53rd INTERNATIONAL CHEMISTRY OLYMPIAD

2021

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 and where ECF is not allowed.

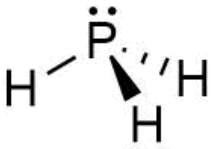
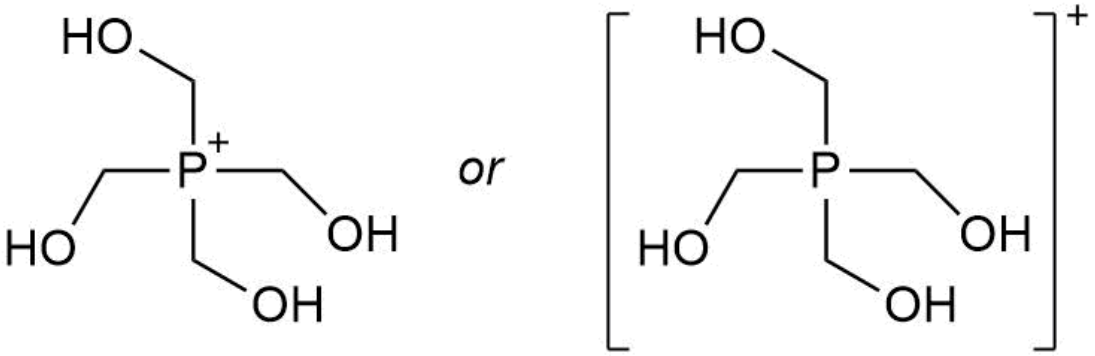
For answers with missing or incorrect units, penalise one mark for the first occurrence in **each** question and write **UNIT** next to it. Do not penalise for subsequent occurrences in the same question.

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

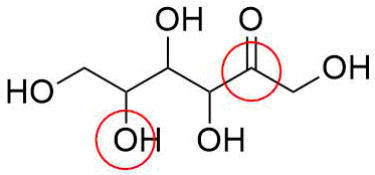
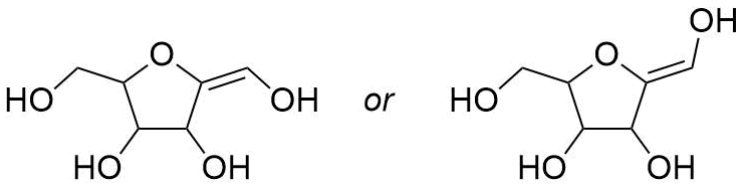
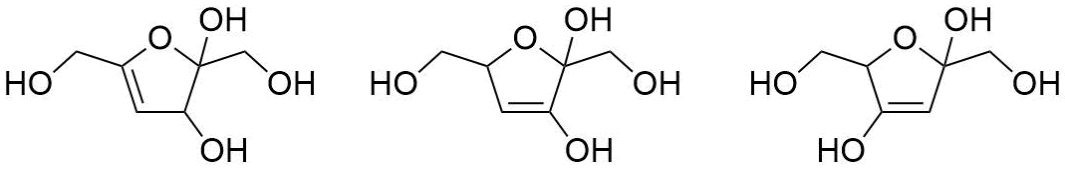
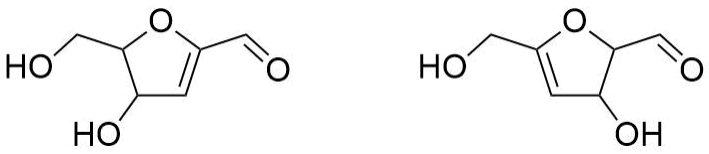
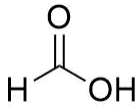
State symbols are not required for balanced equations and students should not be penalised if they are absent.

