48th INTERNATIONAL CHEMISTRY OLYMPIAD

2016

UK Round One

STUDENT QUESTION BOOKLET

* * * * *

- **The time allowed is 2 hours.**
- **Attempt all 5 questions.**
- **Write your answers in the special answer booklet.**
- **In your calculations, please write only the essential steps in the answer booklet.**
- **Always give the appropriate units and number of significant figures.**
- **You are provided with a copy of the Periodic Table.**
- **Do *NOT* write anything in the right hand margin of the answer booklet.**
- **The marks available for each question are shown below; this may be helpful when dividing your time between questions.**

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

Some of the questions will contain material you will not be familiar with. However, by logically applying the skills you have learnt as a chemist, you should be able to work through the problems. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may still find subsequent parts straightforward.

This resource was downloaded from https://rsc.li/2WmGF2V

1																	18
H 1 1.008	2											13	14	15	16	17	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01					**symbol** atomic number mean atomic mass						**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
Na 11 22.99	**Mg** 12 24.31	3	4	5	6	7	8	9	10	11	12	**Al** 13 26.98	**Si** 14 28.09	**P** 15 30.97	**S** 16 32.06	**Cl** 17 35.45	**Ar** 18 39.95
K 19 39.102	**Ca** 20 40.08	**Sc** 21 44.96	**Ti** 22 47.90	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.71	**Cu** 29 63.55	**Zn** 30 65.37	**Ga** 31 69.72	**Ge** 32 72.59	**As** 33 74.92	**Se** 34 78.96	**Br** 35 79.904	**Kr** 36 83.80
Rb 37 85.47	**Sr** 38 87.62	**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.94	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.4	**Ag** 47 107.87	**Cd** 48 112.40	**In** 49 114.82	**Sn** 50 118.69	**Sb** 51 121.75	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.30
Cs 55 132.91	**Ba** 56 137.34	**La*** 57 138.91	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.85	**Re** 75 186.2	**Os** 76 190.2	**Ir** 77 192.2	**Pt** 78 195.09	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.37	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
Fr 87	**Ra** 88	**Ac⁺** 89															

***Lanthanides**	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.4	**Eu** 63 151.96	**Gd** 64 157.25	**Tb** 65 158.93	**Dy** 66 162.50	**Ho** 67 164.93	**Er** 68 167.26	**Tm** 69 168.93	**Yb** 70 173.04	**Lu** 71 174.97
⁺Actinides	**Th** 90 232.01	**Pa** 91	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103

$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$ $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ standard pressure $= 10^5\ \text{N m}^{-2}$ $0\ ^\circ\text{C} = 273\ \text{K}$

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

Daily fluctuations in energy usage and in energy generation from renewables lead to a need for energy storage methods. Energy may be stored chemically using the sulfur-iodine cycle. The cycle has also been proposed as a means of producing hydrogen fuel more efficiently than by electrolysis.

At high temperature the sulfur-iodine cycle involves the three gas-phase equilibria:

(1) $I_2(g) + SO_2(g) + 2H_2O(g) \rightleftharpoons H_2SO_4(g) + 2HI(g)$

(2) $2H_2SO_4(g) \rightleftharpoons 2SO_2(g) + 2H_2O(g) + O_2(g)$

(3) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(a) Use the data and the equations at the end of the question to answer the following questions for **reaction (3).**

(i) Calculate the standard enthalpy change at 298 K, $\Delta_r H^{\ominus}(298\ K)$.

(ii) Calculate the standard entropy change at 298 K, $\Delta_r S^{\ominus}(298\ K)$.

(iii) Calculate the standard Gibbs energy change at 298 K, $\Delta_r G^{\ominus}(298\ K)$.

(iv) Calculate the equilibrium constant, K_{298}, at 298 K.

(v) Calculate the equilibrium constant, K_{723}, at 723 K. Assume $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are independent of temperature.

(b) Conditions are chosen so that the three equilibrium reactions above all proceed from left to right. Assuming that the products of **reaction (1)** are all consumed in **reactions (2)** and **(3)**, write an overall equation for the sulfur-iodine cycle.

