49th INTERNATIONAL CHEMISTRY OLYMPIAD

2017

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. Benzene rings may be drawn with localised or delocalised bonding.

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

Question	1	2	3	4	5	**Total**
Marks Available	8	11	23	21	12	**75**

1. This question is about the Green Pool of Rio

(a) +1 **1**

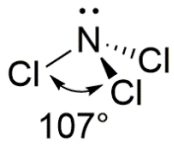
(b) $H_3O^+ + ClO^- \rightleftharpoons ClOH + H_2O$ **1**
or
$H^+ + ClO^- \rightleftharpoons ClOH$
or
$H_2O + ClO^- \rightleftharpoons ClOH + OH^-$

ClOH may be written as HOCl for this and all subsequent occurences in this question.

(c) $ClOH + HCl \rightarrow Cl_2 + H_2O$ **1**
or
$ClO^- + Cl^- + 2H_3O^+ \rightarrow Cl_2 + 3H_2O$
or
$ClO^- + Cl^- + 2H^+ \rightarrow Cl_2 + H_2O$

(d) $H_2O_2 + ClO^- \rightarrow Cl^- + H_2O + O_2$ **1**
or
$H_2O_2 + NaOCl \rightarrow NaCl + H_2O + O_2$
or
$H_2O_2 + ClOH \rightarrow HCl + H_2O + O_2$

(e) (i) $NH_3 + 3NaOCl \rightarrow NCl_3 + 3NaOH$ **1**
or
$NH_3 + 3ClOH \rightarrow NCl_3 + 3H_2O$
or
$NH_3 + 3ClO^- \rightarrow NCl_3 + 3OH^-$

(e) (ii) 

(Trigonal pyramidal) **1**

½ mark for shape, ½ mark for correct angle. Accept 106°-108° for angle. Shape must be drawn unambigously but name of shape is not required. Lone pair is not required.

(f) $2NH_3 + NaClO \rightarrow N_2H_4 + NaCl + H_2O$ **1**
or
$2NH_3 + ClO^- \rightarrow N_2H_4 + Cl^- + H_2O$
or
$2NH_3 + ClOH \rightarrow N_2H_4 + HCl + H_2O$

(g) $Cu(OH)_2$ **1**

Question Total 8

2. This question is about atmospheric chemistry

(a) $H_2S + {\cdot}OH \rightarrow {\cdot}SH + H_2O$ **1**

Dots marking radicals are not required.

(b) $FeS + 2HCl \rightarrow FeCl_2 + H_2S$ **1**

(c) rate of production of H_2S = rate of consumption of H_2S

7.65×10^5 molecules cm^{-3} $s^{-1} = k \times [OH] \times [H_2S]$

7.65×10^5 molecules cm^{-3} $s^{-1} = 4.7 \times 10^{-12}$ cm^3 $s^{-1} \times 1.1 \times 10^6$ $cm^{-3} \times [H_2S]$

$[H_2S] = 1.48 \times 10^{11}$ molecules cm^{-3} **2**
$[H_2S] = 1.5 \times 10^{11}$ molecules cm^{-3}

Please note that "molecules" can be omitted from the units. Correct answer with units scores full marks. One mark can be awarded if the following statement or equivalent is written: 7.65 × 10⁵ molecules cm⁻³ s⁻¹ = k × [OH] × [H₂S]

(d) $[H_2S] = 1.48 \times 10^{11}$ cm^{-3}
$[H_2S] = 1.48 \times 10^{17}$ m^{-3}
$[H_2S] = 2.46 \times 10^{-7}$ mol m^{-3}
$[H_2S] = 8.38 \times 10^{-6}$ g m^{-3}
$[H_2S] = 8.38$ µg m^{-3}

$[H_2S] = 8.4$ µg m^{-3} (2 s.f.) **1**

Correct answers scores mark. Intermediate steps in calculation not required.

(e) (i) $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$ **1**

Allow $H_2S + {}^3/_2O_2 \rightarrow H_2O + SO_2$

(e) (ii) $2H_2S + SO_2 \rightarrow 2H_2O + {}^3/_8 S_8$ **1**
or
$16H_2S + 8SO_2 \rightarrow 16H_2O + 3S_8$
or
$2H_2S + SO_2 \rightarrow 2H_2O + 3\ S$

(f) *Accept 3.7,* 3.8 or 3.9 years **1**
One mark for correct reading of graph.

