Cambridge Chemistry Challenge Lower 6th

June 2024

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.

Periodic Table

Group Number

Symbol
atomic number
mean atomic mass

Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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

s-block, p-block, d-block, 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 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

1. This question is about arsenic

Arsenic, As, is an element in Group 15 of the periodic table. Arsenic occurs in nature in various minerals, including the sulfides orpiment and realgar, and in arsenopyrite, FeAsS, but the most important commercial compound is the very poisonous arsenic(III) oxide – also called arsenic trioxide.

Whilst less than 0.1 g of arsenic trioxide taken orally can be fatal, it is used as a medicine to treat cancer. Even more remarkable, if regular small doses are taken, it is possible to become accustomed to the poison and doses of 0.5 g can be tolerated. In days gone by, this was practised in the Alpine region of Styria and when the graves of such arsenic-eaters were dug up, the bodies were found to be perfectly preserved; this has been suggested as a possible origin of the vampire myth…

Fig. 231. Arsenic-eaters of Styria.

The Arsenic-eaters of Styria.

(a) (i) Give the full electron configuration of arsenic.

(ii) Suggest the highest and lowest possible oxidation states of arsenic.

(iii) Which TWO elements from the periodic table would you expect to be likely to form binary compounds (i.e. compounds containing two different elements only) with arsenic in its HIGHEST oxidation state?

(iv) Give the formula for these two compounds.

(v) Which Group from the periodic table has elements most likely to form a binary compound of arsenic in its LOWEST oxidation state.

(vi) Suggest the formula for a compound of arsenic in its LOWEST oxidation state.

In the gas phase, arsenic can form molecules with the formula As_2 and As_4, depending on the temperature. In the non-planar As_4 molecule, all the bond lengths are the same. Arsenic burns in oxygen gas to form arsenic(III) oxide which has a RMM of 395.68 and in whose structure, every bond is equivalent. At temperatures, over 800 °C some molecules of arsenic(III) oxide are formed with a RMM of 197.84.

(b) (i) Draw the structure for the molecules As_2 and As_4, showing all bonds and any lone pairs.

(ii) Give the equation for arsenic burning in oxygen to form arsenic trioxide.

(iii) Suggest a structure for the molecule of arsenic trioxide with RMM of 395.68.

(iv) Suggest a structure for the molecule of arsenic trioxide with RMM of 197.84.

The picture opposite shows workers in 17th century China roasting arsenic ores. In the text of the book, the worker is warned they must be around 25m up-wind of the apparatus since all grass and trees down-wind are killed in the process. The author also states that the worker should be reassigned to alternative work after two years, since after that time, if they continue, their hair will fall out.

The mineral arsenopyrite, FeAsS, is commonly used in this process. In this compound the arsenic and sulfur atoms have the same integer oxidation state.

Heating FeAsS in the absence of air produces arsenic metal. Roasting FeAsS in air produces arsenic(III) oxide with the other products depending on the quantity of oxygen used. When the molar FeAsS : O_2 ratio is 1 : 0.75, only one additional product is formed. When the FeAsS : O_2 ratio is 1 : 2.5, two additional products are formed.
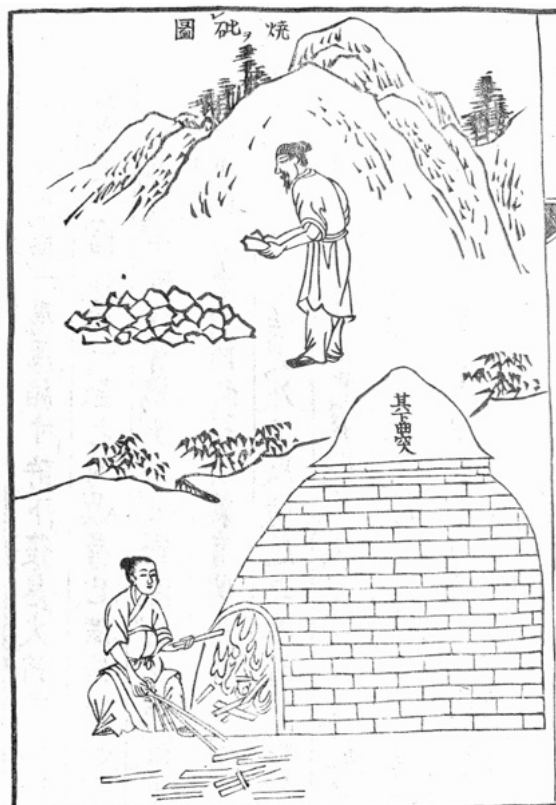
Roasting arsenic ores in 17th century China.

