

**49th INTERNATIONAL
CHEMISTRY OLYMPIAD
2017
UK Round One
STUDENT QUESTION BOOKLET**

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- 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 | 8 | 11 | 23 | 21 | 12 | 75 |

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.

1**18**

| | | | | | | | | | | | | | | | | | |
|---------------------------|---|----------------------------|---------------------------|---------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| H 1 1.008 | | | | | | | | | | | | | | | | | He 2 4.003 |
| Li 3 6.94 | symbol atomic number mean atomic mass | | | | | | | | | | | | | | | | Ne 10 20.18 |
| Na 11 22.99 | | | | | | | | | | | | | | | | | Be 4 9.01 |
| 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 43 101.07 | 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 84 209 | At 85 210 | Rn 86 222 |
| 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 |

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$$

$$0 \text{ }^\circ\text{C} = 273 \text{ K}$$

1. This question is about the Green Pool of Rio

When the water in the diving pool at the Rio Olympic Games turned green, it was suggested that the growth of algae was to blame; this was strongly contested by the organisers. Even after the official report was published, there is still much speculation as to the actual reason behind the colour change.

One of the most commonly used compounds in the chlorination of swimming pools is sodium hypochlorite, NaClO.



(a) Determine the oxidation state of chlorine in sodium hypochlorite, NaClO.

Once dissolved, an equilibrium is established between ClO^- and its conjugate acid.

(b) Give an equation for this equilibrium.

This equilibrium is highly pH dependent and under acidic conditions chlorine is produced.

(c) Give an equation for the generation of chlorine from hypochlorite and HCl.

The organisers eventually explained the green colour in the pool as being due to the growth of algae after the inadvertent addition of a large quantity of hydrogen peroxide, which destroyed the hypochlorite and formed chloride ions.

(d) Give an equation for the reaction between hydrogen peroxide and hypochlorite.

Hypochlorites also have a tendency to react with ammonia and ammonia-like compounds to form compounds containing nitrogen and chlorine. One such compound is nitrogen trichloride, which can cause eye irritation and the distinctive smell of swimming pools.

(e) (i) Give an equation for the formation of nitrogen trichloride.

(ii) Draw a structure for nitrogen trichloride, showing its shape, and state the approximate Cl–N–Cl bond angle.

Depending on reacting ratios, another possible outcome of the reaction between ammonia and hypochlorite is the formation of hydrazine, $\text{H}_2\text{N}-\text{NH}_2$, and chloride ions.

(f) Give an equation for this reaction.

Copper(II) sulfate is sometimes added to swimming pools and this was also suggested as the cause of the green colour. Copper(II) ions were also blamed for the green tint given to the bleached hair of the American swimmer Ryan Lochte. The copper(II) ions precipitate on the hair due to the high pH of certain shampoos.

(g) Suggest a formula for the blue precipitate on Ryan Lochte's hair that made it go green.

2. This question is about atmospheric chemistry

Studying the reactions which take place in the atmosphere is crucial to help understand global climate and thus minimise our impact on the environment. Hydrogen sulfide, H_2S , is a molecule which displays interesting chemistry in the atmosphere. H_2S is present in natural gas and is also particularly common near volcanos.



A sulfur boulder in the crater of a volcano.

The main process by which H_2S is naturally removed from the air is its reaction with the OH radical (the main day-time oxidising agent in the atmosphere). The reaction happens in a single encounter between H_2S and the OH radical.

- (a)** Give an equation for the reaction of H_2S with the OH radical to form water and another radical.

In order to determine the rate constant of the reaction in **(a)**, dry H_2S was generated in the laboratory by reacting iron(II) sulfide with hydrochloric acid.

- (b)** Give an equation for the generation of H_2S in the laboratory.

The average emission rate of H_2S in the air at a volcanic region can be taken to be 7.65×10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$. The concentration of H_2S was measured to be constant over time, which means that the rate with which H_2S is produced is the same as the rate at which H_2S is consumed at this volcanic region.

