48^{th} INTERNATIONAL CHEMISTRY OLYMPIAD 2016

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 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.

Comments in blue have been added to some questions, these are not required for the marks, but may be of interest in subsequent discussion on the questions.

Question	1	2	3	4	5	Total
Marks Available	12	23	31	21	13	**100**

1. This question is about energy storage using a chemical cycle

(a) (i) $\Delta_r H^o$ (reaction (3)) = $\Delta_f H^o$ ($I_{2(g)}$) – 2 $\Delta_f H^o$ (HI) = (62.4 – 2 × 26.5) kJ mol^{-1}
= +9.4 kJ mol^{-1} **1**
Plus sign not required.

(ii) ΔS^o (reaction (3)) = (131 + 261 – 2 × 207) J K^{-1} mol^{-1}
= −22 J K^{-1} mol^{-1} **1**
Minus sign must be present.

(iii) $\Delta_r G^o$(reaction (3)) = 9.4 kJ mol^{-1} – (298 K × −0.022 kJ K^{-1} mol^{-1})
= +16.0 kJ mol^{-1} **1**
Plus sign not required. Allow error carried forward from (i) and/or (ii)

(iv) $K_{298} = \exp(-\Delta G/RT)$ = exp (15956 / (8.314 × 298))
= 1.60 × 10^3 **2**
Allow error carried forward from (iii). Do not penalise if equilibrium constant has units.

(v) $\Delta_r G^o$(reaction (3)) = 9.4 kJ mol^{-1} – (723 K × −0.022 kJ K^{-1} mol^{-1})
= 25.3 kJ mol^{-1}
$K_{723} = \exp(-\Delta G/RT)$ = exp (25306 / (8.314 × 723))
= 0.0148 **2**
Allow error carried forward from (i) and/or (ii). Do not penalise if equilibrium constant has units.

(b) Products of reaction (1) cancel out when they occur in the following proportion:
2 × reaction (1) + reaction (2) + 2 × reaction (3).
This simplifies down to the following reaction:
$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)}$ **2**
State symbols not required. Accept the equation with mole ratio 1:1:½. Award 1 mark if the reactions are combined in the correct ratio but simplifying is done incorrectly.

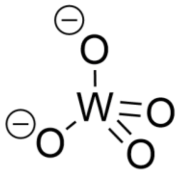
(c) 2 × $\Delta_r H^o$ (1) + $\Delta_r H^o$ (2) + 2 × $\Delta_r H^o$ (3) = –2 × $\Delta_f H^o$ ($H_2O_{(g)}$)
[2 × $\Delta_r H^o$ (1) + 439 + 2 × 9.4] kJ mol^{-1} = 484 kJ mol^{-1}
$\Delta_r H^o$(1) = +13 kJ mol^{-1} **2**
Plus sign not required. Allow error carried forward from (i).

(d) Energy stored = 242 kJ **1**
For the sequence: 2 × reaction (1) + reaction (2) + 2 × reaction (3) there are two moles of sulfur atoms.
This sequence has an overall $\Delta_r H^o$ = 484 kJ mol^{-1}
All this energy is 'stored' as separate hydrogen and oxygen and can be released when these are recombined.
Therefore, per mol of sulfur, the energy stored is 242 kJ.

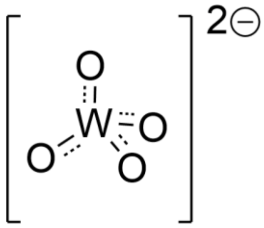
Question Total 12

2. This question is about the chemistry of tungsten

(a)



or



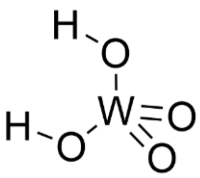
½

Bond Angle: 109.5° ½

Must have attempted to draw a tetrahedral shape to be given credit, i.e. do not credit square planar structures.

(b) (i) $CaWO_{4\ (s)} + Na_2CO_{3\ (aq)} \rightarrow CaCO_{3\ (s)} + Na_2WO_{4\ (aq)}$ **1**
State symbols not required.

