52nd INTERNATIONAL CHEMISTRY OLYMPIAD

2020

UK Round One

MARK SCHEME

Although we would encourage students to always quote answers to an appropriate number of significant figures, do not penalise students for significant figure errors. Allow where a student's answers differ slightly from the mark scheme due to the use of rounded/non-rounded data from an earlier part of the question.

In general, 'error carried forward' (referred to as ECF) can be applied. We have tried to indicate where this may happen in the mark scheme.

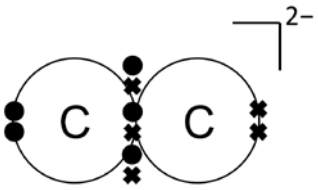
For answers with missing or incorrect units, penalise one mark for the first occurrence in **each** question and write **UNIT** next to it. Do not penalise for subsequent occurrences in the same question.

Organic structures are shown in their skeletal form, but also accept displayed formulae as long as the representation is unambiguous.

State symbols are not required for balanced equations and students should not be penalised if they are absent.

No half marks are to be awarded. One blank tick box has been included per mark available for each part. Please mark by placing a tick in each box if mark is scored.

Question	1	2	3	4	5	6	**Total**
Marks Available	10	10	17	12	17	20	**86**

1.	**This question is about calcium carbide**	**Mark**
(a)	(i) $CaO + 3C \rightarrow CaC_2 + CO$ *Must be fully correct for mark.*	☑
	(ii)  *Charge must be indicated for mark to be awarded.*	☑
(b)	$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$ *Must be fully correct for mark.*	☑
(c)	Moles of HCl(aq) = 0.0346 dm^3 × 0.250 mol dm^{-3} = 8.65 × 10^{-3} mol Moles of $Ca(OH)_2$ in 20.0 cm^3 = 8.65 × 10^{-3} mol / 2 = 4.325 × 10^{-3} mol in 20.0 cm^3 Moles of $Ca(OH)_2$ in 50.0 cm^3 = 2.5 × 4.325 × 10^{-3} mol = 0.0108 mol *(One mark)* Moles of CaC_2 = 0.0108 mol M_r (CaC_2) = 64.1 g mol^{-1} Mass of CaC_2 = 0.0108 mol × 64.1 g mol^{-1} = 0.693 g Percentage by mass CaC_2 = 0.693 g / 0.752 g = 92.2% *(One mark)* *Correct answer scores both marks regardless of working.*	☑ ☑
(d)	2 calcium atoms and 4 carbon atoms. *1 mark for each correct answer.*	☑ ☑
(e)	Molar volume of CaC_2 = 64.1 g mol^{-1} / 2.20 g cm^{-3} = 29.14 cm^3 = 2.914 × 10^{-5} m^3 *One mark for correct molar volume in m^3.* Volume of CaC_2 unit cell = 2 × 2.914 × 10^{-5} m^3 / 6.02 × 10^{23} mol^{-1} = 9.68 × 10^{-29} m^3 = 96.8 $Å^3$ *One mark for correct molar volume in m^3 or in $Å^3$.* Length of side z = 9.68 × 10^{-29} m^3 / (3.88 × 10^{-10} m)^2 = 6.43 × 10^{-10} m = 6.43 Å *One mark* *Correct answer scores three marks regardless of working.*	☑ ☑ ☑
	Total out of 10	**10**