For a reaction that happens in a single encounter between two species A and B, the rate of reaction is given by:

$$\text{rate} = k \times [\text{A}] \times [\text{B}]$$

where k is the corresponding rate constant, and [A] and [B] denote the concentrations of A and B, respectively.

- (c)** Calculate the concentration of H_2S in the atmosphere in units of molecules cm^{-3} .

You should assume that the only removal process of H_2S from the atmosphere is its reaction with the OH radical, and that the average concentration of the OH radical is 1.1×10^6 molecules cm^{-3} . The rate constant for the reaction in part **(a)** was measured to be $k = 4.7 \times 10^{-12} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$.

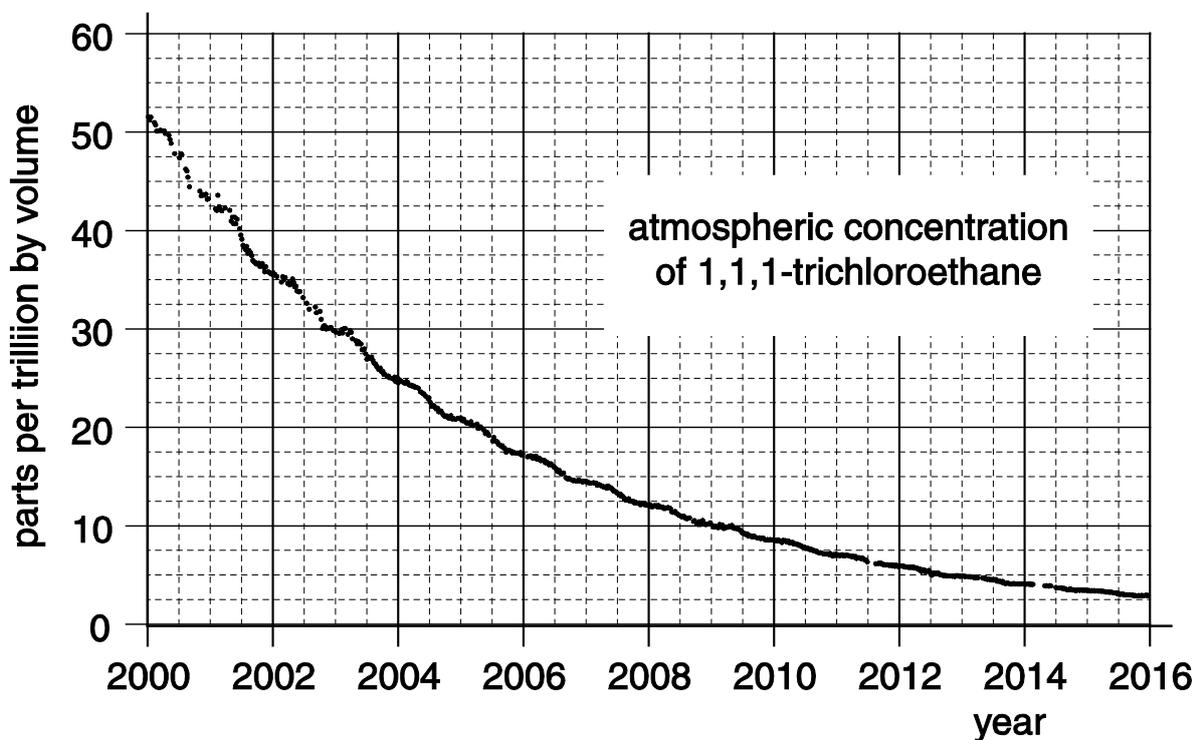
- (d)** The average concentration of H_2S is usually expressed in units of $\mu\text{g m}^{-3}$. Express the concentration of H_2S found in part **(c)** in units of $\mu\text{g m}^{-3}$.

Natural gas often contains sulfur in the form of H_2S . To minimise the sulfur emission from the desulfurization of natural gas, H_2S is partially combusted to form SO_2 which then reacts with the remaining H_2S to form elemental sulfur.

