54th INTERNATIONAL CHEMISTRY OLYMPIAD 2022

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.

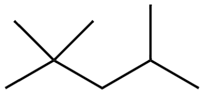
For answers with missing or incorrect units, penalise one mark for the first occurrence in **each** question and write **UNIT** next to it. Do not penalise for subsequent occurrences in the same question.

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

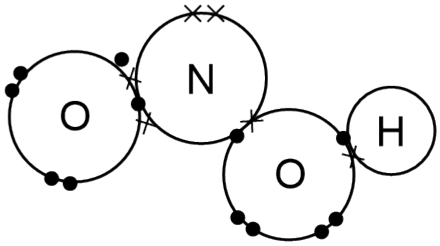
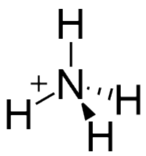
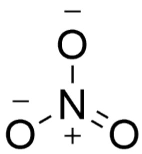
State symbols are not required for balanced equations and students should not be penalised if they are absent.

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	24	13	19	12	**86**

1.	**This question is about E10 petrol**	**Mark**
(a)	 *Only accept skeletal formula.*	☑
(b)	$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ *Must be fully correct for mark.*	☑
(c)	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ *Must be fully correct for mark. Accept if ethanol written as C_2H_6O.*	☑
(d)	$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$ Total bond enthalpy of reactants = $[(7 \times 347) + (18 \times 413) + (12.5 \times 498)]$ kJ mol^{-1} = 16,088 kJ mol^{-1} Total bond enthalpy of products = $[(16 \times 805) + (18 \times 464)]$ kJ mol^{-1} = 21,232 kJ mol^{-1} Enthalpy of combustion = [16088 – 21232] kJ mol^{-1} = –5144 kJ mol^{-1} *Must be negative for mark. Must be scaled for one mole of C_8H_{18} (i.e., not based on a balanced equation with $2C_8H_{18}$ and $25O_2$).*	☑
(e)	**Ethanol:** –1276 kJ mol^{-1} / 46.07 g mol^{-1} = –27.70 kJ g^{-1} –27.70 kJ g^{-1} × 0.789 g cm^{-3} = –21.86 kJ cm^{-3} **Octane:** –5144 kJ mol^{-1} / 114.22 g mol^{-1} = –45.04 kJ g^{-1} –45.04 kJ g^{-1} × 0.703 g cm^{-3} = –31.66 kJ cm^{-3} Energy released from 1 litre (1000 cm^3) of E5 fuel = (950 cm^3 × 31.66 kJ cm^{-3}) + (50 cm^3 × 21.86 kJ cm^{-3}) = 31170 kJ Energy released from 1 litre (1000 cm^3) of E10 fuel = (900 cm^3 × 31.66 kJ cm^{-3}) + (100 cm^3 × 21.86 kJ cm^{-3}) = 30680 kJ *Both correct energy released values scores all three marks. If calculation done via route above, then the first mark is awarded for the value of –21.86 kJ cm^{-3} for ethanol (or 21.86 kJ cm^{-3}). The second mark is awarded for the value of –31.66 kJ cm^{-3} for octane (or 31.66 kJ cm^{-3}). The third mark is for both correct energy released values. A total of one out of three can be given if the ethanol and octane values have been calculated incorrectly but combined in the correct proportions for E5 and E10.* *Alternatively, students may use a different route.* In 1 litre of E5 fuel Amount of ethanol = 50 cm^3 × 0.789 g cm^{-3} / 46.07 g mol^{-1} = 0.8563 mol Amount of octane = 950 cm^3 × 0.703 g cm^{-3} / 114.22 g mol^{-1} = 5.847 mol Energy released = (0.8563 mol × 1276 kJ mol^{-1}) + (5.847 mol × 5144 kJ mol^{-1}) = 31170 kJ In 1 litre of E10 fuel	☑ ☑ ☑

	Amount of ethanol = 100 cm^3 × 0.789 g cm^{-3} / 46.07 g mol^{-1} = 1.713 mol Amount of octane = 900 cm^3 × 0.703 g cm^{-3} / 114.22 g mol^{-1} = 5.539 mol Energy released = (1.713 mol × 1276 kJ mol^{-1}) + (5.539 mol × 5144 kJ mol^{-1}) = 30680 kJ *Both correct energy released values scores all three marks. If calculation done via this route, then the first mark is awarded if the moles of ethanol and octane in 1 litre of E5 fuel are both correct. The second mark is awarded if the moles of ethanol and octane in 1 litre of E10 fuel are both correct. The third mark is for both correct energy released values.* *Allow ECF for incorrect value of enthalpy of combustion of octane from part (d), or where the value of −6666 kJ mol^{-1} has been used.*	
(f)	30680 kJ / 31170 kJ × 100 = 98.4% *Allow ECF for incorrect energy values calculated in part (e).*	☑
(g)	90/95 × 100 = 94.7%	☑
	Total out of 9	**9**

