HWA CHONG INSTITUTION
2022 C1 H2 CHEMISTRY PROMOTIONAL EXAM
MARK SCHEME & TEACHING SOLUTIONS

Paper 1

1	2	3	4	5	6	7	8	9	10
C	A	B	A	D	A	D	B	D	D
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
C	D	C	B	C	A	C	A	B	C

Comments

1 **C** Obtain the proton number based on the identity of the element in the Data Booklet. Calculate the no. of neutrons by taking mass number (indicated as superscript on the element) minus proton number:

A	No. of protons = **2**; no. of neutrons = 2 – 2 = **0**
B	No. of protons = **4**; no. of neutrons = 8 – 4 = **4**
C	No. of protons = **20**; no. of neutrons = 40 – 20 = **20**
D	No. of protons = **82**; no. of neutrons = 210 – 82 = **128**

Only ^{40}Ca has both numbers matching the given nuclear magic numbers.

2 **A**

1	Each nitrogen atom in cyanogen has one lone pair of electrons, hence statement is correct.
2	Both carbon atoms in cyanogen are sp hybridized – there are two electron groups around each carbon atom and the shape around each carbon is linear, hence statement is correct.
3	There should be three σ bonds: C–N, C–N and C–C, hence statement is incorrect.

3 **B**

A	The zig-zag chains are flat and unlikely to form regular 3D spaces in the lattice structure like the tetrahedral 3D arrangement for ice, hence statement is incorrect.
B	Each hydrogen bond in HF is stronger than that in H_2O since F is more electronegative than O, and hence draw away more electron density from H atom, resulting in a greater partial positive charge on H so attraction between the H and the lone pair of another HF molecule is stronger. Statement is correct.

C	The question states that the bond angle around F atom is similar to that around O in ice, hence bond angle around each F atom should be 104.5°. Statement is incorrect.
D	Solid HF exists as discrete HF molecules held together by intermolecular hydrogen bonding. It is still a simple molecular structure, not giant covalent. Statement is incorrect.

4 **A**

1	More gas added into a flask of fixed volume, hence total pressure in the flask will increase. Or consider PV = nRT, where n increases and V is constant, so P will increase. Statement is correct.
2	Mole fraction of a gas in a mixture is "no. of moles of that gas / total no. of moles of gas", since total moles of gas has increased, the mole fraction of each gas will decrease. Statement is correct.
3	Partial pressure of each gas is defined as the pressure that each gas exerts on the flask as though it is alone in the flask. Since the no. of moles of N_2 and O_2 did not change and the volume of the flask did not change, their partial pressures will be unchanged. Or consider partial pressure = mole fraction × total pressure = $(n_{gas} / n_{total}) \times P_{total}$. P_{total}/n_{total} is a constant (use PV = nRT), so if n_{gas} remain the same, partial pressure of that gas remains the same.

5 **D** The **empirical formula** of a compound is the **simplest formula** which shows the **ratio** of the **atoms** of the different elements in the compound.

The **molecular formula** of a compound is the **formula** which shows the **actual number** of **atoms** of each element in one molecule of the compound.

1	NaC*l* is an ionic compound and hence it does not have a molecular formula. Ionic compound formulae are always empirical formula since the actual number of ions is a very large number and it is the simplest ratio of atoms that is reflected in an ionic formula.
2	Water is a simple molecular compound that comprise 2 H atoms and 1 O atom, which means that its formula is both the empirical formula and molecular formula.
3	Propene is a simple molecular compound that comprise 3 C atoms and 6 H atoms, hence its molecular formula is C_3H_6. The simplest ratio of atom would be CH_2 which is the empirical formula.

6 **A** Calculate the number of moles of particles for each option and compare them. The option with the lowest number of moles of particles will give the smallest number of particles since 1 mole of particles contain Avogadro's number (6.02×10^{23}).

A	No. of moles of atoms in 15 g Fe = (15 ÷ 55.8) = 0.269 mol
B	No. of moles of ions in 50 g NaCl = (50 ÷ 58.5) × 2 = 1.71 mol
C	No. of moles of molecules in 15 dm^3 of N_2 = (15 ÷ 24) = 0.625 mol
D	No. of moles of molecules in 10 cm^3 of C_6H_{14} = (10 × 6.55) ÷ 86.0 = 0.762 mol

7 **D**

1	The enthalpy change of formation refers to the energy change in forming a substance from its constituent elements (not atoms!) at their standard state. The correct representation of $\Delta H^{\ominus}_{\text{formation}}(NH_3)$ is: $\frac{1}{2} N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$
2	Bond energy refers to the energy required to break one mole of the covalent bond in the gaseous state, the equation is incorrect because it shows the breaking of only half a mole of the Br–Br bond. The correct representation of $\Delta H^{\ominus}_{\text{bond energy}}$(Br–Br) is: $Br_2(g) \rightarrow 2Br(g)$
3	Ionisation energy refers to energy required to remove one mole of electrons from one mole of the gaseous atoms. The equation is incorrect because Mg should be in the gaseous state. The correct representation of $\Delta H^{\ominus}_{\text{ionisation energy}}$(Mg) is: $Mg(g) \rightarrow Mg^+(g) + e^-$

8 **B** $\Delta H_{\text{solution}}$ = – L.E. + sum of $\Delta H_{\text{hydration}}$ of the ions formed

$$= -(-2195) + (-1577) + 2(-363) = -108 \text{ kJ mol}^{-1}$$

9 **D**

A	At point A, entropy is zero, meaning the particles are at their maximum state of order (no disorder), hence statement is incorrect.
B	Between points C and D, the liquid water is increasing in temperature. It is not at equilibrium. Dynamic equilibrium between the solid and liquid states occurs at BC, while dynamic equilibrium between the liquid and gaseous states occurs at DE. Hence statement is incorrect.
C	At BC, the temperature remains constant so average kinetic energy does not change. Hence statement is incorrect.
D	At DE, the liquid state is converting to gaseous state while at BC the solid state is converting to liquid state. Gas particles have a greater disorder compared to liquid particles, so the increase in entropy in converting from liquid to gas is larger. Statement is correct.

10 **D** A catalyst does not change the initial and final energy levels of the reactants and products, hence the enthalpy change of reaction does not change. This would rule out options B & C immediately.

Catalysis offers an alternative reaction pathway that has a lower activation energy. This means that option A is wrong. This leaves option D as the answer as the diagram shows that the enthalpy change of reaction is unchanged while the activation energy is clearly lower for the catalyzed reaction pathway.

11 **C**

^{242}Cm	4	$\xrightarrow{\text{160 days}}$	2	$\xrightarrow{\text{160 days}}$	1	$\xrightarrow{\text{160 days}}$	½	$\xrightarrow{\text{160 days}}$	¼
^{248}Bk	1	$\xrightarrow{\text{320 days}}$			½	$\xrightarrow{\text{320 days}}$			¼

From the table below, it takes ^{242}Cm 4 half-lives (160 × 4 = 640 days) to go from 4 to ¼, while it takes ^{248}Bk 2 half-lives (320 × 2 = 640 days) to go from 1 to ¼.

Hence at the end of 640 days, the ratio of ^{242}Cm : ^{248}Bk = ¼ : ¼ which gives a 1 : 1 ratio.

12 **D**

1	Comparing Expts 1 & 2, [CH_2ICH_2I] and [I_2] remain constant, but the light intensity increases by 4× while the rate increase by 2×. Hence the rate is proportional to $\sqrt{\text{light intensity}}$.
2	Comparing Expts 3 & 4, [CH_2ICH_2I] and light intensity remains constant but [I_2] increases by 2× while the rate remains constant. Hence the rate is independent of [I_2].
3	Comparing Expts 2 & 3, [CH_2ICH_2I] increases by 2× and the light intensity and [I_2] remain constant, while the rate increases by 2×. Hence the rate is directly proportional to [CH_2ICH_2I].

13 **C** This question tests understanding and application of Le Chatelier's principle – that a change imposed on a system at equilibrium cannot be completely offset by a shift in the position of equilibrium.

Hence when additional 0.5 mol of P was added, not all of it was reacted when the position of the equilibrium shifted right. Therefore [P] left should be more than 2.0 mol dm^{-3} (since some of the 0.5 mol of P added remained behind), and should not exceed 2.5 mol dm^{-3} (otherwise no reaction and shift in the position of the equilibrium would have occurred).

The decrease in the amount of Q should reflect the 2 : 1 stoichiometry in the chemical equation. Consequently, Q should decrease less than 0.25 mol since not all of the 0.5 mol of P reacted. This means that [Q] should be between 0 and 1 mol dm^{-3}.

Similarly, the increase in the amount of R should be less than 0.5 mol (since less than 0.5 mol of P reacted), and therefore [R] should be more than 2.0 mol dm^{-3} but less than 2.5 mol dm^{-3}.

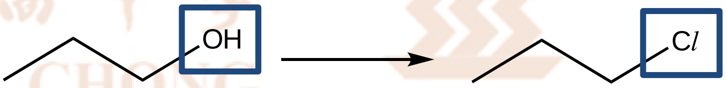
14 **B** The graph must be interpreted correctly in order to anaylse which of the options are correct.

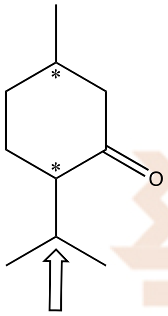
The graph shows that the % of X increases (POE shifts to the right) as P increases. Hence an equilibrium reaction with fewer moles of gas on the RHS will fit this increase.

The graph also shows that the % of X decreases (POE shifts to the left) when the T increases from 298 K to 500 K. Hence an equilibrium reaction which is endothermic in the backward direction (exothermic in the forward reaction) will fit this decrease.

A	There are more number of moles of gas on the RHS, thus this reaction will not fit the changes described when T increases.
B	There are less number of moles of gas on the RHS and the reaction is exothermic. This reaction will fit the changes described when T increases.
C	Although there are less number of moles of gas on the RHS, the reaction is however endothermic. Thus, this reaction will not fit the changes described when T increases.
D	The number of moles of gas are the same on the RHS and LHS. The reaction is also endothermic. Thus, this reaction will not fit the changes described when T increases.

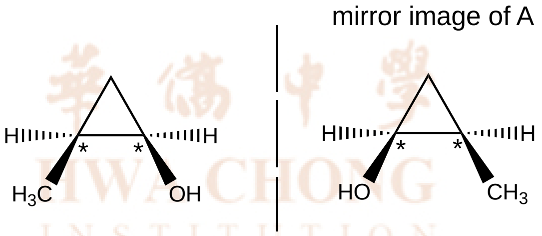
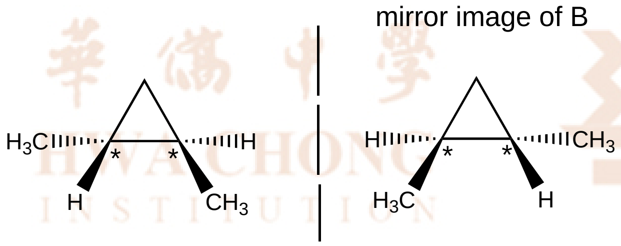
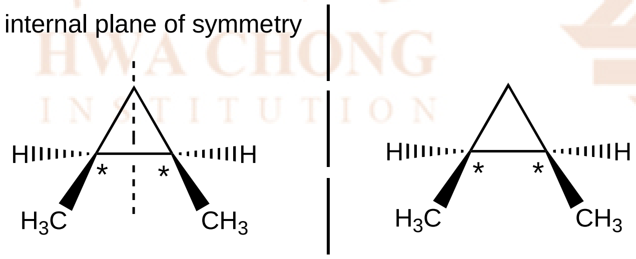
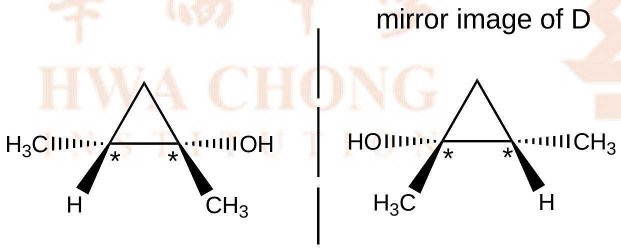
15 **C** It is important to understand the definitions for the types of reactions well to answer this question.