(c) (i) What is the oxidation state of the arsenic in FeAsS?

(ii) Give an equation for heating FeAsS in the absence of oxygen.

(iii) Give an equation for the roasting of FeAsS in limited oxygen (FeAsS : O_2 ratio = 1 : 0.75).

(iv) Give an equation for the roasting of FeAsS in excess oxygen (FeAsS : O_2 ratio = 1 : 2.5).

Arsenic(III) oxide dissolves in water to give an acid, arsenic(III) acid, H_3AsO_3. This reacts with sodium hydroxide to give a mixture of sodium arsenite [sodium arsenate(III), Na_3AsO_3] and sodium meta-arsenite, $NaAsO_2$. The latter has a polymeric structure, $[Na^+]_n\ [AsO_2^-]_n$.

(d) (i) Suggest a structure for H_3AsO_3 and for Na_3AsO_3.

(ii) Suggest a structure for the polymeric structure of sodium meta-arsenite. Draw the repeating structure; include three $[AsO_2^-]$ units in your answer.

Arsenic(III) oxide can be oxidised to arsenic(V) acid, H_3AsO_4, using concentrated nitric acid. The gas NO is also formed during this reaction.

(d) (iii) Give the equation for the oxidation of arsenic(III) oxide to arsenic(V) acid.

When aqueous copper(II) sulfate is added to arsenic(III) acid dissolved in aqueous sodium carbonate, a green precipitate is formed. This poisonous substance, known as Scheele's Green, was commonly used as a pigment used to colour everything including wallpaper and even some foods. On heating a 0.500g sample, it decomposed to yield 0.024 g of water, 0.264 g of arsenic(III) oxide, and 0.212 g of black copper oxide. When Scheele's Green is boiled with aqueous sodium hydroxide, red copper(I) oxide is formed.

(e) (i) Determine the empirical formula for the pigment Scheele's Green.

(ii) Give the equation for the reaction between Scheele's Green and hot sodium hydroxide.

2. This goes-on-forever-question is about "forever chemicals".

Perfluorinated alkyl substances (PFAS) are substances in which every hydrogen in an alkane has been replaced by a fluorine atom. PFAS are useful since they have excellent water-repelling and non-stick properties. This has led to their widespread use in cooking pans, cosmetics, insulation, water-proof clothing, dental floss, and many other products.

As a result of their resistance to degradation, they have been labelled "forever chemicals" and have been suspected of being harmful to health. PFAS easily bioaccumulate and they have been detected in drinking water and agricultural products.

PFAS are forever,

not just for C_3L_6 exams.

A common perfluorinated compound is the addition polymer PTFE, commonly referred to as Teflon™. This is used in kitchen utensils and Gortex™ clothing. The monomer of Teflon has the formula C_2F_4. The monomer is prepared by the thermal decomposition of chlorodifluoromethane, diluted with an inert gas. During this reaction, a reactive intermediate (difluorocarbene) with the formula CF_2 is formed, together with one other by-product.

(a) (i) Give the overall equation for the formation of C_2F_4 from chlorodifluoromethane.

(ii) Draw the structure of the monomer C_2F_4, indicating approximate bond angles.

(iii) Draw a dot-and-cross diagram for the reactive intermediate difluorocarbene, CF_2.

In the absence of air, if a sufficient activation energy is provided, C_2F_4 undergoes a violent exothermic reaction to form carbon and tetrafluoromethane.

(b) (i) Give the equation for this violent reaction.

(ii) During the reaction, carbon in the C_2F_4

        is oxidised   is reduced   disproportionates.

