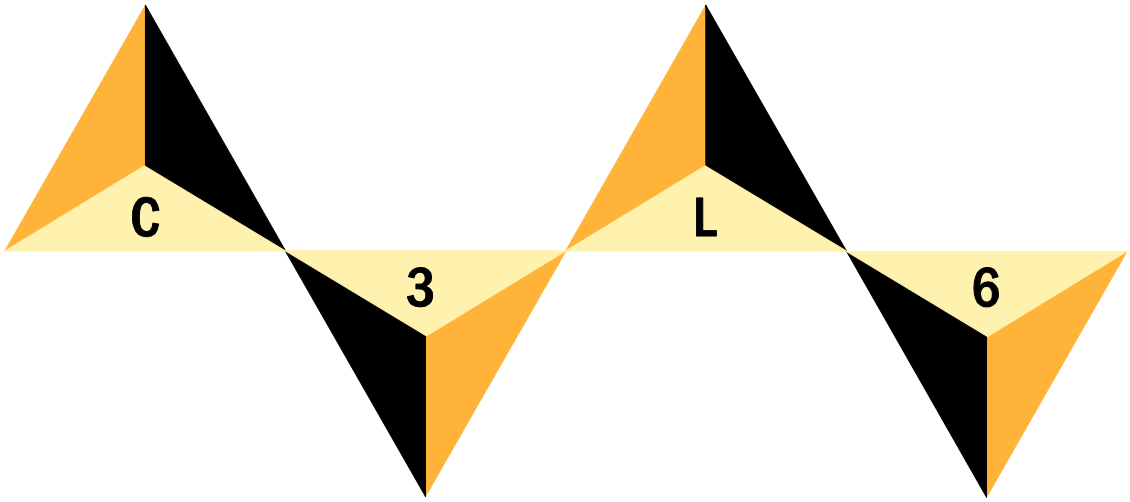



# Cambridge Chemistry Challenge Lower 6th

## June 2023

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 A-level 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 minutes under exam conditions.
- 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 and necessary constants are included on the next page.

| Period | 1 | 2 | | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | s-block | | | d-block | | | | | | | | | | p-block | | | | | |
| 1 | **H** 1 1.008 | | | | | | | | | | | | | | | | | | **He** 2 4.003 |
| 2 | **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 |
| 3 | **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 |
| 4 | **K** 19 39.10 | **Ca** 20 40.08 | | **Sc** 21 44.96 | **Ti** 22 47.87 | **V** 23 50.94 | **Cr** 24 52.00 | **Mn** 25 54.94 | **Fe** 26 55.85 | **Co** 27 58.93 | **Ni** 28 58.69 | **Cu** 29 63.55 | **Zn** 30 65.38 | **Ga** 31 69.72 | **Ge** 32 72.63 | **As** 33 74.92 | **Se** 34 78.97 | **Br** 35 79.90 | **Kr** 36 83.80 |
| 5 | **Rb** 37 85.47 | **Sr** 38 87.62 | | **Y** 39 88.91 | **Zr** 40 91.22 | **Nb** 41 92.91 | **Mo** 42 95.95 | **Tc** 43 | **Ru** 44 101.07 | **Rh** 45 102.91 | **Pd** 46 106.42 | **Ag** 47 107.87 | **Cd** 48 112.41 | **In** 49 114.82 | **Sn** 50 118.71 | **Sb** 51 121.76 | **Te** 52 127.60 | **I** 53 126.90 | **Xe** 54 131.29 |
| 6 | **Cs** 55 132.91 | **Ba** 56 137.34 | * | **Lu** 71 174.97 | **Hf** 72 178.49 | **Ta** 73 180.95 | **W** 74 183.84 | **Re** 75 186.21 | **Os** 76 190.23 | **Ir** 77 192.22 | **Pt** 78 195.08 | **Au** 79 196.97 | **Hg** 80 200.59 | **Tl** 81 204.38 | **Pb** 82 207.2 | **Bi** 83 208.98 | **Po** 84 | **At** 85 | **Rn** 86 |
| 7 | **Fr** 87 | **Ra** 88 | + | **Lr** 103 | **Rf** 104 | **Db** 105 | **Sg** 106 | **Bh** 107 | **Hs** 108 | **Mt** 109 | **Ds** 110 | **Rg** 111 | **Cn** 112 | **Nh** 113 | **Fl** 114 | **Mc** 115 | **Lv** 116 | **Ts** 117 | **Og** 118 |

*Group Number*

**Symbol**
atomic number
mean atomic mass

f-block

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanoids: | * | **La** 57 138.91 | **Ce** 58 140.12 | **Pr** 59 140.91 | **Nd** 60 144.24 | **Pm** 61 | **Sm** 62 150.36 | **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** 70 173.05 |
| Actinoids: | + | **Ac** 89 | **Th** 90 232.04 | **Pa** 91 231.04 | **U** 92 238.03 | **Np** 93 | **Pu** 94 | **Am** 95 | **Cm** 96 | **Bk** 97 | **Cf** 98 | **Es** 99 | **Fm** 100 | **Md** 101 | **No** 102 |

The Avogadro constant $N_A = 6.022 \times 10^{23}$ mol$^{-1}$

## 1. This question is about electron counting and curly arrows

It could be said that chemistry is all about electrons since bonding interactions are formed as electrons are transferred or shared between atoms. During chemical reactions, electrons are redistributed between different atoms as bonds are made and broken. At all stages, all electrons must be accounted for – electrons are never created or destroyed in chemical reactions.

If an isolated atom has the same total number of electrons as its atomic number, it is a neutral atom; otherwise, it is a charged ion. Only electrons in the outermost shell, the so-called valence shell, are used in bonding. The number of electrons in the valence shell for a neutral atom, $N_{neutral}$, is equal to the Group Number for elements in Groups 1 to 12 of the periodic table, and (Group Number minus 10) for elements in Groups 13 to 18.



Chemists love curly arrows. Yum, yum!

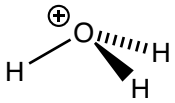
**(a) (i)** How many valence electrons do each of the following atoms have?

Cl Sr Nb Xe

**(ii)** How many valence electrons do each of the following ions have?

$S^{2-}$ $O^{+}$ $N^{+}$ $Tl^{+}$ $B^{3+}$ $Na^{-}$

In molecules, individual atoms may often be shown with charges, such as on the oxygen in $H_3O^+$:



Such charges are known as *formal charges*. They are a result of how we allocate the electrons within the species. If it is assumed that each bond represents a pair of electrons shared equally between two atoms, the oxygen atom in $H_3O^+$ has three electrons used in bonds to the hydrogen atoms, and so together with a lone pair, the oxygen formally has five electrons around it. (To clarify, a shared pair of electrons counts as one electron to each atom, whereas for a lone pair, both electrons are with the atom concerned.) Since an oxygen atom needs six electrons in its valence shell to be neutral, if it formally has five, it must have a charge of +1.

The problem with this model is the assumption that the electrons are shared equally between two atoms – they are not. Since oxygen is more electronegative than hydrogen, the electrons in each O–H bond are more associated with the oxygen rather than the hydrogens. In fact, calculations suggest the oxygen atom in $H_3O^+$ actually has a slight negative charge.

**(b)** Which of the following BEST describes the charge on EACH hydrogen atom in $H_3O^+$?

i) just less than +1 ii) +1 exactly

iii) at least +1 iv) just less than + 1/3

v) +1/3 exactly vi) at least +1/3

We can calculate the formal charge for any atom by comparing how many electrons an atom X actually has in its valence shell, $N_X$, and subtracting it from the number the neutral atom X needs in its valence shell, $N_{neutral}$:

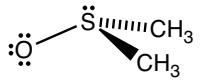



$$\text{Formal charge} = N_{neutral} - N_X$$

where we calculate $N_X$ by summing up one electron for each bond to X (two for each double bond, and three for each triple bond), and two for every lone pair on atom X.

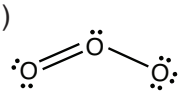
**(c)** Add the formal charges to the non-neutral atoms in the following structures. (All lone pairs have been shown.)

(i)



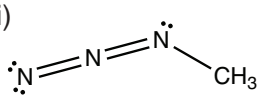
dimethyl sulfoxide
(a common solvent)

(ii)



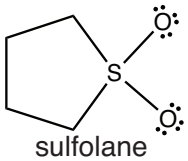
ozone

(iii)



methyl azide
(explosive solid)

(iv)

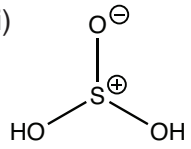


sulfolane
(an organic solvent)

In practice, formal charges would usually be shown on structures and this might be used to calculate how many lone pairs atoms would have if drawn in that way.