- (e)** **(i)** Give an equation for the combustion of H_2S .
(ii) Give an equation for the reaction of H_2S with SO_2 .

It is very hard to measure the concentration of OH radicals directly, so we often have to resort to indirect methods. In addition to H₂S, the OH radical is able to oxidise other compounds in the atmosphere, such as 1,1,1-trichloroethane. Since the atmospheric emission of 1,1,1-trichloroethane stopped in the 1990s, its change in concentration can be used to indirectly estimate the average global concentration of the OH radical. The concentration profile of 1,1,1-trichloroethane over time shows a simple exponential decay, typical of reactions following first-order kinetics.

- (f) (i) Using the graph below, estimate the half-life ($t_{1/2}$) of 1,1,1-trichloroethane to the nearest 0.1 years.
- (ii) Convert your answer to **f(i)** into seconds. [Take 1 year to be 365.25 days.]



Assuming that the concentration of the OH radicals is constant over time, and that the only removal process of 1,1,1-trichloroethane from the atmosphere is its reaction with OH, we can find the observed rate constant (k_{obs}) of the reaction using the following expression:

$$t_{1/2} = \frac{\ln 2}{k_{\text{obs}}}$$

The observed rate constant, k_{obs} , is a product of the second order rate constant ($k_{2\text{nd}} = 1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and the concentration of the OH radicals.

- (g) Using your value for the half-life of 1,1,1-trichloroethane, calculate the average global atmospheric concentration of OH radicals in molecules cm^{-3} .

(Note: you may not get exactly the same result as the concentration given in the first part of the problem.)

3. This question is about the chemistry of Iron Man

Despite his name, the metal suit of comic book superhero 'Iron Man' is actually stated in the 2008 film to be an alloy of titanium and gold.

In July 2016, researchers found a certain titanium-gold alloy with the formula Ti_3Au that was about four times harder than pure titanium and most steel alloys. It was also biocompatible, making it ideal for artificial hip and knee joints, and for screws and implants to fix bone fractures.

Currently, a thin film of titanium nitride, TiN , is used to increase the hardness of titanium, for example on cutting tools. This gives the titanium a beautiful gold colour which Iron Man may have chosen to make his suit look pretty.



Thin films of TiN are typically prepared by a technique called chemical vapour deposition where the TiN is formed on substrates heated above $320\text{ }^\circ\text{C}$ in an atmosphere of titanium(IV) chloride and ammonia. An unbalanced equation for this reaction may be represented as:



- (a) (i) What is the oxidation state of the titanium in titanium nitride, TiN ?
- (ii) Which element is being oxidized in the reaction between $TiCl_4$ and NH_3 ?
- (iii) Which element is being reduced in the reaction between $TiCl_4$ and NH_3 ?
- (iv) Balance the above equation.

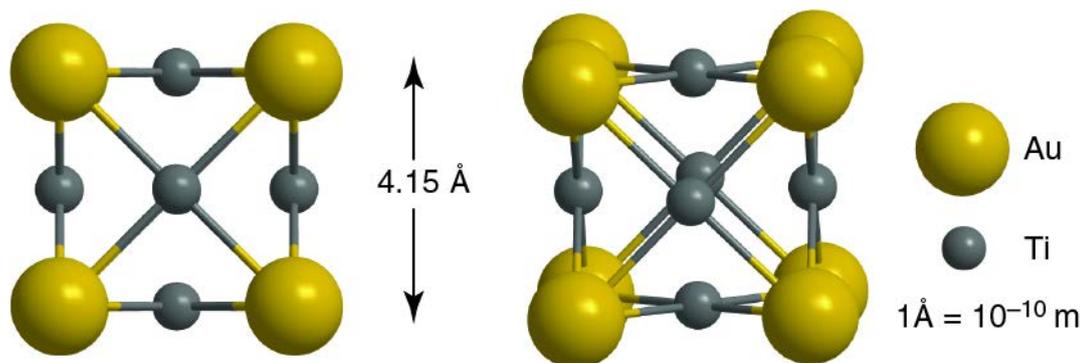
To make the titanium-gold alloys, the two elements are heated together in the appropriate proportions under an inert atmosphere of argon.