If said 3.7 years then 1.168×10^8 s **1**

If said 3.8 years then 1.199×10^8 s

If said 3.9 years then 1.231×10^8 s

One mark for correct value in seconds. Conversion calculation not required. Allow ECF from their answer in years for the value in seconds.
1 year = 365.25 days/year × 24 hours/day × 60 minutes/hour × 60 seconds/minute
1 year = 3.156×10^7 s. Therefore their value in seconds should be the value in years multiplied by 3.156×10^7

(g) $[OH] = \ln 2 / (k_{2nd} \times t_{1/2})$
$[OH] = 0.693 / (1.0 \times 10^{-14} \times t_{1/2})$
$[OH] = 6.93 \times 10^{13} / t_{1/2}$

If they found $t_{1/2}$ = 3.7 years, then
$[OH] = 5.93 \times 10^5$ molecules cm^{-3} **2**

If they found $t_{1/2}$ = 3.8 years, then
$[OH] = 5.78 \times 10^5$ molecules cm^{-3}

If they found $t_{1/2}$ = 3.9 years, then
$[OH] = 5.63 \times 10^5$ molecules cm^{-3}

Correct answer with units scores full marks. Please note that "molecules" can be omitted from the units. One mark may be awarded for obtaining the expression:
$[OH] = 6.93 \times 10^{13} / t_{1/2}$
Allow ECF from their answer to part (f) using the above formula.

Question Total 11

3. This question is about the chemistry of Iron Man

(a) (i) +3 **1**

(a) (ii) Nitrogen **1**

(a) (iii) Titanium **1**

(a) (iv) $6TiCl_4 + 8NH_3 \rightarrow 6TiN + 24HCl + N_2$ **2**
or
$3TiCl_4 + 4NH_3 \rightarrow 3TiN + 12HCl + ½\ N_2$

No partial credit.

(b) Masses used to make one mole (3 × 47.90 g) + 196.97 g = 340.67 g

Masses needed to make 40 kg:
Ti = 40 kg × (3 × 47.90 g) / 340.67 g = 16.87 kg = 17 kg **½**
Au = 40 kg × 196.97 g / 340.67 g = 23.13 kg = 23 kg **½**

Correct answers score ½ mark each. Must have correct value to score ½ mark for each part, i.e. no marks for calculation.

(c) (i) 12 **1**

Within any one plane there are four titanium atoms surrounding a gold atom. Three planes need to be considered, the xy, xz and yz, giving a total of 12. (This explanantion is not required.)

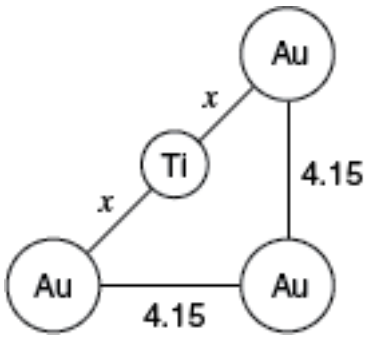
(c) (ii) 4 **1**

From the left hand view, there are clearly four gold atoms surrounding the titanium atom. There are no others. (This explanantion is not required.)

(c) (iii) 8 **1**

From the right hand view looking at the titanium atom at the top, there are four titanium atoms shown that are half way down the cube that are the nearest titanium atoms to the titanium atom at the top. There are also four atoms in the cube that would sit above the cube shown, making a total of eight. (This explanantion is not required.)

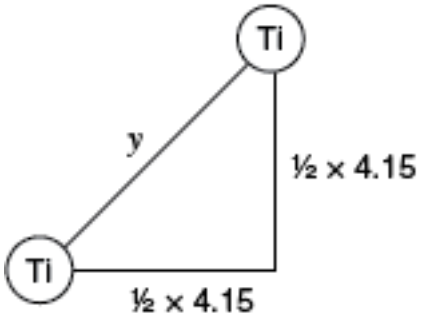
(d) (i)



$(2x)^2 = (4.15\ Å)^2 + (4.15\ Å)^2$
$4x^2 = 34.445\ Å^2$
$x^2 = 8.6113\ Å^2$
$x = \sqrt{(8.6113\ Å^2)}$ **2**
$x = 2.93\ Å$

Correct answer with units scores full marks. One mark may be awarded for drawing the above diagram or equivalent and realisation that a Pythagoras caculation is needed.