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	9	9	16	13	21	17	**85**

1.	This question is about life on Venus	Mark
(a)	 *Shape must be clearly pyramidal rather than trigonal planar for the mark. Lone pair does not have to be drawn in. Wedges and dashes are not needed if shape is clear.*	☑
(b) (i)	phosphine: −3 phosphoric acid: +5 or 5 *Both must be correct for mark.*	☑
(ii)	$PH_3 + 2O_2 \rightarrow H_3PO_4$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(c) (i)	$PCl_3 + 3LiH \rightarrow PH_3 + 3LiCl$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(ii)	$Ca_3P_2 + 3H_2O \rightarrow 2PH_3 + 3CaO$ *or* $Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(iii)	$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(d) (i)	SO_4^{2-} *Charge must be present and correct for mark.*	☑
(ii)	 *Fully correct structure is worth two marks. No partial credit. 3D shape is not required.*	☑ ☑
	Total out of 9	**9**

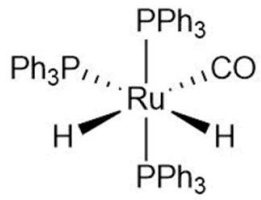
2.	This question is about capturing carbon	Mark
(a)	$CaO + CO_2 \rightarrow CaCO_3$ *Must be fully correct for mark.*	☑
(b)	$CaCO_3 \rightarrow CaO + CO_2$ *Must be fully correct for mark.*	☑
(c)	$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(d)	$2SO_2 + 2CaCO_3 + O_2 \rightarrow 2CaSO_4 + 2CO_2$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(e)	$Ca(OH)_2 + K_2CO_3 \rightarrow 2KOH + CaCO_3$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(f)	Standard enthalpy change of reaction = $\Sigma(\Delta_f H^{\ominus}$ products) − $\Sigma(\Delta_f H^{\ominus}$ reactants) = [−1151.2 + −285.8 −(−393.5 + 2 × −424.8)] kJ mol^{-1} = −193.9 kJ mol^{-1} *Working does not have to be displayed if answer is correct.*	☑
(g)	The standard enthalpy change is positive ✔ The standard enthalpy change is zero The standard enthalpy change is negative More information is needed to calculate the standard enthalpy change *No marks if more than one box ticked.*	☑
(h)	✔ The entropy change of the universe is positive The entropy change of the universe is negative The entropy change of the universe is zero More information is needed to calculate the entropy change of the universe The entropy change of this direct air capture process is positive ✔ The entropy change of this direct air capture process is negative The entropy change of this direct air capture process is zero More information is needed to calculate the entropy change of this direct air capture process *One mark for each correct statement ticked. If more than two statements are ticked or if two contradictory statements are ticked (e.g. statement one and statement two) then no marks should be awarded for this part.*	☑ ☑
	Total out of 9	**9**

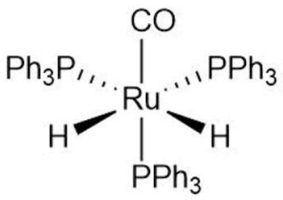
3.	This question is about levulinic acid	Mark
(a)	ester aldehyde ✔ketone acetal ✔carboxylic acid alkene alcohol hemiacetal *Must tick both carboxylic acid and ketone only for the mark.*	☑
(b)	$C_5H_8O_3$	☑
(c)	 *Must circle both C and O atoms for mark.*	☑
(d)	(i) **Alkene A**  *Either cis or trans isomer for mark.*	☑
	(ii) **Other trisubstituted alkenes**  *Three correct structures scores two marks. Two correct structures with up to one incorrect structure scores one mark. All other answers score zero marks.*	☑ ☑
(e)	**Compounds C and D**  *Both must be correct for mark. Students do not have to identify which one is which.*	☑
(f)	**Compound F** 	☑

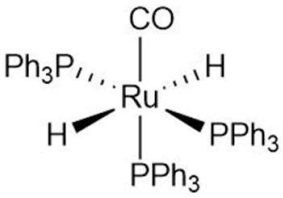
(g) +2

Accept 2, 2+ or II.

(h)

Catalyst	
 Has enantiomer	
Yes	No ✔

 Has enantiomer	
Yes	No ✔

 Has enantiomer	
Yes	No ✔

Has enantiomer	
Yes	No

Two marks are available for the two correct structures. Two correct structures and no incorrect or duplicated structures is worth two marks. If they have drawn at least one correct structure but there are also incorrect sturctures or duplicates then answer is worth one mark. One mark is available for the correct ticking. This mark is only available if students have drawn at least one correct structure themsleves. All structures (including the catalyst structure given) must be ticked as 'No' for this mark. If any structures are not octahedral or have the wrong ligand set then automatically no marks for ticking.