2.	**This question is about the chemistry of nitrous oxide**	**Mark**
(a)	 	☑
(b)	**A** is HNO_3	☑
(c)	**B^+**  **C^-**  *One mark each. The ammonium ion must look approximately tetrahedral in shape and not square planar. The nitrate ion must look approximately trigonal planar. Delocalised structures are allowed for the nitrate ion.*	☑ ☑
(d)	**D** is NO **E** is NO_2 **F** is N_2O_3 **X** is N_2O_4 *One mark each.*	☑ ☑ ☑ ☑
(e)	$N\equiv\overset{+}{N}-\overset{-}{O}$ *or* $^{-}N=\overset{+}{N}=O$ *Either of the two above structures are acceptable. No structure with five bonds to nitrogen is acceptable.*	☑
	Total out of 9	**9**

3.	**This question is about cubane**	**Mark**
(a)	C_8H_8	☑

(b)

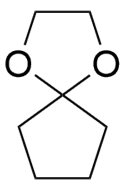
Molecule	Number of peaks in ^{13}C NMR
Cubane	1
Cubane-carboxylic acid	5
Cubane-1,2-dicarboxylic acid	4
Cubane-1,3-dicarboxylic acid	5
Cubane-1,4-dicarboxylic acid	3

3 marks for all five correct. 2 marks for three or four correct. 1 mark for one or two correct.

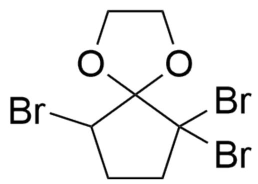
☑ ☑ ☑

(c)

A



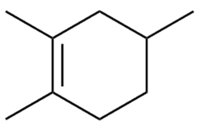
B



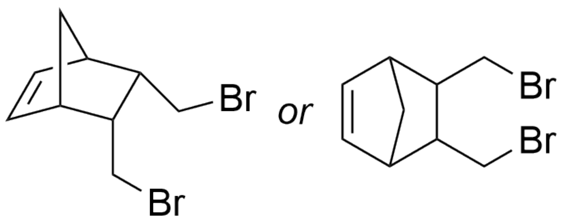
☑ ☑

(d)

W



X

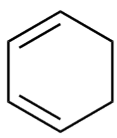


Either representation is acceptable. Stereochemistry is not required.

☑ ☑

(e)

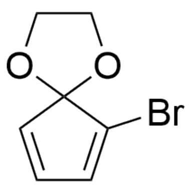
Y



☑

(f)