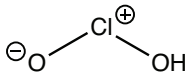
**(d)** Add all the lone pairs to every atom in each of the following structures. (Note the shapes given are not necessarily representative of their real shapes.)

(i)



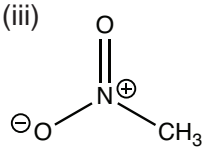
sulfuric(IV) acid

(ii)



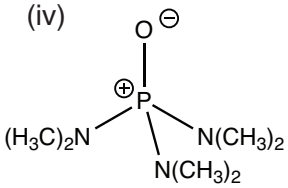
chloric(III) acid

(iii)



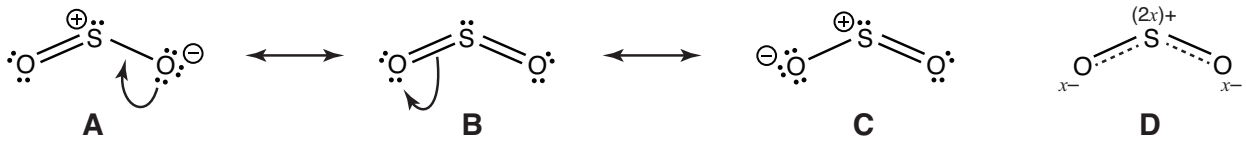
nitromethane

(iv)



HMPA

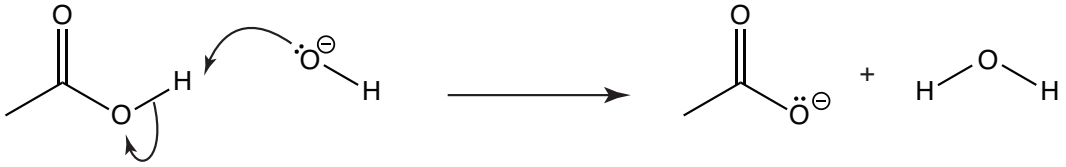
There are often different ways of drawing structures depending on how we consider the electrons to be allocated. There are pros and cons with the different ways, for example, some structures may suggest unrealistic charges (like in $H_3O^+$), others structures may break the '8-electron rule'. Curly arrows may be used to formally show 'movement' of electrons, or how it is possible to interconvert structures. The arrow starts where the electrons are (e.g. on a lone pair, or in a bond), and the head shows where the electron pair ends up – usually on an atom as a lone pair, or between two atoms as a new bond. An example for sulfur(IV) oxide is shown below.



**A** **B** **C** **D**

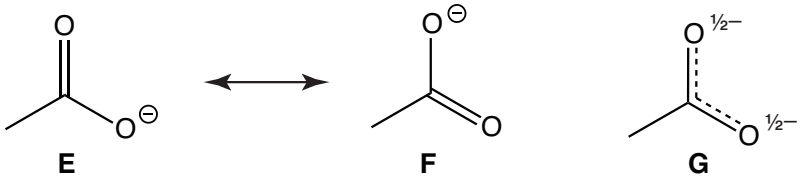
The curly arrows show how to reallocate electrons to convert a structure to the one to the right of it. The special double-headed straight arrow is used to indicate that the structures are the same but just with their electrons distributed in a different way. Structures **A** and **C** must make an equal contribution to how the real molecule is since they are the same but reflected. This suggests each S-O bond is perhaps between a single and a double bond, and the charge on each oxygen is actually the same (as suggested in **D**). Structure **B** shows a different way of assigning the electrons, but suggests there are more than 8 electrons around the sulfur (10). This is acceptable for elements from Period 3 in the Periodic Table and below, but not for elements from Period 2.

Curly arrows are particularly useful for understanding the redistribution of electrons during chemical reactions. For example, consider the reaction between hydroxide ion and ethanoic acid:



(Note that lone pairs are only shown as necessary – not all are shown.)

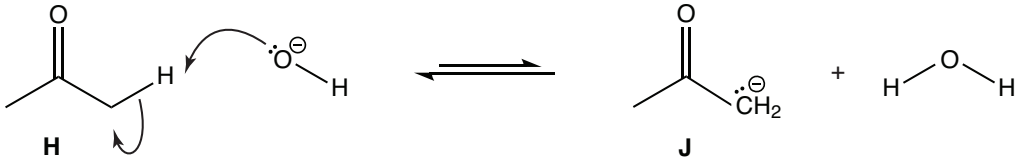
It turns out that the two C–O bonds in the ethanoate ion are equal in both length and strength. We can show this by formally redistributing the electrons from structure **E** to structure **F**. In reality, the ion is more like **G** with equal charges on the oxygens (but not exactly one half each since the oxygens still pull more electron density from the carbons and even the hydrogen atoms in the ion).