A	An addition reaction is when an organic molecule, usually containing a double bond (e.g. C=C) reacts with another molecule to give only one product. However, the chemical equation describes the 2-chloropropane becoming 1-propene, which means that HCl has been removed from the starting molecule. Thus the reaction is **elimination.** Option is incorrect.
B	The chemical equation describes an alcohol molecule and carboxylic acid molecule coming together to form a bigger molecule, an ester, with the elimination of water, an example of a small molecule. The product, an ester, does not contain a double bond that was formed after the removal of a small molecule. Thus type of reaction is **condensation**. Option is incorrect.
C	1-propene has been converted to propane. This means that hydrogen atoms have been added across the carbon-carbon double bond. Hence **reduction** has occurred. Option is correct.
D	Substitution is when one atom or group of atoms replaces another atom or group in a molecule. 

			For instance, if substitution were to occur, the –OH group is replaced by another group, e.g. Cl^-. However propan-1-ol has been converted to propanoic acid. This is the oxidation of a primary alcohol to a carboxylic acid (to be learnt in Topic 16 Hydroxy compounds). Alternatively, the oxidation of propan-1-ol can also deduced by the change in oxidation number of carbon. Oxidation number of C in $CH_3CH_2\underline{C}H_2OH$ changed from –1 to +3 in $CH_3\underline{C}OOH$. Hence **oxidation** occurred. Option is incorrect.
16	**A**	**1**	One important thing to note when reading skeletal structures is that hydrogen atoms are not shown, and that carbon always forms 4 bonds. Statement is correct.
		2	The number of stereoisomers of menthone depends on the number of chiral centres, or if any *cis-trans* isomers exist. Since there is no cis-trans isomerism in this molecule, the number of stereoisomers would be based on the number of enantiomers. This is based on the number of chiral centres in the molecule, and whether its mirror image is superimposable on itself. A chiral center is an atom with a tetrahedral geometry around it that is bonded to four different groups. There are only 2 chiral centres in menthone, indicated by the asterisk.  this is not a chiral centre This carbon is not a chiral centre as there are 2 identical methyl groups bonded to it. Hence the number of stereoisomers is $2^2 = 4$. Statement is correct.
		3	Due to oxygen being more electronegative than carbon, the electron density in the C=O bond will be attracted towards oxygen. Hence the carbon bonded to the oxygen thus carries a partial positive charge and is known as an electrophilic site. Statement is wrong.

17 **C** Molecules that are optically active contain chiral centre(s) and have non-superimposable mirror images. These 4 molecules contain chiral centres but the presence of chiral centres do not always mean that the molecule has a non-superimposable mirror image and hence optically active.

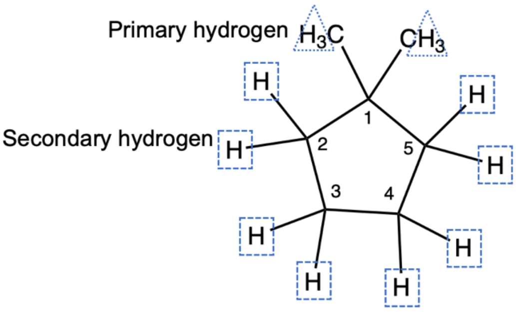
The presence of an internal plane of symmetry will mean that the molecule is identical (superimposable) to its mirror image and is optically inactive.

A	 There is no internal plane of symmetry in the molecule. Mirror image of A is non-superimposable on itself. It is optically active.
B	Same reasoning as **A**. 
C	There are 2 chiral centres in this molecule. However, an internal plane of symmetry is present. The mirror image of the molecule is superimposable on itself and hence the molecule is optically inactive (achiral compound, also known as a meso compound). 
D	Same reasoning as **A**. 

18 **A** Methane and chlorine react together in the presence of ultraviolet light in a process known as free radical substitution (FRS).

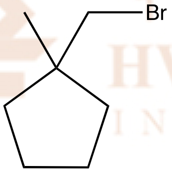
1	For hydrogen gas to be produced during FRS, 2 hydrogen radicals need to collide in termination step. However the formation of hydrogen radicals is unlikely due to the strong C-H bond. Statement is incorrect.
2	Bond breaking occurs at every step in the mechanism for FRS. As a quick recap: Initiation: breaking of X−X bond to form halogen radicals. Propagation: breaking of C−H bond to form C−X bond. Termination: breaking of another X−X bond to form halogen radicals. Statement is incorrect.
3	The formation of CH_3Cl can happen in propagation step, or during the termination step. Propagation: $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$ Termination: $Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$ Statement is correct.

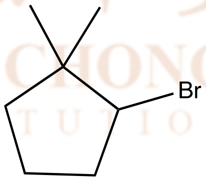
19 **B** To find out the possible mono-brominated products when 1,1–dimethylcyclopentane undergoes FRS, we have to know the position of all the hydrogen atoms.

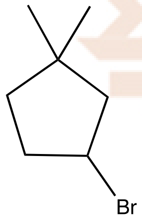


There are a total of 6 1° hydrogens and 8 2° hydrogens. Substitution of any of the above hydrogens will give a mono-brominated product. However, due to an internal plane of symmetry, the mono-substitution of hydrogen on carbon-2 or carbon-5 will give the same product. The case is similar for mono-substitution of hydrogen on carbon-3 or carbon-4, and the 2 primary hydrogens in the methyl groups on carbon-1.

Hence there will be a total of 3 different mono-substituted products.



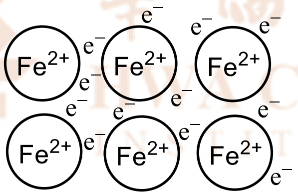




20	**C**	**1**	Carbon monoxide is oxidized to form carbon dioxide. Statement is incorrect.
		2	NO and NO_x are reduced to form nitrogen gas. Statement is correct.
		3	Unburnt hydrocarbons are oxidized to form carbon dioxide and water. Statement is correct.

Paper 2

1 (a)



[1] diagram

- *Fe^{2+} (or Fe^{3+}) cations arranged in a regular manner (min 2 × 2 layer to show lattice structure).*
- *no. of electrons = 2 × no. of Fe^{2+} OR 3 × no. of Fe^{3+}*

The <u>metallic bonding</u> **[0.5]** in iron is the electrostatic <u>forces of attraction</u> between the Fe^{2+} (accept Fe^{3+}) <u>cations</u> and the sea of <u>delocalised electrons</u> **[0.5]**.

- This question was in general well-done.
- Some students need to read the question carefully and take care to **<u>label</u>** the diagram accordingly.
- Some students <u>incorrectly</u> described the structure of iron instead of describing the **bonding** as required. For the explanation portion, to get full credit, students are required to name the bonding (metallic) as well as give a short description of the nature of the metallic bonding.
- Do note that marks were not deducted if answers only showed some electrons (no specific number) to illustrate the concept of "sea" of electrons, although it is more accurate for the negative charges of the electrons to balance the positive charges of the metal cations.
- <u>Zero mark</u> for diagram for the following cases:
  - ☒ Random drawings of "–" and "+" without proper labelling
  - ☒ Electrons drawn in a regular manner (electrons should be drawn as delocalised and interspersed throughout the whole structure, including among the cations)

(b) (i) Electronic configuration of Cu^+ is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ **[1]**
Electronic configuration of Zn^+ is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ **[1]**

- Electronic configuration of Cu is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ (✗ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$). See Section 3.4 of Topic 1 Lecture notes.
  Electronic configuration of Zn is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$.
  An electron is removed from the 4s subshell to obtain the electronic configuration for Cu^+ and Zn^+.

Some students misread the question and incorrectly gave the electronic configuration for Cu and Zn atoms instead.

(ii)
- Second IE of Cu involves removal of a 3d electron **[0.5]**. Second IE of Zn involves removal of a 4s electron **[0.5]**.
- The 3d subshell is closer to the nucleus **[0.5]** than the 4s subshell. The electron to be removed from Cu experiences greater electrostatic attraction towards the nucleus **[0.5]**. Hence, more energy required to remove the 3d electron from Cu, resulting in greater second IE for Cu.

- Discussion of IE involves a comparison of energy required to remove electrons. Hence, it is important for students to first identify the subshell from which the electron is to be removed during second ionization of each unipositively-charged on.
- Some students started off the answer with a definition of second IE. This is not necessary to gain the mark.
- Some students attempted to explain the difference in second IE of Cu and Zn using shielding effect. However, they failed to recognize that Zn has a higher nuclear charge than Cu as it has one more proton in its nucleus compared to Cu. Hence, while there is an increase in shielding effect from Cu^+ to Zn^+, there is also an increase in nuclear charge, leading to the effective nuclear charge of Cu^+ and Zn^+ to be largely invariant. Hence, in this case, the greater proximity of the 3d electron to be removed to the nucleus in Cu^+ vs the 4s electron in Zn^+ is the most significant factor to explain the higher second IE of Cu.
- Students need to take greater care when using the following terminologies:
  - ○ "subshell" vs "orbital"
  - ○ "nuclear charge" vs "nuclear attraction"

(c) (i) By Le Chatelier's principle, a low temperature favours the forward exothermic reaction, which results in a high yield of NH_3 **[1]**. However, at low temperatures, the rate of reaction is too slow to be economical **[1]**.

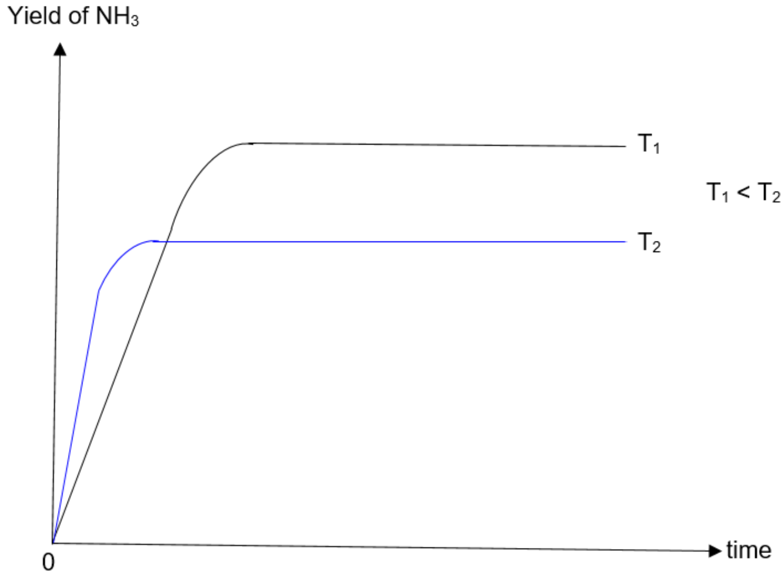
OR

By Le Chatelier's principle, a high temperature ensures the rate of reaction is high. **[1]**

However, high temperature favours the backward endothermic reaction which results in a low yield of NH_3 **[1]**.

☒ Some students linked Le Chatelier's principle/shift in position of equilibrium/extent of forward reaction to rate of reaction. This is not valid.

☒ It is also not valid to link increase in rate to increase in the yield of NH_3 at high temperature. As can be seen from the diagram below, increase in rate shortens the time taken to reach equilibrium. However, the yield is governed by the position of equilibrium, which lies more to the left at higher temperature, resulting in low yield.



Students need to link their analysis on shift in position of equilibrium to the **<u>impact on the yield of NH$_3$</u>**, as this is the focus in the industrial production of NH$_3$.

(ii) Amount of NH$_3$(g) = $\dfrac{3300 \times 1000 \times 1000}{14.0 + 3(1.0)}$ = 1.941×10^8 mol **[0.5]**

Amount of N$_2$(g) required = $\dfrac{(1.941 \times 10^8)}{2} \times \dfrac{100}{15}$ = 6.471×10^8 mol **[1]**

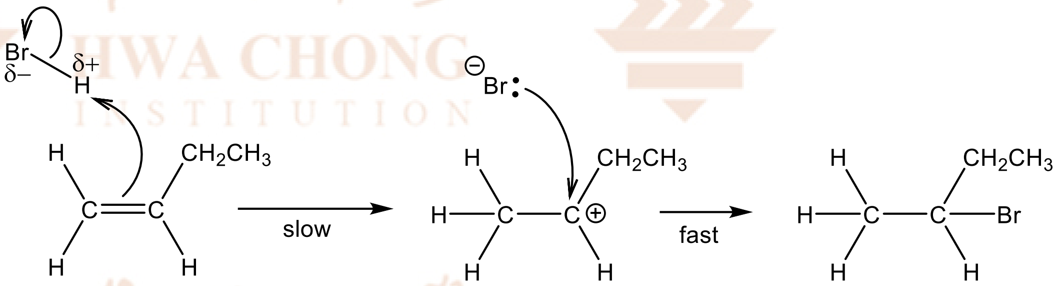
Volume of N$_2$(g) required = $(6.471 \times 10^8)(24.0\ \text{dm}^3)$
= 1.553×10^{10} dm^3
= $\underline{1.55 \times 10^{10}\ \text{dm}^3}$ (to 3 sf) **[0.5]** *ecf*

- This question was in general well-done.
- However, students were prone to careless <u>mistakes</u>, such as:
  - ☒ Not converting the mass of NH$_3$ to grams (g) when calculating its amount
  - ☒ Use of the wrong P and T in the ideal gas equation
  - ☒ Did not consider 15 % yield or used it wrongly
- To be awarded the mark for ecf, relevant workings has to be shown.
- You are recommended to write your answer using scientific notation, i.e. 1.941×10^8, instead of a long string of numbers (194117648). Intermediate steps can be given to 4 or 5 sf. There is no need to use the long string of numbers.

(iii) Volume of air required = $1.553 \times 10^{10} \times \dfrac{100}{78.08}$ = $\underline{1.99 \times 10^{10}\ \text{dm}^3}$ (to 3 s.f.) **[1]** *ecf*

This question is in general very well-done. Students just have to be able to recognise from the question that the percentage composition of nitrogen in the air is 78.08%.

2 (a) (i) **[1]** Electrophilic addition



[1] for first step

deduct 0.5m for each **type** of mistake made, looking out for

- Structure of but-1-ene
- Two curly arrows (one from π bond of C=C to H of HBr, the other from H–Br bond to Br of HBr)
- Partial charges on HBr (δ+ on less electronegative H and δ– on more electronegative Br)
- Label step 1 as slow step
- Carbocation with positive charge on correct carbon
- Balance atoms and charges in step 1 with Br^- (if step 1 and step 2 are separated)

[1] for second step

deduct 0.5m for each **type** of mistake made, looking out for

- Lone pair on Br^-
- One curly arrow from lone pair on Br^- to positively charged carbon on carbocation
- Structure of final product 2-bromobutane

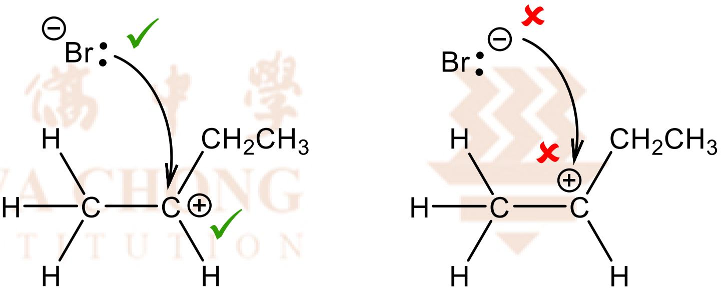
Common mistakes included

☒ missing out on writing the name of the mechanism as **electrophilic addition**

☒ missing out on labeling the first step as the **slow** step / rate determining step

Do note that for this question, no mark was deducted for

- missing the word “fast” in the second step despite the second step being the fast step;
- drawing the arrow from lone pair on Br^- to the positive charge on the positively charged carbon of carbocation in the second step although **the arrow should instead be pointing to the carbon** with the positive charge.



(ii) Bond energy is the energy required to break 1 mole of a covalent bond in the gaseous state. **[1]**

No mark was awarded if answers

☒ included thermodynamics standard conditions of “298K and 1 bar” because a covalent bond to be broken may **not** necessarily be in the gaseous state at 298K and 1 bar;

☒ stated that bond energy is the energy required to break 1 mol of a covalent bond "into gaseous atoms" because the focus of the definition is about breaking 1 mol of gaseous covalent bond and not the state of the products.

☒ stated that 1 mol of covalent bond is broken to give <u>1 mol of atoms</u> in the gaseous state. E.g. when 1 mol of H−H bond is broken, 2 mol of H atoms are formed.

(iii) ΔH = BE(C=C) + BE(H–Br) − BE(C–C) – BE(C–H) − BE(C–Br)
= 610 + 366 – 350 – 410 – 280
= <u>− 64.0 kJ mol^{-1}</u>

[1] quote **all five** bond energies (BE) correctly
[1] if missed out 1 or 2 BE, ecf second mark if working shows application of **BE(bonds broken)−BE(bonds formed)**

Bond breaking requires energy input (endothermic process) whereas bond formation releases energy (exothermic process).

Based on the electrophilic addition mechanism in 2(a)(i),

☒ In the slow step, π bond of the C=C and H–Br bond are broken and C–H bond is formed. Students may either choose to break both the σ and π bonds in C=C then form back the C–C, or just break the π bond only.
Note that BE(π bond of C=C) = BE(C=C) – BE(C-C) = 610 – 350 = 260 kJ mol^{-1}.
For students who broke the C=C bond, it is necessary to form back the C–C bond, otherwise two separate products would be formed instead.

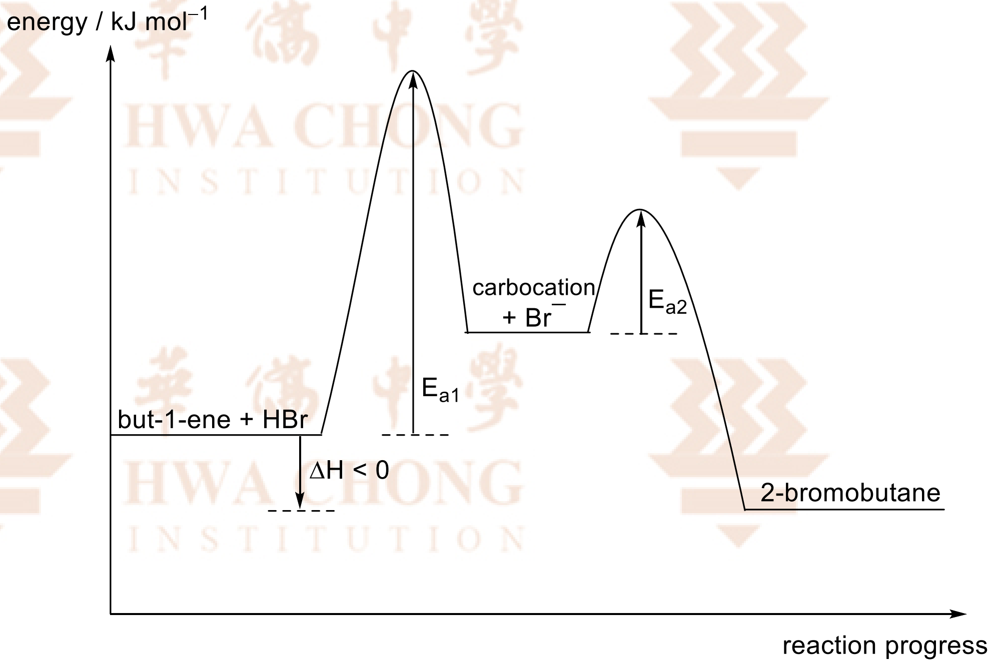
☒ In the fast step, C–Br bond is formed.

Students who attempted to first break all the bonds and then form all the bonds again, often made mistakes counting the numbers of each type of bond esp. the C-H bonds. During the interpretation of skeletal structure, it is good practice to note the number of H atoms bonded to each C to avoid this mistake. Others who calculated the enthalpy changes for step 1 and step 2 separately also often made careless mistakes.

(iv) The activation energy is the <u>energy barrier the reactants must overcome</u> in order to become the products. **[1]**

Alternative answers accepted include "the <u>minimum</u> energy the reactants must possess in order to become products" but <u>no</u> mark was awarded if candidates did <u>not</u> include the word "minimum".

(v)



[0.5] label axes (also accepted reaction pathway / reaction coordinate for x-axis label)
[0.5] label E_{a1} and E_{a2} where $E_{a1} > E_{a2}$
[0.5] label ΔH with correct arrow direction (ecf sign from (a)(iii))
[0.5] label reactants (but-1-ene and HBr), intermediates (carbocation and Br^-) and product (2-bromobutane), number of atoms and charges must be balanced.

Based on the electrophilic addition mechanism in 2(a)(i),

- There are **two steps** and therefore there should be **two peaks**. Since the first step is the slow step, the activation energy for the first step (E_{a1}) must be higher than that of the second (fast) step (E_{a2}).
- The **arrow for ΔH must point down** to indicate an **exothermic** reaction where ΔH is negative.
- The intermediate level must include both the carbocation and **Br^-**. The latter is often missed out.