(ii) $Na_2WO_{4\ (aq)} + 2HCl_{(aq)} \rightarrow H_2WO_{4\ (aq)} + 2NaCl_{(aq)}$ **1**
State symbols not required.



1

Correct 3D tetrahedral structure not required as long as connectivity and bonding are correct.

(iii) $H_2WO_{4\ (aq)} \rightarrow WO_{3\ (s)} + H_2O_{(g)}$ **1**
State symbols not required.

(iv) $WO_{3\ (s)} + 3H_{2\ (g)} \rightarrow W_{(s)} + 3H_2O_{(l)}$ **1**
State symbols not required.

(c) (i) x = 1
3 × O = −6
1 × Li = +1
Therefore W = **+5** **1**
Accept if 5 is written rather than +5.

(ii) x = 0.3
3 × O = −6
1 × Li = +0.3
Therefore W = **+5.7** **1**
Accept if 5.7 is written rather than +5.7.

(d) Assuming air to be made only of nitrogen (N_2)
Density of SF_6 relative to air = 32.06 + (6 × 19.00) / (2 × 14.01)
= 146.06 / 28.02
= 5.21

1

Density of WF_6 relative to air = 183.85 + (6 × 19.00) / (2 × 14.01)
= 297.85 / 28.02
= 10.63

1

(e) $pV = nRT$

1 mol of gas occupies: $V/n = RT/p$

$= (8.314\ J\ K\ mol^{-1} \times 298\ K) / 100000\ N\ m^{-2}$

$= 0.02476\ m^3\ mol^{-1}$

$= 2.476 \times 10^4\ cm^3\ mol^{-1}$

Density of WF_6 = $297.85\ g\ mol^{-1} / 2.476 \times 10^4\ cm^3\ mol^{-1}$

$= 0.0120\ g\ cm^{-3}$ **2**

Give credit if they use 24 dm^3 for 1 mol of gas as a known value at STP.

(f) $WF_{6\ (g)} + 4H_2O_{\ (l)} \rightarrow H_2WO_{4\ (aq)} + 6HF_{\ (aq)}$ **1**

$WF_{6\ (g)} + 3H_2O_{\ (l)} \rightarrow WO_{3\ (s)} + 6HF_{\ (aq)}$

Accept either. State symbols not required.

(g) (i) Positive **1**

This is because there are more moles of gas on the right than the left.

(ii) $\Delta_r H^o = \Delta_f H^o (H_2SO_{4\ (g)}) + 6 \times \Delta_f H^o (HF_{\ (g)}) - \Delta_f H^o (SF_6) - 4 \times \Delta_f H^o (H_2O)$ **1**

$= -735 + (6 \times -273) - (-1210 + 4 \times -242)\ kJ\ mol^{-1}$

$= -195\ kJ\ mol^{-1}$ **1**

1 mark for correct expression if numerical calculation is done incorrectly.Correct answer scores full marks.

(iii) **B** SF_6 is kinetically stable but thermodynamically unstable **1**

(h) Tungsten = 1 atom inside unit cell + 4 × atoms on face + 8 × atoms on corner

= 1 + (4 × ½) + (8 × ⅛) = **4 atoms** **1**

Calcium = 6 × atoms on face + 4 × atoms on edge

= (6 × ½) + (4 × ¼) = **4 atoms** **1**

Oxygen = 16 × atoms inside unit cell

= 16 atoms **1**

(i) Volume of Unit Cell = 0.524 nm × 0.524 nm × 1.137 nm

$= 3.122 \times 10^{-28}\ m^3 = 3.122 \times 10^{-22}\ cm^3$

Molar mass of $CaWO_4$ = $(40.08 + 183.85 + 4 \times 16.00)\ g\ mol^{-1}$

$= 287.93\ g\ mol^{-1}$

Mass of one formula unit = $287.93\ g\ mol^{-1} / 6.02 \times 10^{23}\ mol^{-1}$

$= 4.783 \times 10^{-22}\ g$ **1**

Mass of one unit cell

$= 4 \times 4.783 \times 10^{-22}\ g = 1.913 \times 10^{-21}\ g$ **1**

Density = $1.913 \times 10^{-21}\ g / 3.122 \times 10^{-22}\ cm^3$

$= 6.13\ g\ cm^{-3}$ **1**

1 mark for calculation of mass of formula unit, 1 mark for four formula units per unit cell and 1 mark for answer. Correct answer scores full marks.