**E** **F** **G**

**(e)** In your answer booklet, draw the curly arrows and any necessary lone pairs to convert structure **E** to structure **F**.

Hydroxide ion can also deprotonate propanone, **H**, to form the enolate ion **J**:



**H** **J**

The enolate ion is better represented with the negative charge on the oxygen rather than on the carbon.

**(f)** **(i)** Use curly arrows to show how **J** may be converted to a form with the charge on oxygen. (You will also need to draw the structure of the form with the charge on oxygen.)

**(ii)** How do you think the C–O bond strength in the enolate ion compares with that in the ketone?

Same Stronger Weaker

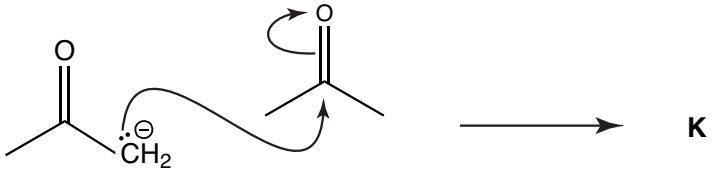
**(iii)** How do you think the (carbonyl-C)–$CH_2$ bond strength in the enolate ion compares with that in the ketone?

Same Stronger Weaker

**(iv)** Even though there is more electron density in total on the oxygen, most of the time the enolate ion acts as a nucleophile attacking from carbon. Circle the best reason for this.

**A** Oxygen is more electronegative than carbon
**B** The electrons on carbon are higher in energy than those on oxygen
**C** The electrons on carbon are lower in energy than those on oxygen

The enolate ion can even act as a nucleophile and attack some unreacted propanone:



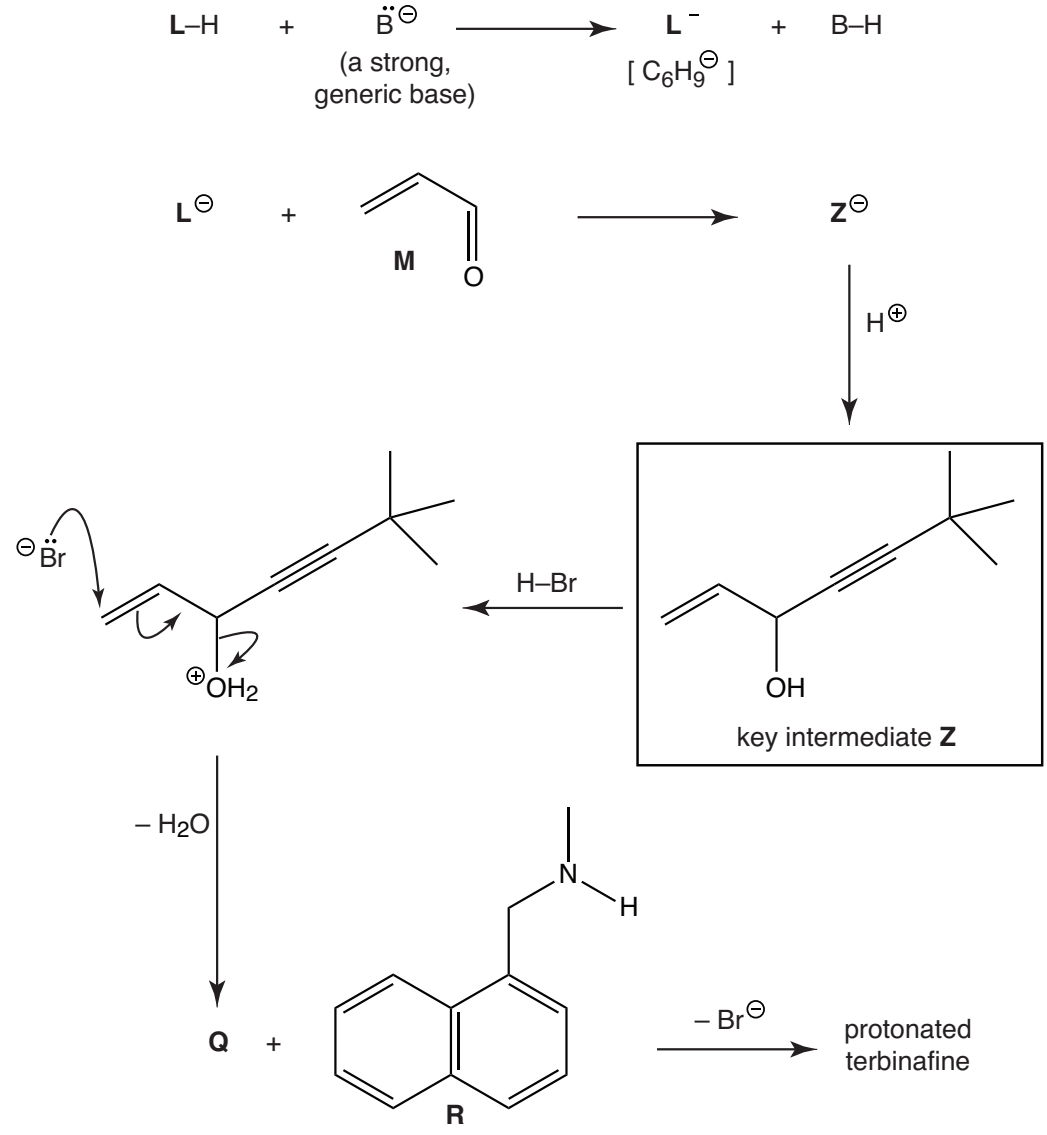
**K**

**(v)** Draw the structure of the product **K**.

We can use curly arrows to help understand this simple synthesis of the drug terbinafine, the active ingredient in products such as Lamisil™, used in treating athlete's foot.




The synthesis starts with a hydrocarbon, denoted **L**–H, which is deprotonated using a strong base to form anion $\mathbf{L}^-$ (with formula $C_6H_9^-$). $\mathbf{L}^-$ then reacts with acrolein, **M**, to initially form anion $\mathbf{Z}^-$ which is then protonated to form the key intermediate, **Z** (shown below). **Z** reacts with acid HBr to form compound **Q,** losing water in the process. In the final step, **Q** reacts with **R** to form protonated terbinafine.




**(g)** **(i)** Give the structure of **L**–H and draw a curly arrow mechanism for the formation of $\mathbf{L}^-$.

**(ii)** Draw a curly arrow mechanism for the reaction between of $\mathbf{L}^-$ and **M** to give $\mathbf{Z}^-$ (the structure of $\mathbf{Z}^-$ should also be drawn out, of course).

**(iii)** Give the structure of **Q**.

**(iv)** Draw a curly arrow mechanism for the reaction between **Q** and **R**, and hence draw the structure of protonated terbinafine.

## 2. This question is about the crazy chemistry of bismuth.

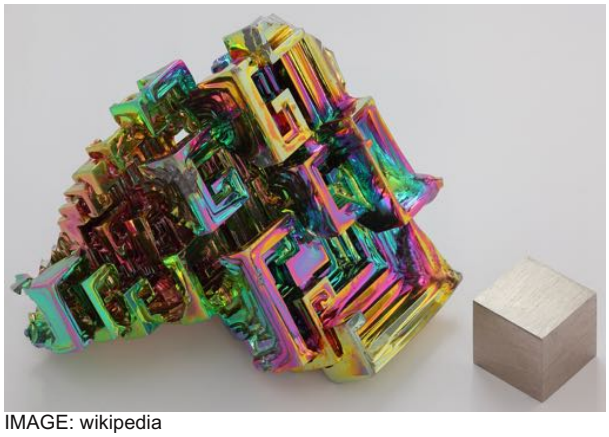


IMAGE: wikipedia

Bismuth, Bi, is a particularly fascinating element. Directly underneath two poisonous elements arsenic and antimony in Group 15, and coming after the toxic elements mercury, thallium and lead in Period 6, and before the dangerously radioactive elements in the periodic table, bismuth metal has been used as a 'safe' and even 'healthy' alternative to lead, for example in fishing weights and even shotgun pellets. The metal crystallises in artificial-looking step-shapes, often with beautiful iridescent colours due to a thin layer of oxide.

**(a) (i)** When heated in a flow of chlorine gas, bismuth forms bismuth(III) chloride. Give the equation for this reaction.

**(ii)** Predict in which of the following ranges you expect the bond angle in gaseous bismuth(III) chloride to fall:

a) 95º–108º b) 108º–110º c) 110º–119º d) 119º–121º e) >121º

**(iii)** When heated to redness in air, bismuth burns with a blue flame to give an oxide containing 89.70% bismuth. Give the formula for this oxide. What is the oxidation state of the bismuth in this oxide?

**(iv)** What do you predict the maximum oxidation state of bismuth to be?

**(v)** Bismuth only forms one simple halide in which the bismuth is in its maximum oxidation state. Give the formula of this compound.

For many years bismuth was thought to be the last non-radioactive element in the periodic table, but calculations suggested this ought not be the case. Finally, in 2003, researchers detected the emission of an alpha particle (a helium nucleus) from bismuth-209 and determined its half-life to be an incredible $2.01\times10^{19}$ years (over a billion times the age of the universe). This means you would have to wait about 25 minutes* for one atom in a mole of Bi to have a 50% chance of decaying!

**(b)** Which isotope is formed when bismuth-209 emits an alpha-particle?

When bismuth(III) chloride is reacted with methyl magnesium iodide, $CH_3MgI$, trimethyl bismuthane, $Bi(CH_3)_3$, is formed as a colourless oil which spontaneously combusts in air. Remarkably, this reactive liquid is currently being investigated for use in ionization detectors for use in Positron Emission Tomography to produce high-resolution images of brains. The standard enthalpy change of combustion, $\Delta_cH^o$, has been measured for liquid $Bi(CH_3)_3$.

**(c) (i)** Give the equation for the complete combustion of $Bi(CH_3)_3$.

**(ii)** Use the data below to calculate the standard enthalpy change of formation of $Bi(CH_3)_3(l)$.

$\Delta_cH^o$ [ $Bi(CH_3)_3(l)$ ] = –2912 kJ mol$^{-1}$ $\Delta_fH^o$ [ $CO_2(g)$ ] = –394 kJ mol$^{-1}$

$\Delta_fH^o$ [ $H_2O(l)$ ] = –286 kJ mol$^{-1}$ $\Delta_fH^o$ [ $Bi_2O_3(s)$ ] = –574 kJ mol$^{-1}$

*We thought about asking you to calculate this, but our brains fried trying to work it out ourselves…

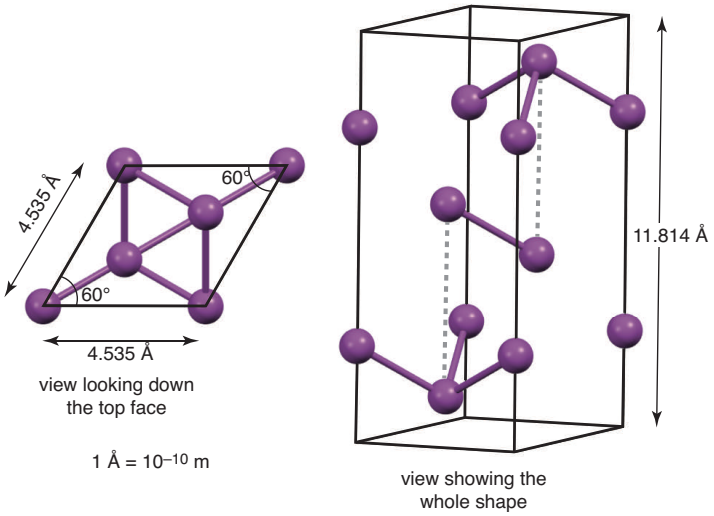
**(d) (i)** Use the following data to derive an algebraic expression for the average Bi–$CH_3$ bond strength, $\boldsymbol{x}$, in $Bi(CH_3)_3(g)$. Your expression should be in terms of the quantities $\boldsymbol{a} - \boldsymbol{f}$ and you should indicate the coefficients for each of these quantities in your answer booklet.

| thermodynamic quantity | symbol | value / kJ $mol^{-1}$ |
|---|---|---|
| $\Delta_f H^\circ$ [ $Bi(CH_3)_3(l)$ ] | $\boldsymbol{a}$ | from **(c)(ii)** |
| $\Delta_f H^\circ$ [ $CH_4(g)$ ] | $\boldsymbol{b}$ | –75 |
| $\Delta_v H^\circ$ [ $Bi(CH_3)_3(l)$ ] | $\boldsymbol{c}$ | 35 |
| $\Delta_{at} H^\circ$ [ $H_2(g)$ ] | $\boldsymbol{d}$ | 218 |
| $\Delta_{at} H^\circ$ [ $Bi(s)$ ] | $\boldsymbol{e}$ | 208 |
| C–H bond strength in $CH_4(g)$ | $\boldsymbol{f}$ | 429 |