Further interpretation of the energy profile diagram,

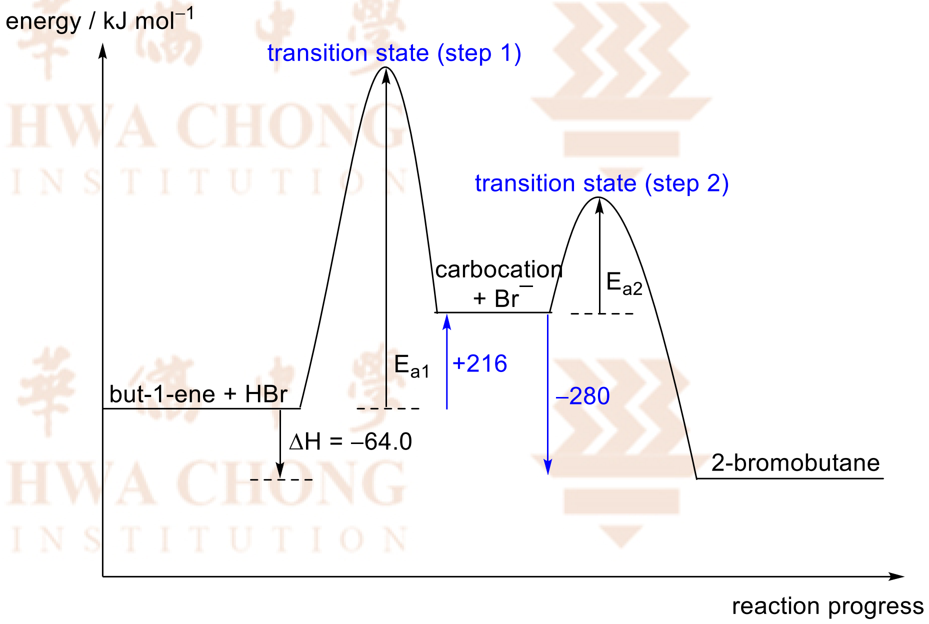
☒ In the slow step, π bond of the C=C and H–Br bond are broken and C–H bond is formed. Hence ΔH(step 1) = BE(C=C) − BE(C—C) + BE(H—Br) – BE(C—H) = 610 – 350 + 366 – 410 = +216 kJ mol^{-1}. As ΔH(step 1) is positive, intermediates are less stable than reactants, **energy level of intermediates is higher than energy level of reactants**.

☒ In the fast step, C–Br bond is formed. Hence ΔH(step 2) = − BE(C—Br) = − 280 kJ mol^{-1}. As ΔH(step 2) is negative, product is more stable than intermediates, **energy level of product is lower than energy level of intermediates**.

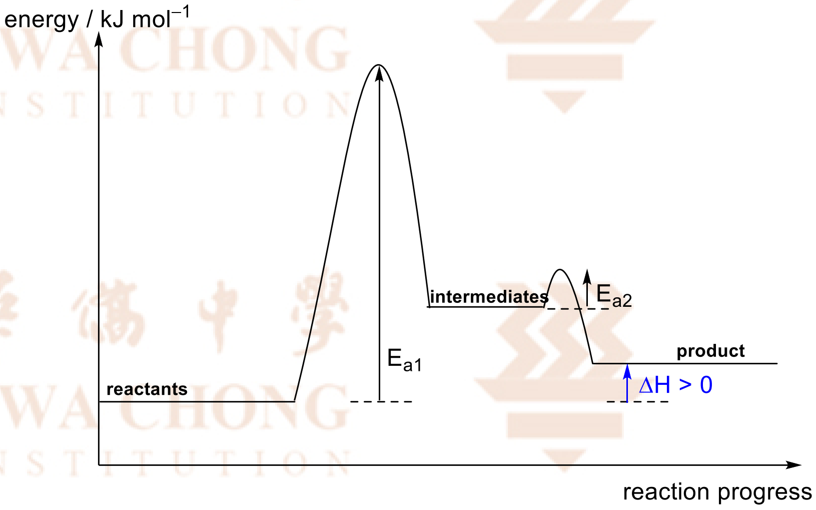
☒ Hence, ΔH(overall) = 216 – 280 = − 64.0 kJ mol^{-1}. As ΔH(overall) is negative, product is more stable than reactants, **energy level of product is lower than energy level of reactants**.

☒ In addition, at each peak is the transition state. Note that **a transition state is different from a reaction intermediate** such as the carbocation for an electrophilic addition.

☒ ΔH(step 1) and ΔH(step 2) are <u>not</u> E_{a1} and E_{a2} respectively. No info is given in the question regarding the values of E_{a1} and E_{a2}.



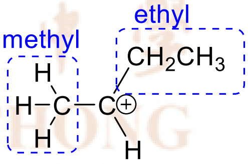
If ΔH calculated in (a)(iii) was incorrect and **positive**, error carried forward (ecf) for the energy profile diagram is allowed, as such the ecf diagram should look similar as the following:



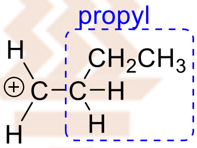
The arrow for ΔH must point up to indicate an endothermic reaction where ΔH is positive.

(vi) Formation of 2-bromobutane involves a more stable secondary carbocation **[1]**.

A secondary carbocation has one more inductively electron-donating alkyl group on the positively charged carbon than a primary carbocation which forms 1-bromobutane **[1]**.
OR
The carbocation which forms 2-bromobutane has two inductively electron-donating alkyl groups on the positively charged carbon compared to one in the carbocation which forms 1-bromobutane **[1]**.



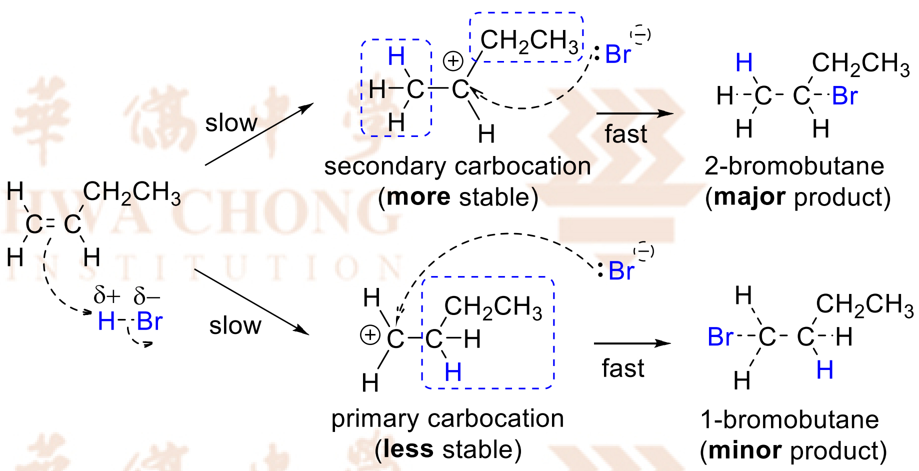
secondary carbocation
with two alkyl groups



primary carbocation
with one alkyl group

Part of the Topic 11 Alkenes Learning Outcome 11.3(g) stated "……explain the composition of products in terms of the **stability of the carbocation intermediates**."

Alkyl groups e.g. methyl ($-CH_3$), ethyl ($-CH_2CH_3$), and propyl ($-CH_2CH_2CH_3$) are electron donating groups. Therefore, the greater the number of alkyl substituents on the positively charged carbon of a carbocation, the **more stable the carbocation** would be, as the electron donating groups **disperse the positive charge** on the carbon.

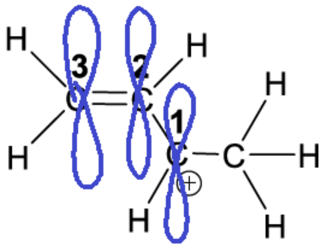


The π electron cloud on C=C of but-1-ene (nucleophile) attacks the electron-deficient H atom of HBr (electrophile) to give the more stable secondary carbocation. The nucleophile bromide anion (Br^-) attacks the positively charged carbon of the **more stable secondary carbocation** (electrophile) to give **2-bromobutane as the major product**.

No credit was given to answers

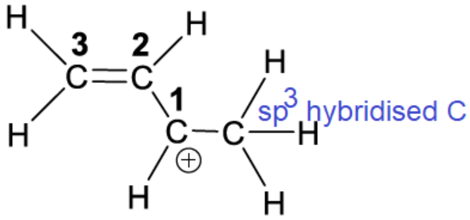
- ☒ with wrong identification of the types / classification of carbocations such as tertiary vs. primary or tertiary vs. secondary
- ☒ which discussed the stability of products rather than that of the carbocations

(b) (i) The three adjacent carbon atoms (carbon-1, carbon-2 and carbon 3) each contains one unhybridised p orbital perpendicular to the plane of its sp^2 hybrid orbital. These three p orbitals **[0.5]** overlap side-on **[0.5]** to allow delocalisation of electrons.



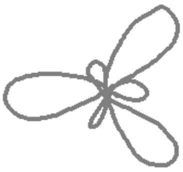
carbocation **C**

There are three electron groups around carbon-3, hence carbon-3 is sp^2-hybridised. Carbon-3 utilises one 2s orbital and two 2p orbitals in the formation of three sp^2 hybrid orbitals. Refer to Topic 2 Lecture Notes Section 6.2.2 (p. 62).

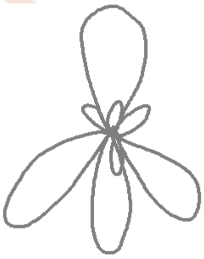


carbocation **C**

Therefore, carbon-3 contains one unhybridised p orbital that is perpendicular to the plane of its sp^2 hybrid orbitals. This is the same for carbon-2 and carbon-1. There are four electron groups around the unlabeled carbon attached to carbon-1, hence this carbon is sp^3-hybridised with **all three of its 2p orbitals used for hybridisation,** together with a 2s orbital, to give four sp^3 hybrid orbitals. Some students incorrectly thought that there is one unhybridised p orbital on the unlabeled carbon next to carbon-1, when in fact there is not.

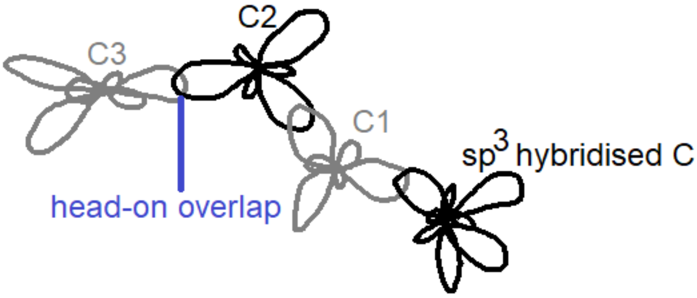


three sp^2hybrid orbitals arranged in trigonal planar

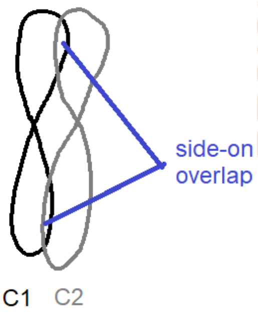


four sp^3 hybrid orbitals arranged in tetrahedral

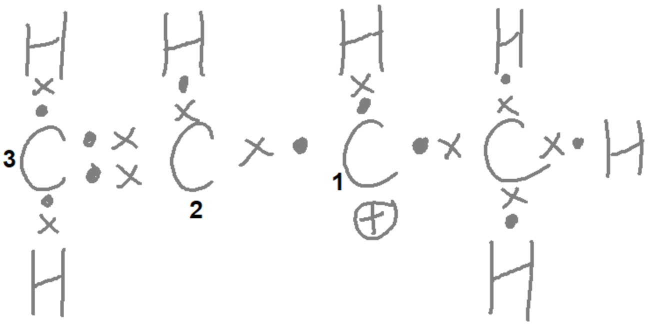
One C=C bond consists of one σ bond and one π bond. One sp^2 hybrid orbital on carbon-3 overlaps head-on with one sp^2 hybrid orbital on carbon-2 to give a carbon-carbon σ bond.