    In your answer booklet, circle any / all of the correct terms which apply for this reaction.

(iii) Which of the following energy profiles would be most appropriate for this reaction? (Circle one in your answer booklet.)
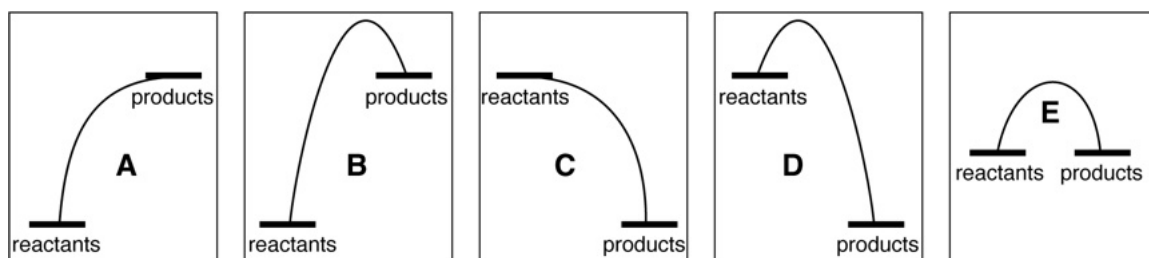
PFAS have remarkable non-stick properties since the molecules have no permanent dipole moments, and because it is also extremely hard to induce any temporary dipole moment in the fluorine atoms that surround the molecule. A molecule has a permanent dipole moment if there is an asymmetrical net imbalance of charge. Thus the molecule HCl has a permanent dipole, whereas even though each C–O bond has a dipole, the linear, symmetrical arrangement of the two C–O bonds in CO_2 means this molecule does not.
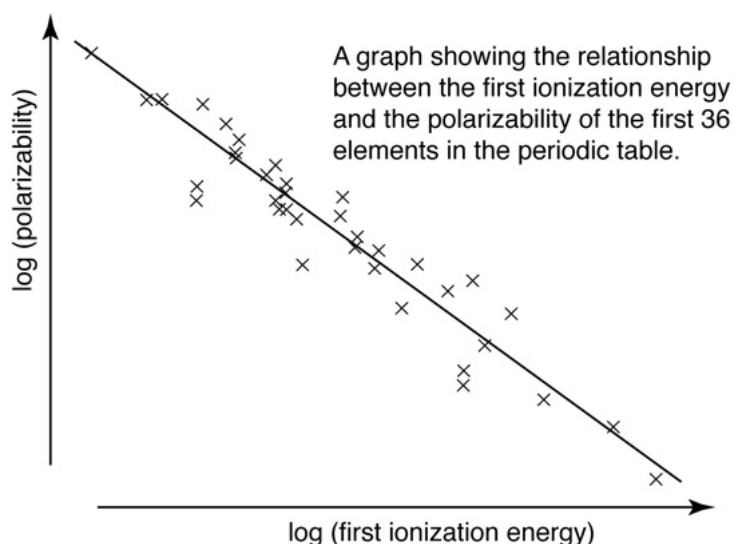
(c) Some of the following molecules DO have a permanent dipole moment and some DO NOT. They are in a random order.

the isomers of difluoroethene

difluoromethane, chlorodifluoromethane, tetrafluoromethane

difluorocarbene (CF_2).

(i) Draw the structures (with realistic shapes) of those molecules that DO have a permanent dipole moment.

(ii) Draw the structures (with realistic shapes) of those molecules that DO NOT have a permanent dipole moment.

A graph showing the relationship between the first ionization energy and the polarizability of the first 36 elements in the periodic table.

How hard it is to induce a dipole in an atom or molecule depends on its so-called *polarizability*. The easier it is to distort the electron cloud within the atom or molecule, the larger its polarizability. Perhaps not surprisingly, there is a reasonable correlation between the first ionization energy of an atom and its polarizability, as shown in the graph on the right.

(d) (i) Arrange the following elements in order of <u>increasing</u> polarizability:

Fe   K   F   Se   Na   Cl.

(ii) Which element (from the whole periodic table) has the smallest polarizability?