(c) The standard enthalpy change of reaction at 298 K for **reaction (2)** is +439 kJ mol^{-1}. Use the value of $\Delta_f H^{\ominus}$ (298 K) for $H_2O(g)$ in the table below to calculate the standard enthalpy change of reaction at 298 K for **reaction (1)**.

(d) How much energy, per mol of sulfur atoms at 298 K, is stored with one revolution around the sulfur-iodine cycle?

Data:

	HI(g)	$H_2(g)$	$I_2(g)$	$H_2O(g)$
$\Delta_f H^{\ominus}$ (298 K) / kJ mol^{-1}	26.5		62.4	−242
$S^{\ominus}$ (298 K) / J K^{-1} mol^{-1}	207	131	261	189

Useful equations: $\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

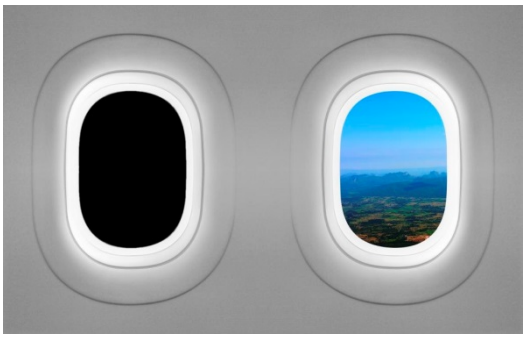
$\Delta G = \Delta H - T\Delta S$

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

Useful constant: $R = 8.314\ J\ K^{-1}\ mol^{-1}$

2. This question is about the chemistry of tungsten

The chemistry of the transition metal tungsten has certain similarities to that of the main-group element sulfur since both atoms have a total of six valence electrons. Both elements reach their maximum +6 oxidation states when combined with electronegative elements fluorine and oxygen.



Whilst tungsten(VI) fluoride is used in the semiconductor industry, the oxide is used in electrochromic windows. These change colour when an electrical voltage is applied, as shown in the aircraft windows on the right.

Most tungsten occurs naturally in the tungstate anion, WO_4^{2-}, analogous to the sulfate, SO_4^{2-}. A common tungsten mineral is Scheelite, calcium tungstate, $CaWO_4$.

(a) Draw a structure showing the bonding in the WO_4^{2-} ion and give the O-W-O bond angle.

Treatment of scheelite with aqueous sodium carbonate gives a solution of sodium tungstate and a white insoluble salt. Addition of hydrochloric acid to aqueous sodium tungstate produces tungstic acid, which on heating gives tungsten(VI) oxide. This may be reduced with hydrogen to give pure tungsten metal.

(b) **(i)** Give the equation for the reaction between scheelite and aqueous sodium carbonate.

(ii) Give the equation for the reaction of aqueous sodium tungstate with hydrochloric acid and suggest a structure for tungstic acid.

(iii) Give the equation for the formation of tungsten(VI) oxide from tungstic acid.

(iv) Give the equation for the formation tungsten metal.

In electrochromic windows, a voltage is applied between a transparent layer of tungsten(VI) oxide and a source of ions such as a lithium salt, and the following reaction takes place during which some of the lithium ions are incorporated into the structure of the oxide:

$$WO_3 + xLi^+ + xe^- \longrightarrow Li_xWO_3$$

The product, Li_xWO_3, is known as a *tungsten bronze*, and its colour depends on the value of x. The value of x can vary from 0 to 1; a typical value giving a blue-black colour is when x = 0.3.

(c) **(i)** Calculate the oxidation state of the tungsten when x = 1.

(ii) Calculate the average oxidation state of the tungsten when x = 0.3.

Both elemental sulfur and tungsten react with fluorine gas to form the hexafluorides. SF_6 and WF_6 are both gases at room temperature and pressure, with WF_6 being the most dense gas known under these conditions. WF_6 is extremely toxic due to its rapid reaction with water to form two substances. In contrast, SF_6 is inert in water and non-toxic.

(d) By assuming air to be made up of nitrogen gas only, calculate the densities of SF_6 and WF_6 relative to air.

(e) Calculate the actual density of $WF_6(g)$ in g cm^{-3} at 298 K and standard pressure.

(f) Suggest an equation for the reaction of WF_6 with water.

