C 3 L 6

Cambridge Chemistry Challenge Lower 6th

June 2011

Some of the material in this booklet might be familiar to you, but other parts may be completely new. The questions are designed to be more challenging than those on typical AS papers, but you should still be able to attempt them. Use your scientific skills to work through the problems logically.

If you do become stuck on one part of a question, other parts might still be accessible, so do not give up. Good luck!

- The time allowed is 90 mins.
- Attempt all the questions.
- Write your answers in the answer booklet provided, giving only the essential steps in any calculations.
- Specify your answers to the appropriate number of significant figures and give the correct units.
- Please do not write in the right-hand margin.
- A periodic table is included in this booklet.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1 1.008																	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01											**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											**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															

symbol
atomic number
relative atomic mass

***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

1. This question is about molecules with the formula C_3L_6

By tradition, the symbol "L" is sometimes used in chemistry when looking at reactions which compare compounds with "normal" hydrogen (the isotope ^{1}H) with those containing deuterium (the isotope ^{2}H). For example, CF_3OL would refer to either the compound $CF_3O^{1}H$ or to $CF_3O^{2}H$.

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For the remainder of this question, assume that "hydrogen" and the symbol "H" refer only to the isotope ^{1}H, and deuterium and the symbol "D" refer only to the isotope ^{2}H.

(a) There are two compounds with the formula C_3H_6. Give their names and the particular class of compounds each belongs to.

Like every other member in its class, one isomer of C_3H_6, isomer **A**, reacts rapidly with bromine to form a single product. When **A** reacts with bromine compound **F** is formed.

(b) Draw the structure for **A** and the product formed when it reacts with bromine, **F**.

The second isomer of C_3H_6, isomer **B**, has a number of unique properties. The other members in the same class of compounds only react with bromine in the presence of light and form HBr as a side product. However, **B** reacts with bromine in the absence of light (but much less rapidly than **A**) and forms a single compound **G**. **F** and **G** are isomers.

(c) Draw the structure for **B** and the product formed when it reacts with bromine, **G**.

The standard enthalpies of formation, $\Delta_f H^{\ominus}$, of both **A** and **B** have been found by first measuring the standard enthalpies of combustion, $\Delta_c H^{\ominus}$, of each. These values are given in the table below, together with the standard enthalpies of combustion of carbon and hydrogen.

	A	**B**	carbon	hydrogen
$\Delta_c H^{\ominus}$ / kJ mol^{-1}	–2058	–2091	–393.5	–241.8

(d) (i) Give the equation for the complete combustion of C_3H_6.

(ii) Calculate the standard enthalpy of formation of **A**.

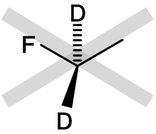
(iii) Calculate the standard enthalpy of formation of **B**.

Gaseous **B** needs to be stored carefully since it can convert explosively to the elements, to isomer **A**, or to other hydrocarbons.

(e) Calculate the standard enthalpy change for the reaction **B** $\longrightarrow$ **A**.

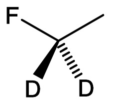
In order to investigate the mechanism for the conversion of reaction **B** $\longrightarrow$ **A**, samples of the compounds have been prepared with some of the normal hydrogen replaced by deuterium. When drawing structures for the rest of the question use skeletal formulae and so do not explicitly draw in any hydrogen atoms, but do show any deuterium atoms. Also, remember that the four single bonds around a carbon atom are arranged tetrahedrally. Examples of how to draw structures correctly are shown below for two isomers of $C_2H_3D_2F$.

I



Structure **I** is incorrectly drawn. The bold bond comes out of the plane of the paper, the hashed bond goes in, but the bonds do not form a proper tetrahedral shape.

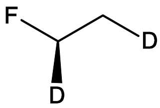
II



CD_2FCH_3

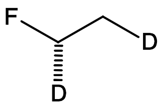
Structure **II** is drawn correctly. In this compound, both deuterium atoms are in the same environment.

III



$CDFHCH_2D$

IV



$CDFHCH_2D$

Structures **III** and **IV** are correctly drawn. In each compound the deuterium atoms are in different environments.

Structures **III** and **IV** are non-superimposable mirror images (called enantiomers). Each contains a carbon with four different atoms or groups attached.

Replacing one of the hydrogens in compound **A** or **B** with a deuterium gives compounds of formula C_3H_5D.

(f) **(i)** Draw the structure(s) of the all the compound(s) that could be formed when one H in **A** is replaced by a D.

(ii) Draw the structure(s) of the all the compound(s) that could be formed when one H in **B** is replaced by a D.

If two of the hydrogens in **A** are replaced with deuterium seven structures with formula $C_3H_4D_2$ are possible. These isomers are labelled **A1**, **A2**, **A3**, **A4**, **A5**, **A6**, and **A7**.

In isomer **A1**, the two deuteriums are in exactly the same environment. For all the other isomers, the two deuteriums are in different environments.

(g) Draw the structure of **A1**.

All the isomers **A1**-**A7** react with deuterium gas (D_2) in the presence of a metal catalyst adding two deuteriums to the molecule and giving isomers with the formula $C_3H_4D_4$. During this process, some of the isomers **A1**-**A7** form a single compound. Other isomers produce a pair of compounds (called enantiomers), each of which are non-superimposable mirror images containing a carbon atom with four different substituents attached.

On deuteration, **A1** gives a pair of enantiomers **X1** and **X2**.

(h) Draw the structures of **X1** and **X2** (you are not required to say which is which).

Compounds **A2** and **A3** also form the compounds **X1** and **X2** on deuteration.

(i) Draw the structures of **A2** and **A3** (you are not required to say which is which).

A4 and **A5** give the same single compound **Y** on deuteration.

(j) (i) Draw the structure of **Y**.

(ii) Draw the structures of **A4** and **A5** (you are not required to say which is which).

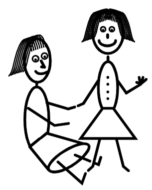
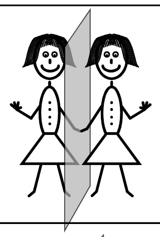
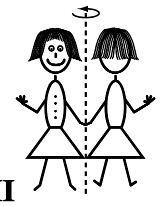
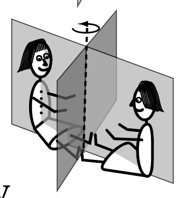
A6 forms the single compound **Z** on deuteration.

(k) Draw the structures of **A6** and **Z**.

Compound **A7** also forms a pair of enantiomers on deuteration, but they are different from **X1** and **X2**.

(l) Draw the structure of **A7**.

It can be useful to classify molecules by the type of symmetry they contain. Molecules may or may not contain a plane of symmetry and they may or may not contain rotational symmetry. A person has a plane of symmetry, but no rotational symmetry. Two identical twins can be arranged in different ways that exhibit different symmetries as shown below.

	NO plane of symmetry	Plane of symmetry
NO rotational symmetry	 **I**	 **II**
Rotational symmetry	 **III**	 **IV**

Arrangement **I** has no symmetry.

Arrangement **II** has a plane of symmetry, but no rotational symmetry.

Arrangement **III** has rotational symmetry, but no plane of symmetry.

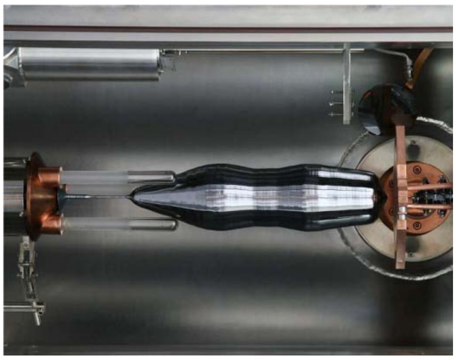
Arrangement **IV** has rotational symmetry, and planes of symmetry.

When two of the hydrogens in compound **B** are replaced with deuterium, a number of isomers of formula $C_3H_4D_2$ can be produced.

(m) In the answer book draw all of these isomers in the appropriate place on the symmetry table.

2. This question is about "The Avogadro Project"

In January 2011 the results were published of the Avogadro Project – the most accurate determination ever of the Avogadro constant. This international project involved counting the number of atoms in a perfectly spherical, single crystal of isotopically-enriched silicon.



The source of the silicon was the compound Na_2SiF_6. This compound contains one negatively charged ion and all the fluorines are in the same environment.

(a) (i) What is the oxidation state of the silicon in Na_2SiF_6?

(ii) What shape do you expect for the anion contained in Na_2SiF_6?

(b) On heating to over 300 °C, Na_2SiF_6 decomposes to form a white crystalline solid **W** and a colourless gas, **X**, which contains silicon.

(i) Give the formula for **W**.

(ii) Give the formula for colourless gas **X**. What shape do you expect this to be?

(iii) Give the equation for the formation of **W** and **X** from Na_2SiF_6.

