RAFFLES INSTITUTION
2017 YEAR 5 H2 CHEMISTRY PROMOTION EXAMINATION

SECTION A

1	2	3	4	5	6	7	8	9	10
D	D	A	D	C	B	D	B	A	A

11	12	13	14	15	16
C	C	B	B	D	C

1 Answer: D

$$\text{relative molecular mass} = \frac{\text{weighted average mass of 1 molecule of the substance}}{\frac{1}{12} \text{ x mass of 1 atom of carbon-12}}$$

Students need to find the option which most closely describes the above.

A. Incorrect. If only the relative isotopic mass of the most abundant isotope was considered for each atom, it will not be able to account for the mass of the different isotopes of the same element, which is required for the weighted average mass.
B. Incorrect. The denominator should have been the mass of $\frac{1}{12}$ of one ^{12}C atom.
C. Incorrect. The denominator should have been the mass of $\frac{1}{12}$ of 1 mole of ^{12}C atoms.
D. Correct. This option most accurately defines relative atomic mass.

2 Answer: D

$\mathbf{G^{2+}}$ ion has the same number of electrons as PH_3, i.e. $\mathbf{G^{2+}}$ ion has 18 electrons.
So, **G** must have 20 electrons. As the 4s orbital will be filled before the 3d orbitals, the ground state electronic configuration of **G** will be $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$.

3 Answer: A

1. Incorrect. Cu_2O contains Cu^+ ion.
   The ground state electronic configuration of Cu is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$.
   To form Cu^+ ion, the electron will be removed from the 4s orbital.
   The ground state electronic configuration of Cu^+ is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$.
   Cu^+ ion does not have an unpaired d electron.
2. Incorrect. $Zn(NO_3)_2$ contains Zn^{2+} ion.
   The ground state electronic configuration Zn is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$.
   To form Zn^{2+} ion, the 2 electrons will be removed from the 4s orbital.
   The ground state electronic configuration of Zn^{2+} is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$.
   Zn^{2+} ion does not have an unpaired d electron.
3. Correct. $Ti_2(SO_4)_3$ contains Ti^{3+} ion.

   The ground state electronic configuration of Ti is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2$.
   To form Ti^{3+}, 2 electrons will be removed from the 4s orbital, followed by 1 electron from a 3d orbital.

The ground state electronic configuration of Ti^{3+} is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1$.
Ti^{3+} ion has an unpaired d electron.

Hence, only option 1 is correct.

4 Answer: D

The actual bond length of N(1)≡N(2) (0.112 nm) in N_2O is between that of N=N (0.120 nm) and N≡N (0.110 nm), which indicates that the N(1)≡N(2) bond in N_2O is stronger than a N=N bond but weaker than a N≡N bond.

Also, the actual bond length of N(2)→O (0.119 nm) in N_2O is between that of N–O (0.147 nm) and N=O (0.115 nm), which indicates that the N(2)→O bond in N_2O is stronger than a N–O bond but weaker than a N=O bond.

This is due to the delocalisation of the π electrons between N(1) and N(2) over the N(2)→O bond, which weakens the N(1)≡N(2) bond but strengthens the N(2)→O bond.

5 Answer: C

amount of **L** = $\frac{0.058}{46.0} = 1.2608 \times 10^{-3}$ mol

partial pressure of **L** = $\frac{1.2608 \times 10^{-3} \times 8.31 \times 373}{80 \times 10^{-6}} = 4.8850 \times 10^4$ Pa

partial pressure of **J** = $101000 - 4.8850 \times 10^4 = 5.2150 \times 10^4$ Pa

mole fraction of **J** = $\frac{52150}{101000} = 0.516$

6 Answer: B

$$\left|\text{lattice energy}\right| \propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$$

q_+ = charge on cation
q_- = charge on anion
r_+ = radius of cation
r_- = radius of anion
$(r_+ + r_-)$ = inter-ionic distance

A. Incorrect. Though the radius of oxide ion is greater than that of the fluoride ion, it does not explain why the LE of MgO is more exothermic than that of NaF.
B. Correct. The higher charge on Mg^{2+} ion compared to Na^+ ion contributes to the more exothermic LE of MgO.
C. Incorrect. The radius of the atom is not needed for predicting the magnitude of the LE of ionic compounds using the mathematical relation above.
D. Incorrect. The difference in electronegativity is not needed for predicting the magnitude of the LE of ionic compounds using the mathematical relation above.

7 Answer: D

Students need to choose an option with a suitable method for monitoring the rate of the reaction. Also, in order to find the order of reaction with respect to H_2SO_4, the experiment needs to be repeated with different initial $[H_2SO_4]$ each time at the same temperature to determine how the rate of the reaction changes with the initial $[H_2SO_4]$.

A. Incorrect. The method for monitoring the rate of reaction is suitable as $[H^+]$ changes during the course of the reaction. However, the experiment should be repeated using a different initial $[H_2SO_4]$ each time.
B. Incorrect. The method for monitoring the rate of reaction is suitable as $[I_2]$ changes during the course of the reaction. However, the experiment should be repeated using a different initial $[H_2SO_4]$ each time.
C. Incorrect. The method for monitoring the rate of reaction is suitable as electrical conductivity changes during the course of the reaction. However, the experiment should be repeated using a different initial $[H_2SO_4]$ each time at a constant temperature.
D. Correct. The method for monitoring the rate of reaction is suitable as $[I_2]$ and its colour intensity changes during the course of the reaction and the experiment is repeated using a different initial $[H_2SO_4]$ each time.

8 Answer: B

The total volume of the reaction mixture in experiments 1 to 4 is kept constant (100 cm^3). Hence, initial [reactant] $\propto$ volume of reactant used.

t is the time taken for the complete disappearance of the red colour of the indicator. We are monitoring the time taken for a fixed and small amount of Br_2 to be formed. Hence, initial rate $\propto 1/t$.

Consider experiments 1 and 2. When the volume of H_2SO_4 is doubled, the initial $[H_2SO_4]$ doubled. With the other concentrations of reactants kept constant, the initial rate of the reaction quadrupled. Hence, the order of reaction with respect to H_2SO_4 is 2.

Consider experiments 2 and 3. When the volume of $KBrO_3$ doubled, the initial $[KBrO_3]$ doubled. With the other concentrations of reactants kept constant, the initial rate of the reaction doubled. Hence, the order of reaction with respect to $KBrO_3$ is 1.

Using experiments 3 and 4,

$$\frac{\text{rate(3)}}{\text{rate(4)}} = \frac{\frac{1}{13}}{\frac{1}{208}} = \frac{k(3)}{k(4)}\frac{10^1}{5^1}\frac{25^n}{50^n}\frac{60^2}{15^2}$$

n = 1

Hence, the order of reaction with respect to KBr is 1.

A. Incorrect. Compared to experiment 4, the volume of each reactant and the total volume of the reaction mixture have doubled. The initial [reactants] remain the same as those in experiment 4. The rate, and hence, t, should be the same as that in experiment 4 (208 s).

B. Correct. Rate = $k[KBrO_3][KBr][H_2SO_4]^2$. The overall order of the reaction is 4.
C. Incorrect. The units of the rate constant are $mol^{-3}\ dm^9\ s^{-1}$.
D. Incorrect. Increasing the concentration of phenol added will increase the amount of Br_2 needed to react with phenol before discolouration of the red colour is observed. Hence, t will be larger.