The π bond between carbon-3 and carbon-2 is due to the side-on overlap between one 2p orbital on carbon-3 and one 2p orbital on carbon-2.

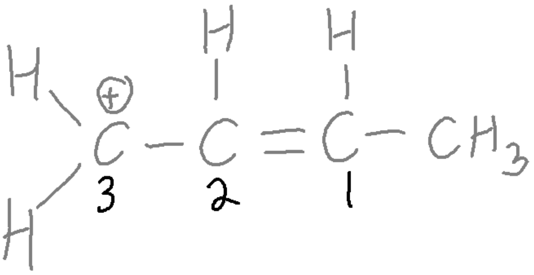


Carbon-1 loses one electron in the formation of the carbocation **C**, hence the dot-and-cross diagram of carbocation C shows that there are only 3 electrons contributed by carbon-1. Some students <u>incorrectly</u> thought that there is one lone electron in the p orbital on each of the three carbons: carbon-1, carbon-2 and carbon-3, when in fact there is only one lone electron in the p orbital on each of these two carbons: carbon-2 and carbon-3. Some students <u>incorrectly</u> thought that there is one π bond between carbon-3 and carbon-2 and another π bond between carbon-2 and carbon-1, when in fact there are only 2 electrons shared among carbon-3, carbon-2 and carbon-1 through side-on overlap of the three p orbitals on each of these three carbon atoms.

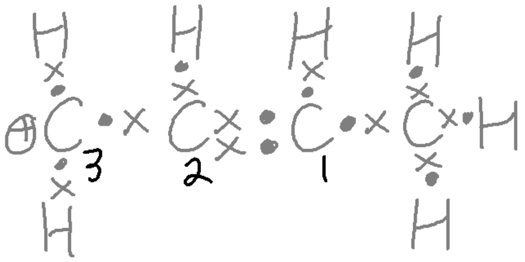


dot-and-cross diagram of carbocation **C**

Bromide anion (Br^-) attacks carbon-1 to give product **A**. The positive charge on carbocation **C** can be delocalised across carbon-3, carbon-2 and carbon-1 through side-on overlap of the three p orbitals on each of these three carbon atoms. Another resonance structure of carbocation **C** and its dot-and-cross diagram are as follows:



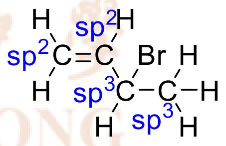
another resonance structure of carbocation **C**

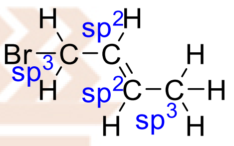


dot-and-cross diagram of this other resonance structure of carbocation **C**

Bromide anion (Br^-) attacks carbon-3 to give product **B**. Do note that any one form of the resonance structure does <u>not</u> represent the actual structure. The real structure is a hybrid of all the possible resonance structures. You may wish to refer to Topic 12 Arenes on the two resonance structures of benzene.

(ii)





	A	**B**
no. of C(sp^2)-C(sp^2) bonds	1	1
no. of C(sp^2)-C(sp^3) bonds	1	2
no. of C(sp^3)-C(sp^3) bonds	1	0
	[0.5] for **A**	**[0.5]** for **B**

If there are **four** electron groups around a carbon atom, the carbon atom is sp^3-hybridised.
If there are **three** electron groups around a carbon atom, the carbon atom is sp^2-hybridised.
If there are **two** electron groups around a carbon atom, the carbon atom is sp-hybridised.
Refer to Topic 2 Lecture Notes p. 64.

One C=C bond consists of one σ bond and one π bond. One C–C bond consists of one σ bond. Do note that the question asked for the number of carbon-carbon σ bonds only.

(iii) An sp^2 hybrid orbital has more s character / less p character than an sp^3 hybrid orbital. **[0.5]**

The effectiveness / degree of the overlap increases as follows: between two sp^3 orbitals < between a sp^2 and a sp^3 orbital < between two sp^2 orbitals. **[0.5]**

OR

The overlap between two sp^2 orbitals is most effective hence the sp^2—sp^2 bond is shortest and strongest.

OR

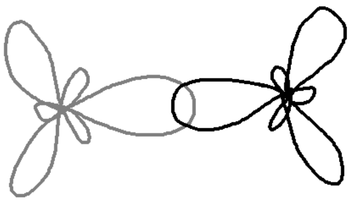
The overlap between two sp^3 orbitals is least effective hence the sp^3—sp^3 bond is longest and weakest.

Each type of hybrid orbital (sp^3 vs. sp^2 vs. sp) has different characteristics depending on the atomic orbitals from which it originates. Recall that a p orbital is dumb-bell shaped (thus, elongated) while an s orbital is spherical. Hence, a hybrid orbital that has more p character (hybrid orbital made up of a larger percentage of p orbitals than s orbitals), tends to form less effective overlap **during head-on overlap with another orbital**, resulting in longer and weaker σ bond. Refer to Topic 2 Lecture Notes p. 64.

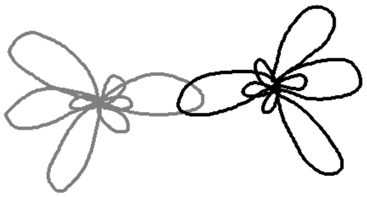
hybrid orbital	ratio of s:p orbitals	% s character	% p character
sp^3	1:3	25%	75%
sp^2	1:2	33.3%	66.6%
sp	1:1	50%	50%

Do note that the question asked you to compare the strength of the carbon-carbon σ bonds only. Any mention of how the π bond affects the strength of σ bond will not be given credit.

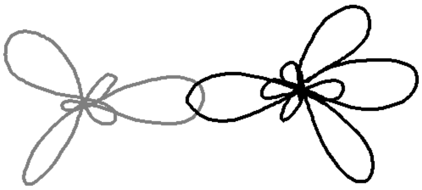
☒ Several students incorrectly expressed their answers as if a hybrid orbital is a bond when in fact they are different. For example, sp^2-sp^2 bond has more s character is incorrect. Instead, it should be sp^2 **hybrid orbital** has more s character.



head-on overlap between two sp^2 hybrid orbitals



head-on overlap between two sp^3 hybrid orbitals



head-on overlap between one sp^2 hybrid orbital and one sp^3 hybrid orbital

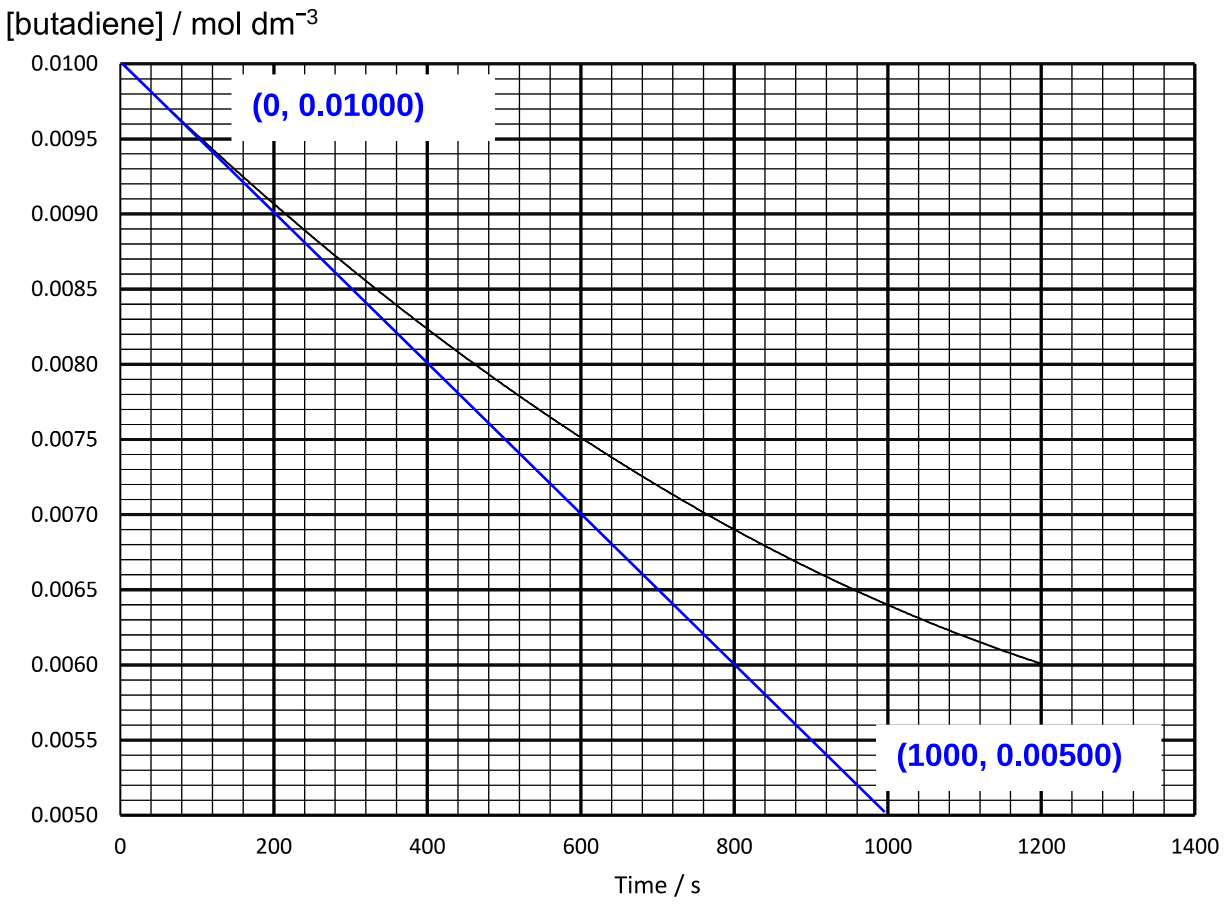
The overlap between two sp^2 orbitals is more effective than between one sp^2 hybrid orbital and one sp^3 hybrid orbital hence the sp^2—sp^2 bond is shorter and stronger than the sp^2—sp^3 bond. The overlap between two sp^3 orbitals is less effective than between one sp^2 hybrid orbital and one sp^3 hybrid orbital hence the sp^3—sp^3 bond is longer and weaker than the sp^2—sp^3 bond.

(iv) **B** is more stable as **B** has one stronger sp^2–sp^3 bond in place of an sp^3–sp^3 bond in **A**. **[1]**

It is important to notice that **A** and **B** each has 3 carbon-carbon σ bonds for a fair comparison and therefore a complete comparison between **A** and **B** is necessary to obtain full credit. This means that answers which only state "**B** is more stable as **B** has one stronger sp^2–sp^3 bond" OR "**B** is more stable as **B** does not have the weaker sp^3–sp^3 bond like A" will **not** be given full credit.

It is not necessary to state that an sp^2–sp^3 bond is stronger than an sp^3–sp^3 bond as this information was given in (b)(iii).

