of NH_4NO_3. **[1]**

Reject: heat loss

Comments:
- As stated in the question, the dissolution of $NH_4NO_3(s)$ is an endothermic process. Hence, the temperature of the solution decreases initially and subsequently increases due to the heat gain (NOT loss) from the surroundings.

B1(c) $\Delta H_{hyd}(NH_4^+(g)) = LE(NH_4Cl) + \Delta H_{soln}(NH_4Cl) - \Delta H_{hyd}(Cl^-(g))$
$= -705 + 17 - (-381)$
$= -307$ kJ mol^{-1} **[1]**

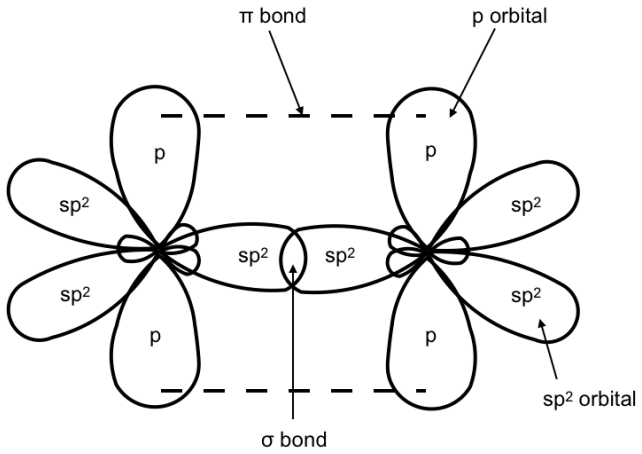
$\Delta H_{soln}(NH_4NO_3) = -LE(NH_4NO_3) + \Delta H_{hyd}(NH_4^+) + \Delta H_{hyd}(NO_3^-(g))$
$= 646 - 307 - 314$
$= +25.0$ kJ mol^{-1} **[1]**

Comments:
- In general, for the dissolution of $M_aX_b(s)$ in water,
  $\Delta H_{soln}(M_aX_b) = a\Delta H_{hyd}(M^{b+}) + b\Delta H_{hyd}(X^{a-}) - LE(M_aX_b)$
  $= \Sigma\Delta H_{hyd} - LE(M_aX_b)$

B2(a)(i) Type of hybridisation: sp^2 **[1]**

Comments:
- Students should write the number in superscript form.
  - Common errors include sp2 or sp_2.
- Students should avoid using capital letters.
  - Common errors include SP^2 or Sp^2.

B2(a)(ii)



[1] diagram showing three sp^2 hybrid orbitals & one p orbital on each C atom
(with p and sp^2 labels, no need for σ and π labels)

The σ bond is formed by the head-on overlap of the sp^2 hybrid orbitals on each C atom. The π bond is formed by the side-on overlap of the unhybridised p orbital on each C atom. **[1]**

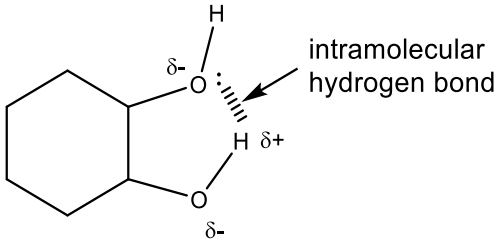
no need to show small lobe for hybrid orbitals
must show the overlap of relevant orbitals to form σ bond
no need to show overlap of p orbitals

Comments:
- The question states that students are supposed to use "**a fully labelled** diagram" in their description of the bonding in C=C bond. Hence, students should only draw one diagram and label clearly the type of orbitals and bonds formed.
- There is no need to show the central C atom when drawing the orbitals.
- Common errors include:
  - Drawing of incomplete orbitals (e.g. showing only half a p-orbital and/or one out of the three sp^2 hybrid orbitals)
  - Missing labels of the type of orbitals and bonds in the diagram
- Some students only drew the hybrid orbitals and missed out the p orbitals involved in the π bond. These students tend to give answers on the bond angle using VSEPR and failed to answer the question.

B2(b)(i) oxidation number of C atom in cyclohexa-1,3-diene: –1
oxidation number of C atom in **A**: 0 **[1] for both correct ans**

Comments:
- Majority of the students did not manage to determine the oxidation numbers of the circled C atoms and left the question blank. Please revise section 1.2 of the 'Introduction to Organic Chemistry' notes.
- For cyclohexa-1,3-diene, the circled C atom is bonded to **1** H and 2 C atoms. Since there is no electronegativity difference between the C atoms and C is more electronegative than H, the circled C atom will 'gain' an electron and its oxidation number is –1.
- For compound A, the circled C atom is bonded to **1** H, **1** O and 2C atoms. Since C is more electronegative than H but less electronegative than O, there is no overall 'gain' or 'loss' of electrons by the circled C atom and thus its oxidation number is 0.