The gas **X** was passed through a series of gas centrifuges in order to enrich the silicon-28 isotope. After enrichment, it was reacted with calcium hydride at 180 °C. This formed a new crystalline solid **Y** and another colourless gas containing silicon, **Z**. Air must be rigorously excluded since on exposure to the air, gas **Z** spontaneously ignites.

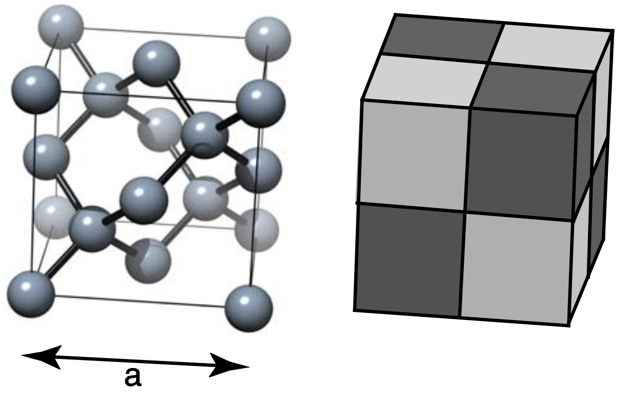
(c) (i) Give the formulae for **Y** and **Z** and an equation for their formation from calcium hydride and **X**.

(ii) Give an equation for the combustion of gas **Z** in air.

(d) Gas **Z**, containing the enriched silicon-28 is converted to solid silicon by thermal decomposition at temperatures around 800 °C. The by-product of this reaction is another colourless gas, which is flammable in air (but not spontaneously flammable).

Give the equation for the thermal decomposition of **Z**.

From the lump of isotopically enriched silicon, a single crystal of silicon-28 was grown. The structure on the left shows the repeating pattern, or unit cell, for silicon. By stacking these cubes together, the structure of the solid is revealed. Atoms that are directly bonded to one another are connected by the bonds (the heavier lines). In the unit cell, silicon atoms are placed with their centres at each corner of the cube, and in the centre of each face. If we divide the unit cell into eight smaller cubes, as shown on the right, there is also one silicon atom right in the middle of every alternate cube (the darker shaded ones).



The length of the cube is **a** pm (1 pm = 1×10^{-12} m). The total number of silicon atoms contained within the cube is denoted **n**. The single crystal was fashioned into a perfect sphere of volume **V** cm^3, and mass **m** g. The relative atomic mass of silicon is $\mathbf{A_r}$.

(e) (i) By counting up the contributing fractions, calculate a value for **n**, the number of number of silicon atoms per unit cell.

(ii) Give an expression for the number of atoms in the sphere in terms of **a**, **n**, and **V**. Take care with the units!

(iii) Give an expression for the Avogadro constant in terms of **a**, **n**, **V**, $\mathbf{A_r}$, and **m**.

(f) By considering the atoms within one of the smaller cubes, or otherwise, derive an expression for the Si–Si bond length in terms of distance **a**.

In the experiment, the silicon was isotopically enriched in silicon-28. Analysis of the sample showed the fraction of silicon atoms that were ^{29}Si was 41.2×10^{-6} and the fraction that were ^{30}Si was 1.3×10^{-6}. The remainder is assumed to be silicon-28.

(g) Given the following accurate masses, determine the relative atomic mass, $\mathbf{A_r}$, for this sample of silicon.

Isotope	^{28}Si	^{29}Si	^{30}Si
Relative isotopic mass	27.97692653	28.97649470	29.97377017

(h) The volume of the sphere, **V**, used in the experiment was 431.059060 cm^3 and its mass, **m**, was 1000.087559 g. The length of the unit cell, **a**, as determined from the crystal structure was 543.0996234 pm. Use these values together with your values for **n** and $\mathbf{A_r}$ to calculate the Avogadro constant to 9 significant figures.

Acknowledgements

C3L6 would like to thank our sponsors:

University of Cambridge International Examinations

University of Cambridge Department of Chemistry

St Catharine's College, Cambridge

Question 2 was based on the papers:

Measurement Science and Technology, **17**, (2006) 1854-1860
"*Large-scale production of highly enriched* ^{28}Si *for the precise determination of the Avogadro constant*" by P. Becker *et al*.

Physical Review Letters, **106**, (Jan 2011) 030801
"*Determination of the Avogadro Constant by Counting the Atoms in a* ^{28}Si *Crystal*" by B. Andreas *et al*.

The picture of the crystal of silicon being grown is taken, with permission, from the PRL paper.

The photograph of the silicon sphere is used courtesy of CSIRO – Australian Centre for Precision Optics.