(c) (i)



$$\text{Initial rate} = -\text{ gradient} = -\frac{y_1 - y_2}{x_1 - x_2} = -\frac{0.01 - 0.0050}{0 - 1000}$$

$$= 5.00 \times 10^{-6}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

[1] tangent + working + final answer within **range 4.5×10^{-6} to 5.5×10^{-6}** mol dm^{-3} s^{-1}
Deduct [0.5] if initial rate is **not** positive but award [0.5] if gradient calculated correctly.

Initial rate can be found from the gradient of the tangent at time = 0 of a concentration-time graph. Therefore, a good tangent to obtain gradient for the initial rate must appropriately overlap the front / initial part of the curve. If your initial rate was correctly calculated and falls within the acceptable range 4.5×10^{-6} to 5.5×10^{-6}, the tangent you drawn is considered a good tangent.

Since [reactant] decreases during a reaction, d[reactant]/dt is negative. The negative sign is added to give a positive value to rate. Refer to Topic 6 Lecture Notes Section 2.1 (p. 49)

It is recommended to choose two well-separated coordinates, a suggestion for the two coordinates to be away from one another by more than half the length a maximum tangent (that falls within the grid) that can be drawn for the curve.

It is recommended to leave your final answer to 3 or 4 significant figures unless otherwise stated by the question.

(ii) $$k = \frac{\text{rate}}{[\text{butadiene}]^2} = \frac{5.00 \times 10^{-6}}{(0.01)^2} = 0.0500\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

[1] working + final answer
[1] units

Units of k = $\frac{units\ of\ rate}{units\ of\ conc^2} = \frac{mol\ dm^{-3}\ s^{-1}}{(mol\ dm^{-3})^2} = mol^{-1}\ dm^3\ s^{-1}$

It is recommended to leave your final answer to 3 or 4 significant figures unless otherwise stated by the question.

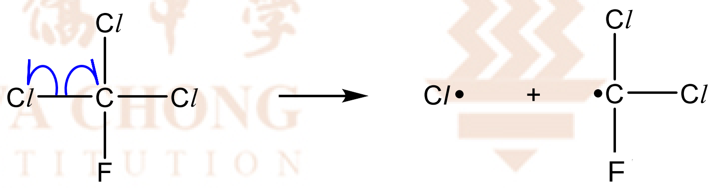
3 **(a)** Condensation involves the formation of intermolecular forces which release energy. **[1]**

From Table 3.1, we can tell that all the refrigerants exist as simple covalent molecules. To convert from gaseous to liquid phase, these simple covalent molecules form stronger intermolecular forces of attraction, which releases energy.
Simply stating "energy is released during condensation" is not accepted as it is just rephrasing the word 'exothermic'. The key is to explain *why heat is released*. Stating "energy released in forming bonds is greater than energy taken in when breaking bonds" misses the point of the question as it does not acknowledge the context here where no "bonds" are broken ☹
The use of the term "bonds" is ambiguous as it may mean "covalent bonds" which is not formed here.
The term "condensation" refers to the gas to liquid phase transition, as shown in the question context. Answers which refer to the organic chemistry reaction or assume water molecules must be formed are not accepted.

(b) They have low boiling points and can be easily liquefied by pressure a little above atmospheric pressure / They are chemically and biologically inert (and hence safe to use and handle). **[1]**

This question is about identifying a property of CFCs which made them suitable as refrigerants. Its low boiling point makes it easy to undergo repeated liquid-gas transitions, as mentioned in the question stem.
Answers that only mentioned low boiling point without any reason were not accepted. Answers that made comparison to other refrigerants and mentioned that CFCs have higher boiling points (hence easier to transport or store etc.) were also rejected. The other refrigerants came after CFCs, and cannot be used to explain why CFCs were chosen in the first place.

(c) **(i)**



[0.5] arrows **[0.5]** $\bullet\mathrm{CC}l_2\mathrm{F} + \mathrm{C}l\bullet$
Type of bond breaking: <u>homolytic</u> fission **[1]**

Homolytic fission makes radicals, which are species with unpaired electron. The two electrons from the $\mathrm{C{-}C}l$ bond breaks homolytically, with one electron going to C and $\mathrm{C}l$ each. This is represented by two half (fish-hook) arrows. Note that it is the $\mathrm{C{-}C}l$ and not the C–F bond that breaks, in order to form the chlorine radical.

(ii) step 1: $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$ **[1]**
step 2: $ClO\bullet + O_3 \rightarrow 2O_2 + Cl\bullet$ **[1]**

Most students were able to balance the steps correctly, and figure out that the other product must be O_2 and $2O_2$ (O_4 does not exist!) in steps 1 and 2 respectively.
Note that elementary steps must add up to give the overall equation, $2O_3 \rightarrow 3O_2$.

(iii) Cl_2 / $Cl–OCl$ (or Cl_2O) **/** $ClO–OCl$ (or Cl_2O_2) **[1]** *for any one*

Trace amounts of other products are obtained when two radicals collide into each other (similar to termination step of free radical substitution), hence any correct combination of two radicals was accepted. Note that $ClO–ClO$ is not accepted as the two O atoms should be bonded together, i.e. $ClO–OCl$.

(iv) C-F (and C-H) bond in HFCs is stronger than C-C*l* bond in CFCs and will not be broken by UV light to form F (and H) radicals, hence no ozone depletion potential. **[1]**

Alternative answer (assuming comparison was made with CFCs and HCFCs):
HFCs do not contain C*l* atom and hence cannot form $Cl\bullet$ radicals that causes ozone depletion.
However, answers that simply mentioned that HFCs 'do not contain C*l* atom' OR 'will not form C*l* radicals' were not accepted due to missing reason or consequence.
Note that the ozone depletion mechanism is not exactly a "free radical substitution" - even though it involves free radicals, it is not a substitution reaction.

(d) $q_2 = mc_{liq}\Delta T = (700 \times 2.24 \times 8) = 12544 = 12.5$ kJ **[1]**

No. of moles of propane = 700/44 = 15.9 mol
$q_3 = n\Delta H_{vap} = (15.9 \times 24500) = 389550 = 390$ kJ **[1]**

$q_1 = 12.5 + 390 + 78.3 = 481$ kJ **[1]** *ecf*

Many students were penalized for number of significant figures (s.f.) in their presentation of q_2, q_3 and q_1. Since the question asked for q_2, q_3 and q_1 individually, all answers need to have the correct number of s.f., not just the final answer for q_1.
Note that units of q, the quantity of heat, is J or kJ, and **not** kJ mol^{-1}! Do not confuse heat (q) with enthalpy change (ΔH). There is also no sign necessary for q.
For q_2, a common error is to use (8+273) for ΔT – note that the change in temperature, ΔT, whether in °C or K, is numerically the same! Another common error is to use the wrong c_{liq} of 4.18 (specific heat capacity for water) instead of 2.24 provided in the question ☹
q_3 is NOT equivalent to enthalpy change of vaporisation which is for 1 mole of propane. We must multiply by the number of moles of propane (check the units for hint!)

Paper 3

1 (a) (i) Si: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ **[1]**

Rejected: formulae with subscripts instead of superscript

Most students answered this correctly.

(ii) Similarity (one of the following): **[1]**

- The 3s and 3p orbital both belong to the third principal quantum shell
- The 3s and 3p orbital can each hold a maximum of two electrons (of opposite spins)
  Rejected:
  ✘ *Answers that are too vague (e.g. "3s and 3p orbitals can both hold electrons")*

Difference (one of the following): **[1]**

- The 3s orbital is spherical while the 3p orbital has a dumb-bell shape
- The 3s orbital is lower in energy than the 3p orbital
  Rejected:
  ☒ *Answers with insufficient details, e.g. "the 3s orbital and 3p orbital have "different" energy levels"*
  ☒ *Answers that do not focus on the difference between 'a' 3s and 'a' 3p orbital, as required by the question. E.g. "there is only one 3s orbital while there are three 3p orbitals"*
  ☒ *Answers that refer to the orbital's "distance" from the nucleus. Since all orbitals include a region of space that starts at the nucleus, it is technically not possible to determine which orbital is 'further'. Note that this is different from referring to the electron's position from the nucleus.*

Many students could come up with suitable similarities and differences, although quite a number incorrectly wrote that a 3p orbital could contain 6 electrons (very common error), showing a confusion between the terms 'orbital' and 'subshell'.
Note that the shape of the orbitals should be three-dimensional shapes, and references to "circular" or "oblong" shapes were penalized.

(iii) Difference (any one of the following): **[1]**

- The 3p orbital is higher in energy than the 2p orbital
- The 3p orbital is larger (in size) than the 2p orbital
- The 3p orbital belongs to the third quantum shell, while the 2p orbital belongs to the second quantum shell
  Rejected:
  ☒ *Answers with insufficient details, e.g. "the 3p and 2p orbitals have different energy levels" – please describe the difference.*
  ☒ *Answers that refer to the orbital's "distance" from the nucleus (see details under rejected answers in (ii)).*

Since both 2p and 3p orbitals have the same dumbbell shape, the most straightforward difference is to think of their size. Here again it is important to note that the orbital size changes in three-dimensions, so it isn't sufficient to suggest that the shape of the 3p orbital is *longer* or *wider*.

(b) (i)

	Ca	Mg	Si	O
%	18.51	11.22	25.95	44.32
A_r	40.1	24.3	28.1	16.0
No. of moles in 100 g	0.4616	0.4617	0.9235	2.77
Ratio	1	1	2	6

Hence, empirical formula is $\underline{CaMgSi_2O_6}$

[1] correct working shown
[1] correct answer

Most students could correctly work out the empirical formula for basalt. A handful of candidates carelessly used the symbol for sulfur (S) instead of silicon (Si) and were penalized.

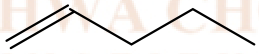
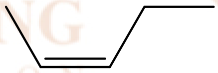
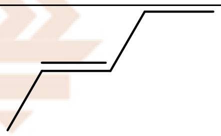
(ii) SiO_3^{2-}

[1] for correct formula (charge must be correct)

This proved slightly more challenging, with many students incorrectly suggesting the oxide anion (O^{2-}) as the possible anion. However, many others could still work out the correct answer.

Strategy: based on the empirical formula which shows the mole ratio of Ca and Mg as 1:1, and the information in the question which tells us that the Ca^{2+} and the Mg^{2+} salts both have the same anion, we are left with 2xSi, 6xO, and a 4- charge to be shared across the two salts equally, hence giving us SiO_3^{2-} x2.

(c) (i)

D	E and F	
 pent-1-ene	 *cis*-pent-2-ene	 *trans*-pent-2-ene

[0.5] each correctly drawn structure (can be displayed, skeletal, condensed or mixed, but must be unambiguous) – must correspond to the correct letter (D, E or F).
[0.5] each name corresponding to correct structure
Accept if labels 'cis' and 'trans' are written separately from "pent-2-ene".

A number of students did not clearly label which of their structures were D, E or F, and were penalized.
Many students could correctly work out the three structures, though several forgot to give their names, which the question asked for. A handful overlooked the detail in the question that said they were "straight-chain alkenes", that is they are **not branched**, and so suggested incorrect structures, particularly for the structure of D.
Students who used skeletal structures tended to make less errors than those who used displayed structures, many of which either forgot H atoms, or added extra H atoms where there shouldn't be as many.

(ii) Cis-trans isomerism exists between E and F. It arises because there is restricted rotation around the C=C double bond in molecules E and F **[1]** and there are non-identical groups on each carbon in the bond with restricted rotation (i.e. the C=C bond). **[1]**

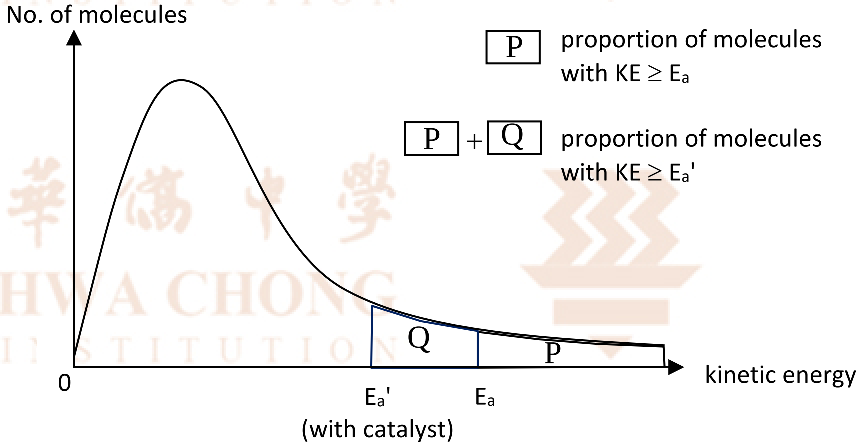
Rejected: "restricted movement"; "fixed rotation", "limited movement", or any implication that the restricted rotation occurs in any other part of the molecule (other than around the C=C bond).

Many vague or ambiguous phrasings were seen here, which revealed a poor understanding of what 'restricted rotation' meant. It is important to say around which bond there is restriction of rotation.

Several also confused the meaning of "each end of the C=C bond" with "each side of the C=C bond" which do not refer to the same thing.

- Each *end* of the C=C bond refers to each C atom in the double bond. We use this term to explain the second criteria in how cis-trans isomerism arises (i.e. non-identical groups on each *end* of the C=C bond).
- Each *side* of the C=C bond requires us to imagine splitting the bond along its axis: we use this to determine if the isomer is the *cis* isomer (if the identical groups are on the same *side* of the C=C bond) or the *trans* isomer (if the identical groups are on opposite *sides* of the C=C bond).

(iii)



The catalyst provides an alternative reaction pathway of lower activation energy (E_a') compared to the uncatalysed reaction (E_a).

The proportion/fraction of (reactant) particles that have KE ≥ activation energy hence increases from area P to area P+Q, leading to increased frequency of effective collisions, hence rate of reaction increases even without an increase in initial concentrations of reactants. Hence, rate constant (k) must have increased (since Rate = $k[A]^x[B]^y$).

[3] To earn the marks, students must fulfill the following:

- Diagram: correct axis labels, two E_a labels (with and without catalyst, symbols must be defined or explained in text), correct shape of graph (starts from 0 but no need to label 0).

- Explicit mention that catalyst lowers activation energy, thus proportion of particles with KE ≥ activation energy increases *as shown by areas shaded/labelled on graph*. Labels on graph must be clear (can be shaded or lettered areas).
- Reference to frequency of effective collisions increasing, rate increasing, and rate constant increasing with a valid justification from Boltzmann distribution graph (e.g. given same starting conditions / given same initial concentrations of reactants).

In general, responses here showed that students studied this concept well.

Common errors included:

☒ A number of students overlooked the fact that the question asked for the effect *on the rate constant*.

☒ Some students used Arrhenius' equation to justify the increase in the value of the rate constant, but this was not accepted, as the question wanted justification from the Maxwell-Boltzmann distribution diagram.

☒ A significant number of students inverted the labels on the axes of the Boltzmann distribution diagram.

(iv) At low pressures, concentration/partial pressures of reactants are low, there are many active sites available on the catalyst. As the concentration/partial pressures of reactants increase, more reactants can be adsorbed onto active sites. Hence, rate of reaction increases proportionately to the increase in each reactants concentration/pressure (first order).

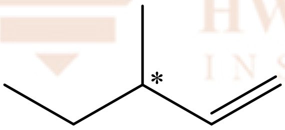
At higher pressures, the active sites on the catalyst are saturated. Products must desorb from the active sites before new reactants can be adsorbed. Increasing the concentration/partial pressure of the reactants thus has no effect on the rate (zero order).

[2] To earn both marks, students must:

- Make reference to active sites of the catalyst being available at low pressures and saturated at higher pressures.
- Show understanding that pressure is linked to concentration/partial pressure of the reactants, with the use of correct terminology and keywords (active sites, saturated, adsorb/desorb).

This question was poorly answered. Only a handful of students read the question stem carefully enough to realise that the catalyst was playing a big role in the observation. For revision, do revisit the concept of heterogeneous catalysis under Topic 6 – Kinetics (also see Topic 6 Tutorial Q9(a)).

(d) **G:**



[1] correct structure *(need not be skeletal, as long as unambiguous)*

Structure can be drawn as one of the enantiomers, or as the general structure (as shown above).

Since G is able to rotate plane-polarised light, it must have a chiral carbon, that is a C atom bonded to 4 different groups. Based on the structural formula and information in the question, we know G has one C=C double bond. With that, there is only one possible arrangement that allows for a chiral centre.

Note: it is best to avoid condensed formulae for substitutents, particularly when these contain an alkene functional group, as such formula give no clear information about the structure:

e.g. avoid "-C_2H_3" but instead write "-$CH=CH_2$"
e.g. avoid "-C_2H_5" but instead write "-CH_2CH_3"

(e) **(i)** Since pressure and amount of each species is constant during cooling

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Thus, volume of carbon dioxide at 150 °C can be found:

$V_{(CO2)} = \frac{V_2}{T_2} \times T_1 = \frac{48.5}{(20+273)} \times (150+273) = \underline{70.0\ \text{cm}^3}$

[1] correct use of ideal gas relationship to find volume of CO_2 at 150 °C

A significant number of students forgot to convert the temperature units from degrees Celsius to Kelvin, and as a result could not calculate the correct volume.

(ii) $\frac{x}{1} = \frac{70}{10} \Rightarrow x = 7$

$\therefore \frac{x + {}^{y}/_{4}}{1} = \frac{95}{10} \Rightarrow y = 10$

Hence, the formula of **J** is $\underline{C_7H_{10}}$.

[0.5] correct working for either *x* or *y* (no e.c.f. from e(i) given).
[0.5] correct formula for **J** (with working)

Many students did not reach this question part. However, for students who managed to correctly calculate the volume of CO_2 at 150 °C in (i), this part was straightforward.
It is important to realise that *x* and *y* are **not** volumes, but because we are dealing with gases, their ratios are equivalent to volume ratios.

2 (a) (i) No. of moles of $S_2O_3^{2-}$(aq) used = $0.500 \times \frac{25.56}{1000} = 0.01278$ mol **[0.5]**

No. of moles of I atoms in $I_xCl_y^-$ = 0.01278 mol = 0.0128 mol (3 s.f.) **[0.5]**

The question requires the no. of moles of I **atoms** to be calculated, not I_2 molecules.

(ii) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

No. of moles of AgCl(s) formed = $\frac{0.92}{(107.9 + 35.5)} = 6.416 \times 10^{-3}$ mol **[0.5]**

No. of moles of Cl atoms in $I_xCl_y^-$ = 6.42×10^{-3} mol **[0.5]**

Answers which only showed the no. of moles of AgCl(s) formed, without any reference to the no. of moles of Cl **atoms**, are penalised.

(iii) Mole ratio of I : Cl in $I_xCl_y^-$ = 0.01278 : 6.42×10^{-3}
= 2 : 1 **[0.5]**
Hence, formula of the anion: **I_2Cl^-** **[0.5]**

No. of moles of I_2Cl^- = 6.416×10^{-3} mol

M_r of the metallic salt = $\frac{2.10}{6.416 \times 10^{-3}} = 327.3$ **[0.5]**

A_r of metal = 327.3 − (126.9 × 2) – 35.5 = 38.0

Identity of the Group 1 metal: Potassium / K **[0.5]**

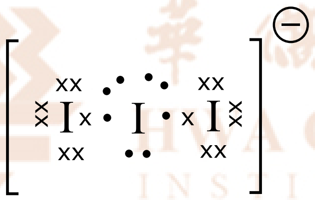
Working must be shown in determining the formula of the anion. "**Determine** often implies that the quantity concerned cannot be measured directly but is obtained by calculation, substituting measured or known values of other quantities into a standard formula, e.g. relative molecular mass." – Glossary of Terms in 9729 syllabus.

Hence, we expect the working to be clearly shown when you are asked to determine a quantity. Answers without working are penalized.

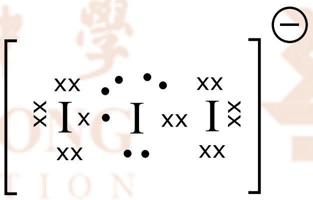
(b) (i) A dynamic equilibrium refers to a reversible reaction in which the forward and reverse reactions are taking place at the same rate **[0.5]** resulting in no overall changes in concentrations/concentrations remaining constant. **[0.5]**

Many answers omitted the point about "no overall changes in concentrations/concentrations remaining constant", but this is necessary to describe a system at equilibrium.

(ii)



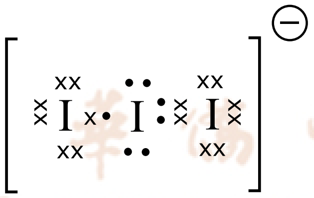
or



[1]

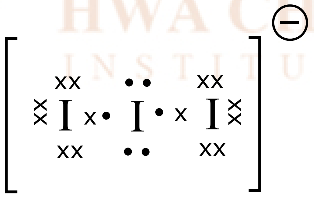
Rejected:

☒



The central iodine has 2 bond pairs and 2 lone pairs, so the shape of the anion would be bent.

☒



The central iodine has only 6 electrons (i.e. electron deficient). The central iodine also only has 2 bond pairs and 2 lone pairs, so the shape of the anion would be bent.

Do note that dot-and-cross diagrams are **not** the same as Lewis structures. Answers which gave structures, even if correct, were not given any credit.

The overall charge of the anion should be written outside a square bracket. Some answers were missing the negative charge altogether.

The question gave the shape of the anion to be linear, hence the central iodine should have 2 bond pairs and 3 lone pairs.

(iii) When I_2 is added to KI(aq), increase in $[I_2]$ shifts the position of equilibrium 1 to the right to decrease $[I_2]$ **[1]**. Thus I_2 reacts with I^- to form I_3^- which can form ion-dipole interactions with water molecules. **[1]**

☒ A common mistake is to misread/misinterpret the question, thinking that I^- was added to the equilibrium mixture, when it was actually **I_2 that is added to KI(aq)**. Thus, it should be $[I_2]$, not $[I^-]$, which increases.

The force of attraction between the I_3^- anion and H_2O molecules is ion-dipole interaction, as I_3^- is an ion while H_2O is a polar molecule with a net dipole moment.

(iv) $K_c = \dfrac{[I_3^-]}{[I_2][I^-]} = \dfrac{0.850}{(0.040)^2} = 531.25 = 531$ (3 s.f.) $\text{mol}^{-1}\ \text{dm}^3$ **[1]**

The final answer should be given to 3 or 4 s.f.
Some wrong units were given but there was no penalty.

(v) <u>K_c >> 1 (or large K_c)</u> means <u>the reaction has gone to completion / position of equilibrium lies far to the right.</u> **[1]** *(Also accept the equilibrium mixture contains more products compared to reactants / reaction has a high yield)*

Rejected:

☒ *there are more products, without comparison to the amount of reactants*

The magnitude of K_c indicates how far the position of equilibrium lies to the right. Thus, students were expected to make reference to the value of K_c which they calculated in (b)(iv) to explain that the **large** K_c indicated that the reaction goes to completion. Refer to Topic 07 Lecture Notes Section 4.

(vi) Let x be the no. of moles of I_2 added,

	I_2(aq)	+	I^-(aq)	$\rightleftharpoons$	I_3^-(aq)
initial /mol	$\frac{0.04 \times 100}{1000} + x$ $= 0.004 + x$		$\frac{0.04 \times 100}{1000}$ $= 0.004$		$\frac{0.85 \times 100}{1000}$ $= 0.085$
change/mol	-0.001		-0.001		$+0.001$
equilibrium/mol	$0.003 + x$ **[0.5]**		0.003 **[0.5]**		0.086

$$531.3 = \frac{\left(\frac{0.086}{V}\right)}{\left(\frac{0.003 + x}{V}\right)\left(\frac{0.003}{V}\right)}$$

$$= \frac{(0.086)}{(0.003 + x)\left(\frac{0.003}{100/1000}\right)} \Rightarrow x = 0.002396 \text{ mol } \textbf{[1]}$$

$$[I_2]_{\text{new eqm}} = \frac{(0.003 + 0.002396)}{0.100} = 0.0540 \text{ mol dm}^{-3} \text{ (3 s.f.) } \textbf{[1]}$$ *ecf no.of moles of I_2*

The "change" row in the ICE table represents the change in the amounts of the reactants and products **during** the equilibrium shift to <u>achieve a new equilibrium after a change has been introduced</u>. The amount of added solid iodine (*x*) should thus appear in the "initial" row, because this addition is a change introduced <u>before</u> the position of equilibrium started to shift to achieve a new equilibrium.

Since the equilibrium amount of I_3^- was given in terms of no. of moles, it would have been easier to complete the ICE table in terms of no. of moles, rather than concentration. Students who used concentration terms in the ICE table would have found that they needed to do unit conversions several times.

Question asked for the amount **in moles** of I_2 added but some answers did not show the conversions from concentration to number of moles. In some answers, there was no attempt at determining the new equilibrium concentration of I_2.

(vii) ΔS for the forward reaction is negative as there is a decrease in the number of moles of aqueous particles during the forward reaction, **[1]** resulting in less ways to distribute the particles and their energy.

For the reaction to be spontaneous, $\Delta G = \Delta H - T\Delta S < 0$
Since ΔH and ΔS are −ve $\Rightarrow \Delta G = (-\text{ve}) - T(-\text{ve})$
As T increases, magnitude of TΔS increases, ΔG becomes less negative **[0.5]**. Thus the forward reaction becomes non-spontaneous when the T is too high / reaction becomes less spontaneous as T increases. **[0.5]**

Rejected:

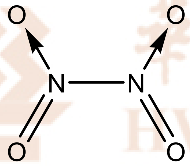
☒ *increase in T favours the backward endothermic reaction, resulting in a shift if the position of equilibrium to the left to decrease temperature and hence reaction becomes less spontaneous*

There is 1 mol of aqueous product compared to 2 mol of aqueous reactants. Hence there is a decrease in the number of moles of aqueous particles, indicating a negative ΔS.

To gain the second mark, $\Delta G = \Delta H - T\Delta S$ equation should be used to discuss the sign of ΔG, the indication of spontaneity of the forward reaction.

The second mark was not awarded if answers mentioned that "increase in T favours the backward endothermic reaction, resulting in a shift if the position of equilibrium to the left to decrease temperature and hence reaction becomes less spontaneous". Students who gave this answer missed the point of the question. The question required students to explain how the spontaneity of a system which is already at equilibrium (indicated by ΔG) changes with temperature. By mentioning the shift in equilibrium, students were incorrectly explaining how the position of equilibrium shifts to reduce a change (in this case, an increase in temperature). This merely explained how the equilibrium system reacts to a change in conditions, but it did not address the point of how spontaneity of the reaction is affected by temperature.

3 (a) (i)



[1]

trigonal planar **[1]**

The question specifically says that 2 molecules of NO_2 dimerises to give 1 molecule of N_2O_4. This is a clue that the lone electron on each NO_2 molecule can be used to form a covalent bond between the 2 N atoms. Any other answers were not accepted.

(ii) The <u>lone electron-bond pair repulsion</u> in NO_2 <u>is weaker than bond pair-bond pair repulsion</u>. **[1]**

Rejected:

☒ *any reference to lone pairs was <u>not</u> relevant*

For a central atom with 3 bond pairs surrounding it, the geometry around the atom is trigonal planar with a bond angle of 120° around it. In NO_2, instead of having 3 bond pairs surrounding the N, there are only 2 bond pairs and one lone electron. With only one electron, it will definitely repel the other bond pairs much weaker as compared to a typical bond pair-bond pair repulsion. As a result, the 2 bond pairs will be pushed further from each other and increases the bond angle.

(b) (i) $K_p = \frac{P_{(N_2O_4)}}{{P_{(NO_2)}}^2}$ **[1]**

Rejected:

☒ *expressions with square brackets*

Square brackets are used to represent concentration, in which case you would have been writing an expression of K_c rather than K_p.

(ii)

	$2NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
I / kPa	x		-
C / kPa	$-2a$		$+a$
E / kPa	$x - 2a$		a

total initial P – total final P = 100 kPa = x – (x − 2a + a) = a

Equilibrium partial pressure of N_2O_4 = <u>100 kPa</u> **[1]**

When the question states that the total pressure inside the vessel decreased by 100 kPa, it meant that the total initial P – total final P = 100 kPa. By using the ICE table as shown above, we can determine in terms of kPa, is the equilibrium partial pressure of N_2O_4. There was **no need** to convert the units to Pa.

"**Determine** often implies that the quantity concerned cannot be measured directly but is obtained by calculation, substituting measured or known values of other quantities into a standard formula, e.g. relative molecular mass." – Glossary of Terms in 9729 syllabus.

Hence, the working should be clearly shown when you are asked to determine a quantity. Answers without working were penalized.

(iii) $K_p = \frac{P_{(N_2O_4)}}{P_{(NO_2)}{}^2}$

Equilibrium partial pressure of NO_2 = x – 200 kPa (see ICE table from **(ii)**)

$$6.25 \times 10^{-2} = \frac{100}{(x - 200)^2}$$

$$x - 200 = \sqrt{\left(\frac{100}{6.25 \times 10^{-2}}\right)} = 40$$

x = 200 + 40 = 240 kPa **[1]** *ecf from **(ii)***

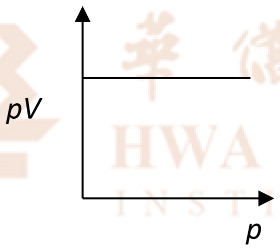
If the K_p is given with units in kPa, **do not** attempt to convert the units to Pa. The same goes if you are given K_p in other units such as atm. Just use the units that are given to you unless otherwise stated. The equilibrium partial pressures of N_2O_4 and NO_2 (not the initial pressures) should be substituted into the K_p expression,. Hence the p(NO_2) substituted in should be (x – 200) rather than x. **You are not expected to solve quadratic equations by formula** in the H2 Chemistry syllabus. In this question, you can just square root both sides and take the positive root to be the answer.

(iv) When the volume was decreased, total pressure increases **[0.5]**. This causes the equilibrium position to shift to the right **[1]** where there are less moles of gas so as to reduce the pressure **[0.5]**.

The less moles of gas there are in a system, the lower the pressure will be. When we increase the total pressure by decreasing the volume, the system will try to minimize this change by shifting the position of equilibrium towards the side that has less moles of gas so as to decrease the pressure. In this case, there is 1 mole of gas on the right and 2 moles of gas on the left, so naturally, the position of equilibrium shifts to the right hand side.

Note: Some students had difficulty understanding which direction the position of the equilibrium will shift towards. When the forward reaction is favoured, the position of equilibrium will shift to the right; when the backward reaction is favoured, the position of equilibrium will shift to the left.

(c) **(i)**



[1]

pV = nRT

Given a fixed mass of gas, n will be a constant, since a constant mass would imply a constant number of moles of the gas. Since temperature is also constant, and R is also a constant, pV must be a constant *at any pressure*. Hence the graph is a horizontal line across as pV is always the same value.

(ii) The gas particles of a real gas have non-negligible volume compared to the volume of the container. **[1]**
There are intermolecular forces of attraction between real gas particles. **[1]**

The question requires you to state the properties of a real gas that could lead to *pV* being different from that of an ideal gas. Answers should be given in terms of the **properties of a real gas** rather than the properties of an ideal gas, which was irrelevant.

(iii) Intermolecular forces of attraction**.** As *p* increases, particles become closer together and intermolecular forces of attraction become stronger, and there is greater deviation from ideality as the volume of gas becomes smaller than the volume expected if it were ideal
OR
there is greater deviation from ideality as the observed pressure is less than what it would be if the gas was ideal, causing *pV* to be even lower. **[1]**

As pressure increases, the intermolecular forces of attraction between the particles become more significant as the particles are closer together. There are 2 possible effects. If the particles are attracted to one another more and more as pressure increases, due to intermolecular forces of attraction, that will cause the volume of the gas to become even smaller **than expected**. Note that you cannot just state that the volume of the gas decreases because a decreasing volume is a natural consequence of increasing pressure. It is the fact that the **gas volume is smaller than that predicted for an ideal gas** that *pV* decreases. The second effect of more significant intermolecular forces is that the particles will strike the walls of the container with less force than expected. This results in the **observed pressure being smaller than what you would expect for an ideal gas**. Both the volume and the observed pressure being smaller than expected can be used to explain why the *pV* value decreases as pressure increases and intermolecular forces become more significant.

(iv) Low pressure **[1]**
Rejected:
☒ *large container (a large container containing many moles of gas will still have a high pressure)*

At low pressures, particles are far apart and so the intermolecular forces between particles are negligible. At the same time, the volume of the particles are also negligible compared to the volume of the container.

(v) Extrapolating the line to *p* = 0 (this is where a gas is most ideal),
$pV = 2538$ Pa m^{-3} **[1]**
(accept range of $2536 \leq pV \leq 2540$)

The lower the pressure is, the more ideal the gas is. Since the lowest pressure theoretically possible is 0 kPa, we should extrapolate the line until *p* = 0 kPa and take the value of *pV* to be the y-intercept. This should be the *pV* of an ideal gas.

(vi) $pV = \left(\frac{m}{M_r}\right)RT$

$2538 = \left(\frac{56}{M_r}\right) \times 8.31 \times 150$

M_r = 27.5 **[1]** *(deduct 0.5 m if answer not to 1 d.p.)*
ecf if pV is wrong

> The ideal gas equation should be used to get the answer. There was no need to convert any of the units in this question. =)