9 Answer: A

rate = $k[H_2O_2][I^-]$
Since $[H_2O_2] << [I^-]$, rate ≈ $k'[H_2O_2]$, where $k' = k[I^-]$
Since the reaction is approximated to a pseudo-first order reaction,

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[I^-]} = 80 \text{ s (reaction I)}$$

Since the $[I^-]$ in reaction **II** is half of that in reaction **I**,

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k \times \frac{1}{2} \times [I^-]} = \frac{80}{\frac{1}{2}} = 160 \text{ s (reaction II)}$$

$[H_2O_2]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	ratio of H_2O_2 to I_2	no. of half-lives	time taken / s
0.0200	0	-	0	0
0.0100	0.0100	1 : 1	1	160
0.0050	0.0150	1 : 3	2	320
0.0025	0.0175	1 : 7	3	480

10 Answer: A

Since the initial volumes of SO_2 and O_2 added were equal, an equal number of moles of SO_2 and O_2 has been added, and the initial partial pressure must be the same.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Initial pressure /atm	x	x	0
Change in pressure /atm	–2y	–y	+2y
Equilibrium pressure /atm	x – 2y	x – y	2y

$P_T = (x - 2y) + (x - y) + 2y = 2x - y$
$P_{SO_3} = 2y$

$$\frac{P_{SO_3}}{P_T} = \frac{2y}{2x - y} = 0.5$$

Solving, y = 0.4x

$$\text{Mole fraction of } SO_2 = \frac{P_{SO_2}}{P_T} = \frac{x - 2y}{2x - y} = \frac{x - 2(0.4x)}{2x - 0.4x} = \frac{1}{8}$$

11 Answer: C

The mixture is kept within a movable syringe, so this is a constant pressure system.

1. Correct. When the plunger is pulled, the total volume of the system increases. As the number of moles of gases remains constant, all the concentrations of gases are simultaneously decreased, accounting for the sudden dip in concentration of H_2. Since the decrease in the denominator of Q_c is greater than the decrease in the numerator, we have

$$Q_C = \frac{[H_2S]^2[CH_4]}{[CS_2][H_2]^4} > K_C$$

The system restores equilibrium by favouring the backward reaction. The concentrations of H_2S and CH_4 decrease, while the concentrations of CS_2 and H_2 increase until

$$Q_C = \frac{[H_2S]^2[CH_4]}{[CS_2][H_2]^4} = K_C$$

2. Incorrect. As the forward reaction is endothermic ($\Delta H^{\ominus} > 0$), lowering the temperature would cause the backward exothermic reaction to be favoured, producing more H_2. However, there is no sudden change in number of moles of gases and in volume. Thus, there will not be a sudden dip in concentration of H_2.

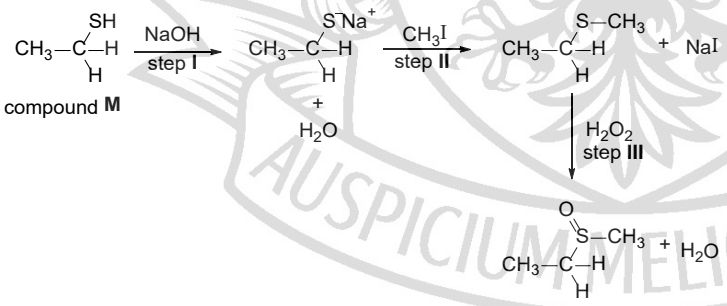
3. Correct. At constant temperature, in order for the pressure inside the syringe to be the same as that of the surroundings, the volume of the system must increase when a small amount of Ar(g) is added. As the number of moles of reactant gases remains constant, all the concentrations of reactant gases are simultaneously decreased, accounting for the sudden dip in concentration of H_2. Since the decrease in the denominator of Q_c is greater than the decrease in the numerator, we have

$$Q_C = \frac{[H_2S]^2[CH_4]}{[CS_2][H_2]^4} > K_C$$

The system restores equilibrium by favouring the backward reaction. The concentrations of H_2S and CH_4 decrease, while the concentrations of CS_2 and H_2 increase until

$$Q_C = \frac{[H_2S]^2[CH_4]}{[CS_2][H_2]^4} = K_C$$

12 Answer: C



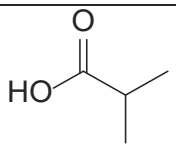
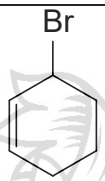
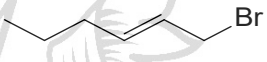
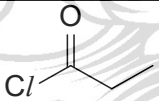
In Step **I**, OH^- neutralises H^+ from CH_3CH_2SH, forming a salt ($CH_3CH_2S^-Na^+$) and H_2O.

In Step **II**, the nucleophile $CH_3CH_2S:^-$ attacks the C(δ+) bonded to I in CH_3I. The substitution of the I atom results in the formation of $CH_3CH_2SCH_3$ and I^-. This is a nucleophilic substitution reaction.

In Step **III**, the sulfur atom gains an oxygen atom. This is an oxidation reaction.

Hence, there is no addition reaction.

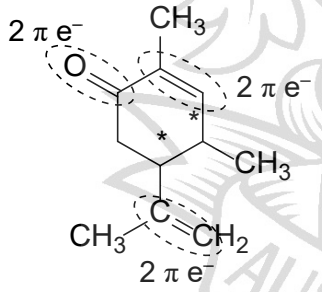
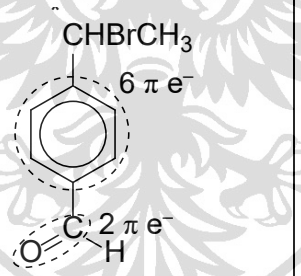
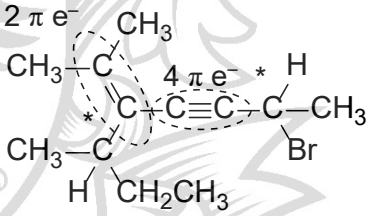
13 Answer: B

1.	 molecular formula: C_2H_4O empirical formula: C_2H_4O	 molecular formula: $C_4H_8O_2$ empirical formula: C_2H_4O
2.	 molecular formula: C_6H_9Br empirical formula: C_6H_9Br	 molecular formula: $C_6H_{11}Br$ empirical formula: $C_6H_{11}Br$
3.	 molecular formula: C_3H_5OCl empirical formula: C_3H_5OCl	 molecular formula: C_3H_5OCl empirical formula: C_3H_5OCl

Therefore, only options 1 and 3 are correct.

14 Answer: B

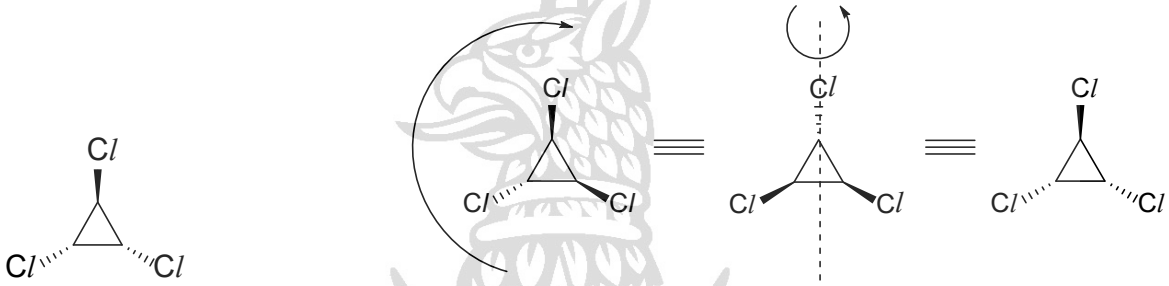
Chiral carbons are marked with *.

 - two chiral carbons - six π electrons	 - one chiral carbons - eight π electrons	 - two chiral carbons - six π electrons
P	**Q**	**R**

Hence, only compounds **P** and **R** have chiral carbons and six π electrons.

15 Answer: D

A. Incorrect. The two structures are identical.



B. Incorrect. The two compounds are constitutional (or positional) isomers as the Br atoms can be bonded either to the same carbon atom or to different carbon atoms of the ring.

C. Incorrect. The two compounds are constitutional (or positional) isomers as the C*l* atoms can be bonded either to the same carbon atom or to different carbon atoms of the C=C bond.

D. Correct. They are cis-trans isomers.

16 Answer: C

For hexabromination to occur, Br_2 needs to be in excess. Ultraviolet light is required for the homolytic fission of the Br–Br bond in the initiation step to generate the Br● radicals.

SECTION B

B1 (a)(i) The energy absorbed to break the 6 Co-O coordinate bonds is greater/more than the energy released when 4 Co-C*l* bonds are formed. **[1]** OR
Energy needed to break the more extensive ion-dipole interactions between $Co(H_2O)_6^{2+}$ & H_2O and Cl^- & H_2O is greater than energy released in the formation of ion-dipole interactions between $CoCl_4^{2-}$ & H_2O in the products. **[1]**

(a)(ii) ΔS: Positive Sign/+/plus/>0
Since $\Delta H > 0$, ΔS must be positive in order for the reaction to be spontaneous ($\Delta G < 0$) **[1]**
OR
7 particles (1 ion and 6 molecules) are formed from 5 particles (5 ions). There is an increase of two particles, leading to an increase in disorder and entropy. **[1]**

(b)(i) $K_c = \dfrac{[CoCl_4^{2-}]}{[Co(H_2O)_6^{2+}][Cl^-]^4}$ **[1]** $mol^{-4}\ dm^{12}$ **[1]** (units must be consistent with K_c expression)

(b)(ii)

	$Co(H_2O)_6^{2+}$ +	$4Cl^-$ ⇌	$CoCl_4^{2-}$ +	H_2O
Initial conc ($mol\ dm^{-3}$)	0.4	6	0	-
Change in conc ($mol\ dm^{-3}$)	$-(3.3 \times 10^{-3})$	$-4(3.3 \times 10^{-3})$	$+3.3 \times 10^{-3}$	-
Eqm conc ($mol\ dm^{-3}$)	0.3967	5.987	3.3×10^{-3}	-

$$K_c = \frac{(3.3\times10^{-3})}{(0.3967)(5.987)^4}$$
$= 6.47 \times 10^{-6}\ mol^{-4}\ dm^{12}$

[1] for factoring in dilution, **[1]** for correct calculation of equilibrium concentrations of reactants, **[1]** for final answer based on working shown

(b)(iii) Colorimetry **[1]** could be used to measure the intensity of the colour absorption. The concentration $CoCl_4^{2-}$ could then be determined by comparing the absorption of the sample with that of a solution with a known concentration.

(c)(i) K_c becomes larger from low temperatures to high temperatures. **[1]**

Since $\Delta H^{\ominus}$ is positive, the forward reaction is endothermic. At higher temperatures, the forward reaction is favoured over the backward exothermic reaction. The rate of the forward reaction increases more than the rate of backward reaction. K_c increases. **[1]**

(c)(ii) There will be no effect on K_c since K_c is not affected by concentration changes. K_c is only affected by temperature. **[1]**

(d)(i) $Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$

As heat is applied, the system will favour the forward endothermic reaction / shift the position of equilibrium to the right to absorb heat / counteract the increase in temperature. **[1]** More blue coloured $CoCl_4^{2-}$ will be formed. This conversion of faint pink to blue causes the ink to become more visible. **[1]**
OR
As heat is applied, H_2O is driven off and vaporised completely. This leads to an increase in concentration of all ionic species. By Le Chatelier's Principle, equilibrium position will shift right to partially offset the increase in concentration of all ionic species ($Q_c < K_c$), favouring the side with fewer ions. **[1]** More blue coloured $CoCl_4^{2-}$ will be formed. This conversion of faint pink to blue causes the ink to become more visible. **[1]**

(d)(ii) No, it will not be able to. The H_2O which vaporised away cannot be replaced by cooling down the paper. Hence, there is no backward reaction to re-form $Co(H_2O)_6^{2+}$. **[1]**
OR
Yes, it will be able to. Cooling allows H_2O to condense onto the paper, which can react with $CoCl_4^{2-}$ to re-form the $Co(H_2O)_6^{2+}$ / allow the backward reaction to occur. **[1]**

Comments for B1

(a)(i) The question requires students to provide a plausible reason as to why Reaction 1 is an endothermic reaction. Many students wrote vague statements such as "the energy used in bond breaking is more than the energy released in bond formation". Many students also mentioned that the Co-O bond must be stronger than the Co-C*l* bond, without adding that the stronger bond is due to the greater electronegativity difference between Co and O. A purpose of giving the diagrams is to allow students to count the number of bonds in $CoCl_4^{2-}$ and in $Co(H_2O)_6^{2+}$. Not many students made use of the diagrams to figure out that the difference in number of bonds is a key factor which influences ΔH of Reaction 1.

(a)(ii) This question is best answered using $\Delta G = \Delta H - T\Delta S$. Since reaction 1 occurs ($\Delta G<0$), and that $\Delta H>0$, the sign of ΔS can be easily deduced. Many students focused on counting only the number of aqueous ions or only the number of liquid molecules. The reaction should always be considered as a whole system, not by individual components. Some students mentioned that the increase in entropy could be explained by the decrease in number of H_2O molecules solvating the ions, as a result of the decrease in number of ions. This explanation is not incorrect, but it is not always the most important factor. For example: in the dissolution of NaC*l*, water molecules surround the ions and this leads to a decrease in entropy ($\Delta S<0$). However, there is an overall increase in entropy ($\Delta S>0$) because the ions in the rigid ionic lattice (very orderly) become freely-moving ions in the aqueous solution. Hence, answers which did not consider the "bigger picture" were not accepted.

(b)(i) Many students included $[H_2O]$ in the expression. Students should remember that in aqueous systems, H_2O is the solvent, and its concentration is high and assumed to be constant. $[H_2O]$ is thus not included in the K_c expression. A sizeable number of students made the mistake of using [HC*l*] instead of $[Cl^-]$ in the K_c expression. Another common mistake was to include s^{-1} in the units. Students probably mixed up *equilibrium constant* and *rate constant*.

(b)(ii) Very poorly done. Most students did not realise that the mixing of two solutions led to dilution, and hence, lower initial concentrations of the ions. Other common mistakes include swapping the initial concentrations of Cl^- and $Co(H_2O)_6^{2+}$, not multiplying the change of $[Cl^-]$ by a factor of 4, and forgetting to raise $[Cl^-]$ to the power of 4 in the calculation of K_c (even though the student gave the correct K_c expression).

(b)(iii) Generally well done. Many students could cite the use of colorimetry as a possible method of determining the concentration of a coloured species. Some students suggested measuring the rate of change of concentration or colour of the sample. Note that this question is asking for a method to determine $[CoCl_4^{2-}]$, not to monitor the change in $[CoCl_4^{2-}]$ during a reaction.

(c)(i) In an equilibrium reaction, when temperature increases, both the rate of forward reaction and the rate of backward reaction increase. However, the rate of the endothermic reaction increases more. In this case, the concentrations of reactants and products will simultaneously change until K_c settles on a new value. Thus, it is important to discuss both [reactants] and [products] in the answer. Phrases such as "product to reactant ratio increases" or "concentration of products increases" were not specific enough, so they were not accepted.

(c)(ii) Poorly done. Many students focused on how the position of equilibrium changed instead of whether K_c would change when NaC*l*(s) was added.

(d)(i) Since it is given that *Reaction 1* is a reversible reaction, where the forward reaction is endothermic, students need to apply Le Chatelier's Principle to answer this question and are encouraged to structure their answers as follows:

Tips: In using Le Chatelier's Principle to answer question, the answer contains three parts: "where", "why" and "how".

By Le Chatelier's Principle, equilibrium position will shift left to partially offset the decrease in [A] by producing more A until a new equilibrium is reached.

where | why | how

Both forward and backward reactions involve bond breaking and bond forming processes. Also, increase in temperature will lead to an increase in the rates of both the forward and backward reactions. Hence, answers which discuss only the energetics (e.g. endothermic reaction can occur as it absorbs heat to break the Co-O bonds) or only the kinetics (e.g. $Co(H_2O)_6^{2+}$ and Cl^- have sufficient energy to overcome E_a to result in a higher frequency of effective collision) of the reaction does not explain why the forward reaction is favoured over the backward reaction when temperature is increased.

Note that the reaction system is a heterogeneous equilibrium (in an aqueous medium). When H_2O evaporates as a result of heating, the concentrations of $Co(H_2O)_6^{2+}$, Cl^- and $CoCl_4^{2-}$ will increase, leading to $Q_c < K_c$. It is incorrect to say that the equilibrium position shifts right due to a decrease in concentration of H_2O or products.

(d)(ii) Answers should clearly state that the decrease in temperature favours the backward reaction, which in this case, cannot occur due to the absence of H_2O as a reactant.

Avoid stating that the reactants and products are in the solid state. H_2O, which is one of the products of the reaction, is in the gaseous state after heat is applied.

Do read the question carefully. While adding water to the 'completely dry' paper could reverse the reaction, students should not suggest this in their answers because the question specified that the change has to be a decrease in temperature.

2 (a) Alkanes have strong C–C and C–H bonds which need a lot of energy to break. **[1]**
Alkanes lack regions of high or low electron densities OR Alkanes are non-polar and fully saturated compounds.**[1]**

(b) Propane molecules have a larger electron cloud, which is more easily polarised compared to that of ethane molecules **[1]**. This results in stronger instantaneous dipole-induced dipole interactions between propane molecules **[1]**. More energy is required to overcome these stronger interactions between propane molecules during the boiling process.

(c)(i) OS of C changes from –3 to +4 **[1]**

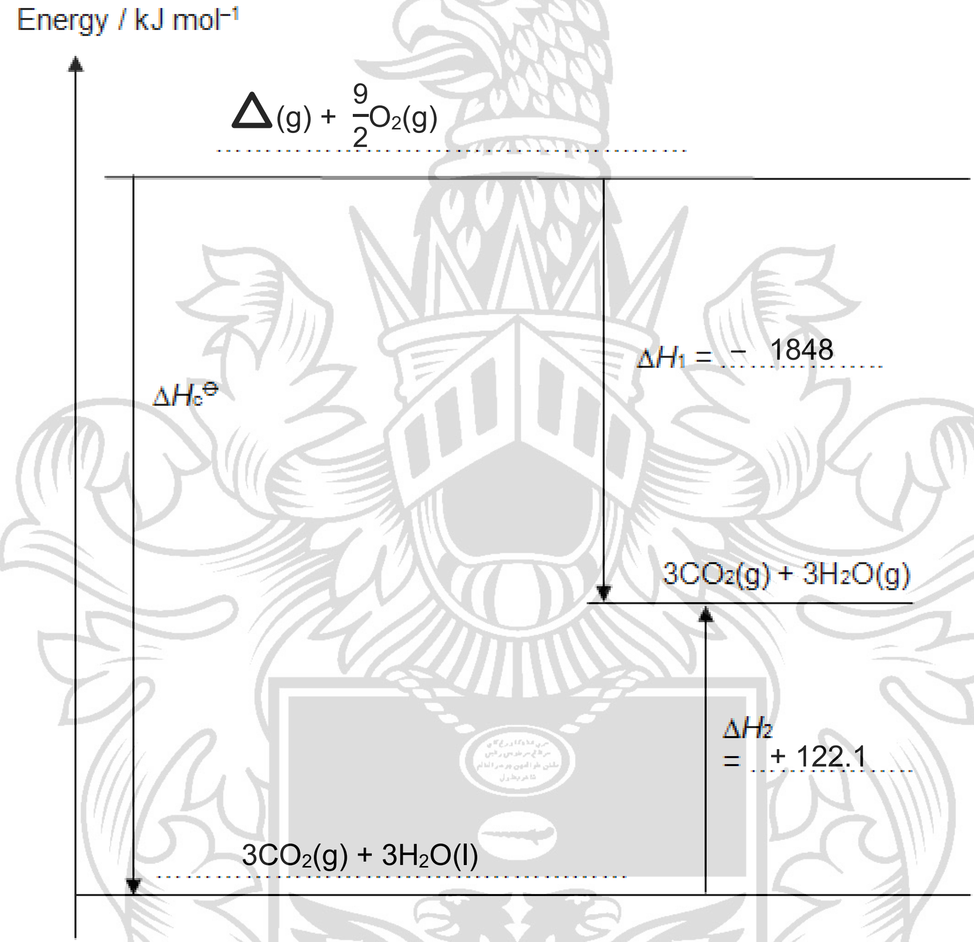
(c)(ii) From ethane to propane to butane, there is an additional $-CH_2-$ group. The regular increase in the magnitude of $\Delta H_c^{\ominus}$ (~657–659 kJ mol^{-1}) from ethane to butane represents the $\Delta H_c^{\ominus}$ value for the combustion of the $-CH_2-$ group. **[1]**

(c)(iii) Methane has the lowest CO_2 emissions per unit of energy released. Since natural gas consists mainly of methane, it is the most environmentally friendly choice. **[1]**

(d)(i) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = -890.3 - 298(-7.10/1000) = -888$ kJ mol^{-1} **[1]**

(d)(ii) Though the reaction is feasible, <u>activation energy has to be supplied</u> **[1]** for the reaction to proceed. The spark provides the activation energy needed for methane and oxygen to react.

(e)(i)



ΔH_1 = ΣBE of bonds broken in reactants – ΣBE of bonds formed in products
= [3BE(C–C) + 6BE(C–H) + 9/2 BE(O=O)] – [6BE(C=O) + 6BE(O–H)]
= 3(350) + 6(410) + 9/2(496) – 6(805) – 6(460)
= –1848 kJ mol^{-1} **[1]**

$\Delta H_2 = 3 \times \Delta H_{vap} = 3(+40.7) = +122.1$ kJ mol^{-1} **[1]**

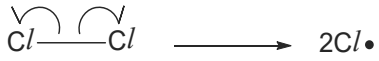
Applying Hess' Law,
$\Delta H_c^\ominus = \Delta H_1 - \Delta H_2 = -1848 - (+122.1) = -1970$ kJ mol^{-1} (units required) **[1]**