(d) (ii)



$y^2 = (½ \times 4.15\ Å)^2 + (½ \times 4.15\ Å)^2$
$y^2 = 4.306\ Å^2 + 4.306\ Å^2$
$y^2 = 8.6113\ Å^2$
$y = \sqrt{(8.6113\ Å^2)}$ **2**
$y = 2.93\ Å$

Correct answer with units scores full marks. One mark may be awarded for drawing the above diagram or equivalent and realisation that a Pythagoras caculation is needed.

(e) (i) 12 **1**

Consider the central gold atom in the right hand view, there are two titanium atoms surrounding the gold atom on each of the six faces of the cube, making a total of 12. (This explanantion is not required.)

(e) (ii) 4 **1**

Consider the titanium atom in the top left of the right hand view. There are two gold atoms to its left which are nearest neighbours. The gold atom in the centre of the cube shown is also a nearest neighbour, as is the gold atom in the centre of the cube that would be above this (which is not shown). This makes a total of four. (This explanantion is not required.)

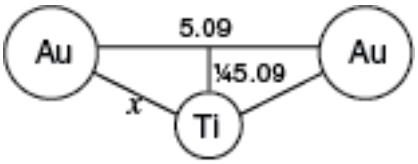
(e) (iii) Nearest: 2 **1**

The two titanium atoms on the centre of the front face are half the length of the cube edge apart. If you consider the one at the top of these two on the front face. It has a nearest neighbour half the length of the cube below it in the cube shown and it also has one half the length of the cube above it, in the cube that would be above the one shown. (This explanantion is not required.)

Next-nearest: 8 **1**

Consider the titanium atom at the top of the front face. It has four next nearest neighbours that reside in the same cube. These are the two on the top face of the cube and the one nearest to the front on each of the side faces. There are also another four in similar position in the cube that would lie in front of the one shown. This makes a total of eight. (This explanantion is not required.)

(f) (i)

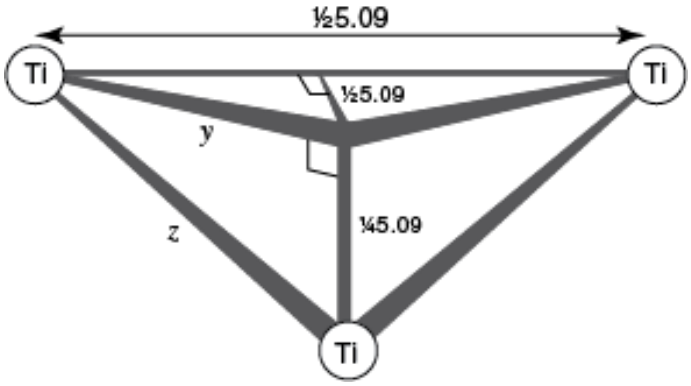


$x^2 = (½ \times 5.09\ Å)^2 + (¼ \times 5.09\ Å)^2$
$x^2 = 6.477\ Å^2 + 1.619\ Å^2$
$x^2 = 8.096\ Å^2$
$x = \sqrt{(8.096\ Å^2)}$
$x = 2.85\ Å$

2

Correct answer with units scores full marks. One mark may be awarded for drawing the above diagram or equivalent and realisation that a Pythagoras caculation is needed.

(f) (ii)



$y^2 = (½ \times 5.09\ Å)^2 + (¼ \times 5.09\ Å)^2$
$y^2 = 6.477\ Å^2 + 1.619\ Å^2$
$y^2 = 8.096\ Å^2$
$y = \sqrt{(8.096\ Å^2)}$
$y = 2.85\ Å$

$z^2 = (2.85\ Å)^2 + (¼ \times 5.09\ Å)^2$
$z^2 = 8.096\ Å^2 + 1.619\ Å^2$
$z^2 = 9.715\ Å^2$
$z = \sqrt{(9.715\ Å^2)}$
$z = 3.12\ Å$

4

Correct answer with units scores full marks. Two marks may be awarded for drawing the above diagram or equivalent fully correct with known lengths labelled and a third mark for the calculation of length y.