(i)

one singlet	one doublet and one singlet
one doublet	one triplet and one singlet
one triplet	✔ one triplet and one doublet
two singlets	three singlets
two doublets	three doublets
two triplets	three triplets

(j)

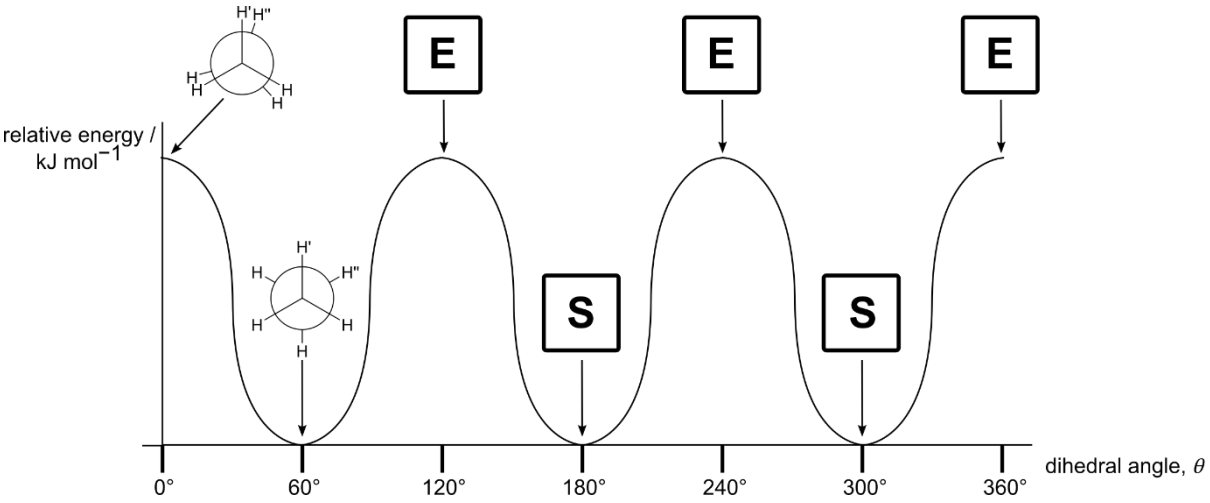
H^J–H^K 6 Hz	H^K–P^W 28 Hz
H^J–P^W 31 Hz	H^K–P^X 28 Hz
H^J–P^X 31 Hz	H^K–P^Y 74 Hz
H^J–P^Y 15 Hz	

All seven correct scores three marks. Five or six correct scores two marks. Three or four correct scores one mark. Two, one or zero correct scores no marks.

Total out of 16 **16**

4.	This question is about 'social distancing' within molecules	Mark

(a)



All must be correct for mark.

☑

(b)

A	B	C	D	E	F
2	6	3	4	1	5

Fully correct and scores three marks.

A	B	C	D	E	F
3	6	2	5	1	4

Fully correct and scores three marks.

☑

Two marks can be awarded if four or five numbers are in the correct position based on either of the correct answers above. One mark can be awarded if three of the numbers are in the correct position based on either of the correct answers above.

☑

☑

A	B	C	D	E	F
2	6	3	5	1	4

It is important to note that the above example only scores two marks (i.e. it cannot be given full credit because the first half matches the first correct answer and the second half matches the second correct answer). This is because structures do not form a sequence of continuous rotation around the central bond.

(c) (i)

	$G_1 \leftrightharpoons AP$	**$AP \leftrightharpoons G_2$**	**$G_2 \leftrightharpoons G_1$**
$\Delta G^{\ominus}$	−3.63 kJ mol^{-1}	+3.63 kJ mol^{-1}	0 kJ mol^{-1}
K	4.33	0.231	1

One mark for +3.63 kJ mol^{-1} for **$AP \leftrightharpoons G_2$** ☑

One mark for 0 kJ mol^{-1} for **$G_2 \leftrightharpoons G_1$** ☑

These two values can be stated based on the realisation that **G_1** and **G_2** must have the same energy and that **$AP \leftrightharpoons G_2$** is in the reverse direction of **$G_1 \leftrightharpoons AP$.** ☑

$\Delta G^{\ominus} = -RT\ln K$

e.g. K for **$G_1 \leftrightharpoons AP$**

$$K = e^{-\Delta G^{\ominus}/RT}$$

K = e^−(−3630 J mol^{-1} / 8.314 J K^{-1} mol^{-1} × 298 K) = 4.33

One mark for all three K values correct. ECF can be awarded for K values from values of $\Delta G^{\ominus}$ only if all three values are correct based on ECF.