Consider the following gas-phase reaction:

$$SF_6(g) + 4H_2O(g) \longrightarrow H_2SO_4(g) + 6HF(g)$$

(g) **(i)** Would you expect the standard entropy change for this reaction to be positive or negative?

(ii) Use the data below to calculate the standard enthalpy change for this reaction.

	$SF_6(g)$	$H_2O(g)$	$H_2SO_4(g)$	$HF(g)$
$\Delta_f H^\ominus$ / kJ mol^{-1}	–1210	–242	–735	–273

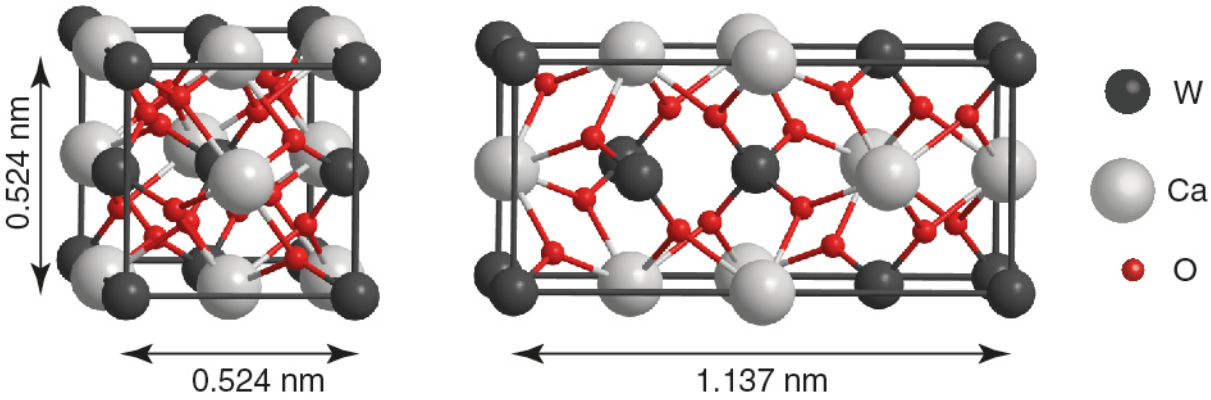
(iii) Which of the following is correct regarding the reaction between SF_6 and water? Circle one answer in your answer booklet.

A SF_6 is kinetically stable and thermodynamically stable

B SF_6 is kinetically stable but thermodynamically unstable

C SF_6 is kinetically unstable but thermodynamically stable

D SF_6 is kinetically unstable and thermodynamically unstable.



Two views of the unit cell of scheelite, $CaWO_4$.

The cell dimensions are: 0.524 × 0.524 × 1.137 nm.

The view on the right is obtained by rotating the one on the left by 90°.

The word ‘tungsten’ itself is actually an older Swedish name for the mineral Scheelite. It literally means heavy (*tung*) stone (*sten*) since Scheelite is considerably more dense than the rocks commonly found with it.

The *unit cell* for Scheelite is shown above. A unit cell is determined by X-ray crystallography and shows the arrangement of atoms which generates the bulk structure when the cells are stacked together. Some of the atoms are contained completely within the boundaries of the unit cell, whilst for those atoms centred on the corners, edges, or faces, only fractions are contained within one unit cell.

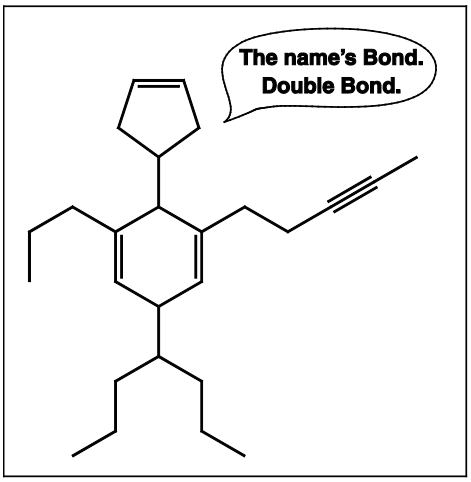
(h) By considering the number of fractions of atoms within one unit cell, count the net numbers of tungsten atoms, calcium atoms, and oxygen atoms within one unit cell.