Question Total 23

3. This question is about Double Bond Equivalents, DBE

(a) (i) C_nH_{2n} ½
(ii) C_nH_{2n-2} ½
(iii) C_nH_{2n-2} ½
(iv) C_nH_{2n-6} ½

(b)

DBE = 3	Ring	Double Bond	Triple Bond
	3	0	0
	2	1	0
	1	2	0
	1	0	1
	0	3	0
	0	1	1

If all correct (in any order) **2**
Minus ½ mark for any missing or incorrect line down to 0

DBE = 4	Ring	Double Bond	Triple Bond
	4	0	0
	3	1	0
	2	2	0
	2	0	1
	1	3	0
	1	1	1
	0	4	0
	0	2	1
	0	0	2

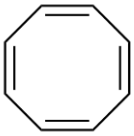
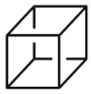
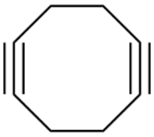
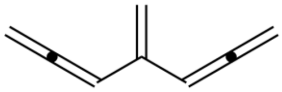
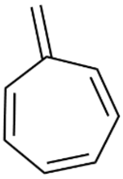
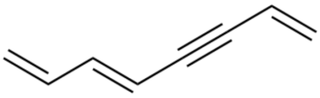
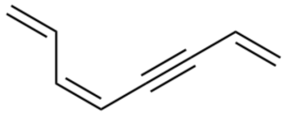
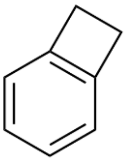
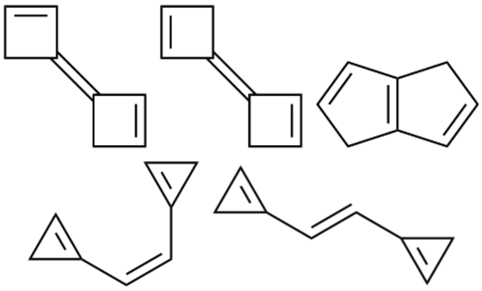
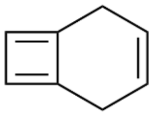
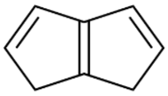
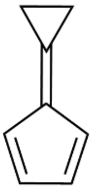
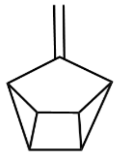
If all correct (in any order) **3**
Minus ½ mark for any missing or incorrect line down to 0

(c) (i) 4 ½
(ii) 9 ½
(iii) 61 ½
(iv) 4 ½
(v) 4 ½
(vi) 3 ½

(d)

Spectrum	Number of atoms in each region (must add to 8)					Structural information deduced			
	Triple Bond (Alkyne)	**Double Bond (Alkene)**	**Single Bond**	**Allene Central**	**Allene Flanking**	**Number of Triple Bonds**	**Number of Double Bonds**	**Number of Rings**	
A	0	8	0	0	0	0	4	1	**½**
B	0	0	8	0	0	0	0	5	**½**
C	4	0	4	0	0	2	0	1	**½**
D	0	2	0	2	4	0	5	0	**1**
E	0	8	0	0	0	0	4	1	**½**
F	2	6	0	0	0	1	3	0	**½**
G	0	6	2	0	0	0	3	2	**½**
H	0	6	2	0	0	0	3	2	**½**
I	0	2	6	0	0	0	1	4	**½**

Each line must be fully correct to score the mark

A 	**B** 	**2**
C 	**D** 	**4**
E 	**F**  *This is the correct structure*  *This structure also fits the NMR data*	**4**
G  *This is the correct structure*	 *These structures also fit the NMR data*  This structure is unstable as is antiaromatic but also fits the NMR data so give full credit	**2**
H  *This is the correct structure*  *This structure also fits the NMR data*	**I** 	**4**

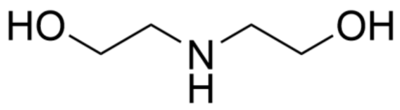
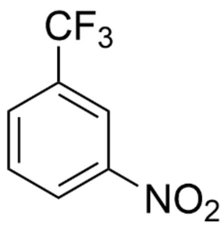
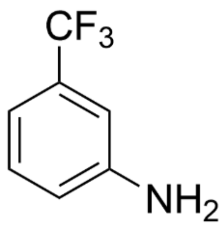
Structures A and B are worth 1 mark each, Structures C-I are worth 2 marks each. *Marks are awarded for each fully correct structure in the correct place. Correct structures in an incorrect place score zero. No partial marks are awarded for a structure. No error carried forward is allowed if structure is wrong but consistent with the student's answer in the previous table. Where more there is more than one possibility only one structure needs to be drawn. There may be other possibiltilies which can be given full credit but only if they are* ***fully*** *consistent with all NMR data listed. Please contact the Committee if you find any alternatives.*

Question Total 31

4 This question is about the synthesis of Addyi

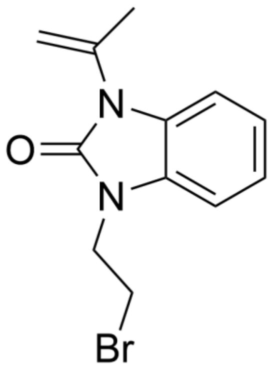
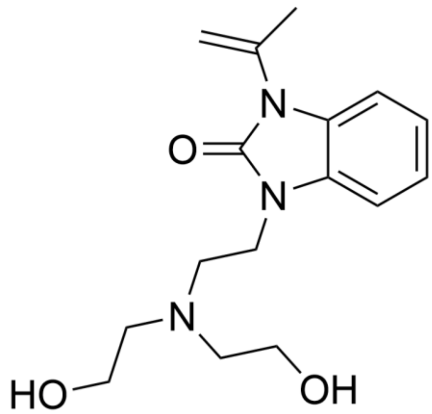
(a) Carbon: 45.70/12.01 = 3.805
Hydrogen 10.55/1.008 = 10.47
Nitrogen 13.32/14.01 = 0.951
Oxygen 30.43/15.99 = 1.90
Simplest whole number ratio = 4:11:1:2
Empirical formula = $C_4H_{11}O_2N$ **2**
If oxygen is forgotten then can award 1 mark if calculation is done correctly.

(b)

Compound **A**	Compound **B**	Compound **C**
 *1 mark* *No carry forward if they propose a structure that matches their incorrect empirical formula in (a).*	 *1 mark* *Wrong isomer 0 marks.*	 *1 mark* *Allow error carried forward if wrong isomer is drawn for* ***B*** *and same wrong isomer is drawn for* ***C*** *but functional group change is correct.*

3

(c)