2.	This question is about hydrogen as a fuel	Mark
(a)	$\Delta H^{\ominus}_r = \Sigma\Delta H^{\ominus}_f$ (Products) − $\Sigma\Delta H^{\ominus}_f$ (Reactants) $\Delta H^{\ominus}_r$ = −393.5 kJ mol^{-1} − (−74.8 kJ mol^{-1} + 2 × −285.8 kJ mol^{-1}) = +253 kJ mol^{-1}	☑
(b)	**Reaction 2:** $2H^+(aq) + 2e^- \rightarrow H_2(g)$ *(Reduction occurs at the cathode). Either "Reaction 2" or the reaction equation gets the mark.*	☑
(c)	$\Delta H^{\ominus}$ = 2 × 285.8 kJ mol^{-1} = +571.6 kJ mol^{-1} *Sign must be correct for mark. A negative value scores zero marks.*	☑
(d)	$\Delta S^{\ominus}$ = 2 × 163.0 J K^{-1} mol^{-1} = +326.0 J K^{-1} mol^{-1} $\Delta G^{\ominus}$ = 571.6 kJ mol^{-1} – 298 K × 0.326 kJ K^{-1} mol^{-1} = +474.5 kJ mol^{-1} *(one mark)* $E^{\ominus}$ = 474.5 × 10^3 J mol^{-1} / (4 × 96485 C mol^{-1}) = −1.23 V *(one mark)* *Correct final answer scores both marks. One mark for calculation of $\Delta G^{\ominus}$ and one mark for calculation of $E^{\ominus}$.* *ECF: Allow ECF from part (c).*	☑ ☑
(e)	$E^{\ominus}$ = −1.23 V *(the same answer as in part (d) – the other half reaction is the standard hydrogen electrode with $E^{\ominus}$ = 0.00 V)* *ECF: Accept if answer is same as part (d) or answer is –1.13 V if no answer achieved for part (d).*	☑
(f)	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^{\ominus}_r = \Sigma\Delta H^{\ominus}_f$ (Products) − $\Sigma\Delta H^{\ominus}_f$ (Reactants) $\Delta H^{\ominus}_r$ = 2 × −285.8 kJ mol^{-1} −393.5 kJ mol^{-1} + 74.8 kJ mol^{-1} = −890 kJ mol^{-1}	☑
(g)	$\Delta H^{\ominus}_r$ = −285.8 kJ mol^{-1} *The same reaction as the standard enthalpy change of formation of water, which is given.* *This is the only correct answer – no ECF for this part.*	☑

(h)	relative $M_r(H_2) = 2$ relative $M_r(CH_4) = 16$ Ratio = heat released with H_2 / heat released with CH_4 = (−285.8 kJ mol^{-1} / $2^{½}$) / (−890.3 kJ mol^{-1} / $16^{½}$) = 0.908 *or* 0.908 to 1 *or* 1 to 1.101. *ECF: Answer = (answer to part (g) × $16^{½}$) / ($2^{½}$ × answer to part (f))* *Answer with given values = (−352.8 kJ mol^{-1} / $2^{½}$) / (−943.2 kJ mol^{-1} / $16^{½}$)* *= 1.058* *Correct final answer scores two marks. This must be the correct way around, i.e. value lower than 1. One mark is given for the inverse ratio of 1.101 or 1.101 to 1. All other values score no marks.*	☑ ☑
	Total out of 10	**10**

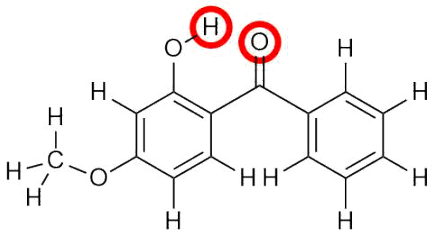
3.	This question is about sun cream	Mark

(a)

ester	aldehyde	ketone
		✔
carboxylic acid	ether	phenol
	✔	✔

Must all be correct for mark.

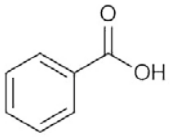
(b)



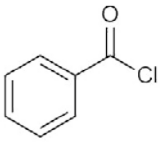
Only these two atoms must be circled for the mark.