- (b) Assuming Iron Man's suit requires 40 kg of alloy to make, calculate the masses of titanium and gold needed to prepare this mass of alloy with the formula Ti_3Au .

There are two different forms of the alloy with the formula Ti_3Au , distinguished as the α -form and β -form. The arrangements of the atoms in the different forms are shown using a *unit cell*. 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.

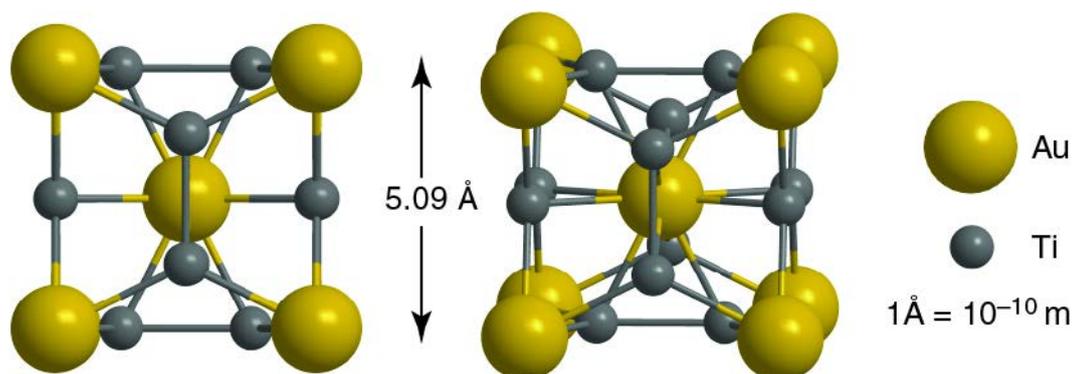
The unit cells for both α - Ti_3Au and β - Ti_3Au are based on regular cubes. How hard the alloys are depends on the number of bonding interactions each atom has, and the lengths of the bonds.

Two views of the unit cell of the α -form are shown below. The unit cell has a gold atom centred at each corner of the cube, and a titanium atom in the centre of each face. The length of the cube edge is 4.15 \AA .



- (c) In the bulk structure of $\alpha\text{-Ti}_3\text{Au}$ generated by stacking the unit cells together, the titanium atoms are surrounded by gold atoms and other titanium atoms.
- (i) How many titanium atoms surround each gold atom?
 - (ii) How many gold atoms surround each titanium atom?
 - (iii) How many titanium atoms surround each titanium atom?
- (d) (i) Calculate the Ti–Au distance.
- (ii) Calculate the shortest distance between two titanium atoms.

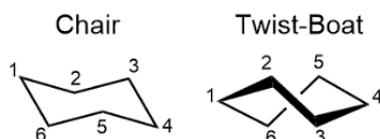
The β -form also has a gold atom centred at each corner of the cube, but also one in the centre of the cube. The length of the cube edge is 5.09 \AA . The titanium atoms are arranged with two on each face, with the two separated by exactly half the length of the cube edge. The Ti–Ti pair are arranged centred on the face, parallel to one of the edges of the cube. The Ti–Ti pairs on adjacent faces of the cube are aligned at right-angles.



- (e) In the bulk structure of $\beta\text{-Ti}_3\text{Au}$ generated by stacking the unit cells together, the titanium atoms are surrounded by gold atoms and other titanium atoms. However there are now *two* separations between the titanium atoms: nearest neighbours, and next-nearest.
- (i) How many titanium atoms surround each gold atom?
 - (ii) How many gold atoms surround each titanium atom?
 - (iii) How many titanium nearest neighbours and next-nearest neighbours are there around each titanium atom?
- (f) (i) Calculate the Ti–Au distance.
- (ii) Calculate the separation between a titanium atom and its next-nearest neighbour.