(i) Use your answer in **(h)** and the dimensions of the cell to calculate the density of the ‘heavy stone’ scheelite in g cm^{-3}.

3. This question is about Double Bond Equivalents, DBE

The idea of Double Bond Equivalents, DBE, the number of double bonds and / or rings that a compound contains, can be extremely useful when working out possible structures from formulae.

Mr Bond, shown on the right, has 007 DBE.



(a) The general formula for a non-cyclic alkane is C_nH_{2n+2}. Give the general formulae for the following:

(i) an alkene or cycloalkane **(ii)** an alkyne (a hydrocarbon containing a C≡C triple bond)

(iii) a cycloalkene **(iv)** a di-alkyne.

For each extra ring or π-bond that a hydrocarbon has, an extra two hydrogens are lost compared with the alkane. The total number of rings and/or π-bonds that a structure has is known as the number of Double Bond Equivalents, DBE. For structures with multiple rings, the number of rings may be determined by counting the minimum number of cuts through bonds needed to be made in order to leave the structure ring-free.

(b) The table below shows the possible combinations of rings, double bonds and triple bonds for DBE = 1 and DBE = 2. In your answer booklet, extend the table to show the possible combinations for DBE = 3 and DBE = 4.

DBE	Ring	Double bond	Triple bond
1	1	0	0
	0	1	0
2	2	0	0
	0	2	0
	1	1	0
	0	0	1

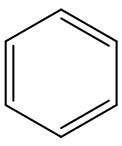
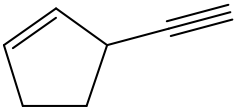
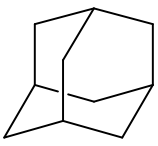
The number of DBE in a hydrocarbon may be calculated by comparing the actual number of hydrogens (X) in a given hydrocarbon of formula C_nH_X with the number of hydrogens (A) in the non-cyclic alkane with the same number of carbon atoms (C_nH_A):

$$DBE = ½ \times (A - X)$$

As an example, to work out the DBE for cyclohexene, C_6H_{10}, since the number of hydrogens in hexane (the alkane with 6 carbons) is 14, DBE(cyclohexene) = ½ × (14 – 10) = 2.

(c) Determine the number of double bond equivalents in:

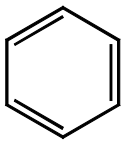
(i) C_5H_4 **(ii)** $C_{18}H_{20}$ **(iii)** C_{60}

(iv)  **(v)**  **(vi)** 

The types of DBE may be revealed using spectroscopic techniques, such as NMR.

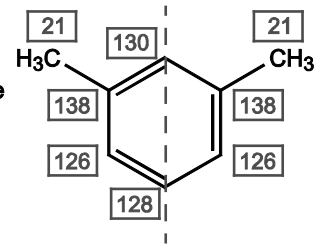
In ^{13}C NMR, the number of signals in the spectrum depends on the number of different carbon environments in a structure. For example, in benzene, each carbon atom is equivalent and so the spectrum shows only one peak, whereas in 1,3-dimethylbenzene there are 5 different environments as shown below:

In benzene, all the carbons are in equivalent environments and so the spectrum shows only one peak at 128 ppm.



In 1,3-dimethylbenzene, ignoring how the π-bonds in the ring are drawn, a plane of symmetry (or rotation axis) runs through the molecule (shown by the dashed line). This means there are only 5 different environments and so 5 peaks appear in the spectrum as indicated.

[Note the unique carbons at 130 ppm and 128 ppm must lie on the axis.]



Carbon atoms in the following environments typically give peaks in the regions indicated:

- Triple-bonded alkyne carbons: 70-100 ppm
- Double-bonded alkene carbons: 100-160 ppm
- Carbons with four single bonds to carbons or hydrogens: 0-50 ppm

In the rather unusual allene group, $R_2C=C=CR_2$, the central carbon gives a peak over 200 ppm, and the carbons attached directly to the central allene carbon, flanking it either side, now fall in the same region as the triple-bonded carbons, i.e.

- Allene central carbon: >200 ppm
- Allene flanking carbons: 70-100 ppm

Using advanced NMR techniques, in addition to telling how many carbon atoms are in a particular environment, it is also possible to tell how many hydrogen atoms are attached to a particular carbon. We may denote this as (CH_3), (CH_2), (CH), or (C) for carbons with 3, 2, 1, or 0 hydrogens attached. The spectrum for 1,3-dimethylbenzene may be summarised as:

2 × 138 (C), 130 (CH), 128 (CH), 2 × 126 (CH), 2 × 21 (CH_3).

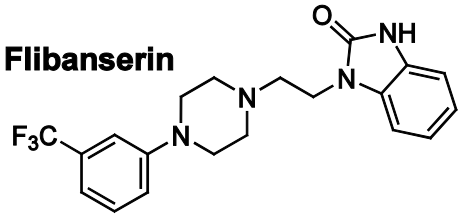
(d) The following data are taken from the ^{13}C NMR spectra of isomers with the formula C_8H_8 which has **five** DBE. For each spectrum, first complete the table in your answer booklet and hence suggest how many triple bonds, double bonds, and rings each compound contains. Then suggest a skeletal structure consistent with the data. [You do not need to assign values to particular carbons.]

Spectrum	Signals / ppm
A	8 × 132 (CH)
B	8 × 47 (CH)
C	4 × 96 (C), 4 × 20 (CH_2)
D	2 × 210 (C), 134 (C), 113 (CH_2), 2 × 93 (CH), 2 × 79 (CH_2)
E	147 (C), 2 × 138 (CH), 2 × 131 (CH), 2 × 127 (CH), 112 (CH_2)
F	142 (CH), 136 (CH), 127 (CH_2), 120 (CH_2), 117 (CH), 112 (CH), 91 (C), 89 (C)
G	2 × 146 (C), 2 × 127 (CH), 2 × 122 (CH), 2 × 30 (CH_2)
H	154 (C), 151 (C), 2 × 136 (CH), 2 × 128 (CH), 2 × 37 (CH_2)
I	157 (C), 101 (CH_2), 2 × 26 (CH), 4 × 19 (CH)

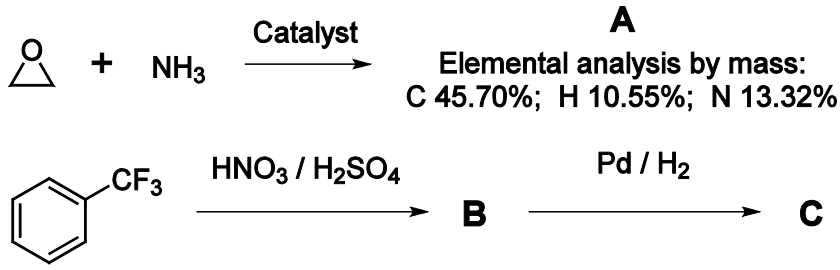
4. This question is about the synthesis of Addyi

In 2015, the drug Addyi (chemical name Flibanserin) made the news by becoming the first drug to be approved for the treatment of female hypoactive sexual desire disorder. The structure of Addyi is shown below.

Flibanserin



In making this molecule, two precursor molecules **A** and **C** are first synthesised as shown in the scheme below.

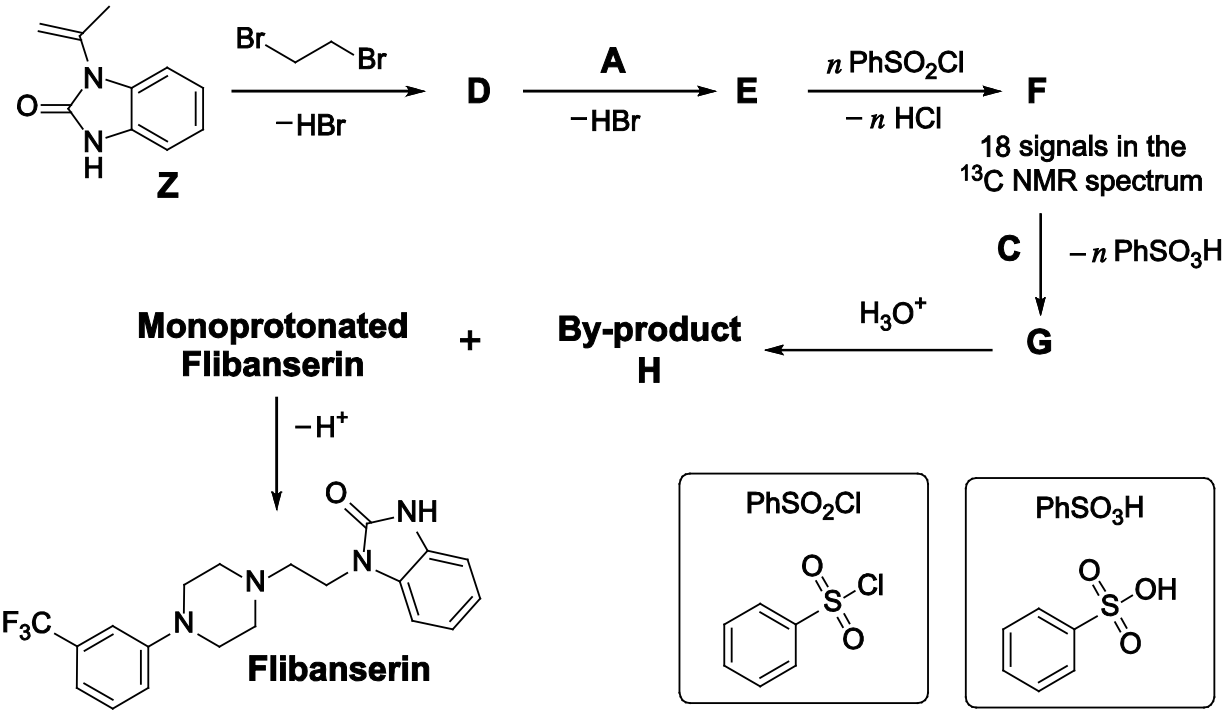


(a) Calculate the empirical formula of **A**.

(b) Draw the structures of Compounds **A**, **B** and **C**.

The remainder of the synthesis starts with Compound **Z** and is shown below. In this scheme all reactions are balanced.

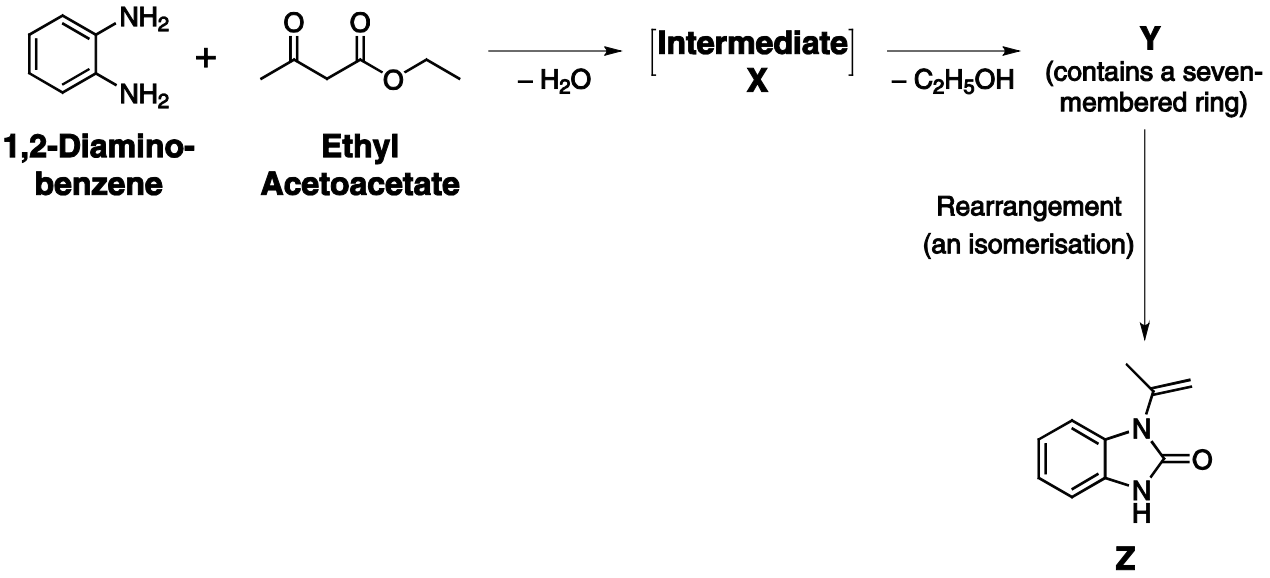
(c) Draw the structures of Compounds **D**, **E**, **F** and **G** and the By-Product **H**.