Both equations balanced correctly with correct state symbols **[1]**

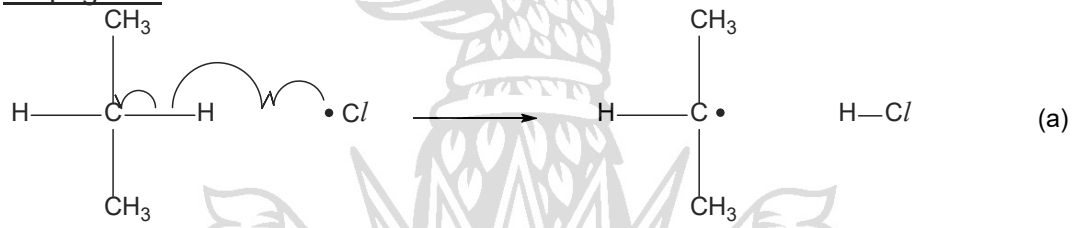
(e)(ii) C-C-C bond angle = <u>60°</u>; <u>sp^3</u> hybridised **[1]**
There is significant <u>angle/ring strain</u> due to repulsion between bonding electron pairs which are overly close. As the bond angle of 60° deviates significantly from the ideal 109.5°, there is <u>ineffective overlap of sp^3 orbitals</u>. Thus, the weaker C–C bonds require less energy to break. This results in the actual ΔH_c being more exothermic than the calculated ΔH_c. **[1]**

(f)(i) and (ii) Correct curly arrows in propagation **[1]**, correct equation for termination **[1]**

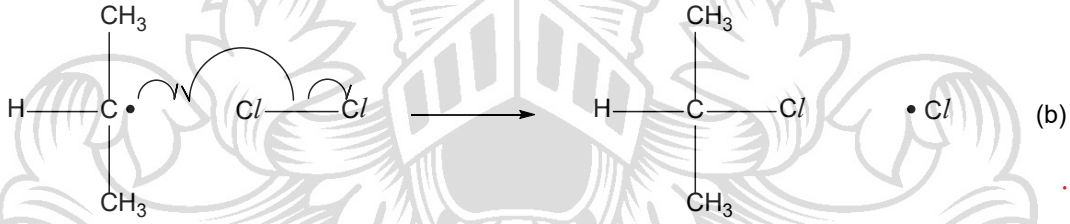
Initiation



Propagation



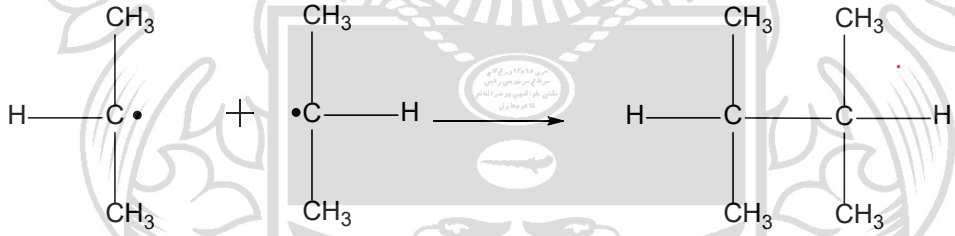
(a)



(b)

Then (a), (b), (a), (b)….

Termination



(g)(i) Secondary free radical is more stable than primary free radical. **[1]**

(g)(ii) The free radical has a C atom with an unpaired electron/is electron deficient. Since a secondary free radical has 2 electron donating groups directly attached to this C atom compared to only one in a primary free radical, the secondary radical is more stable.**[1]**

(g)(iii) Homolytic fission of the C–H bond in $(CH_3)_2CH–H$ results in the formation of a more stable secondary free radical, $(CH_3)_2\dot{C}H$. **[1]**

Comments for B2

(a) The term 'unreactive' refers to a compound being inert/stable and unlikely to undergo a chemical reaction. A dissolution process, e.g. dissolving methanol in water, involves a change in phase and is NOT a chemical reaction as the compounds remain unchanged.

Hence, answers for this question should focus on discussing the strength of covalent bonds, and lack of electron rich and electron deficient regions in alkanes instead of their solubility in polar solvents or strength of intermolecular forces of attraction.

Students must use the correct terminology in their answers and aim to write concisely. Some examples of poor phrasing include:

Poor phrasing	Correct phrasing
× *Stable* C–C and C–H bonds	✓*Strong* C–C and C–H bonds
× C–H and C–C *bonds are saturated* × All C atoms are fully bonded × All C atoms are sp^3 hybridised and cannot form any more bonds × All atoms have octet structure × Alkanes consist of single bonds	✓*Alkanes are saturated* compounds
× Alkanes have *dipole moment bonds* × The atoms are *neutral and not electrically charged*	✓ Alkanes are *non-polar* (no net dipole moment) due to the non-polar C–C and C–H bonds.
× Alkanes have no lone pairs, no free radicals or vacant orbitals × Alkanes have *no high or low regions of electron densities*	✓ Alkanes *have no regions of high or low electron densities*

(b) Ethane and propane have different number of electrons per molecule. The key reason which accounts for their difference in boiling points should be the <u>difference in size and polarisability of their electron clouds</u>, which leads to difference in <u>strength of</u> (NOT *number* or *extensiveness of*) id-id interactions. Note that it is the electron cloud, NOT the molecule, which is polarised.

The <u>surface area</u> of a molecule affects the <u>extensiveness</u> of id-id interactions. This factor is usually used when comparing compounds with the same molecular formula but different electron cloud sizes, e.g. constitutional isomers such as butane and 2-methylpropane.

Also, ethane and propane are simple molecules. Boiling involves the breaking of intermolecular forces of attraction, NOT the covalent (C–C and C–H) bonds!

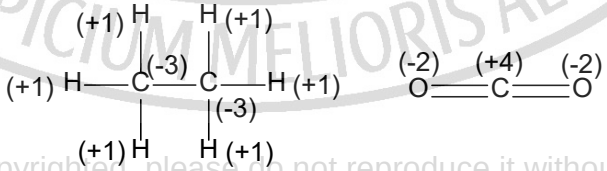
(c)(i) Generally well done.

- The oxidation number of **hydrogen** in all compounds, except metal hydrides, is +1.
- The oxidation number of **oxygen** is −2 in all compounds, except in peroxides, superoxides and OF_2.

In complicated molecules or ions, it is helpful to deduce the oxidation states of the elements based on the structures.

The steps involved are:

1. Pick a bond between 2 atoms.
2. The more electronegative atom "gains" both the electrons in the bond, resulting in a −1 oxidation state.
3. The less electronegative atom "loses" its shared electron, resulting in a +1 oxidation state.



Note: C is more electronegative than H
O is more electronegative than C

(c)(ii) It is clearly stated in the question that students are to suggest what the regular increase in the magnitude of $\Delta H_c^{\ominus}$ represents and NOT what the difference between each member of the homologous series is. It is insufficient to just state that the difference in $\Delta H_c^{\ominus}$ is due to the additional $-CH_2-$ group.

A combustion reaction is always exothermic, with energy released by the reaction.

The types and number of bonds broken and formed should be clearly stated in your answer. The combustion of the additional $-CH_2-$ group involves the *breaking of one C–C, two C–H and 3/2 O=O bonds and the formation of 2 O–H and 2 C=O bonds*.

Note that "methyl group" refers to $-CH_3$, while "methylene group" refers to $-CH_2-$.

(c)(iii) Generally well done.
It must be clearly stated in your answers that methane/natural gas emits the least / a lower amount of CO_2 for the same amount of energy released during combustion.

(d)(i) Generally well done.
Note that '$^{\ominus}$' refers to standard conditions, i.e. combustion occurs at a temperature of 298 K (NOT 293 K, 273 K or the boiling point of methane)

(d)(ii) Most students simply stated that the reaction has a high activation energy / is thermodynamically feasible but kinetically unfeasible, but did not proceed to explain how the combustion can occur when a spark is introduced.

It must be clearly stated in your answers that the spark provides the energy for the reactants to overcome the activation energy, E_a.

(e)(i) BE(C=O) = 740 kJ mol^{-1}; BE(C=O) in CO_2 = 805 kJ mol^{-1}. Quite a number of students calculated ΔH_1 incorrectly as they used the wrong BE(C=O) of 740 kJ mol^{-1}. Thus, they obtained a wrong enthalpy change, ΔH_1 = –1458 kJ mol^{-1}. Cyclopropane should be a gas as it has a boiling point of 240 K (Pg 15 of QP). Please remember to leave your final numerical answers to 3 s.f.

(e)(ii) The correct term to use is ring/angle strain, NOT bond strain/stress/tension/torsion. Due to the poor overlap of the sp^3 orbitals, the C–C bond is weakened (less energy required for bond breaking) and thus more energy is given off during combustion (more exothermic ΔH_c).

(f)(i) Arrows showing homolytic fission should start from a covalent bond, NOT from an atom.

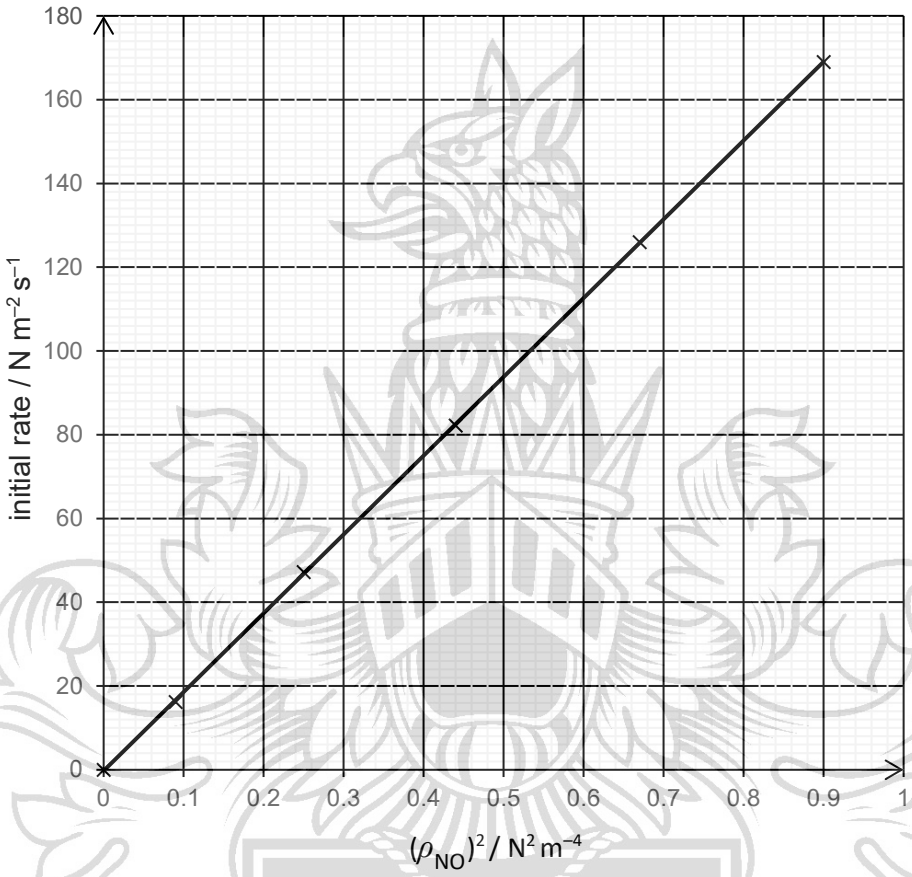
(f)(ii) Some students wrongly expressed $-CH(CH_3)_2$ as $-CHCH_3CH_3$.

(g)(i) Generally well done.

(g)(ii) Many students failed to mention that, compared to a primary free radical, the secondary free radical has more alkyl groups bonded to the electron deficient C atom. Some students wrongly suggested that the free radical has a charge and is a carbocation. Some mentioned that the free radical is electrophilic and attracts the electron donating alkyl group(s), suggesting that the alkyl group(s) and the free radical are different entities.

(g)(iii) Poorly done. Many students did not understand the concept tested. Many mentioned about the stability of alkanes and tried to compare the stability of primary and secondary carbon/hydrogen, instead of considering the stability of the radical formed upon breaking of C–H bond.

C1 (a)(i)



[1] – choice of graph / suitability of the graph plotted
[1] – points plotted and best fit
[1] – occupy at least ½ of the grids (on both axes)

(a)(ii) The graph plotted (rate against $(\rho_{NO})^2$) in **(a)(i)** is a straight line that intersects the origin. That means the initial rate of reaction is directly proportional to the square of the partial pressure of NO, $(\rho_{NO})^2$. **[1]** Thus, the order of reaction with respect to ρ_{NO} is 2. **[1]**

(b) Let rate = $k(\rho_{O_2})^m (\rho_{NO})^2$, where m is the order of reaction with respect to ρ_{O_2}

If the graph of rate against ρ_{NO} is plotted,
gradient of the graph = $2k(\rho_{O_2})^m (\rho_{NO})$.
If m = 0, gradient = $2k(\rho_{NO})$. When ρ_{O_2} is halved, the gradient remains unchanged.
If m = 1, gradient = $2k(\rho_{O_2})(\rho_{NO})$. When ρ_{O_2} is halved, the gradient will be halved. **[1]**
If m = 2, gradient = $2k(\rho_{O_2})^2 (\rho_{NO})$. When ρ_{O_2} is halved, the gradient will be ¼ that obtained in **(a)(i)**.

If the graph of rate against $(\rho_{NO})^2$ is plotted,
gradient of the graph = $k(\rho_{O_2})^m$.
If m = 0, gradient = k. When ρ_{O_2} is halved, the gradient remains unchanged.
If m = 1, gradient = $k(\rho_{O_2})$. When ρ_{O_2} is halved, the gradient will be halved. **[1]**
If m = 2, gradient = $k(\rho_{O_2})^2$. When ρ_{O_2} is halved, the gradient be ¼ that obtained in **(a)(i)**.

Since the question stated that halving ρ_{O_2} will halve the gradient, we conclude that the order of reaction with respect to to ρ_{O_2} is 1. **[1]**

Alternative answer:
Gradient at each point on the graph of rate against $(\rho_{NO})^2$ is directly proportional to the instantaneous rate of reaction.
When the partial pressure of O_2 is halved, the initial rate of reaction is halved. **[1]**
Thus, the rate of reaction is directly proportional to the partial pressure of O_2, ρ_{O_2}. The order of reaction with respect to ρ_{O_2} is 1. **[1]**