Compound **D**	Compound **E**
 *2 marks*	 *2 marks*

4

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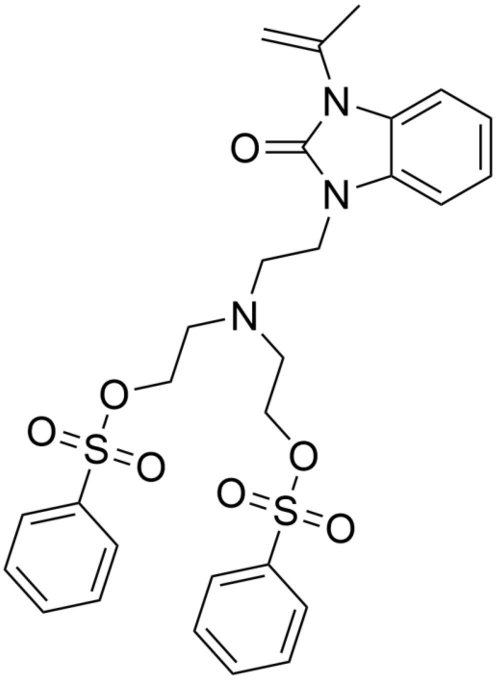
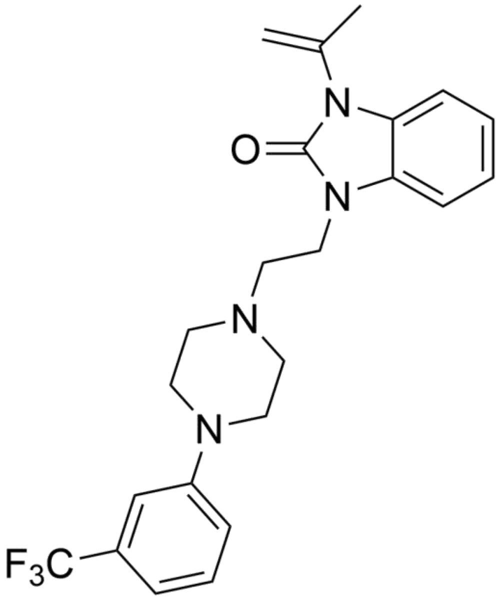
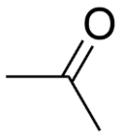
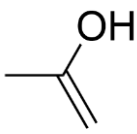

2 marks</td><td>**2**</td></tr>
<tr><td>Compound **G**

2 marks</td><td>By-Product **H**

2 marks
Accept the following alternative for 1 mark.
</td><td>**4**</td></tr>
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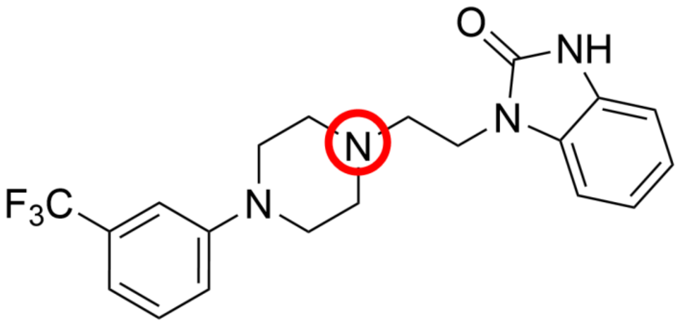
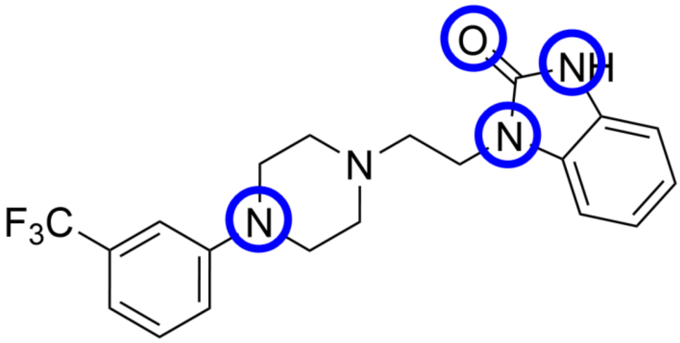
(d)



2

2 marks

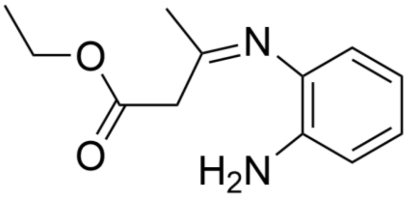
Accept any one of the following for 1 mark.



If more than one atom circled then no marks are awarded.

(e)

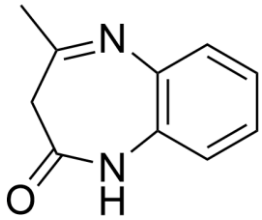
Intermediate X



2 marks

Give full credit to the E isomer of the imine.