C



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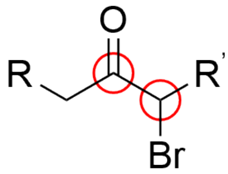
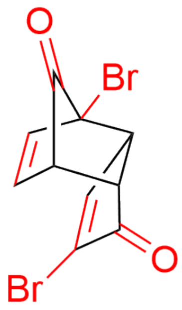
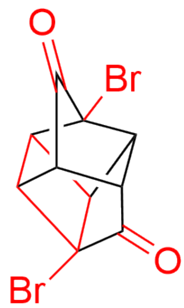
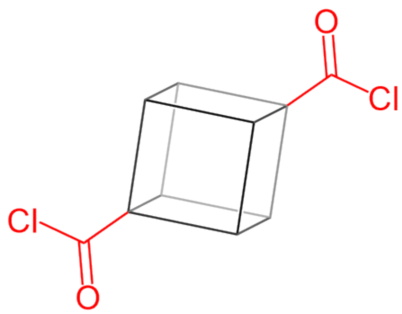
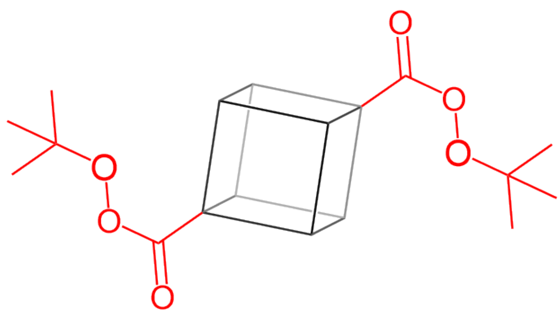
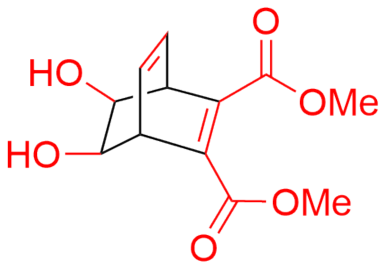
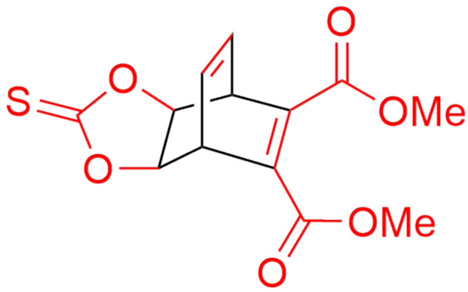
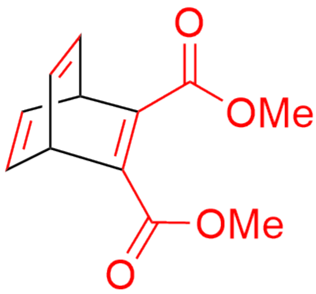
(g)	 *Both must be circled correctly for one mark.*	☑
(h)	**E**  *Two marks for completely correct. For any marks, both carbonyls must be present. Up to one other error, one mark.*	☑ ☑
	F  *Two marks for completely correct. ECF allow from **E** for any chemically reasonable substituent error carried forward.*	☑ ☑
(i)	**G** 	☑
	H 	☑

(j)	**Q**  *Structure must be fully correct. No partial credit.*	☑ ☑
	R  *Structure must be fully correct. No partial credit.*	☑ ☑
	S is CO_2	☑
	T  *Structure must be fully correct. No partial credit.*	☑ ☑
	Total out of 24	**24**

4.	This question is about coronavirus testing				Mark
(a)	Make a very acidic solution	Make a neutral solution	Make a very alkaline solution	Make a buffered ✔ solution	☑
(b)	Very Acidic ✔	Neutral	pH 7.4	Very Alkaline	☑
	Note in this case the buffer concentration is much lower than the acid concentration, so the acid overwhelms the buffer.				

(c)

7.1×10^6 virus particles / cm^3 $\times$ (1000 cm^3 / dm^3) = 7.1×10^9 virus particles / dm^3.

[virus particles] = number of virus particles / N_A =

7.1×10^9 virus particles / dm^3 / 6.02×10^{23} mol^{-1}

= 1.18×10^{-14} mol dm^{-3}

[SP] = 20 $\times$ [virus particles] = 20 $\times$ 1.18×10^{-14} mol dm^{-3}

= 2.36×10^{-13} mol dm^{-3}

☑

(d)

$[NP]_0$ = 1.6×10^{12} cm^{-3} $\times$ (1000 cm^3 / dm^3) / N_A = 2.66×10^{-9} mol dm^{-3}

Species	Original Concentration	After Equilibrium Concentration
SP	2.36×10^{-13} mol dm^{-3}	2.36×10^{-13} mol dm^{-3} $- x$
NP	2.66×10^{-9} mol dm^{-3}	2.66×10^{-9} mol dm^{-3} $- x$
SPNP	0	x

$x \le [SP]_0$ so any change in [NP] is small, so [NP] $\approx$ $[NP]_0$ $\approx$ 2.66×10^{-9} mol dm^{-3}

$K = \frac{[SPNP]}{[NP][SP]} = 1.2 \times 10^{10}$ mol^{-1} dm^3

$\approx \frac{x}{[NP]_0([SP]_0 - x)}$

$x = K[\mathrm{NP}]_0([SP]_0 - x)$

$x(1 + K[\mathrm{NP}]_0) = K[\mathrm{NP}]_0[SP]_0$

$x = \frac{K[NP]_0}{(1+K[NP]_0)}[SP]_0$ = 0.97 $[SP]_0$ = 2.29×10^{-13} mol dm^{-3}

☑ ☑

Correct final answer scores both marks. One mark for correct $[NP]_0$ and one *mark for correct solution of equations. Allow ECF from part (c). Answer = 0.97* $\times$ (answer from (c)). *Answer = 9.7×10^{-12} mol dm^{-3} if [SP] = 1.0×10^{-11} mol dm^{-3}.*

(e)

(i) Area of strip A = 3 mm^2.

Number of AB = 3 mm^2 $\times$ 1.2×10^9 mm^{-2} = 3.6×10^9.

☑

(ii) Volume of strip V = 0.3 mm^3 = 3×10^{-7} dm^3

Amount of SPNP = 2.29×10^{-13} mol dm^{-3} $\times$ 3×10^{-7} dm^3 = 6.86×10^{-20} mol

Number of SPNP = 6.86×10^{-20} mol $\times$ 6.02×10^{23} mol^{-1} = 4.13×10^4.

☑ ☑

$[SP] = [SP]_0 - [SPNP] = 7.2 \times 10^{-15}$ mol dm^{-3}

[NB 7×10^{-15} mol dm^{-3} if full accuracy not maintained]

Amount of SP = 7.2×10^{-15} mol dm^{-3} $\times$ 3×10^{-7} dm^3 = 2.1×10^{-21} mol

Number of SP = 2.1×10^{-21} mol $\times$ 6.02×10^{23} mol^{-1} = 1.3×10^3.

One mark for number of SPNP and one mark for number of SP. Error carried forward can be given. Number of SP = $1.81 \times 10^{17} \times [SP]$, and number of SPNP = $1.81 \times 10^{17} \times [SPNP]$.

If using [SPNP] = 9.7×10^{-12} mol dm^{-3}, number of SPNP = 1.8×10^6, number of SP = 0.

If using [SPNP]= 1.0×10^{-11} mol dm^{-3}, number of SPNP =1.8×10^6, number of SP = 0.

(f) If y SPNP bind to AB to make y ABSPNP then we have:

$[SPNP] = [SPNP]_0 - y/V$ and $\sigma_{ABSPNP} = y/A$

Rearranging the equilibrium constant

$$\frac{\sigma_{ABSPNP}}{\sigma_{AB}} = [SPNP]\,K$$

$$\frac{A\,\sigma_{ABSPNP}}{A\,\sigma_{AB}} = [SPNP]\,K$$

$$\frac{y}{A\,\sigma_{AB}} = ([SPNP]_0 - y/V)K$$

$$y\,(1 + KA\,\sigma_{AB}/V) = [SPNP]_0 KA\,\sigma_{AB}$$

We note that $1 \ll KA\,\sigma_{AB}/V$, so ☑

$y \approx [SPNP]_0\,V$ ☑

For the complete sample passing, we can use V = 0.10 cm^3

y = 2.29×10^{-13} mol dm^{-3} $\times$ 1×10^{-4} dm^3 $\times$ 6.02×10^{23} mol^{-1} ☑

= 1.38×10^7 ABSPNP

Correct answer scores all three marks. First mark for $1 \ll KA\,\sigma_{AB}/V$, second mark for $y \approx [SPNP]_0\,V$, and third mark for final answer. Note the number of AB >> number of SPNP, which means that σ_{AB} stays large and approximately constant throughout flow and so all SPNP bind. Error carried forward can be given. Answer = 333 $\times$ (number of SPNP in (e)). Error carried forward not given if number of SPNP in (e) = 0.

(g) This test gave 1.38×10^7 ABSPNP in 3 mm^2 so density 4.59×10^6 mm^{-2}. This test had 7.1×10^5 virus particles in test sample.

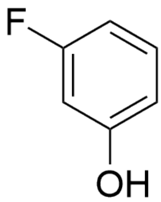
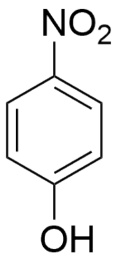
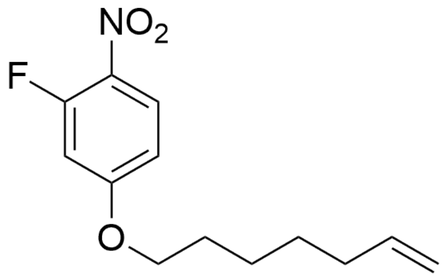
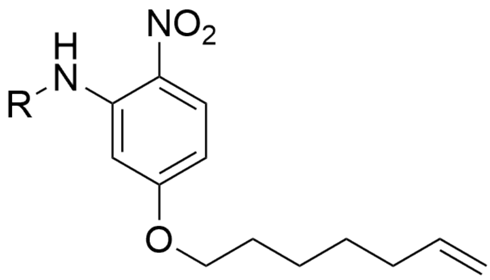
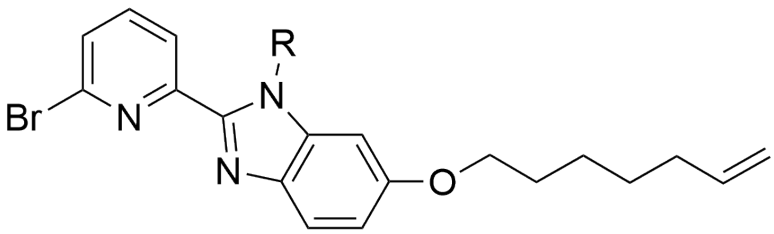
As number of ABSPNP proportional to number of virus particles:

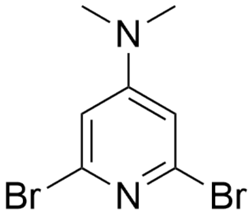
Minimum observable number = $(3 \times 10^6 / 4.59 \times 10^6) \times (7.1 \times 10^5)$ ☑

= 4.64×10^5 virus particles ☑

Correct answer scores both marks. First mark for the density of 4.59×10^6 mm^{-2} and second mark for final answer. Allow error carried forward. Answer = 6.39×10^{12} / (answer to (f))

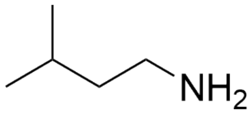
Total out of 13 **13**

5.	This question is about making the smallest Chinese knot	Mark
(a)	(i) **A** 	☑
	(ii) $O=\overset{\oplus}{N}=O$ *Accept if not drawn linear.*	☑
(b)	**B** 	☑
(c)	(i) **C** 	☑
	(ii) **D** 	☑
(d)	**E** 	☑ ☑

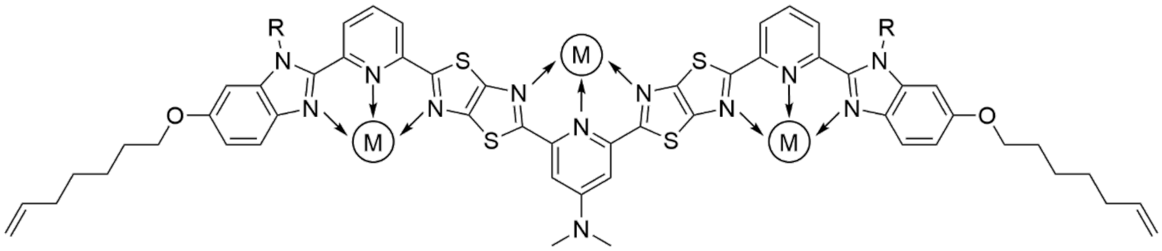
G 

Also accept if Br exchanged for I.

(e)



(f)



Three metals one mark. All nine atoms coordinated correctly two marks.

(g)

tetrahedral	trigonal planar	square planar
octahedral ✔	square pyramidal	hexagonal planar

(h)

M^{2+} = Fe^{2+} and **X^{-}** = BF_4^-

The iron(II) can be identified from the characteristic ion test result.

From the loss of mass when heating, the molecular mass can be obtained.

$6 \times 18.106 = 32.0\%$, therefore the total mass of complex = 337.8 g mol^{-1}

Mass of two anions = 337.8 – ($6 \times 18.106 + 55.85$) g mol^{-1} = 173.314 g mol^{-1}

Mass of one anion = 86.657 g mol^{-1} (Mass of BF_4^- = 86.81 g mol^{-1})

One mark for Fe^{2+}. Two marks for BF_4^-. One of these two can be given for a mass of a single anion as 86.657 g mol^{-1}.

(i)

(i) Chinese knots ✔

Must be this answer only for mark.

(ii) Individual rings ✔ and Linear organic molecules ✔

Must be these two answers and no others for mark.

(iii) Two interlinked rings ✔ and Linear organic molecules ✔

Must be these two answers and no others for mark.

(iv) Chinese knots ✔

Must be this answer only for mark.

Total out of 19 **19**

6.	**This question is about storing vaccines**	**Mark**
(a)	Process 1: $Si(OCH_2CH_3)_4 + 4\ H_2O \rightarrow Si(OH)_4 + 4\ CH_3CH_2OH$ Process 2: $Si(OH)_4 \rightarrow SiO_2 + 2\ H_2O$ *One mark for each correct equation.*	☑ ☑
(b)	Process 3 = Process 5 – (6 × Process 6) + (6 × Process 4) = [−100.3 + (6 × −56.7) – (6 × −61.5)] kJ mol^{-1} = −71.5 kJ mol^{-1} *Answer must be negative for mark.*	☑
(c)	Using the relation between Gibbs free energy and the equilibrium constant, $$\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus} = -RT\ln K_{\mathrm{eq}}$$ and $$\ln K_{\mathrm{eq}} = \ln\frac{1}{[\mathrm{Si(OH)_4}]} = -\ln[\mathrm{Si(OH)_4}]$$ we can rearrange for $$\ln[\mathrm{Si(OH)_4}] = \frac{\Delta H^{\ominus} - T\,\Delta S^{\ominus}}{RT} = \frac{\Delta H^{\ominus}}{RT} - \frac{\Delta S^{\ominus}}{R}$$ Comparing to the relation $$\ln[\mathrm{Si(OH)_4}] = -\frac{1680}{T} - 0.605$$ we identify $\Delta H^{\ominus}$ = −1680 K × 8.314 J K^{-1} mol^{-1} = 14.0 kJ mol^{-1} $\Delta S^{\ominus}$ = 0.605 × 8.314 J K^{-1} mol^{-1} = 5.03 J K^{-1} mol^{-1} *Both correct answers score all three marks. First mark for the dependence of $ln([Si(OH)_4])$ on enthalpy and entropy. Second mark for $\Delta H^{\ominus}$ and third mark for $\Delta S^{\ominus}$.*	☑ ☑ ☑
(d)	$A = c - 1 = 0.56744$	☑
(e)	For $t = 1\ \mu\mathrm{s}$, $f_1 = -0.143809\ \mathrm{nm}^{-1}$ and for $t = 2\ \mu\mathrm{s}$, $f_2 = -0.140792\ \mathrm{nm}^{-1}$. $$a = \frac{f_2 - f_1}{2 - 1} = 3.017 \times 10^{-3}\ \mathrm{nm}^{-1}\mu\mathrm{s}^{-1}$$ $$b = a \times 1 - f_1 = 0.146826\ \mathrm{nm}^{-1}$$ *One mark for correctly calculating each of a and b.*	☑ ☑

(f)	Let $r_1^{-1} = x_1$ and $r_2^{-1} = x_2$. Rearranging the equation for b gives $$x_2 = \frac{b - x_1}{A}$$ Substituting this into the equation for a gives $$\left(1 + \frac{1}{A}\right)x_1^2 - \frac{2\,b}{A}x_1 + \left(\frac{b^2}{A} - \frac{2\,a}{\Gamma}\right) = 0.$$ The first root gives $x_1 = 0.00526\ \mathrm{nm}^{-1}$ and hence $x_2 = \frac{b-x_1}{A} = 0.249\ \mathrm{nm}^{-1}$, which corresponds to $r_1 = 190\ \mathrm{nm}$ and $r_2 = 4.01\ \mathrm{nm}$. The second root gives $x_1 = 0.182\ \mathrm{nm}^{-1}$ and hence $x_2 = \frac{b-x_1}{A} = -0.0621\ \mathrm{nm}^{-1}$, which corresponds to an unphysical $r_2 < 0$ and is therefore discarded. Hence the final answer is $r_1 = 190\ \mathrm{nm}$ and $r_2 = 4.01\ \mathrm{nm}$. *Alternative solution:* can equivalently rearrange for $$x_1 = b - Ax_2$$ which leads to the quadratic $$(A^2 + A)x_2^2 - 2Abx_2 + \left(b^2 - \frac{2a}{\Gamma}\right) = 0.$$ This gives rise to the same values of x_1 and x_2 as above. *Correct r_1 and r_2 scores all three marks. One mark for deriving the quadratic equation for x_1 (or equivalently x_2), one mark for each correctly calculated radius (full marks for r_1 in the range 180-200 nm and for r_2 in the range 3.95-4.05 nm.* *Error carried forward can be given. One mark to be awarded for each radius consistent with the equation for $x_{1,2}$ given above, evaluated with the values of A, a, and b the student has used. The suggested values of A = 0.5, a = 0.0025 and b = 0.125 give r_1 = 249 nm and r_2 = 4.13 nm.*	☑ ☑ ☑
	Total out of 12	**12**