4. This question is about the molecule twistane

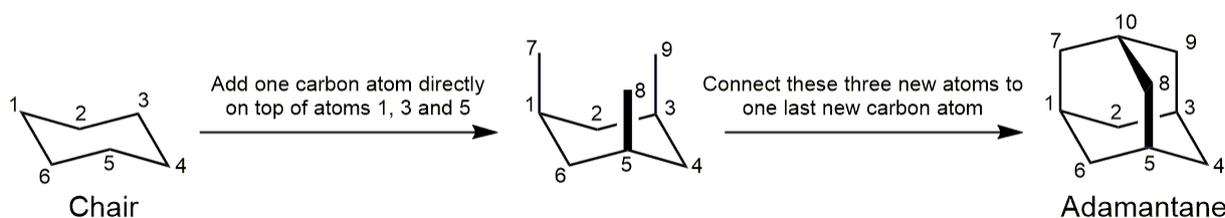
Although the skeletal structure of cyclohexane (C_6H_{12}) is often represented as a regular hexagon, it is actually a flexible molecule that exists in a variety of different shapes referred to as *conformations*. Two of these conformations, the *chair* and the *twist-boat*, are shown below. The carbon atoms in the six-membered rings have been numbered 1-6 to show their connectivity.



The chair is the lowest energy conformation of cyclohexane with all the bond angles almost equal to the ideal angle for a tetrahedral carbon atom. The twist-boat is higher in energy.

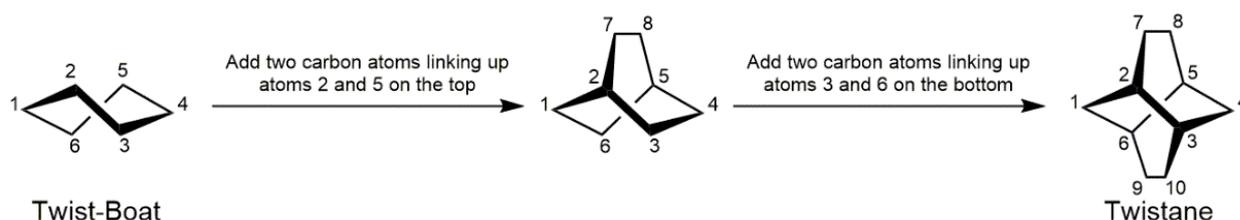
- (a) By how many degrees does the ideal C–C–C angle in the chair form of cyclohexane differ from that in a regular hexagon?

The molecule *adamantane* can be visualised by the addition of a further four carbon atoms onto the chair conformation of cyclohexane as shown below. In doing this, other six-membered rings are created. In adamantane all the six-membered rings are locked in the chair conformation.