(c)

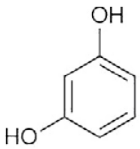
A



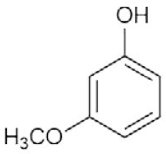
B



C

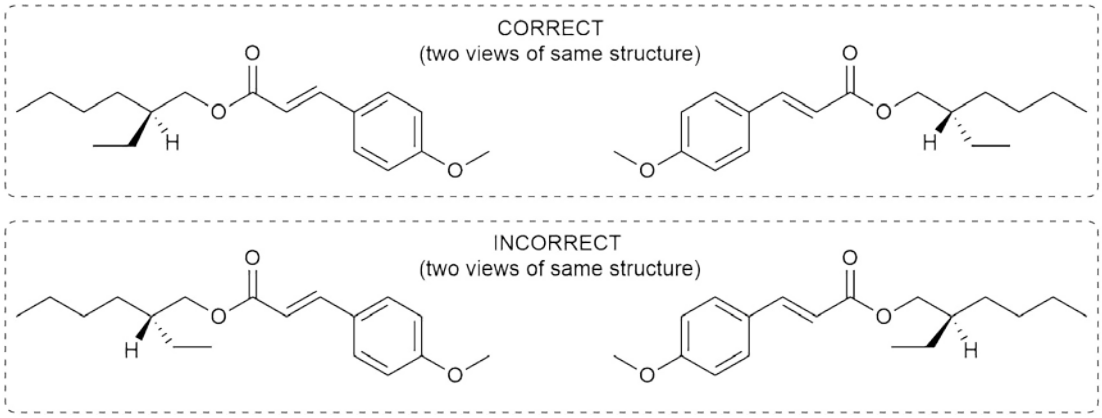


D



One mark each. No ECF to be awarded as there is sufficient information to work backwards as well as forwards.

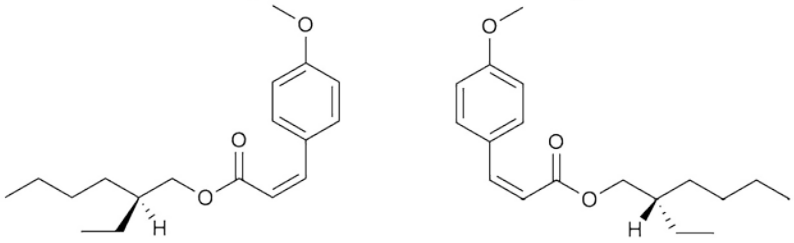
(d) (i)



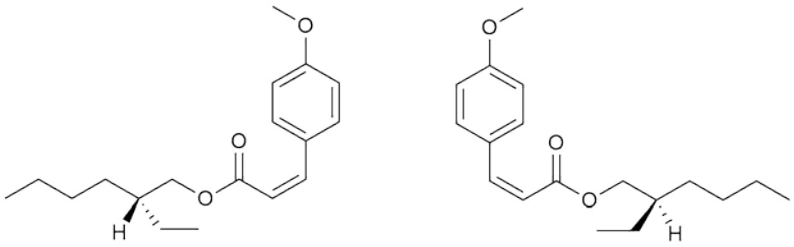
Double bond must be unambiguously trans. Stereochemistry of chiral centre must be clearly indicated as of (S) configuration (as drawn in the CORRECT views) and not of (R) configuration (as drawn in the INCORRECT views). Abbreviations are allowed as long as groups are unambiguously defined.

(ii)

CORRECT
(two views of one correct structure)



(two views of other correct structure)

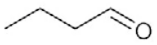


Double bond must be unambiguously cis. No marks if trans. Stereochemistry of chiral centre can be either S or R but must be drawn unambiguously. Abbreviations are allowed as long as groups are unambiguously defined.

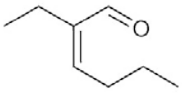
☑

(e)

E



F



No ECF. Accept both cis and trans isomers or if sterochemistry drawn as undefined.

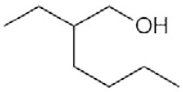
One mark each.

☑

☑

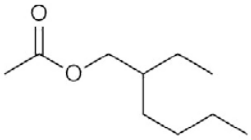
(f)

G



*No stereochemistry required. ECF can be awarded only if structure has no alkene or carbonyl functional groups and is consistent with the structure of **F** (having been reduced) or consistent with the stucture of **H** (the alcohol to make the ester).*

H



No ECF. No stereochemistry required.