(d) Flibanserin is formed initially as its monoprotonated salt. On the structure of Flibanserin in your answer booklet, circle the atom that is protonated.

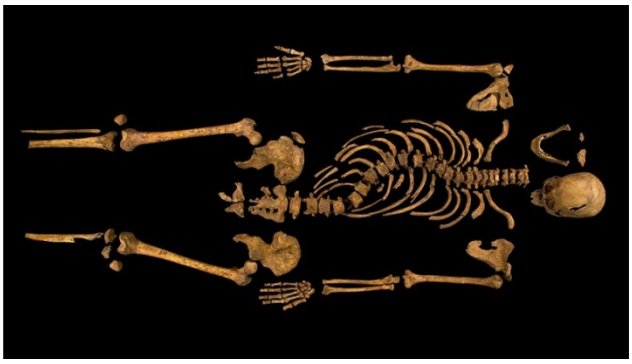
Compound **Z** itself is synthesised from 1,2-diaminobenzene and ethyl acetoacetate. The synthesis is shown in the scheme below, where all reactions are balanced.

(e) Draw the structures of Intermediate **X** and Compound **Y**.



5. This question is about dating King Richard III.

King Richard of York gave battle in vain and was killed in 1485. In 2015, his remains were buried in Leicester Cathedral, after having been found underneath the nearby Greyfriars car park in 2012. The bones were dated from their radiocarbon content.



Bone found in skeletal remains may be considered to be 60% hydroxyapatite ($Ca_5(PO_4)_3(OH)$) by weight, and the rest mostly collagen, a protein, whose major amino acid constituent is glycine (H_2NCH_2COOH).

In the radiocarbon dating of this skeleton, a 1.0 g sample was taken from a rib bone. It was first processed to remove the inorganic content.

(a) Which of the following will be most effective at removing the unwanted **inorganic** content and leave behind the organic component? Circle one option in the answer booklet.

A Wash repeatedly with water and then propanone

B Heat to 400°C

C Wash repeatedly with dilute HCl then dilute NaOH

The remaining organic component, the protein collagen, may be assumed to be polyglycine (a polymer made only from glycine). This is burnt in excess oxygen and the carbon-containing product is reduced back to graphite with hydrogen.

(b) **(i)** Draw the simplest repeat unit of the polymer polyglycine.

(ii) Write a balanced equation for the combustion of polyglycine consisting of *n* repeat units.

(iii) Write a balanced equation for the formation of the graphite from the carbon-containing product.

(iv) What mass of graphite was produced from processing the 1.0 g sample of bone?

Radiocarbon dating relies on the existence of three isotopes of carbon, ^{12}C, ^{13}C and ^{14}C. The two lighter isotopes are stable, but ^{14}C is radioactive with a half-life of 5568 years. The standard abundances of these isotopes in a sample at the time of death may be taken to be:

$$98.93\,\% : 1.07\,\% : 1.215\times10^{-10}\,\%.$$

(c) In a 2.0 mg sample analysed at the time of death, how many ^{14}C atoms on average would be expected to decay in one day?

Rather than counting the actual decay rate, a more sensitive technique is to determine the ratio of ^{12}C, ^{13}C and ^{14}C by counting the atoms of particular masses using mass spectrometry.

The ratio of ^{12}C : ^{14}C in the bone sample was found to be $1 : 1.154\times10^{-12}$.

(d) Using these data, determine how old the bones are and hence the date of death of the man whose bones were being analysed.

Acknowledgements & References

Q2
The image is from © iStock.

Q4
Nouvelle synthese de l' (∝-methyl vinyl)-9 methyl-3s-triazolo[4,3-a]benzimidazole a partir de la methyl-4benzodiazepine-1,5 one-2.
R. Achour et al. *Tetrahedron Letters*, **1988**, *29*, 195-198.

Q5
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