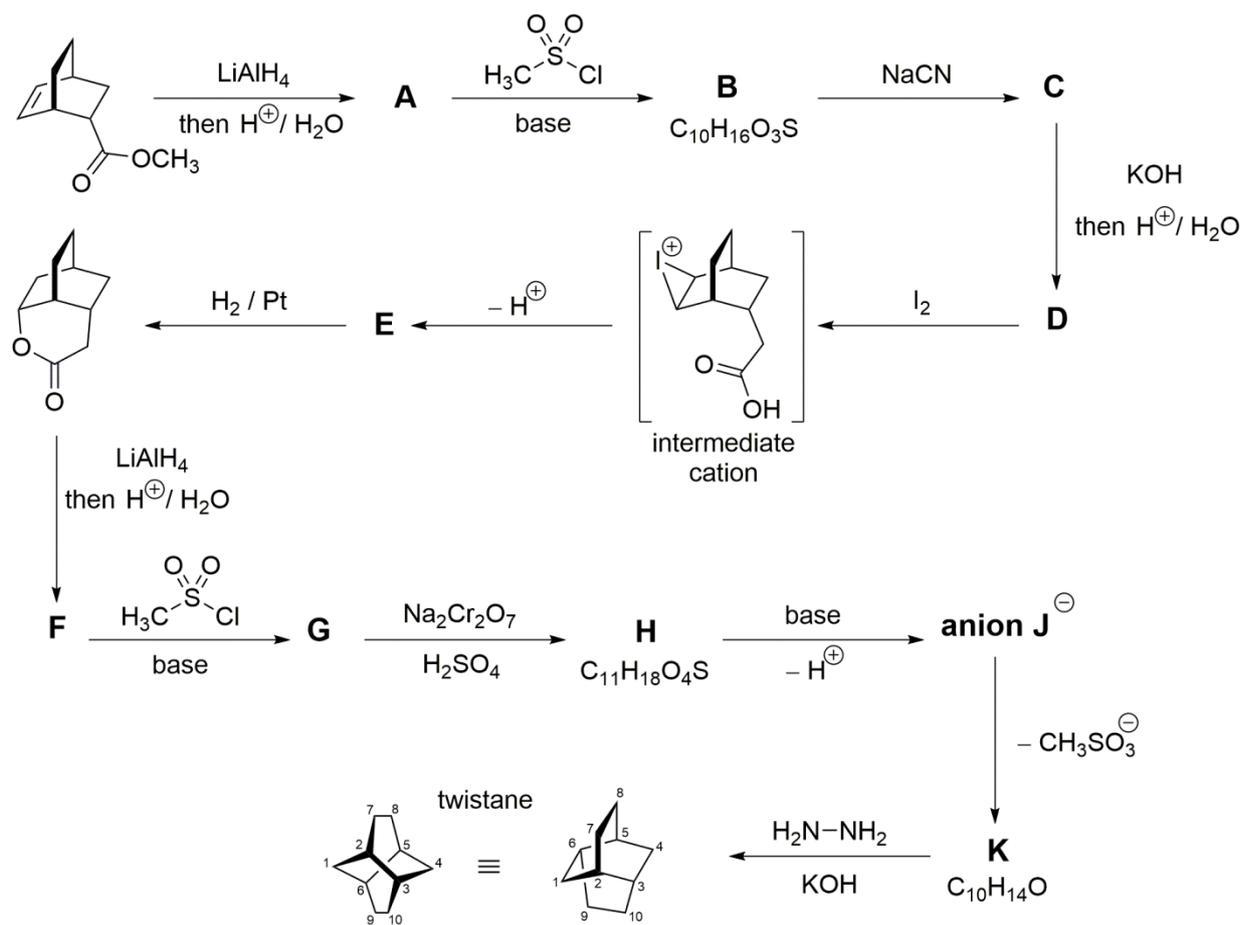
- (b) For each unique six-membered ring in adamantane, write down the numbers of the six carbon atoms in that ring in the order they are connected, beginning with the lowest number (e.g. -1-2-3-4-5-6-).
- (c) How many signals are there in the ^{13}C NMR spectrum of adamantane (i.e. how many unique environments of carbon are there)?

The molecule *twistane* can be visualised by the addition of a further four carbon atoms onto the twist-boat conformation of cyclohexane as shown below. In doing this other six-membered rings are created. In twistane all the six-membered rings are locked in the twist-boat conformation, which gives the molecule its name.



- (d) For each unique six-membered ring in twistane, write down the numbers of the six carbon atoms in that ring in the order they are connected, beginning with the lowest number (e.g. -1-2-3-4-5-6-).
- (e) How many signals are there in the ^{13}C NMR spectrum of twistane?
- (f) Adamantane and twistane are isomers of each other. What is their molecular formula?

As all its rings are in the lowest energy chair conformation, adamantane is a very stable molecule. It was discovered as a component of crude oil in 1933. By contrast, twistane is a very strained molecule as all its rings are in the higher energy twist-boat conformation. It must be specially synthesised, which was first done in 1962. The synthesis is shown below.



No C–C single bonds are broken in the synthesis and so those present in the starting material remain throughout. They have already been drawn in your answer booklet and you must use them for your answers for part (g).