(ii) [**G_1**] = [**G_2**]

[**G_1**] = 0.231 × [**AP**]

%(**AP**) = 1 / (1 + 0.231 + 0.231) ☑

%(**AP**) = 68.4% ☑

Correct answer scores both marks. One mark can be awarded for two independent simultaneous equations which are correct based on answer to part (i).

ECF answer = $\frac{100\%}{1+K_2+K_2K_3}$ *where K_2 is for **AP** ⇋ **G_2** and K_3 is for **G_2** ⇋ **G_1**.*

(d) (7 = 11) , (8 = 10) , 9 , 12 ☑

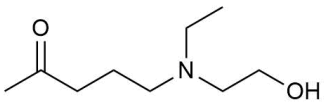
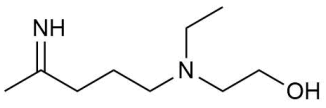
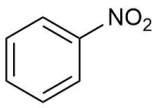
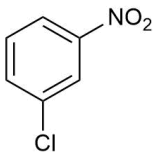
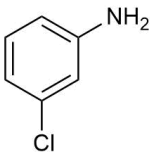
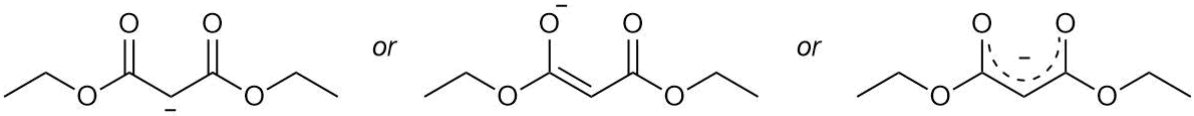
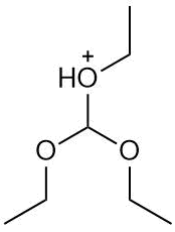
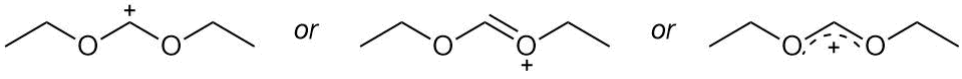
(e)

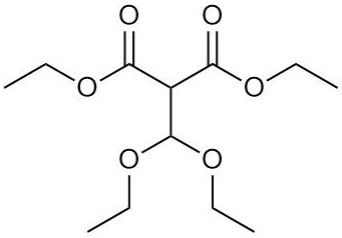
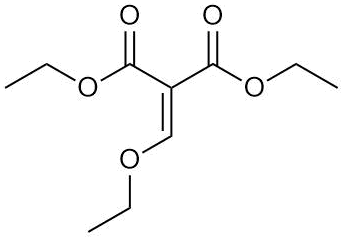
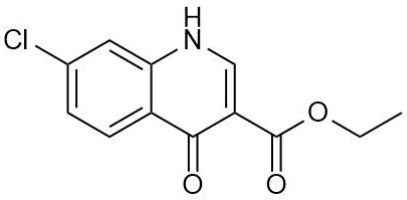
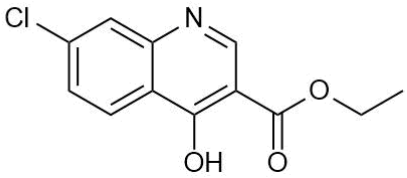
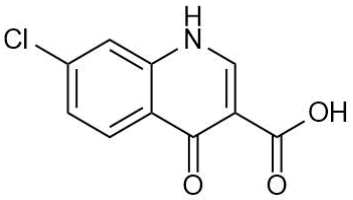
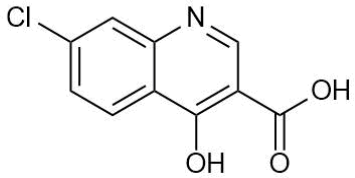
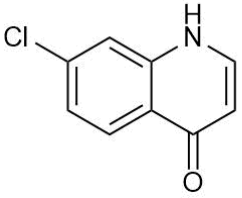
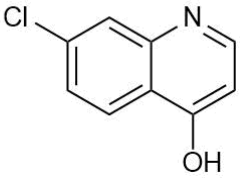
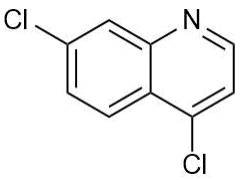
	W	**X**	**Y**	**Z**	**None**
7					✔
8		✔			
9					✔
10			✔		
11					✔
12	✔			✔	