Question Total 23

4. This question is about the molecule twistane

(a) 120° − 109.5° = 10.5° **1**

Accept 10-11°

(b) -1-2-3-9-10-7- *or* -1-7-10-9-3-2-
-1-6-5-8-10-7- *or* -1-7-10-8-5-6-
-3-4-5-8-10-9- *or* -3-9-10-8-5-4- **1**

If a set of numbers does not start with the lowest number it must be marked incorrect. All three correct 1 mark. Two correct ½ mark. If four answers are written, maximum score is ½ if all correct answers are present. If five or more answers are written then zero marks. There is no credit for writing out the example in the question (-1-2-3-4-5-6-), but do not penalise them for writing this answer i.e. do not include in your count of the total number of answers.

(c) 2 **1**

(d) -1-2-3-10-9-6- *or* -1-6-9-10-3-2- **½**
-1-2-7-8-5-6- *or* 1-6-5-8-7-2- **½**
-3-4-5-6-9-10- *or* -3-10-9-6-5-4- **½**
-2-3-4-5-8-7- *or* -2-7-8-5-4-3- **½**

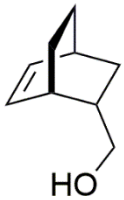
½ mark each. If they do not start with the lowest number then no marks for that answer. For each additional set of numbers over the first four, minus ½ mark per additional set down to zero. There is no credit for writing out the example in the question (-1-2-3-4-5-6-), but do not penalise them for writing this answer i.e. do not include in your count of the total number of answers.

(e) 3 **1**

(f) $C_{10}H_{16}$ **1**

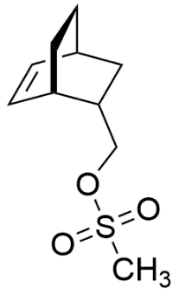
(g) *ECF can be awarded for Compounds **B**,**C**,**G**,**H** and Anion I^- only. It cannot be awarded for the others because there is a known compound to work forward from or back from. An example where ECF could be used for Compound **B**,**C**,**G**,**H** or Anion J^- is in the case of a small error such as an extra CH_2 in the chain. This should of course be penalised when it first occurs, but ECF can be awarded if the rest of the chemistry in subsequent intermediates is correct after the initial mistake.*

Compound A



One mark

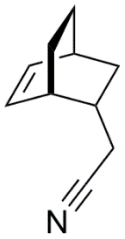
Compound B



One mark

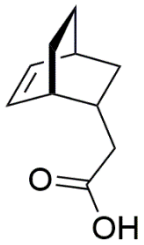
2

Compound C



One mark

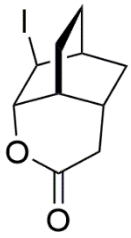
Compound D



One mark

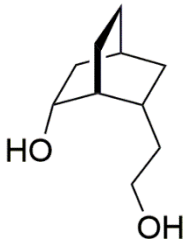
2

Compound E



One mark

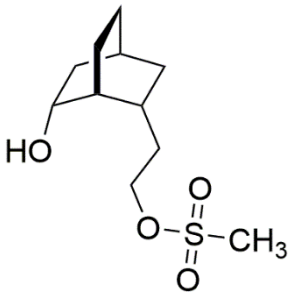
Compound F



One mark

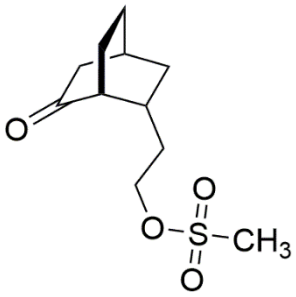
2

Compound G



One mark

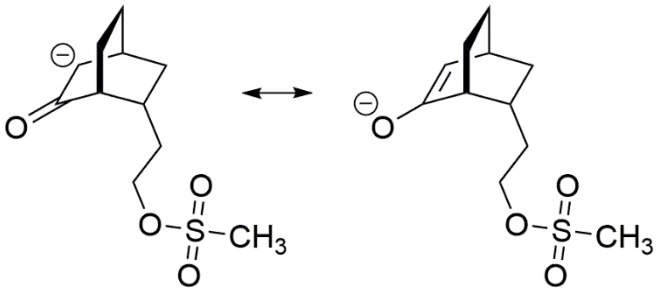
Compound H



One mark

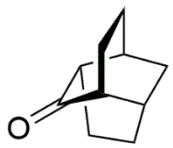
2

Anion J $^{\ominus}$



Only one of the two structures is needed to score two marks. No partial credit.

Compound K



One mark

3

(h) (i) How many planes of symmetry does twistane contain?

None ✓ **1**
One
Two or more

(ii) How many rotational axes of symmetry does twistane contain?

None
One
Two or more ✓ **1**

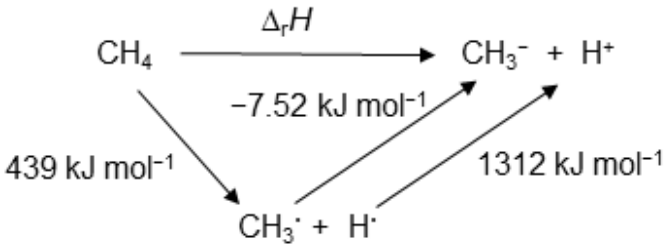
(iii) Is twistane superimposable on its mirror image?

Yes
No ✓ **1**

Question Total 21

5. This question is about Superbases

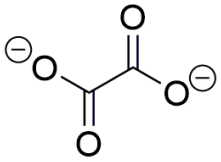
(a) $\Delta_r H$ (reaction 2) = (2.18 × 10^{-18} J) × (6.02 × 10^{23} mol^{-1}) × (10^{-3} kJ/J)= 1312 kJ mol^{-1}



$\Delta_{acid}H^\ominus(CH_4)$ = 439 kJ mol^{-1} + (−7.52 kJ mol^{-1}) + 1312 kJ mol^{-1}
= 1743 kJ mol^{-1} **2**

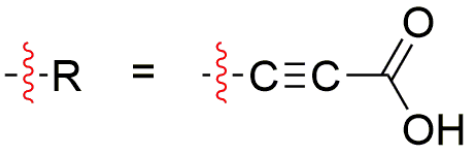
Correct answer with units scores both marks. One mark for correct conversion of enthalpy of reaction 2 into kJ mol^{-1}.

(b)

oxalate ion	**P**	**Q**	
	CO_2	CO	**3**
One mark	*One mark*	*One mark*	

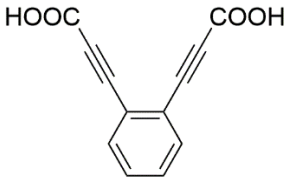
Allow delocalised representation of the anion

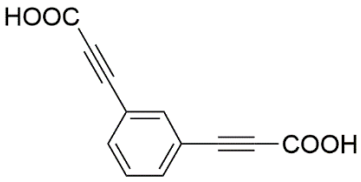
(c) Functional group: carboxylic acid **½**

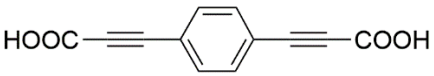


½

½ mark each

(d) 





1

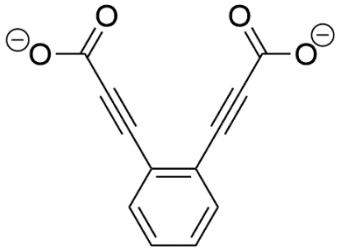
Allow ECF if they have the wrong R group in part (c) as long as they have used the same one here. Allow if they write R instead of drawing out the R group. Do not penalise for non-linear alkyne geometries. No partial credit.

Signals			
6	7	5	**2**

All correct two marks. Two correct one mark. One correct ½ mark. Allow ECF if they have the wrong R group in part (c) as long as they have used the same one here and the number of signals they have suggested here is consistent with their R group. If they have just written R when drawing the disubsituted benzenes then you can award ECF for the number of ^{13}C signals in the benzene ring (which should be 3, 4 and 2 respectively).

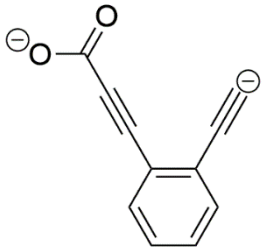
(e)

$B^{2\ominus}$



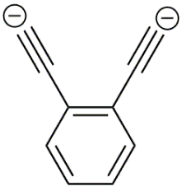
One mark

$C^{2\ominus}$



One mark

$DEB^{2\ominus}$



One mark

3

*If they have drawn the wrong disubstitued benzene isomer then no marks are awarded for **B^{2-}** but can give ECF on **C^{2-}** and **DEB^{2-}**. Allow delocalised representation of the carboxylate anions. Do not penalise for non-linear alkyne geometries.*

Question Total 12