- (g) Draw the structure of compounds **A–H**, anion **J[–]** and compound **K**.
- (h) Answer the following multiple choice questions in the answer booklet.
- (i) How many planes of symmetry does twistane contain?
- (ii) How many rotational axes of symmetry does twistane contain?
- (iii) Is twistane superimposable on its mirror image?

5. This question is about Superbases

The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have stronger bases.

For many years the strongest known base was the methyl anion, but in 2008 a team of scientists synthesised the lithium monoxide anion which was found to be an even stronger base.

2016 has seen the records rewritten again as Australian researchers announced the formation of an organic gas-phase dianion (DEB^{2-}) which has the highest proton affinity ever reported, i.e. is the strongest base.



How strong a base is may be defined by its proton affinity. The proton affinity of species X^- , $\text{PA}(\text{X}^-)$, is given by the standard enthalpy change of the reaction:



- (a) Using the data in the table below, calculate the proton affinity of the methyl anion, $\text{PA}(\text{CH}_3^-)$, in kJ mol^{-1} .

| | | |
|------------|--|----------------------------------|
| Reaction 1 | $\text{CH}_4 \longrightarrow \text{H}^\bullet + \text{CH}_3^\bullet$ | 439 kJ mol^{-1} |
| Reaction 2 | $\text{H}^\bullet \longrightarrow \text{H}^+ + \text{e}^-$ | $2.18 \times 10^{-18} \text{ J}$ |
| Reaction 3 | $\text{CH}_3^\bullet + \text{e}^- \longrightarrow \text{CH}_3^-$ | $-7.52 \text{ kJ mol}^{-1}$ |

With a proton affinity of 1778 kJ mol^{-1} , the lithium monoxide anion was found to be a stronger base than the methyl anion. The lithium monoxide anion is formed in a mass spectrometer when a lithium oxalate anion, LiC_2O_4^- , firstly loses a neutral molecule **P** of mass 44 and subsequently another neutral molecule **Q** of mass 28.

- (b) Draw the structure of the oxalate anion ($\text{C}_2\text{O}_4^{2-}$) and give the formulae for **P** and **Q**.

The organic gas-phase dianion (DEB^{2-}) has the highest proton affinity ever reported of 1843 kJ mol^{-1} . This dianion is produced from compound **A** which belongs to a family of disubstituted benzenes, $\text{C}_6\text{H}_4\text{R}_2$, where both substituents R are the same. Compound **A** has the molecular formula $\text{C}_{12}\text{H}_6\text{O}_4$ and effervesces on addition of sodium hydrogen carbonate.

- (c) Suggest the functional group present in R responsible for the effervescence, and hence deduce a structure for R.
- (d) Draw all of the possible disubstituted benzenes, $\text{C}_6\text{H}_4\text{R}_2$, and state the number of signals you would expect in the ^{13}C NMR for each.

DEB^{2-} was observed in the negative-ion mass spectrum of Compound **A**. It is formed via species B^{2-} and C^{2-} . Compound **A** is found to have 6 signals in its ^{13}C NMR spectrum.



- (e) Determine the structures of intermediates B^{2-} and C^{2-} , and DEB^{2-} .

Acknowledgements & References

Q2

National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division

http://www.esrl.noaa.gov/gmd/dv/data/?parameter_name=Methyl%2BChloroform&frequency=Discrete&site=Multiple

NASA, JPL

<http://jpldataeval.jpl.nasa.gov/download.html>

Q3

The image is © Brendan HunteriStock.

High hardness in the biocompatible intermetallic compound β -Ti₃Au.

E. Svanidze et al Science Advances, 20July 2016

<http://advances.sciencemag.org/content/2/7/e1600319.full>

Q4

Tricyclo[4.4.0.03.8]Decane

H. W. Whitlock, *J. Am. Chem. Soc.*, 1962, 84 (17), pp 3412–3413

Q5

Preparation of an ion with the highest calculated proton affinity

B. L.J.Poad et al. *Chem. Sci.*, 2016, 7, 6245-6250