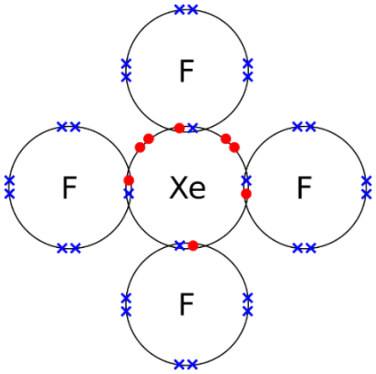
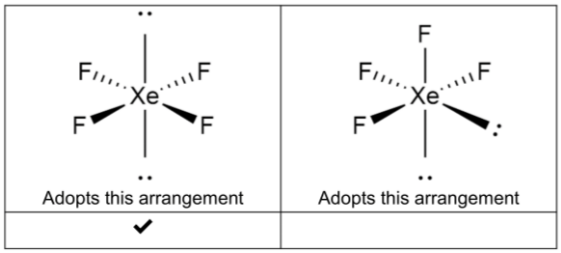
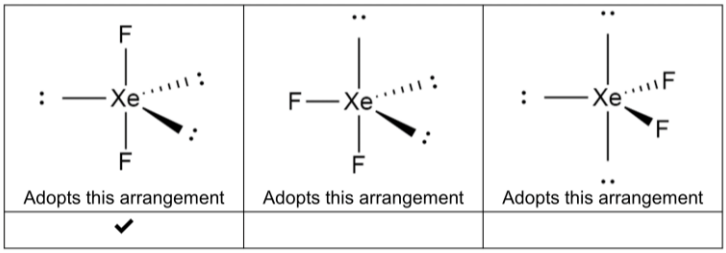
☑ ☑ ☑

All six rows correct three marks. Four or five rows correct two marks. Two or three rows correct one mark.

Total out of 13 **13**

5.	This question is about Donald Trump and the coronavirus	Mark
(a)	5-chloropentan-2-one	☑
(b)	**B**  *One mark*	☑
	C  *One mark*	☑
(c)	Br_2 / UV light; $KMnO_4$; ✔ H_2 / Ni catalyst; acidified $K_2Cr_2O_7$ OsO_4; ethylamine; O_2 / UV light; H_2SO_4 catalyst	☑
(d)	**D**  *One mark*	☑
	E  *One mark*	☑
	F  *One mark. Reduction of NO_2 group to NH_2 can be credited as ECF for **F** if there consistent position of Cl from **E** to **F**.*	☑
(e)	**Anion V^-**  *Any one of the above structures scores two marks. No partial credit.*	☑
	Cation W^+ 	☑
	Cation X^+  *Any one of the above structures scores two marks. No partial credit. No ECF.*	☑

	Intermediate Y  *One mark. No ECF.*	**Reagent Z**  *One mark. No ECF.*	☑ ☑
(f)	**G**  *or*  *Either of the above structures scores two marks. No partial credit.*		☑ ☑
	H  *or*  *Either of the above structures scores two marks. No partial credit. The anion or the sodium salt of the carboxylic acid also should be given full credit. No ECF.*		☑ ☑
	I  *or*  *Either of the above structures scores two marks. No partial credit. No ECF.*		☑ ☑
	J  *No ECF.*		☑
		Total out of 21	**21**

6.	This question is about fluorides of xenon	Mark
(a)	$Xe + 2F_2 \rightarrow XeF_4$ *Must be fully correct for mark. Accept correct fractional coefficients for balancing.*	☑
(b)		☑
(c)	 *One mark for correctly identifiyng both the cis and trans arrangements of the lone pairs and one mark for correctly ticking the trans (square planar) arrangement. The students are not expected to name the arrangements. The square planar arrangement is adopted to maximise the separation between the two lone pairs. Wedges and dashes are not required if shape is clear.*	☑ ☑
(d)	 *The first mark is for drawing at least one arrangement of the correct overall shape (i.e. a trigonal bipyramid). The name of the shape is not required but the shape must be unambiguous from the drawing. The second mark is for having the three correct arrangements (and no additional wrong shapes or duplicates). The third mark is for ticking the linear structure. The students are not expected to name the arrangements. The linear arrangement is adopted to maximise the separation between the three lone pairs. Wedges and dashes are not required if shape is clear.*	☑ ☑ ☑
(e)	$r = k[\text{Xe}]$ or $r = kp_{\text{Xe}}$ *The reaction is first-order with respect to xenon and zeroth-order with respect to fluorine. A correct expression in terms of either concentration, [Xe], or pressure, p_{Xe}, gets one mark.*	☑
(f)	$\frac{k_{\text{cat}}}{k} = \frac{A_{\text{cat}}e^{-E_{cat}/RT}}{Ae^{-E_a/RT}}$ $\boldsymbol{\frac{k_{\text{cat}}}{k} = \frac{A_{\text{cat}}}{A}e^{\Delta E/RT}}$	☑

(g)

$$y = \ln\frac{k_{cat}}{k} = \frac{\Delta E}{RT} + \ln\frac{A_{cat}}{A}$$

$$(y_1) - (y_2) = \frac{\Delta E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

One mark

$$\Delta E = R\frac{y(T_1) - y(T_2)}{T_1^{-1} - T_2^{-1}}$$

One mark

$$\Delta E = \frac{8.314\ \text{J K}^{-1}\text{mol}^{-1}(\ln 23 - \ln 13)}{(373)^{-1}\text{K}^{-1} - (393)^{-1}\text{K}^{-1}}$$

$= 3.480 \times 10^4$ J mol^{-1} = 34.8 kJ mol^{-1}

Correct answer scores full marks. One mark for eliminating A_{cat}/A, one mark for rearranging for ΔE, one mark for correctly calculating the final answer.

(h)

Collect the temperature-independent constants into a single parameter, c, and then rearrange for E_a:

$$k = c\,T^{\frac{1}{2}}e^{-E_a/RT}$$

One mark for eliminating T-independent constants

$$\ln kT^{-\frac{1}{2}} = -\frac{E_a}{RT} + \ln c$$

$$E_a = -R\frac{\ln k_1T_1^{-1/2} - \ln k_2T_2^{-1/2}}{T_1^{-1} - T_2^{-1}}$$

One mark for rearranging for E_a

Note any two temperatures can be used. Using the data at 50 °C and 170 °C.

$$E_a = -8.314\ \text{J K}^{-1}\text{mol}^{-1} \times \frac{\ln 1.55 \times 10^{-10}(323)^{-1/2} - \ln 2.07 \times 10^{-6}(443)^{-1/2}}{(323)^{-1}\text{K}^{-1} - (443)^{-1}\text{K}^{-1}}$$

E_a = 92.7 kJ mol^{-1} *One mark for correctly calculating the final answer.*

The range for the correct answer is strictly 92.4 kJ mol^{-1} ≤ E_a ≤ 93.0 kJ mol^{-1}. This allows for rounding errors, but ensures that students who have neglected the $T^{½}$ term in their calculation do not get credit, as this gives an E_a = 94.3 kJ mol^{-1}. Correct answer scores full marks by any other method but only if in range specified above.

(i)

The only factor that is affected is the reduced mass μ. Denoting the rate constant for the hypothetical 'light' xenon with k',

$$\frac{k'}{k} = \sqrt{\frac{\frac{1}{28} + \frac{1}{m_F}}{\frac{1}{m_{Xe}} + \frac{1}{m_F}}} = \sqrt{\frac{\frac{1}{28} + \frac{1}{19.00}}{\frac{1}{131.29} + \frac{1}{19.00}}} = 1.211$$

k' = 1.211 × 1.70 × 10^{-8} dm^3 mol^{-1} s^{-1}

= 2.06 × 10^{-8} dm^3 mol^{-1} s^{-1}

Correct answer scores full marks. One mark for an expression that eliminates all the unchanged parameters and one mark for correctly calculating the new rate constant.

Total out of 17 **17**