Compound Y



4

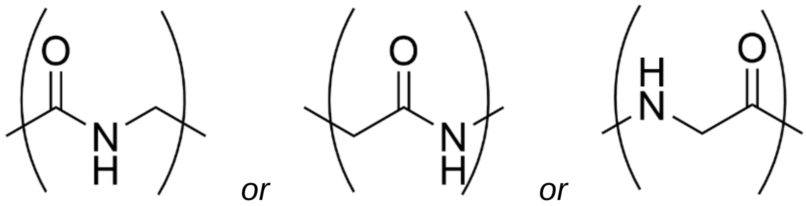
2 marks

Question Total **21**

5. This question is about the radiocarbon dating of King Richard III

(a) **C** Wash repeatedly with dilute HCl then dilute NaOH **1**

(b) (i)



Accept if they label the diagram with an 'n' to show the polymer **1**

(ii) $[NHCH_2CO]_n + 3\frac{1}{4}\ nO_2 \rightarrow 2nCO_2 + nNO_2 + {}^3/_2\ nH_2O$ **2**

$[NHCH_2CO]_n + 2\frac{1}{4}\ nO_2 \rightarrow 2nCO_2 + {}^n/_2N_2 + {}^3/_2\ nH_2O$

Accept either equation or a multiple of either.

(iii) $CO_{2\,(g)} + 2H_{2\,(g)} \rightarrow C(s) + 2H_2O_{(g)}$ **1**
State symbols not required.

(iv) 40% of 1.0 g bone = 0.40 g polyglycine
The entire mass of carbon in polyglycine becomes graphite
Mass of graphite = % carbon in polyglycine × 0.40 g
(2 × 12.01) / (2 × 12.01 + 3 × 1.008 + 16.00 + 14.01) × 0.40 g
= 0.168 g **1**

(c) Amount of C = 0.002 g / 12.01 g mol^{-1} = 1.665×10^{-4} mol
Number of atoms of C = 1.665×10^{-4} mol × 6.02×10^{23} mol^{-1} = 1.00×10^{20}
Number of atoms of ^{14}C initially (N_0)= (1.215×10^{-10} / 100) × 1.00×10^{20} = 1.22×10^{8} **1**

Half life ($t_{½}$) = 5568 years = 5568 × 365 = 2.032×10^{6} days
Decay Constant (k) = ln 2 / $t_{½}$ = ln 2 / 2.032×10^{6} days
= 3.41×10^{-7} day^{-1} **1**

Number of atoms of ^{14}C left = $N_0\exp(-kt)$
Number of atoms of ^{14}C decayed = $N_0 - N_0\exp(-kt)$
= $1.22 \times 10^{8} - 1.22 \times 10^{8} \times \exp(-3.41 \times 10^{-7} \times 1)$
= 41.6
≈ 42 atoms **1**

(d) Decay Constant (k) = ln 2 / $t_{½}$ = ln 2 / 5568 years = 1.245×10^{-4} $year^{-1}$ **1**
$N(^{14}C)/N(^{12}C) = 1.154 \times 10^{-12}$
$N_0(^{14}C)/N_0(^{12}C) = 1.215 \times 10^{-10} / 98.93 = 1.228 \times 10^{-12}$
As $N(^{12}C) = N_0(^{12}C)$
$N(^{14}C)/N_0(^{14}C) = 1.154 \times 10^{-12} / 1.228 \times 10^{-12} = 0.9397$ **1**

For ^{14}C: $N = N_0\exp(-kt)$
$t = -[\ln (N(^{14}C)/N_0(^{14}C))] / k$
$= -[\ln (0.9397)] / 1.245 \times 10^{-4}$ = 500 years **1**
Date of Death = 2012 − 500 = 1512
Accept if any year between 2012-2016 is used as the date of the dating experiment. **1**
No credit if they just write 1485!

Question Total 13
PAPER TOTAL 100