$\boldsymbol{x}$ = ☐ $\boldsymbol{a}$ ☐ $\boldsymbol{b}$ ☐ $\boldsymbol{c}$ ☐ $\boldsymbol{d}$ ☐ $\boldsymbol{e}$ ☐ $\boldsymbol{f}$ kJ $mol^{-1}$

**(ii)** Use your value from **(c)(ii)** and the values of $\boldsymbol{b} - \boldsymbol{f}$ to calculate the Bi–$CH_3$ bond strength.

It is relatively easy to grow beautiful crystals of bismuth since it is one of the few elements whose solid form is less dense than its liquid form. In other words, like ice on water, solid Bi floats on top of liquid Bi.




Shown above is the unit cell for Bi. The 3-D shape outlined in black is called a *right rhombic prism* which consists of 4 rectangular faces, and two faces which are rhombi. How the Bi atoms are arranged in the solid structure is generated by stacking the unit cells directly on top of each other in 3-dimensions. Some of the atoms indicated in the unit cell are only partially within the cell, but when they stack together, the full atom is formed. The two pairs of atoms connected by the dotted lines lie directly on top of each other when viewed from above (as do pairs of atoms on each of the long edges). You should not worry about the 'bonds' connecting atoms – they just indicate the immediate closest neighbours within the cell.

**(e) (i)** By considering how any partial fragments add together, what is the total number of bismuth atoms contained within 1 unit cell?

**(ii)** Calculate the mass in g of the atoms contained in 1 unit cell.

**(iii)** Calculate the volume in **both** $Å^3$ **and** $cm^3$ of the unit cell.

**(iv)** Hence calculate the density of solid bismuth in g $cm^{-3}$.

$BiCl_3$ reacts with water to form bismuth oxychloride, BiOCl, sometimes knows as pearl-white. Pearl-white used to be used to whiten people's faces in times gone by, and is still used today in some makeups. The compound is remarkably non-toxic – in one study rats* fed 5% BiOCl for 2 years showed no ill effects from it!

A story relates how one bewhitened lady who entered the hydrogen sulfide-containing bath waters at Harrogate was shocked when suddenly her makeup went from white to black. This would be due to the formation of bismuth(III) sulfide.



Fig. 234. Lady at her Toilette applying the "Pearl-white" with a Hare's-foot.

**(f)** **(i)** Give an equation for the formation of bismuth oxychloride from $BiCl_3$.

**(ii)** Give an equation for the reaction that shocked the lady in the Harrogate waters. (Hint: this is not a redox reaction.)

When bismuth metal is dissolved in molten bismuth(III) chloride, a new compound (**Z**) is formed that is 83.48% bismuth, by mass. **Z** was once incorrectly called bismuth monochloride. When **Z** is analysed by X-ray crystallography, it is found that the unit cell has a relative formula mass of 6008.12.

**(g)** **(i)** Calculate the empirical formula of compound **Z**.

**(ii)** Calculate the total formula of the unit cell.

Examination of the X-ray crystal structure shows that all the chlorine atoms are contained within bismuth-chlorine species that have the formula $[Bi_2Cl_8]^l$ or $[BiCl_5]^m$ where $l$ and $m$ are the charges of these species. The bismuth atoms not in the two Cl-containing ions are contained within two identical cations, $[Bi_p]^{n+}$.

**(iii)** Assuming that each Bi has an oxidation state of +3, and each chlorine, –1, calculate the values of the charges $l$ and $m$.

**(iv)** Given the total formula of the species contained within the unit cell, write the formula of compound **Z** in the form $(Bi_p)_2(Bi_2Cl_8)_q(BiCl_5)_r$.

**(v)** What is the formula, including charge, of the $[Bi_p]^{n+}$ ion?

**(vi)** Write a balanced equation for the reaction that occurs when bismuth metal dissolves in molten bismuth(III) chloride to give compound **Z**.

* No rats were harmed in the writing of this question.

## Acknowledgements

We would like to thank those who support C3L6:

University of Cambridge Yusuf Hamied Department of Chemistry

St Catharine's College, Cambridge

Cambridge Chemistry Challenge Ltd.