(iii) Which element (from the whole periodic table) has the greatest polarizability?

Although rotation around single bonds is relatively easy, certain arrangements (known as *conformations*) are preferred as they are lower in energy. The preferred (i.e. lowest energy) conformation of an alkane is where the C–C bonds align as far away as possible from one another. This can be visualised using *Newman projections*, as shown in the lower half of the diagram below.


Two conformations of butane.
Conformation **Y** is the lowest energy conformation.
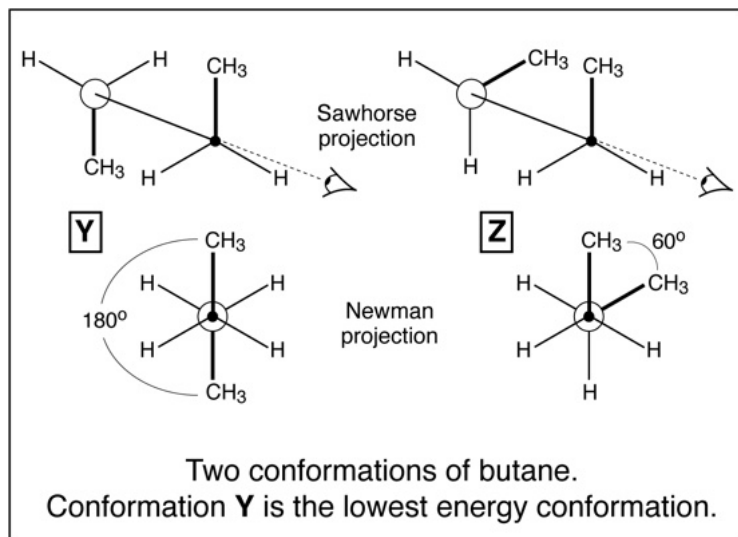
Newman projections for two conformations of butane, **Y** and **Z**, are illustrated and show what you would see if you looked along the central C–C bond.

Conformation **Y** has the C–C bonds as far away from each other as possible (with a so-called CH_3–C–C–CH_3 torsional angle of 180°.

Conformation **Z** (with a CH_3–C–C–CH_3 torsional angle of 60°) is higher in energy than **Y**.

(e) (i) What is the CH_3–C–C–CH_3 torsional angle of the conformation of butane with the overall highest energy?
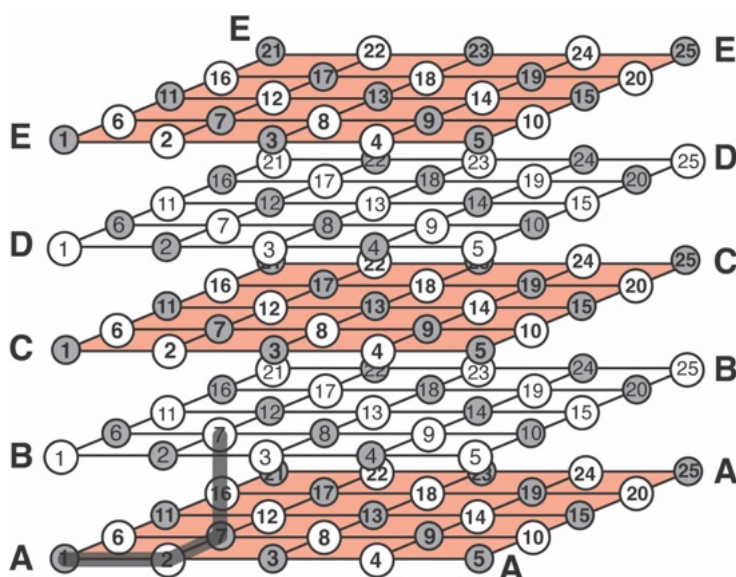
When the torsional angle is not 180°, the carbon backbone develops into a spiral or helix. This can be illustrated using the diagram on the left. The layers **A–E** stack on top of each other, each layer separated by one bond length.
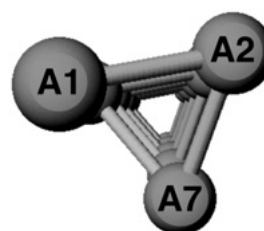
Four atoms are shown joined together:

A1–A2–A7–B7

This represents four atoms where the torsional angle and all bond angles are 90°. (The torsional angle is seen when viewing along **A2–A7**; bond **A1–A2** is at 90° to **A7–B7**.) If this pattern is continued a spiral will develop, as shown below.
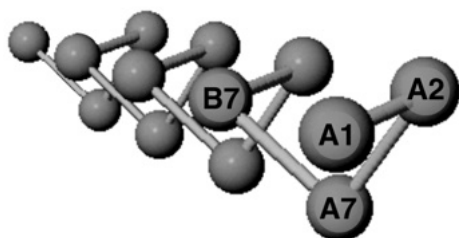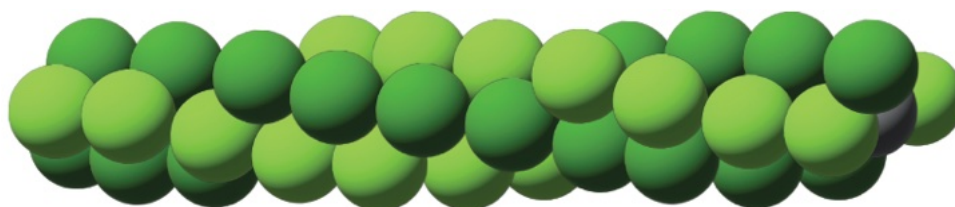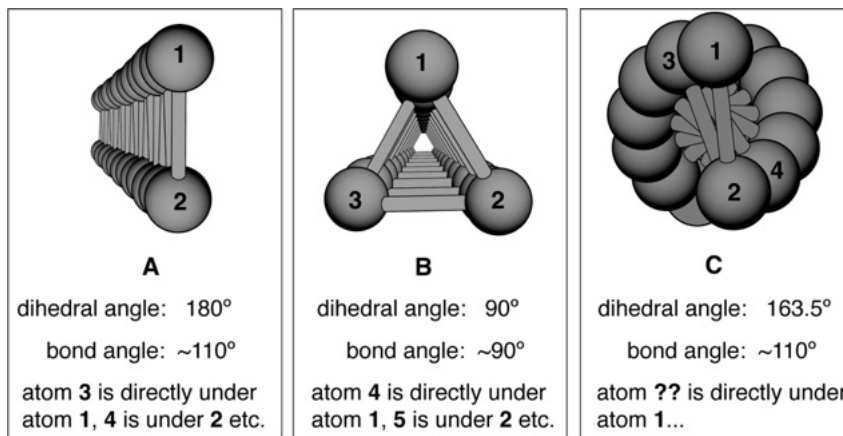

The sprial formed with 90° angles.

View along the axis of the spiral.

(e) (ii) Extend the path trace using the same numbering scheme **A1–A2–A7–B7…** as far as possible on the grid, keeping all angles at 90°. (This will generate the spiral.)

A schematic view of part of a PTFE helix with only the fluorine atoms visible.

With bond angles close to the tetrahedral angle but C–C–C–C torsional angle of 163.5°, perfluorinated alkanes coil into a helix. The central C–C chain is completely enveloped and protected by the outer fluorine atoms which helps make the PFAS so inert.

A	B	C
dihedral angle: 180°	dihedral angle: 90°	dihedral angle: 163.5°
bond angle: ~110°	bond angle: ~90°	bond angle: ~110°
atom **3** is directly under atom **1**, **4** is under **2** etc.	atom **4** is directly under atom **1**, **5** is under **2** etc.	atom **??** is directly under atom **1**...

(e) (iii) Which of the structures **A**, **B**, or **C** above are superimposable on their mirror images? Circle one option in your answer booklet.
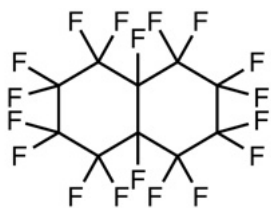
A only   **B** only   **C** only   **A** & **B** only   **A** & **C** only   **B** & **C** only   **all three**

(iv) What is the formula for the shortest perfluoroalkane with structure **C** (drawn accurately above) with one full turn (i.e. where the first and last carbons are exactly aligned)?