B2(b)(ii)



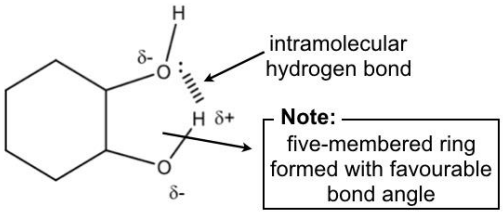
[1]

In **B**, the proximity of –OH groups allow for the formation of intramolecular hydrogen bonds. **[1]** Thus, **B** has fewer sites for intermolecular hydrogen bonding / less extensive intermolecular hydrogen bonding than **A**. **[1]**

Hence, the boiling point of **B** is lower than that of **A** since less energy is required to overcome the less extensive intermolecular hydrogen bonding during boiling.

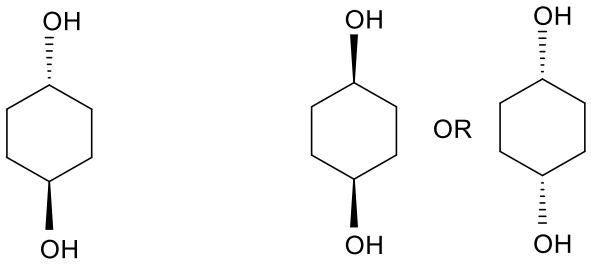
Comments:

- Since hydroxyl (-OH) groups are present in the compounds, students need to identify the predominant forces of attraction (i.e. hydrogen bonding) present.
- Due to the different relative positions of the -OH groups, students need to recognise that only compound B is able to form intramolecular hydrogen bonding. Hence, the diagram drawn should show clearly the **intra**molecular hydrogen bonding in B.



- Lone pair of electrons involved in the hydrogen bonding, and the partial charges on the H and adjacent O atoms should be included in the diagram.
- Since there are two types of hydrogen bonding involved in this question, there is a need to differentiate them by using key terms such as "intramolecular" and "intermolecular".
- Note that although compound B has intramolecular hydrogen bonding, B is still able to form intermolecular hydrogen bonding as there are still sites available for it. The only difference is that there are fewer sites available for intermolecular hydrogen bonding as some of the sites have been used for intramolecular hydrogen bonding.
- Avoid using abbreviations such as "H bonding" in the answers.

B2(b)(iii) cis-trans isomerism **[1]** *accept: geometrical*



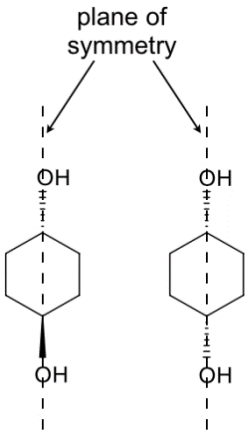
trans isomer cis isomer

[1] for one cis & one trans

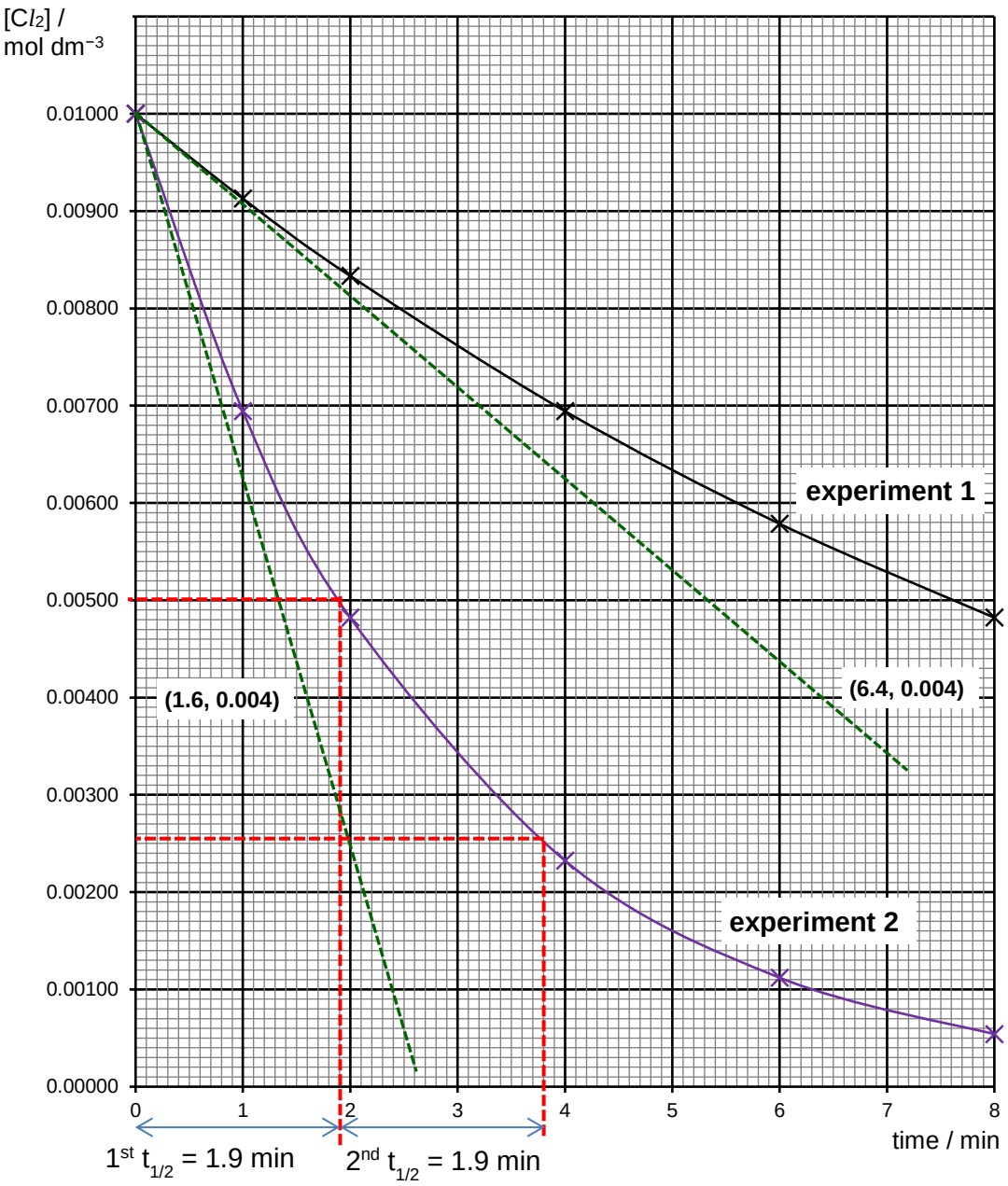
accept: correct chair conformations

Comments:

- The question states that stereoisomers are present. Thus, answers such as “constitutional isomerism” or “positional isomerism” are not accepted.
- Compound A does not display enantiomerism due to the plane of symmetry present in the molecule. This leaves us with cis-trans isomerism, where the *cis* isomer has both hydroxyl (-OH) groups on the same side and the *trans* isomer has the hydroxyl groups on opposite sides.
- When drawing the structures of the isomers, students must use the dash and wedge lines to clearly denote the spatial arrangements of the hydroxyl groups.
- As the question required the drawing of skeletal structures, students should not show C and H atoms in their answers.



B3(a)(i)



[1] for correct plotting of points
[1] for best fit curve

Comments:
- Question was generally well done. Students need to note that for this curve, the best fit curve passes through all the points.
- Students need to exercise more caution when plotting points. A handful plotted points for 0, 1, 2, 3, 4 and 5 min instead of 0, 1, 2, 4, 6 and 8 min.

B3(a)(ii) From graph of experiment 2, 1st $t_{1/2}$ = 2nd $t_{1/2}$ = 1.9 min. Since $t_{1/2}$ is constant, the reaction is first order with respect to ClO_2. **[1]**

Initial rate of Expt 2 = $-\frac{0.004-0.010}{1.6-0}$ = 0.00375 mol dm^{-3} min^{-1}

(A range of 0.00300 to 0.00500 is accepted)

Initial rate of Expt 1 = $-\frac{0.004-0.010}{6.4-0}$ = 0.0009375 mol dm^{-3} min^{-1}

(A range of 0.000850 to 0.00105 is accepted)

[1] for both initial rates

When [NO] $\times$ 2, rate $\times$ $(\frac{0.00375}{0.0009375})$ = 4

Hence rate α [NO]^2 and the order of reaction with respect to NO is 2. **[1, ecf]**

This mark is awarded independently. For example, if gradient ratio = 2.9, order wrt NO can be 1 or 2. If conclusion order = 2 but gradient ratio was 3, do not penalise.

Comments:
- The question explicitly states "draw clearly any construction lines on the graphs". Hence, construction lines to find half-lives and tangents to find gradients should be clearly drawn, as shown in the graph on pg 12.
- It is preferable to use graph of experiment 2 to find $t_{1/2}$ rather than that of experiment 1. When finding two $t_{1/2}$, the initial concentrations used should be significantly different, e.g. initial concentrations of 0.0100 and 0.005 mol dm^{-3} for the first and second $t_{1/2}$ respectively.
- To find the order of reaction with respect to NO, the initial rates of experiments 1 and 2 needed to be compared. To find initial rate, a tangent to each graph should be drawn at t = 0 min. A significant number of students were not able to draw the tangents correctly, especially for graph of experiment 2. Please see your tutor if you were not able to draw the tangent(s) correctly.
- Students should take note that the rate of reaction is always a positive value. For the graph of [reactant] against time, rate = −gradient (since gradient is a negative value).
- An alternative method to find the order of reaction wrt NO is to compare half-lives of experiments 1 and 2. Since NO is used in large excess and the order of reaction wrt ClO_2 is 1,
  rate = k[ClO_2][NO]^m = k'[ClO_2] where m is the order of reaction wrt NO and k' = k[NO]^m
  $t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[NO]^m} \Rightarrow t_{1/2} \propto \frac{1}{[NO]^m} \Rightarrow \frac{t_{1/2} \text{ of expt 1}}{t_{1/2} \text{ of expt 2}} = (\frac{[NO] \text{ of expt 2}}{[NO] \text{ of expt 1}})^m$
  $\Rightarrow \frac{7.6}{1.9} = (\frac{0.20}{0.10})^m$. Solving, m = 2.

  Students who used this alternative method need to show clearly that
  $$t_{1/2} \propto \frac{1}{[NO]^m} \Rightarrow \frac{t_{1/2} \text{ of expt 1}}{t_{1/2} \text{ of expt 2}} = (\frac{[NO] \text{ of expt 2}}{[NO] \text{ of expt 1}})^m$$

B3 (a)(iii) rate = $k[NO]^2[Cl_2]$ **[1, ecf]**

Comments:
• Question was generally well done.

B3 (a)(iv) Using results from experiment 2,
initial rate = $k[NO]_{initial}[Cl_2]_{initial}$
$= k(0.20)^2\ (0.010)$
$= 0.00375$
Solving, $k = 9.375\ mol^{-2}\ dm^6\ min^{-1}$
$= \underline{9.38\ mol^{-2}\ dm^6\ min^{-1}}$ **[1] answer, [1] units**
e.c.f. wrong rate equation & wrong initial rate

Alternatively method *(only if student correctly determined first order wrt Cl_2):*
For experiment 2, since NO is in large excess,
rate = $k[NO]^2[Cl_2] = k'[Cl_2]$ where $k' = k[NO]^2$
$k' = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1.9} = k(0.20)^2$
Solving, $k = \underline{9.12\ mol^{-2}\ dm^6\ min^{-1}}$

Comments:
• For students who used half-life for the calculation of rate constant (i.e. the alternative method), do note that it is $\boldsymbol{k'} = \frac{\ln 2}{t_{1/2}}$ and not $\boldsymbol{k} = \frac{\ln 2}{t_{1/2}}$.
• Many students did not give the units correctly as most wrote s^{-1} instead of min^{-1}.

B3(b)(i) Conversion efficiency for CO = $(1 - \frac{2.1}{15}) \times 100\ \% = \underline{86.0\ \%}$ **[1]**

Comments:
• Question was well done.

B3(b)(ii) $2NO + 2CO \longrightarrow N_2 + 2CO_2$
$2CO + O_2 \longrightarrow 2CO_2$
[1] for 2 equations

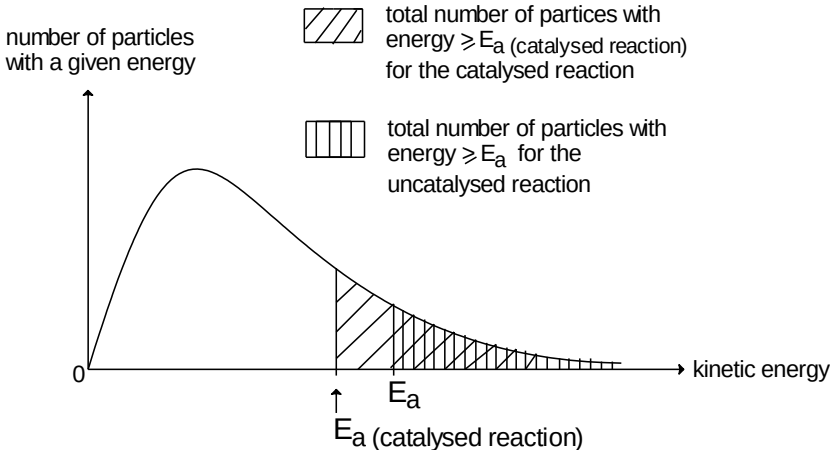
NO is removed by <u>only one process</u> while CO is removed by <u>2 processes.</u>
[1] OWTTE

Comments:
• Many students failed to give the correct equations for the reactions of NO and CO in the catalytic converter. Please revise section 10.2 of the 'Reaction Kinetics' notes.

B3(b)(iii) A catalyst increases the rate of a reaction by providing an alternative reaction pathway of lower activation energy.

In the catalysed reaction, since the activation energy ($E_{a\ (catalysed\ reaction)}$) is lower than that of the uncatalysed reaction (E_a), more reactant particles have energy greater than or equal to the activation energy than in the uncatalysed reaction. **[1]**

This is shown by the larger shaded area for the catalysed reaction in the diagram below.



[1]

Label E_a and E_a(catalysed)
Shape must be correct

- *Start from origin*
- *Tail must approach (but not touch) horizontal axis*
- *areas shaded/allude to shaded areas*
- *reject: if a symmetrical normal distribution is drawn*

The frequency of effective collision increases **[1]** accordingly, and hence the reaction rate increases.

A lower activation energy also results in the reaction having a larger rate constant, and hence an increase in the reaction rate.

Comments:

- Many students failed to draw a reasonable Boltzmann distribution curve. Students need to note the shape of the curve, where it
  - should start from origin
  - is a convex shape from origin to the apex of the curve
  - tapers off with x-axis as the asymptote
- The keyword "frequency" of effective collisions needs to be present. Words such as "number" or "rate" will not be accepted.
- Some students labelled the axes incorrectly.

Section C

C1(a) Total pressure at equilibrium
= nRT / V
= 0.680(8.31)(472) / (3000 × 10^{-6})
= 8.891 × 10^5 Pa
= 8.774 atm

Let y atm be the equilibrium partial pressure of $COCl_2$.

	CO(g)	+ Cl_2(g)	⇌ $COCl_2$(g)
Initial partial pressure / atm	5.05	4.63	0
Change / atm	–y	–y	+y
Equilibrium partial pressure / atm	5.05–y	4.63–y	y

Applying Dalton's Law,
5.05 – y + 4.63 – y + y = 8.774 atm
y = 0.906 atm

Equilibrium partial pressure of $COCl_2$, y = 0.906 atm
Equilibrium partial pressure of CO = 5.05 – y = 4.144 atm
Equilibrium partial pressure of Cl_2 = 4.63 – y = 3.724 atm

[1] use of ideal gas equation to solve for total pressure or y or amount
[1] for all the eqm partial pressure or amounts.

K_p = 0.906 / (4.144)(3.724) = <u>0.0591 atm^{-1}</u> **[1] answer, ecf + [1] units**

Comments:
- 1 atm is equivalent to 101325 Pa, NOT 10^5 Pa (which is equivalent to 1 bar). If unsure, please check these values under Section 1 'Important values, constants and standards' of the *Data Booklet*.
- K_p must be calculated <u>in terms of partial pressures</u>. Using concentration or amount will give an incorrect value.

C1(b)(i) When the volume of the vessel is increased, the <u>total pressure is initially decreased</u> **[1]**. According to Le Chatelier's Principle, the <u>reaction that produces greater amount of gases is favoured</u> so as to counteract the initial decrease in total pressure and <u>position of equilibrium shifts left</u> (or backward reaction favoured) **[1]**. At the new equilibrium, the reaction mixture consists of <u>less</u> $COCl_2$(g) and <u>more</u> CO(g) and Cl_2(g) compared to the mixture before the volume change **[1]**.

accept if explained in terms of concentration or partial pressure
accept Q_p explanation
***[1]** partial pressures of gases decrease*
***[1]** $Q_p > K_p$, backward reaction favoured/POE shift left*
***[1]** correct composition changes*

Comments:
- Composition of a mixture consists of both reactants and products. Hence students need to state whether the reactants **and** products are increased or decreased.
- Students need to state clearly how the composition of the mixture at the new equilibrium **compare** with that at the start (i.e. before the volume of the reaction vessel was increased). It is confusing to simply state that 'the partial pressure / concentration of $COCl_2(g)$ is decreased and the partial pressures / concentrations of CO(g) and $Cl_2(g)$ are increased' as the stress imposed on the system (increase in volume) already caused an initial change in the partial pressures / concentrations of all species in the system.
- It is also incorrect to conclude that the resulting reaction mixture has more reactants (CO(g) and $Cl_2(g)$) than products ($COCl_2(g)$). When the position of equilibrium shifts towards the left (reactants), it means that more reactants would be formed to establish a new equilibrium. It does not necessarily mean that there would be more reactants **than** products at the new equilibrium.

C1(b)(ii) The value of K_p will remain the same as the temperature was kept constant. **[1]**

Comments:
- Students need to show understanding that the value of K_p is only dependent on temperature. Do not merely list some physical properties that do not affect the value of K_p e.g. volume, pressure or concentration.

C1(c)(i) $\Delta H^{\ominus} = 1077 + 244 - 740 - 2(340) = \underline{-99.0 \text{ kJ mol}^{-1}}$ **[1]**

Comments:
- Note that bond energy refers to the energy required to break the bond, not the energy released when forming the bond. Many students who simply memorised the formula of $\Delta \boldsymbol{H} = \Sigma \boldsymbol{H}_{\text{products}} - \Sigma \boldsymbol{H}_{\text{reactants}}$ applied it incorrectly and obtained $\Delta H^{\ominus} = +99.0 \text{ kJ mol}^{-1}$ instead.

C1(c)(ii) $\Delta S^{\ominus} = +283 - (+198) - (+223) = -138 \text{ J K}^{-1} \text{ mol}^{-1}$ **[1]**

$\Delta G^{\ominus} = -99 - 298(-138 \times 10^{-3}) = \underline{-57.9 \text{ kJ mol}^{-1}}$ **[1, ecf]**

Comments:
- To calculate the $\Delta S^{\ominus}$ of a reaction, the following formula should be used
$$\Delta S_{rxn}^{\ominus} = \Sigma n S^{\ominus}(\text{products}) - \Sigma m S^{\ominus}(\text{reactants})$$
- Students need to be mindful of the units of entropy (usually in **J** K^{-1} mol^{-1}) compared to the units of enthalpy and Gibbs free energy (usually in **kJ** mol^{-1}).

C1(c)(iii) Since $\Delta G^{\ominus} < 0$, the equilibrium constant is expected to be > 1. The position of equilibrium lies to the right. **[1, ecf]**

Comments:
- $\Delta G^{\ominus} = -RT \ln K$. Mathematically, an exergonic Gibbs free energy ($\Delta G < 0$) correlates to an equilibrium constant value that is greater than 1. Hence, there should be more products than reactants, implying that the equilibrium position lies to the right.
- Avoid stating that the position of equilibrium shifts to the right (or forward reaction is favoured) as it is assumed that the system is at dynamic equilibrium and no external stress was imposed.

C2(a)(i) Standard enthalpy change of combustion of cubane is the energy released when 1 mol of cubane is completely burnt in excess oxygen at 298K and 1 bar. **[1]**

Accept: energy change
BOD: combusted fully / burnt with excess oxygen

$C_8H_8(s) + 10O_2(g) \longrightarrow 8CO_2(g) + 4H_2O(l)$ **[1]**
[0] missing / wrong state symbols

Comments:
- Combustion reactions are always exothermic. Hence, answers that gave the definition as 'energy required' were not accepted.
- State symbols must be given. H_2O is in the liquid state as this standard enthalpy change takes place at 298K.

C2(a)(ii) $\Delta H_c^{\ominus} = 8(-394) + 4(-286) - (+602)$ **[1]**
$= -4898$ kJ mol^{-1} or -4900 kJ mol^{-1} **[1]** ignore units
[0] wrong / no sign

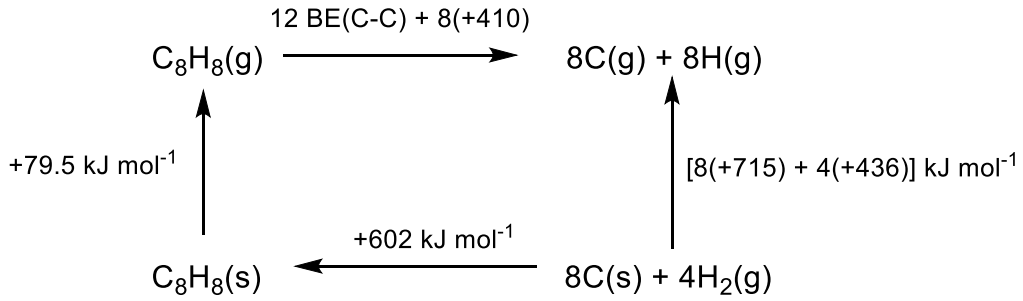
Comments:
- When using $\Delta H_{rxn}^{\ominus} = \Sigma n \Delta H_f^{\ominus}$ **(pdts)** – $\Sigma m \Delta H_f^{\ominus}$ **(rxts)**, the coefficients must be included.
- $\Delta H_f^{\ominus}$ of elements is 0. Hence, $\Delta H_f^{\ominus}[O_2] = 0$. A number of students incorrectly used bond energy of O=O (496 kJ mol^{-1}) to substitute for $\Delta H_f^{\ominus}[O_2]$.

C2(b)(i) Cubane is energetically less stable relative to its elements under standard conditions since $\Delta H_f^{\ominus} > 0$. **[1]**

For the reason, i.e. $\Delta H_f^{\ominus} > 0$, accept also: Endothermic / Higher energy level than elements / Energy level diagram can substitute

Comments:
- It is irrelevant to discuss $\Delta H_c^{\ominus}$ since we are comparing the energetic stability of cubane relative to its elements, not relative to CO_2 and H_2O.

C2(b)(ii)



[2] deduct 1m per one or two errors

Using Hess' Law,
$12\,BE(C-C) + 8(410) = -79.5 - 602 + 8(715) + 4(436)$ **[1]**
$12\,BE(C-C) = +3502.5$
$BE(C-C) = +292$ kJ mol^{-1} **[1] ignore sign, no ecf from cycle**

Comments:
- The question clearly states that cubane has 12 identical C-C bonds and 8 identical C–H bonds. A number of students thought that there are 8 C–C bonds instead.
- Bond energy is the energy required to break one mole of the X–Y bond in the gaseous state and hence $C_8H_8(s)$ has to undergo sublimation to $C_8H_8(g)$ before the 12 C–C bonds and 8 C–H bonds are broken, forming 8C(g) and 8H(g) atoms.

C2(b)(iii) BE(C−C) in cubane = +292 kJ mol^{-1} is less endothermic than BE(C−C) = +350 kJ mol^{-1} due to the angle strain in cubane in which the bond angles are 90^o instead of the usual 109.5^o.
This causes the overlap between hybrid orbitals to be less effective OR greater repulsion between the bond pairs. **[1]**

no ecf
Reject: BE are average values
Reject: highly strained without explanation

Comments:
- Reference should be made as to how the value is different, i.e. students need to specify that it is less endothermic.
- A precise reason as to why it is so much less endothermic has to be given, with reference made to the structure of cubane and how there is less effective orbital overlap or increased repulsion between bond pairs due to the angle strain.

C2(c)(i) $\Delta S^{\ominus}$ is positive since there is an increase in disorder due to the increase in number of gaseous particles from 0 mol in the reactant to 12 mol in the products. **[1]**
This results in $-T\Delta S^{\ominus}$ being negative.

Since $\Delta G^{\ominus} = -3475 - T\Delta S^{\ominus}$, $\Delta G^{\ominus}$ is negative / has same sign as $\Delta H^{\ominus}$ and will have a greater magnitude / value compared to $\Delta H^{\ominus}$. **[1]**

For comparison of value, accept: $\Delta G^{\ominus}$ is more negative than $\Delta H^{\ominus}$

Comments:
- Many students did not compare the value of $\Delta G^{\ominus}$ with that of $\Delta H^{\ominus}$ even though it was stated in the question to do so.
- Some students stated that $\Delta S^{\ominus}$ is positive without giving the reason.

C2(c)(ii) A large volume of gas was produced in a short period of time. **[1] OWTTE**

Accept: sudden expansion of gases/volume or sudden increase in pressure. Ideas of speed of rxn and volume of gases should be accepted.

Comments:
- For an explosive, a large volume of gas should be produced in a short period of time. If it were produced over a long period, it would not have an explosive action.

C2(c)(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

Octabitrocubane produces all gaseous products that are not visible while hydrogen produces visible water/ice that can be tracked. **[1]**

Comments:

- Some students did not know the product of the combustion of H_2, and wrongly thought that H_2 or soot (C(s)) will be produced.
- For those who knew H_2O would be produced, some incorrectly suggested that water vapour (i.e. $H_2O(g)$) can be seen (the humidity in Singapore ranges from 64-96%, but yet we do not 'see' water vapour!). Many students wrote that water vapour is hardly present in air and this is definitely not true.
- For this question, students are required to compare between $H_2O(l)$ and the gaseous products formed by octanitrocubane. Many students mentioned visible liquid water but did not compare with how the gaseous products produced by octanitrocubane are not visible.

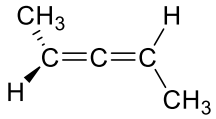
C3(a) constitutional / structural **[1]**

Accept: chain
Reject: positional

Comments:

- Students need to specify the isomeric relationship between compounds A and B, rather than simply stating that A and B have the same molecular formula but different structural formula.
- Compounds A and B are constitutional/structural isomers as they differ in the arrangement of the $–CH_3$ group on the carbon skeleton (CH_3-C=C=C-H).
- Positional isomers are isomers from the same homologous series with the <u>functional group</u> located at <u>different positions</u> on the same carbon skeleton. Since compounds A and B have the same carbon skeleton and position of the C=C bonds (CH_3-C=C=C-H), A and B are NOT positional isomers. Similarly, A and B are NOT stereoisomers (enantiomers, cis-trans isomers) since they have different structural formula/arrangement of atoms (recall: stereoisomers are compounds with the same molecular formula and structural formula but different spatial arrangement of atoms).

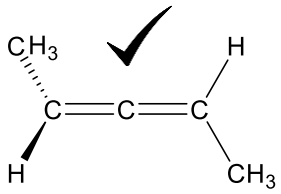
C3(b)(i)



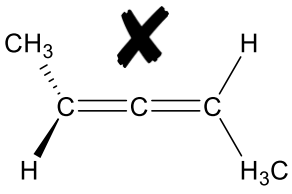
[1]

Comments:

- To draw the enantiomer, students are encouraged to draw the mirror plane and do a mirror reflection of compound B.
- Alternatively, students can swap the position of $–CH_3$ and –H on <u>only one</u> (not both) of the sp^2 C.
- When drawing the compound structure, it is important to show clearly the bond connection between the atoms. Also, avoid inverting the methyl group, i.e. refrain from drawing $H_3C–$.



C-C bonds are shown clearly



C-C bonds are not clearly shown. Also, avoid writing 'H_3C-'

- Since the structure of the enantiomer (stereoisomer) is required, the spatial arrangement of the atoms/groups must be clearly shown, i.e. trigonal planar shape around the sp^2 C and linear shape around the sp C.

C3(b)(ii) **A** does not exhibit enantiomerism as it has an internal plane of symmetry. **[1]**

Reject: Its mirror image is superimposable.
Reject: No chiral carbon

Comments:
- In the context of this question, it is insufficient to state that compound A does not exhibit enantiomerism because it has no chiral carbon (no C atom with four different groups) since compound B exhibits enantiomerism despite having no chiral carbon.
- As the question required reference to the structure of compound A, it is insufficient to state that compound A does not exhibit enantiomerism as it forms superimposable mirror image.
- Since compound A has no chiral carbon, it is NOT a meso compound (Recall: A meso compound is an optically inactive compound with more than one chiral center but has a plane of symmetry).

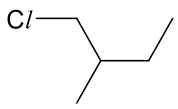
C3(c)(i) Alkanes contain strong C-C and C-H bonds. **[1]**
Alkanes are non-polar (OR lack of electron-rich and electron-deficient sites). **[1]**

Comments:
- This question is generally well done.
- Some students incorrectly used "weak instantaneous dipole–induced dipole" to explain the unreactivity of alkanes. Note that the strength of intermolecular forces affects the b.p./m.p. (physical properties) and not the chemical reactivity of the compound.
- Note also that electron-rich sites/regions with high electron density attracts electrophiles while electron-deficient sites/regions with low electron density attracts nucleophiles.

C3(c)(ii) step I: H_2, Ni, heat **[1]** *accept Pt/Pd (heat)*

step II: limiting Cl_2 (or excess **C**), uv light (or heat) **[1]**

Comments:
- For step I, many students forgot to include H_2 (reagent), the catalyst and/or heat.
- For Step II, many students missed out on the limiting Cl_2. To produce mono–substituted chloroalkanes, limited Cl_2 (or excess hydrocarbon) should be used.
- For the presentation of answers, students need to specify clearly which reagents/conditions are meant for which step of the reaction scheme.

C3(c)(iii) 

[1]

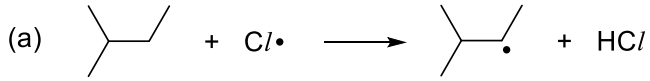
Comments:
- The question states that 'Compounds D and E **each** exists as a pair of enantiomers.' Many students failed to read the question carefully and gave compound E as the enantiomer of compound D.
- Since compound E exists as a pair of enantiomers, E has a chiral carbon/absence of plane of symmetry.

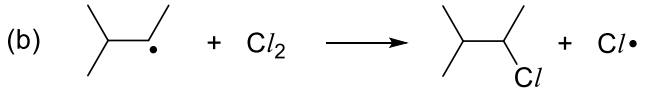
C3(c)(iv) Free radical substitution

initiation

$Cl_2 \longrightarrow 2Cl\bullet$ **[1]**

propagation

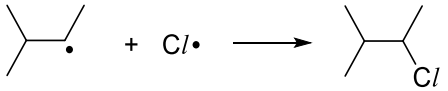
(a)  **[1]**

(b) 

then (a), (b), (a), (b)…

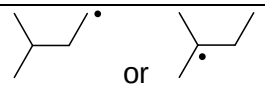
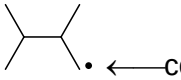
termination

$2Cl\bullet \longrightarrow Cl_2$

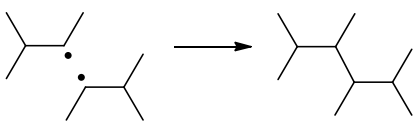
 **[1]**

Comments:

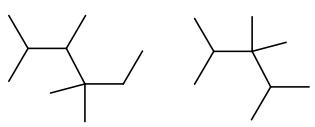
- This question is generally well done. Use of skeletal structures is preferred (unless otherwise stated by the question).
- As the question required the mechanism to show the formation of compound D, the correct radical must be drawn, with the unpaired electron indicated on the correct C atom. Some common mistakes include:

Incorrect radical
 or (these will not lead to formation of compound D)
 ⟵contains extra C atom
 (missing H atom on C•)
$CH_3CH_3\overset{\bullet}{C}HCH_3$ or $(CH_3)_2CHCHCH_3\bullet$ (correct presentation should be $(CH_3)_2\overset{\bullet}{C}HCH_3$)
$C_5H_{11}\bullet$ (structure of the radical must be clearly shown)

- For the termination step showing the reaction between the two alkyl radicals, it is a good practice to place the two alkyl radicals next to each other and form the C–C bond between the two C•.



common mistakes:



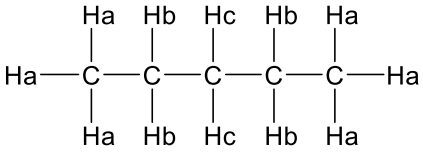
C3(d)(i) Ratio of **F** : **G** = 3 : 2 **[1]**

There are 6 equivalent (primary) H that can be substituted to give **F**, and 4 equivalent (secondary) H that can be substituted to give **G**. **[1] OWTTE**

Marking point (6 : 4 ratio)
No need to classify H as primary/secondary
Students can draw structure and circle equivalent H.
If counted wrongly, but idea of equivalency is correctly explained, award total of 1m.

Comments:

- Some students did not realise that the question is asking them for a probability of forming compounds F and G based on the number of equivalent hydrogens that can be substituted to form F and G.
- Students should only consider the relative stability of the alkyl radicals in determining the ratio of the products F and G when prompted by the question, e.g. when given information on the relative rates of formation of the alkyl radicals.
- Some answers were unclear in stating which secondary H atoms can be substituted to form compound G. Note that in pentane, there are two different secondary H atoms:

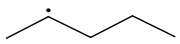
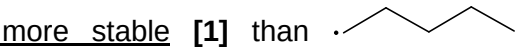


Ha : primary H atoms

Hb & Hc: secondary H atoms

Hb and Hc are **not** equivalent

- The question asked to predict the relative proportions (i.e. ratio) of compounds F and G, NOT the total percentage of F and G formed. Hence, answers stating 50 % F and 33.3% G are not accepted.

C3(d)(ii)  (or secondary radical) is more stable **[1]** than  (or primary radical) due to the presence of more electron-donating alkyl groups **[1]** attached to the electron-deficient carbon.

Therefore it gives rise to a greater proportion of **G** being formed than predicted in **(d)(i)**.

Marking point: secondary radical more stable than primary radical. No need to classify radical, can just compare number of R groups.

Primary H less reactive than secondary H (Max 1m)

No ecf from (i)

Comments:

- Other than the number of equivalent H atoms, the stability of the alkyl radical also affects the proportion of the products formed – the more stable the alkyl radical, the faster it is formed (due to lower E_a) and the greater the amount of the respective substituted product formed.
- Following their answers in (d)(i), most students recognised that compound G is produced in greater amount than expected. Hence, the key to explaining the observed ratio is to compare and explain the relative stability of the **alkyl radicals**. Many students incorrectly compared and explained the stability of compounds G vs F.

- Some students showed confusion between stability vs reactivity. A species that is more stable (i.e. at lower energy level) will be less reactive and vice versa. Hence, a secondary H atom is more reactive (NOT more stable) than a primary H atom.
- Students should practise the use of correct terminologies, e.g. 'radical', 'alkyl groups' and 'electron donating', in their answers.
- Some students incorrectly mentioned tertiary and secondary radicals instead of primary and secondary radicals.