(c) rate = $k(\rho_{O_2})(\rho_{NO})^2$ **[1]**

Units of rate constant, k $= \dfrac{Nm^{-2}s^{-1}}{(Nm^{-2})^3}$

$= \dfrac{Nm^{-2}s^{-1}}{N^3m^{-6}}$

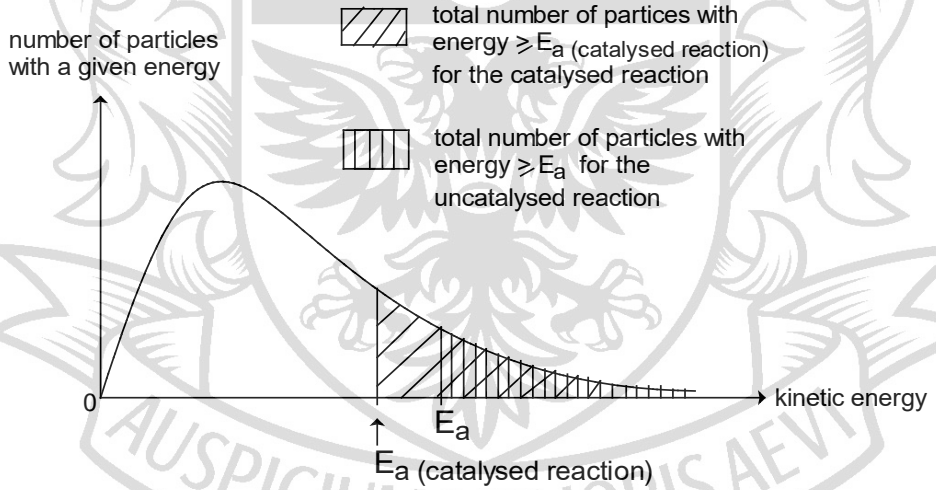
$= N^{-2}m^4s^{-1}$ **[1]**

(d) Step 1: $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$**[1]**

Step 2: $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$ **[1]**

(e) The heterogeneous catalyst is in a different phase / (physical) state from the reactant(s). **[1]**

(f)(i) **Maxwell-Boltzmann distribution of kinetic energies at a temperature T K.**



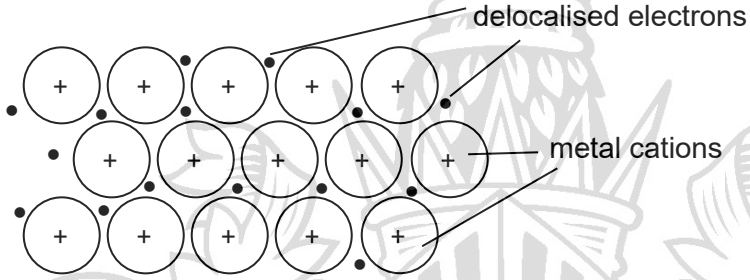
[1]

A catalyst increases the rate of a reaction by providing an alternative reaction pathway, one of lower activation energy ($E_{a\ (catalysed\ reaction)}$) than the uncatalysed reaction.
As such, significantly more reactant molecules have energy greater than or equal to the activation energy for the catalysed reaction (this can be mentioned in the legend). This is shown by the larger shaded area for the catalysed reaction in the above diagram.
This results in an increase in effective collision frequency and hence an increase in the rate of the reaction. 3 points **[2]**; 2 points **[1]**; 0-1 point **[0]**

(f)(ii) $k = A\, e^{-\frac{E_a}{RT}}$

An alternative reaction pathway of lower activation energy results in a larger rate constant *k* and hence an increase in the reaction rate. **[1]**
From the rate equation, if concentrations remain constant, an increase in rate due to the presence of a catalyst would imply an increase in the rate constant *k*.

(g)



[1] – any no. of electrons & cations with any charge

Metals can be considered to be composed of a rigid lattice of positive ions surrounded by a 'sea of electrons'.
The strong metallic bond is the electrostatic attraction between a lattice of positive ions and the delocalised electrons.**[1]**
As the 5d electrons can also be delocalised with the 6s electrons, transition metals like platinum have strong metallic bonds. Since a lot of thermal energy is needed to break these strong metallic bonds, platinum has a high melting point.

(h) Poisoning refers to the molecules/ions which are chemically bonded to the active sites of the nickel catalyst **[1]**, leading to a reduction in the number of active sites available for catalysis reaction. **[1]** (OR other suitable answers)

[Total: 20]

Comments for C1

(a)(i) In order to determine the order of reaction with respect to ρ_{NO}, students need to decide which data given in the question should be used to plot a graph. Data points need to be plotted accurately and a best fit curve/line should be drawn.

Students need to ensure that the plotted graph occupies at least half the grids (along both axes) given in the question paper. Students should also avoid using odd scales for graph plotting.

(a)(ii) Students are required to make reference to the graph plotted in **(a)(i)** when determining the order of reaction with respect to ρ_{NO}.

If the graph of rate against $(\rho_{NO})^2$ is plotted, students need to show understanding that it is a straight line graph that passes through the origin or that the graph has a positive gradient. Only stating that the graph "is a straight line" or "has a constant gradient" is imprecise because these phrases could also apply to a horizontal straight line graph, which will indicate that the reaction is zero order with respect to ρ_{NO}.

If the graph of rate against ρ_{NO} is plotted, students need to quote specific data points from the graph and show that the rate quadrupled when ρ_{NO} doubled.

Students are not allowed to determine the order of reaction by elimination. For example, "since the graph is not a straight line, the reaction must be second order with respect to ρ_{NO}" is not accepted.

(b) Students need to show clearly how the gradient of the graph is related to ρ_{O_2}, regardless of which graph is plotted in **(a)(i)**.

(c) The data presented in the question is in terms of partial pressure (in N m^{-2}). As students are told to "construct" the rate equation, the rate equation should be written in terms of partial pressure (in N m^{-2}) instead of concentration.

The square brackets "[ ]" represent "concentration of". $[\rho_{O_2}]$ is not acceptable.

(d) NO_2 is the catalyst involved in the oxidation of SO_2. Hence, the first equation should show how NO_2 directly oxidises SO_2, while the second equation should show how NO_2 is regenerated.

Students also need to ensure that the stoichiometry of the reaction is correct.
Adding the two equations should give us this net equation: $SO_2 + ½O_2 \rightarrow SO_3$.
For example:
Step 1: $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$
Step 2: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
Overall: $SO_2(g) + O_2(g) + NO(g) \rightarrow NO_2(g) + SO_3(g)$ [This is incorrect.]
Do note that NO(g) and $NO_2(g)$ should not appear in the overall equation. Since 1 mole of NO(g) is produced in Step 1, only 1 mole of NO(g) is involved in Step 2.

(e) The term *heterogeneous* is referring to different physical states between the catalyst and the reactants.

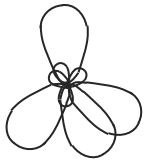
(f)(i) For the Maxwell-Boltzmann distribution curve, a few students mixed up the labels for the x and y axes. A number of students did not start drawing the distribution curve at the origin. Since all particles possess some kinetic energy, the number of particles with 0 J of energy should be zero. Hence, the distribution curve starts at the origin (0,0). Areas under the curve should be labelled clearly to show how the number of particles with $E \geq E_a$ is greater for the catalysed reaction.

(f)(ii) Many students mixed up rate constant k with equilibrium constant K_c. While K_c is affected only by temperature and unaffected by the use of a catalyst (since a catalyst increases both the forward and backward rates to the same extent), rate constant k is affected by **both** temperature and the use of a catalyst. The effects of changing temperature and using a catalyst have on k can be predicted by the Arrhenius equation: $k = Ae^{-\frac{E_a}{RT}}$. k is larger at a higher temperature and when E_a is lower. "When rate is increased by the use of a catalyst, k must have increased if the concentrations of reactants remain unchanged". This argument may not always be correct, e.g. when a homogeneous catalyst is used, the rate equation of the catalysed reaction (which includes the concentration of the catalyst) will be different from that of the uncatalysed reaction.

(g) Many students did not draw the cations in regular rows (at least 2 rows should be shown) and close to one another, interspersed with delocalised electrons. Some students did not elaborate that metallic bonding arises from the electrostatic attraction between the positively charged metal cations and the delocalised valence electrons.

(h)	The terms *nucleophiles* and *electrophiles* are usually used in reactions involving organic compounds and hence should not be used in explaining how heterogeneous catalysis is affected by ions/ molecules with lone pair of electrons.

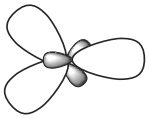
C2 (a)(i)



[1]

sp^3-hybridisation (must show the molecular shape)

(a)(ii)



(must show the molecular shape) **[1]**

(b)(i) C_{60} has a simple molecular structure. The intermolecular forces between C_{60} and benzene molecules are instantaneous dipole – induced dipole interactions which are similar/ comparable to those between C_{60} molecules and between benzene molecules. Thus, C_{60} is soluble in benzene. **[1]**
However, diamond and graphite have giant covalent structures with strong covalent bonds between carbon atoms. To dissolve in solvents, the strong C–C bonds needed to be broken, which is not compensated by the formation of weak interactions with the solvent. Thus, diamond and graphite are insoluble in all solvents. **[1]**

(b)(ii) Each carbon in graphite has an unhybridised p orbital which contains a single electron. The p orbital of one carbon atom overlaps **[1]** collaterally with the p orbitals of its immediate neighbour, resulting in an extended π electron cloud above and below the plane containing the carbon atoms.

The π electrons are delocalised over the whole layer so that graphite is an electrical conductor. **[1]**

The four valence electrons in diamond are all involved in σ-bond formation and are not delocalised. The absence of mobile charge carriers / delocalised electrons causes diamond to be an insulator. **[1]**

The π-electrons in C_{60} are delocalised within the molecule but cannot move from one C_{60} molecule to another. Thus, C_{60} is unable to conduct electricity. **[1]**

(c)(i) $n_{C_{60}} = \frac{60}{12\times60}$ = 0.08333 mol
p = 1.20 x 10^5 kPa = 1.20 x 10^8 Pa; V = 69.9 cm^3 = 6.99 x 10^{-5} m^3
Assuming that H_2 behaves ideally,
$n_{H_2} = \frac{pV}{RT} = \frac{1.20\times10^8\times6.99\times10^{-5}}{8.31\times673}$ = 1.500 mol **[1]**
Mole ratio of C_{60} to H_2 = 0.08333 : 1.500 = 1 : 18
Mole ratio of C_{60} to H = 1 : 36
Thus, molecular formula of the hydrofullerene formed is $C_{60}H_{36}$. **[1]**

(c)(ii) Due to the structure of C_{60}, the bond angle in the carbon-hexagon is 120º. In $C_{60}H_{60}$, each C has 4 regions of electron density. The shape around each C atom should be tetrahedral (or C should be sp^3-hybridised) and the bond angle should be 109.5º. **[1]**

Since the bond angle of 109.5º deviates significantly from the 120º in the carbon-hexagon, the structure of $C_{60}H_{60}$ will be highly strained. **[1]**

[1] – bond angle
[1] – discussion of deviation / shows understanding of strain

(c)(iii) For 100 km of travel,

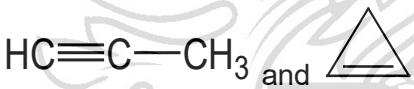
amount of H_2 needed = 100 x $\frac{13.5}{2}$ = 675 mol **[1]**

$C_{60}H_{36} \rightarrow C_{60} + 18H_2$

Amount of $C_{60}H_{36}$ needed = $\frac{1}{18} \times 675 = 37.5$ mol

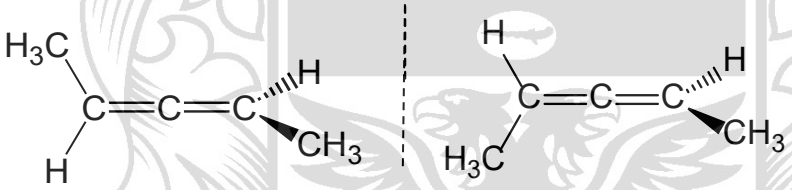
Mass of $C_{60}H_{36}$ = 37.5 (12.0 x 60 + 36) = 2.84 x 10^4 or 28350 g **[1]**

(d)



[1], [1]

(e)(i) Enantiomerism **[1]**



[1] – correct structures with mirror plane, **[1] –** hash/wedge bonds & solid lines

(e)(ii) They differ in the way they rotate plane-polarised light. One isomer rotates plane-polarised light clockwise, while the other isomer rotates plane-polarised light anticlockwise. **[1]**

Comments for C2

(a)(i) & (ii) Generally well done. The respective tetrahedral and trigonal planar arrangements of sp^3 and sp^2 hybrid orbitals should be shown clearly. Each hybrid orbital consists of a small lobe and a large lobe which are directly opposite each other.

(b)(i) The structures and bonding of diamond, graphite and C_{60} should be explicitly stated. To decide whether a solute is soluble in a solvent, it is insufficient to use the phrase "like dissolves like". Students need to compare the relative strengths of solute-solvent interactions to the strength of solute-solute / solvent-solvent interactions.
Solubility is usually a physical process and covalent bonds are not broken during dissolution.

(b)(ii) Many candidates provided answers which do not have sufficient depth, e.g. "graphite has delocalised electrons". Students should describe the collateral overlap of p orbitals because it is critical for the delocalisation of electrons.

Incorrect terms include "electrons are hybridised", "electrons overlap", "π orbitals overlap", "p orbitals collide", "free electrons" (this refers to electrons being removed from the atom), "sp_2", "one valence electron is not used in bonding" (it is used in π bonding for graphite and C_{60}). "p orbitals interact" is vague and not accepted.

Though not necessary, many candidates incorrectly mentioned that C_{60} has a giant covalent structure with no delocalised electrons. The question explicitly stated that C_{60} is a molecule, which means that it is a discrete molecule with covalent bonds within the molecule and intermolecular interactions between molecules. It does not have a giant covalent structure like diamond.

(c)(i) Generally well done. Common errors include taking M_r of H_2 to be 1.0 (instead of 2.0) and assuming the mole ratio of C_{60}:H_2 to be 1:1.

(c)(ii) This question requires candidates to realise that hydrogenating C_{60} is similar to hydrogenating an alkene to alkane. Each C atom will change from being sp^2-hybridised to being sp^3-hybridised. Many candidates mentioned "strain" but did not substantiate their argument with data (i.e. ideal vs actual bond angles). Some candidates did not realise that the question asked about $C_{60}H_{60}$. The concept of "steric strain" is not relevant in this question.

(c)(iii) Generally well done. Careless mistakes included multiplying 13.5 by 10 instead of 100, and rounding 28350 g to 2840 g.

(d) Many candidates did not understand the concept of "constitutional isomers" and attempted to draw stereoisomers of X (when there isn't any). Constitutional isomers have the same molecular formula but different atom connectivity. Many candidates did not consider cyclic compounds and hence did not obtain cyclopropene. Proper representations of organic molecules should be used.

(e)(i) Cis-trans isomerism is not accepted as it requires the four groups to be on the same plane. The occurrence of enantiomerism does not require a chiral carbon (though it is present in most cases). Enantiomerism arises due to the absence of an internal plane of symmetry.

Accurate three-dimensional structures are required in this question. Each of the two bonds on one of the terminal carbon atoms should be denoted by solid lines, while the two bonds on the other terminal carbon atom should have one wedge bond and one hashed bond.

A dotted line should be drawn between the two molecules. This denotes the mirror plane. The bonds drawn must show appropriate carbon atoms being connected together.

(e)(ii) Generally well done. Incorrect concepts include "the enantiomers polarise light in different directions" and "reflect / refract / diffract plane polarised light".