One mark each.

☑

☑

(g)

The same molecular formula ✔

The same melting points

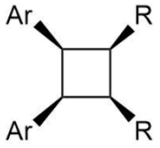
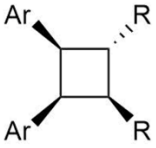
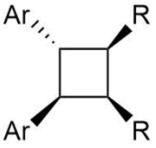
Rotate plane-polarised light in the same direction

If any other answer ticked then no marks.

☑

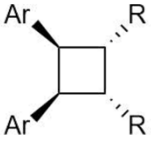
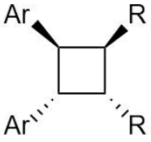
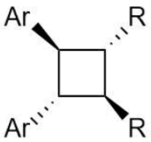
(h)

(i)

Substituents on the same face	Truxinates	
Four		
Has enantiomer?	YES **NO**	
Three		
Has enantiomer?	**YES** NO	**YES** NO

All must be correct for mark.

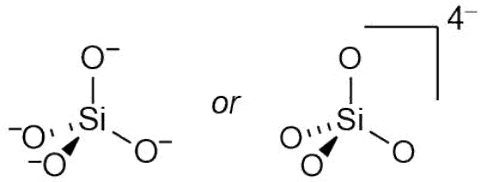
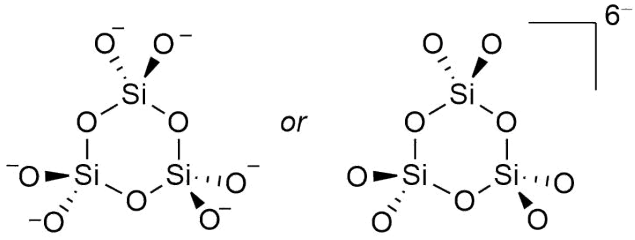
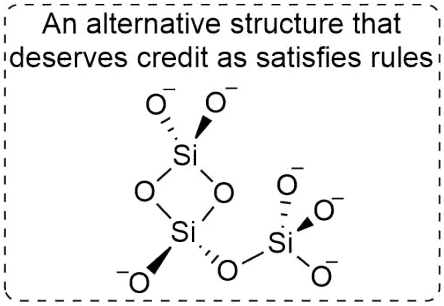
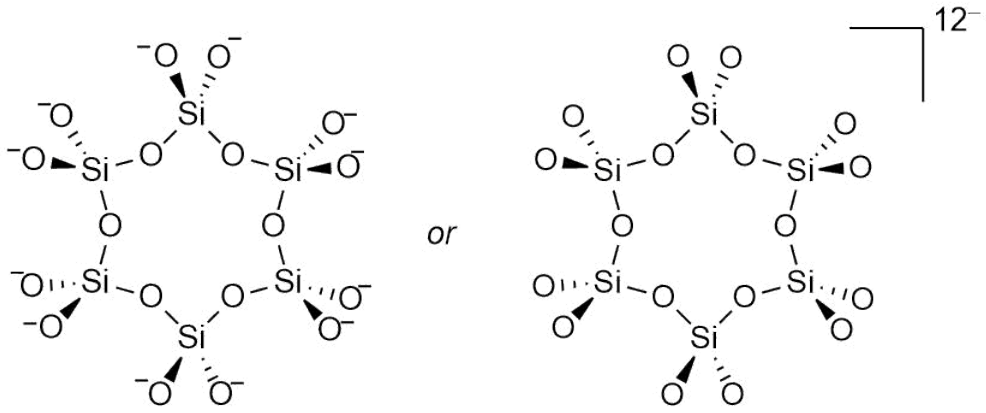
(ii)

Substituents on the same face	Truxinates	
Two		
Has enantiomer?	YES **NO**	**YES** NO
Two (continued)		
Has enantiomer?	**YES** NO	YES NO

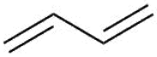
The structures are worth two of the three marks. The structures can be in any order. Three correct structures and one blank box is worth two marks. Two correct structures and two blank boxes is worth one mark. Three correct structures and one incorrect structure or duplicated structure is worth one mark. All other combinations are worth zero marks for this part.

The YES/NO for enantiomers are worth one of the three marks. Must all be correct for the mark. Every structure they have drawn must have the correct YES/NO for that structure. (NB Any structure with a plane of symmetry or a centre of inversion does not have an enantiomer and so is a NO, others are YES). This means ECF is being awarded for the chirality mark, i.e. if the YES/NO are consistent for every structure they have drawn they get the mark.

Total out of 17 **17**

4.	This question is about silicon oxides	Mark
(a)	(i) CO_2	☑
	(ii)  *A total charge of 4− or four individual charges of 1− must be indicated for mark to be awarded.* *(**X** = Na_4SiO_4 – This is not needed for the mark).*	☑
	(iii) $SiO_2 + 2Na_2CO_3 \rightarrow Na_4SiO_4 + 2CO_2$ *Must be fully correct for mark.*	☑
(b)	$CaSiO_3 + 2HCl + 10H_2O \rightarrow SiO_2.11H_2O + CaCl_2$ *Must be fully correct for mark.*	☑
(c)	4	☑
(d)	(i)   *The overall charge must be indicated as 6− or the sum of individual charges must be equal to 6−. 3D shape is not important. Credit can be given for alternative answers as long as formula is correct, overall charge is correct, and has only Si–O bonds and no Si=O double bonds, Si–Si bonds or O–O bonds drawn. An example of an alternative (incorrect) structure which should be credited is shown.*	☑
	(ii)  *The overall charge must be indicated as 12− or the sum of individual charges must be equal to 12−. 3D shape is not important. Credit can be given for alternative answers as long as formula is correct, overall charge is correct, and has only Si–O bonds and no Si=O double bonds, Si–Si bonds or O–O bonds drawn.*	☑ ☑

(e)	From overall formula need to remove 3 × Mg^{2+} and 2 × OH^- This leaves $[Si_4O_{10}]^{4-}$ *The overall charge must be indicated for the mark.*	☑
(f)	Mineral 20.32 g / 24.305 g mol^{-1} = 0.836 mol Mg = n Mg 28.18 g / 28.035 g mol^{-1} = 1.003 mol Si = n Si *(One mark for both)* Talc has ratio of 3 Mg to 4 Si Chrysotile has 3 Mg to 2 Si. Mineral with x talc and (1 − x) chrysotile has ratio 3 Mg to 2 (1+x) Si So n Si / n Mg = 2 (1 + x) / 3 *(One mark)* n Si / n Mg = 1.003 / 0.836 = 2 (1 + x) / 3 x = 0.8 so 80% talc *(One mark)* *Correct final answer with working scores three marks. Exact steps may vary. First mark can be awarded for correct calculation of the number of moles of both Mg and Si. Second mark can be awarded for a correct ratio in terms of x and 1−x (can be either way around). Third mark is only for correct answer as a percentage.*	☑ ☑ ☑
	Total out of 12	**12**

5.	This question is about colourful compounds	Mark
(a)		☑
(b)	(i) ΔE = 6.626 × 10^{-34} m^2 kg s^{-1} × 2.998 × 10^8 m s^{-1} / 210 × 10^{-9} m = 9.46 × 10^{-19} J or 9.46 × 10^{-19} m^2 kg s^{-2}	☑
	(ii) $L^2 = \frac{(2n+1)h^2}{8m_e\Delta E}$ n = 2 *(One mark)* L^2 = 5 × (6.626 × 10^{-34} m^2 kg s^{-1})^2 / (8 × 9.109 × 10^{-31} kg × 9.46 × 10^{-19} m^2 kg s^{-2}) = 3.1844 × 10^{-19} m^2 L = 5.64 × 10^{-10} m = 5.64 Å *(One mark)* *Correct answer in Å scores both marks. First mark can be awarded for explicit statement of n = 2. Do not award second mark if answer is only in m and not in Å.* *ECF: Answer = (5.49 × 10^{-9} / answer to part (i)^{½})* Å	☑ ☑
(c)	(i) $\varepsilon = \lambda / d^2$ = 5714 Å / (2 × 2.052 Å)^2 ε = 339.3 Å^{-1} *No mark if given in different units.*	☑
	(ii) $d^2 = \lambda / \varepsilon$ d^2 = 5687 Å / 339.3 Å^{-1} d^2 = 16.7609 Å^2 d = 4.094 Å N–Zn bond = 2.047 Å *No mark if given in different units.*	☑
	(iii) $\lambda = \varepsilon d^2$ λ = 339.3 Å^{-1} × (4.112 Å)^2 λ = 573.7 nm *No mark if given in different units.*	☑

(d)

$$\frac{k_{1(493K)} = A\exp\left(-\frac{E_a}{RT_{(493K)}}\right)}{k_{1(393K)} = A\exp\left(-\frac{E_a}{RT_{(393K)}}\right)}$$

$\frac{k_{1(493K)}}{k_{1(393K)}} = \exp\frac{E_a}{R}\left(-\frac{1}{T_{(493K)}} + \frac{1}{T_{(393K)}}\right)$ *One mark*

$ln\left(\frac{k_{1(493K)}}{k_{1(393K)}}\right) = \frac{E_a}{R}\left(-\frac{1}{T_{(493K)}} + \frac{1}{T_{(393K)}}\right)$ *One mark*

$$E_a = \frac{Rln\left(\frac{k_{1(493K)}}{k_{1(393K)}}\right)}{\left(-\frac{1}{T_{(493K)}} + \frac{1}{T_{(393K)}}\right)}$$

$$E_a = \frac{8.314\ J\ K^{-1}\ mol^{-1} ln\left(\frac{3.31\times10^{12}\ s^{-1}}{1.32\times10^{12}\ s^{-1}}\right)}{\left(-\frac{1}{493\ K} + \frac{1}{393\ K}\right)}$$

E_a = 14.8 kJ mol^{-1} *One mark*

Correct final answer with working scores full marks. One mark can be awarded for method if they have an expression where A has been removed. Second mark can be awarded if a logarithm has subsequently been taken. Third mark is for final answer.

☑ ☑ ☑

(e)

$$-2\alpha + \beta T = -\alpha\left(2 - \frac{\alpha RT}{E_a}\right)$$

$$-2\alpha + \beta T = -2\alpha + \frac{\alpha^2 RT}{E_a}$$

$$\beta = \frac{\alpha^2 R}{E_a}$$

One mark

$$T\left(\frac{\beta}{\gamma}\right)^{\frac{1}{2}} = \left(\frac{2E_a}{\mu}\right)^{\frac{1}{2}}\frac{\alpha RT}{E_a}$$

$$T\left(\frac{\beta}{\gamma}\right)^{\frac{1}{2}} = T\left(\frac{2E_a}{\mu}\right)^{\frac{1}{2}}\left(\frac{\alpha^2R^2}{{E_a}^2}\right)^{\frac{1}{2}}$$

$$\left(\frac{\beta}{\gamma}\right)^{\frac{1}{2}} = \left(\frac{\alpha^2 R}{E_a}\right)^{\frac{1}{2}}\left(\frac{2E_a R}{\mu E_a}\right)^{\frac{1}{2}}$$

$$\left(\frac{\beta}{\gamma}\right)^{\frac{1}{2}} = (\beta)^{\frac{1}{2}}\left(\frac{2R}{\mu}\right)^{\frac{1}{2}}$$

$$\gamma = \frac{\mu}{2R}$$

Two marks. No partial credit for γ.

☑ ☑ ☑

(f)

$$\ln\left(\frac{k_{2(83\ K)}}{T_{(83\ K)}}\right) = \beta T_{(83\ K)} + i - \left(\ln\left(\frac{k_{2(61\ K)}}{T_{(61\ K)}}\right) = \beta T_{(61\ K)} + i\right)$$

$$\ln\left(\frac{k_{2(83\ K)}}{T_{(83\ K)}}\right) - \ln\left(\frac{k_{2(61\ K)}}{T_{(61\ K)}}\right) = \beta T_{(83\ K)} - \beta T_{(61\ K)}$$

One mark

$$\ln\left(\frac{k_{2(83\ K)} T_{(61\ K)}}{T_{(83\ K)} k_{2(61\ K)}}\right) = \beta\left(T_{(83\ K)} - T_{(61\ K)}\right)$$

$$\beta = \frac{\ln\left(\frac{k_{2(83\ K)} T_{(61\ K)}}{T_{(83\ K)} k_{2(61\ K)}}\right)}{\left(T_{(83\ K)} - T_{(61\ K)}\right)}$$

One mark

$$\beta = \frac{\ln\left(\frac{8.74 \times 10^{10}\,\mathrm{s}^{-1} \times 61\ K}{83\ K \times 6.23 \times 10^{10}\,\mathrm{s}^{-1}}\right)}{(83\ K - 61\ K)}$$

$\beta = 1.389 \times 10^{-3}\ \mathrm{K}^{-1}$ *One mark*

Correct final answer with working scores full marks regardless of method. First mark awarded for expression where the constant i has been removed. Second mark for correct algebraic expression where β is the subject. Third mark is for correct final answer with units.

(g)

$$\beta = \frac{\alpha^2 R}{E_a}$$

$$E_a = \frac{\alpha^2 R}{\beta}$$

$$E_a = \frac{2.235^2 \times 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}}{1.389 \times 10^{-3}\ \mathrm{K^{-1}}}$$

$E_a = 2.235^2 \times 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} / 1.389 \times 10^{-3}\ \mathrm{K^{-1}}$

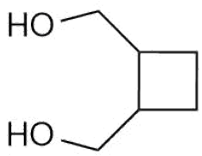
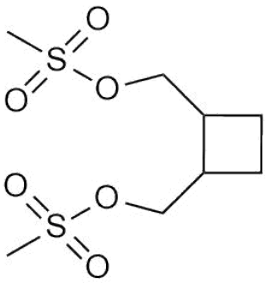
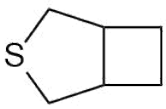
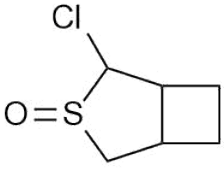
$E_a = 29.9\ \mathrm{kJ\ mol^{-1}}$

ECF: Allow ECF from part (f). Answer = (0.0415 / answer to (f)) kJ mol^{-1}

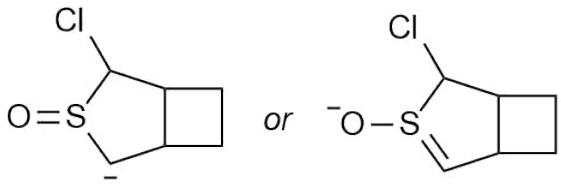
Answer with given value = 43.9 kJ mol^{-1}

Allow ECF from part (e) only if dimensionality is correct in expression for E_a

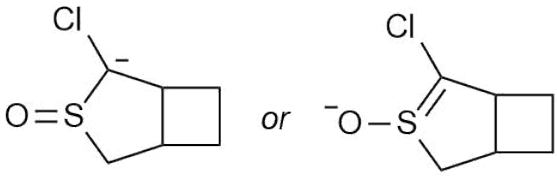
Total out of 17 **17**

6.	This question is about anammox and ladderanes.			Mark
(a)	(i)	nitrogen gas 0	ammonium ion −3	☑
	Both must be correct for mark.			
	(ii)	nitrite ion (NO_2^-) +3	hydrazine (NH_2NH_2) −2	hydroxylamine (NH_2OH) −1	☑ ☑
	All three correct two marks. Two correct one mark. One or zero correct no marks.			
(b)	(i) $NO_2^- + 4e^- + 5H^+ \rightarrow NH_2OH + H_2O$ *Must be fully correct for mark* *Also accept $NO_2^- + 4e^- + 6H^+ \rightarrow [NH_3OH]^+ + H_2O$*			☑
	(ii) $NH_4^+ + NH_2OH \rightarrow NH_2NH_2 + H_2O + H^+$ *or* $NH_4^+ + NH_2OH \rightarrow NH_2NH_2 + H_3O^+$ *or* $NH_4^+ + NH_2OH \rightarrow [NH_2NH_3]^+ + H_2O$ *Must be fully correct for mark* *Also accept analogous equations if hydroxylamine is protonated*			☑
	(iii) $NH_2NH_2 \rightarrow N_2 + 4e^- + 4H^+$ *or* $[NH_2NH_3]^+ \rightarrow N_2 + 4e^- + 5H^+$ *Must be fully correct for mark*			☑
(c)	$NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O$ *Must be fully correct for mark*			☑
(d)	**A**  *One mark. No stereochemistry required.*		**B**  *One mark. No stereochemistry required. ECF is allowed based on A only if their structure of B is consistent with molecular formula.*	☑ ☑
	C  *One mark. No stereochemistry required. No ECF as can work backwards.*		**D**  *One mark. No stereochemistry required. No ECF.*	☑ ☑

Anion E^-

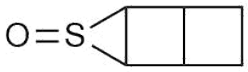


No stereochemistry required. Either of these above is worth two marks.



*Either of these incorrect structures above can be given one mark as the student has correctly realised the acidic carbon is next to sulfur. ECF: Maximum ECF score here is one mark as there is information to work forwards and backwards. ECF one mark only awarded if chlorine is in same place as on structure **D** and anion is on carbon next to sulfur.*

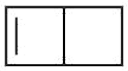
F



One mark. No stereochemistry required. No ECF as can work backwards.

☑ ☑ ☑

G



One mark. No stereochemistry required. No ECF as sufficent new information.

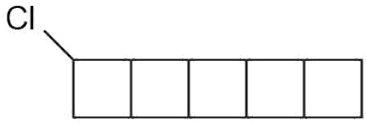
X

S=O

One mark. No ECF as sufficent new information.

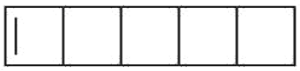
☑ ☑

H



One mark. No stereochemistry required. No ECF as sufficent new information.

I



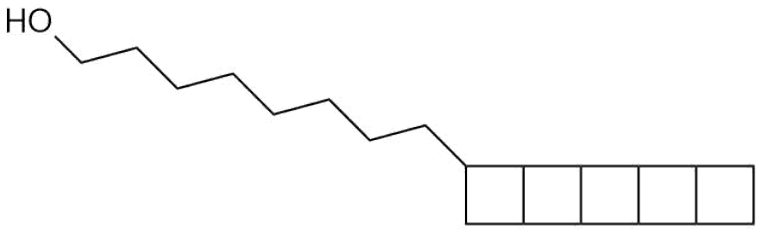
*One mark. No stereochemistry required. ECF can be awarded from **H** only if their structure of **I** has the correct number of signals in the ^{13}C NMR and is consistent with an elimination from their incorrect stucture of **H**.*

☑ ☑

J

One mark. No stereochemistry required. No ECF as sufficent new information. Accept if double bond drawn explicitly as cis or trans.

☑



☑

One mark. No stereochemistry required. Must have exactly and unambiguously eight carbon atoms in the side chain to score the mark.

Total out of 20 **20**