A typical average relative molecular mass, M_{av}, of the polymer PTFE is around 10^7. The density of PTFE, d_{rel}, (relative to water with a density of 1 g cm^{-3}) is found to be related to M_{av} via the equation:
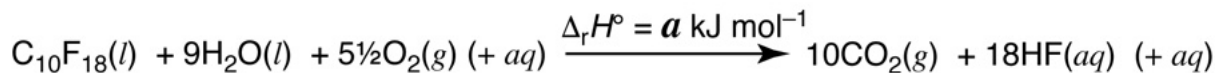
$$d_{rel} = 2.612 - 0.058 \times \log_{10}(M_{av})$$

(f) (i) Calculate the density of a sample of PTFE for which $M_{av} = 10^7$.

(ii) Estimate the number of carbon atoms in a sample of polymer with this M_{av}.

(iii) Calculate the M_{av} for a sample of PTFE with relative density 2.18 .

Perfluorodecalin is another commonly used PFAS. Its structure is shown on the left. The standard enthalpy change for the reaction below has been measured and allows thermodynamic quantities to be calculated for perfluorodecalin. We will use it to estimate the C–F bond strength which helps make the compound so chemically inert.

perfluorodecalin $C_{10}F_{18}$

$$C_{10}F_{18}(l) + 9H_2O(l) + 5\tfrac{1}{2}O_2(g) \ (+ aq) \xrightarrow{\Delta_rH^\circ = a \text{ kJ mol}^{-1}} 10CO_2(g) + 18HF(aq) \ (+ aq)$$

(g) (i) Use the following data to derive an algebraic expression to estimate the average C–F bond strength, z, in perfluorodecalin. Your expression should be in terms of the quantities $a - j$. Give the coefficients for each of these quantities in your answer booklet.

thermodynamic quantity	symbol	value / kJ mol^{-1}
standard enthalpy change for the reaction of perfluorodecalin above	a	–3467
standard enthalpy change for the vapourisation of perfluorodecalin(l)	b	43.3
Standard enthalpy change of formation of $H_2O(l)$	c	–285.8
Standard enthalpy change of formation of $CO_2(g)$	d	–393.5
Standard enthalpy change of formation of $HF(g)$	e	–273.3
Standard enthalpy change of solvation of $HF(g)$	f	–61.6
Standard enthalpy change of atomisation of $C(s)$	g	716.7
Bond dissociation enthalpy of F–F	h	157.0
Average bond dissociation enthalpy of C–C	j	325

$z = \boxed{}\,a \ \boxed{}\,b \ \boxed{}\,c \ \boxed{}\,d \ \boxed{}\,e \ \boxed{}\,f \ \boxed{}\,g \ \boxed{}\,h \ \boxed{}\,j$ kJ mol^{-1}

(ii) Use your expression and the values of $a - j$ to calculate the average C–F bond strength.

A particularly interesting property of perfluorodecalin is its capacity to dissolve gases. It can do this because the solvent molecules have such weak attractions to each other, the gas molecules can easily diffuse between them. Its ability to dissolve oxygen has led it to be used as "artificial blood" when preserving live tissues. The solubility of oxygen (at room temperature and pressure, RTP) can be expressed as 5.03×10^{-3} moles of oxygen/mole of solvent). The density of perfluorodecalin (at RTP) is 1.917 g cm^{-3}.

(h) (i) Calculate the solubility of oxygen in perfluorodecalin in mL/mL at RTP. (Assume one mole of gas occupies 24 dm^3 at RTP.)

Blood haemoglobin has an oxygen capacity of 20.1 mL/100 mL and additionally some is dissolved in the plasma with a solubility of 22.8 mL/L/atm (all at RTP).

(ii) An adult human contains around 5 L of blood. What volume of perfluorodecalin would be required to carry the same amount of oxygen at RTP?

Acknowledgements

We would like to thank those who support C3L6: