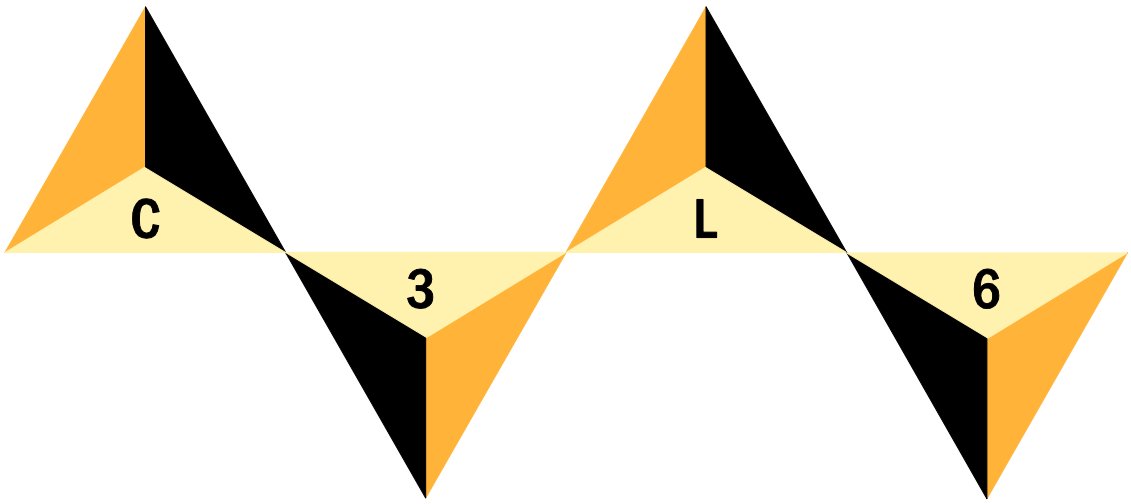


Cambridge Chemistry Challenge Lower 6th

June 2025

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 alkene isomers.

Isomers are simply different arrangements of atoms in space and some arrangements are lower in energy than others. This question looks at different alkene isomers.



For alkene-isomers, it is generally the case that:

- the more alkyl groups directly attached to the double bond, the lower the energy of that isomer
- a *cis* arrangement of two groups on a double bond (where the two groups are on the same side) is higher in energy than a *trans* arrangement (where the two groups are on opposite sides).

In the questions below, skeletal structures should be given
(i.e. you should not draw in the carbon atoms or hydrogen atoms).

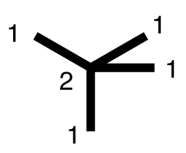
(a) **(i)** Draw the structure for hex-1-ene.

(ii) Give the equation for the hydrogenation of hex-1-ene (the reaction with hydrogen gas to give the alkane).

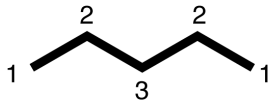
(iii) Draw ALL the isomers of hex-1-ene which form the same alkane as hex-1-ene upon hydrogenation.

(b) One alkene-isomer of hexene contains a carbon atom with four different substituent groups attached to it, making the molecule chiral; draw the structure of this alkene.

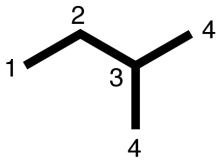
Carbon NMR (nuclear magnetic resonance) is routinely used to help determine structures. At the simplest level, the technique reveals how many unique environments of carbon atoms there are in a structure. Some atoms may be in the same environment if the structure contains mirror planes of symmetry, or rotational symmetry axes. The example below shows the number of signals in the carbon NMR spectrum of three isomers of pentane. Within each molecule, atoms labelled with the same number are in the same environment:



2 signals



3 signals



4 signals

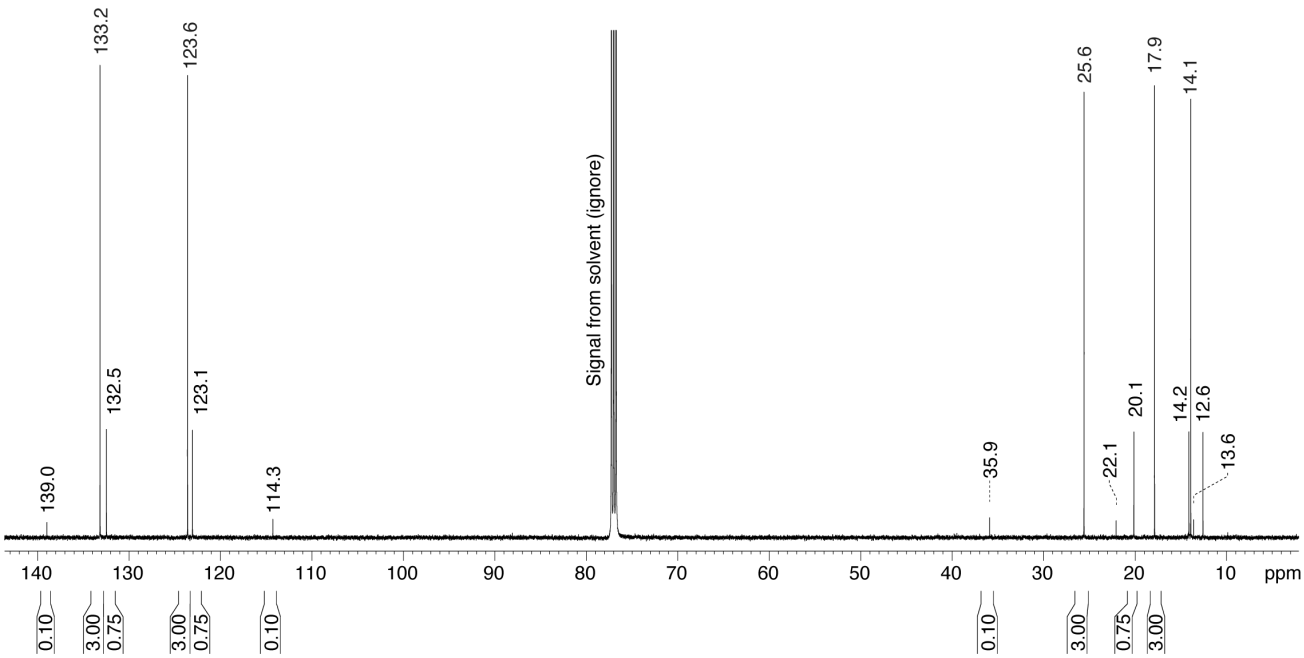
(c) Draw ALL the alkene isomers of hexene that have the following number of signals in the carbon NMR spectra:

(i) 2 signals **(ii)** 3 signals

(iii) 4 signals **(iv)** 5 signals.

(d) Given the effect of branching has less effect on the energy of alkanes, of **all** the alkene isomers of hexene, draw the one for which standard enthalpy of hydrogenation is:

(i) the least exothermic (-109 kJ mol^{-1}) **(ii)** the most exothermic (-127 kJ mol^{-1}).



It is possible to interconvert between certain alkene isomers using an appropriate catalyst. Shown above is a carbon NMR spectrum of an equilibrium mixture of the linear alkene-isomers of pent-1-ene: **A** is the highest-energy isomer, **C** is the lowest-energy isomer, and isomer **B** is in between these two in energy. The numbers shown against each peak are the chemical shifts (in ppm) for a carbon atom in a particular environment. Unlike most carbon NMR spectra, this has been specially recorded so that the heights of each peak (more correctly, the area under each peak) is directly proportional to the number of carbon atoms in that particular environment. The numbers shown beneath the spectrum [0.10, 0.75 and 3.00] show the relative proportions in the equilibrium mixture due to carbon nuclei in a particular environment (not all of these are shown).

(e) In your answer-booklet, draw the structure of each isomer in the mixture (**A**, **B**, and **C**) and list the chemical shifts for the signals for that isomer. For each isomer, underline the shifts corresponding to the two alkene carbons.

[You do not need to assign each peak to a particular carbon atom.]

The equilibrium constant for the interconversion between isomers **A** and **B** (denoted K_{AB}) is given by the following expression:

$$\mathbf{A} \overset{K_{AB}}{\rightleftharpoons} \mathbf{B} \qquad K_{AB} = \frac{[\mathbf{B}]_{eq}}{[\mathbf{A}]_{eq}}$$

where $[\mathbf{X}]_{eq}$ represents the equilibrium concentration of isomer X.

(f) Determine the numerical values of K_{AB}, K_{AC}, and K_{BC}.

For these reactions, we can approximate* the standard enthalpy change of the reaction (for example, **A** → **B**) to be given by the expression:

$$\Delta_r H^\circ_{AB} \approx -RT \ln K_{AB} \quad *$$

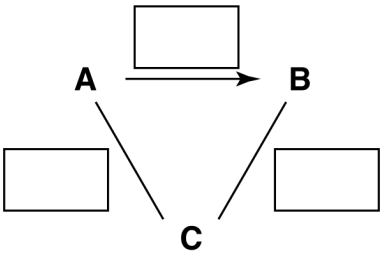
where R is the molar gas constant [R = 8.314 J K^{-1} mol^{-1}] and T is the temperature in kelvin.

*We can do this only when, as here, there is a negligible change in the entropy of the reaction, $\Delta_r S^\circ$.

(g) Use the information above to determine the approximate enthalpy changes at 298 K for the reactions:

(i) **A** → **B** **(ii)** **A** → **C** **(iii)** **C** → **B**

(iv) In your answer-booklet, complete the arrows and values in the enthalpy cycle below: (the arrow for **A** → **B** is given.)



A more accurate value for the standard enthalpy change of the reaction may be determined by measuring how the equilibrium constant for the reaction varies with temperature. The relationship (which ultimately explains Le Chatelier's Principle and is known as the Van't Hoff equation) is:

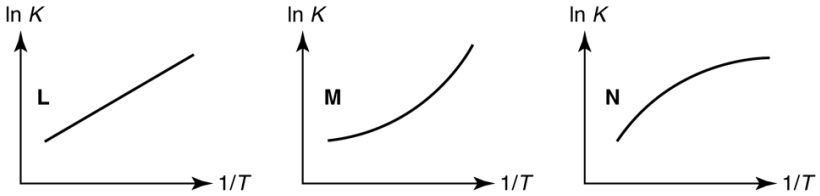
$$\ln K = -\frac{\Delta_r H^\circ}{RT} + \text{constant}$$

(h) **(i)** For an exothermic reaction at equilibrium, if the temperature is increased, does the equilibrium constant shift to:

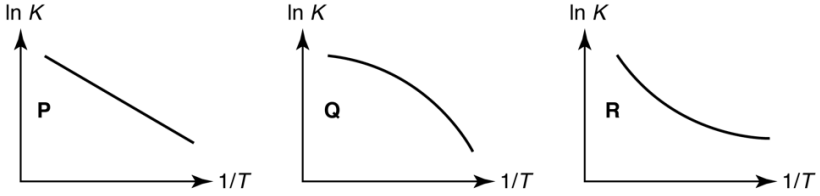
a <u>LARGER</u> value (more products) or

a <u>SMALLER</u> value (more reactants)?

Consider the schematic Van't Hoff plots on the right:



Select which of the plots is for:

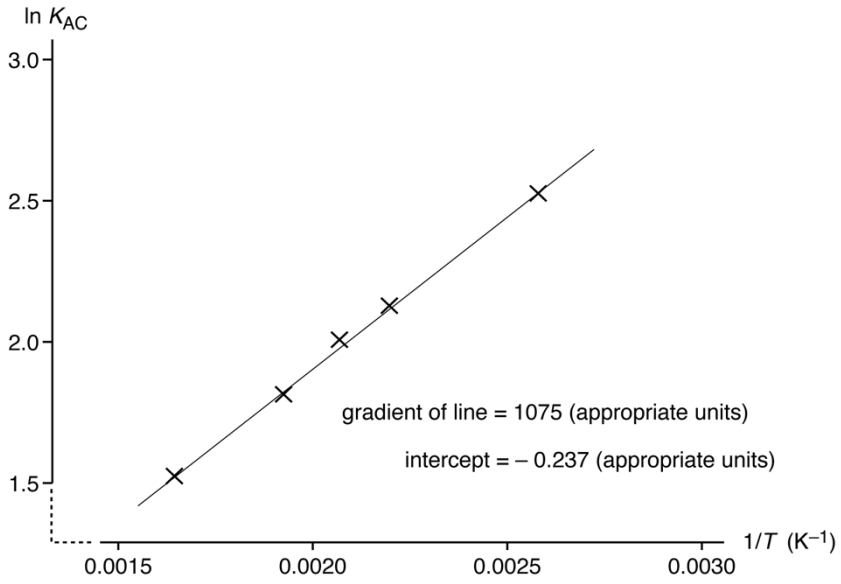


(ii) an <u>exothermic</u> reaction with a value of $\Delta_r H^\circ$ that <u>does not vary</u> with temperature

(iii) an <u>exothermic</u> reaction with a value of $\Delta_r H^\circ$ becomes <u>more exothermic</u> at higher temperatures

(iv) An <u>exothermic</u> reaction with a value of $\Delta_r H^\circ$ that becomes <u>less exothermic</u> at higher temperatures.

How K_{AC} (the equilibrium constant between the linear alkene isomers of pent-1-ene with the highest energy, **A**, and the lowest energy, **C**) varies with temperature has been studied in the gas phase and the following Van't Hoff plot has been made.



(j) Use the Van't Hoff plot to determine $\Delta_r H°_{AC}$.



2. This is a non-boring question about boron.

The element boron (as opposed to the town of Boron in California) is the fifth-lightest element on The Periodic Table, in Group 13. It is estimated that this rare element has an abundance of approximately 0.001% of The Earth's crust. Despite its rarity, boron and its compounds have many uses, from the production of fibreglass for composite materials to the synthesis of novel drugs designed to treat cancer or to overcome the resistance of some bacteria to antibiotics.

The largest single mine of boron is in California, where the compound borax is mined. The atomic mass of boron varies between 10.806 and 10.821, depending on the origin of the boron. This is because the proportions of its two naturally occurring isotopes (^{10}B, A_r = 10.013, and ^{11}B A_r = 11.009) may vary.



A picture of the town Boron and its boron mine taken from the International Space Station by a NASA astronaut.

(a) **(i)** Give the electron configuration of boron in terms of subshells.

(ii) How many protons and how many neutrons are in an atom of ^{11}B?

(iii) Calculate the percentage of ^{10}B found in a sample of naturally-occurring boron with A_r = 10.810.

Drugs containing boron-10 have been used in boron neutron capture therapy. The drugs are delivered to cancerous cells and then irradiated with neutrons. Atoms of ^{10}B can capture a neutron to form an excited ^{11}B atom which then decays by emitting a high-energy alpha-particle (a helium nucleus) which destroys the cell.

(iv) Which other atom is formed when the excited ^{11}B atom decays? What is its mass number?

Boron can combine with the halogens to form an analogous series of halides in which the single boron atom is in its maximum oxidation state. We will denote the fluoride as **A** and the chloride as **B**. The maximum oxidation state is also shown in oxide **C**, formed when boron reacts with oxygen.

(b) **(i)** Give the equation for the reaction between boron and chlorine to form chloride **B**.

(ii) Give the equation for the reaction between boron and oxygen to form oxide **C**.

(iii) Draw the structure of chloride **B**, showing the relevant bond angles.

(iv) How many electrons does the boron atom have in its outer shell in the structure of **B**?

In industry, both fluoride **A** and chloride **B** are prepared from the oxide **C**. The fluoride is prepared by the reaction of oxide **C** with hydrofluoric acid, whilst the chloride is prepared by heating oxide **C** with carbon and chlorine – carbon monoxide is also formed during this reaction.

(c) (i) Give the equation for the formation of fluoride **A** from oxide **C** and hydrofluoric acid.

(ii) Give the equation for the formation of chloride **B** from oxide **C**, carbon and chlorine.

(iii) Use the thermodynamic data below to calculate the standard enthalpy change for the reaction when one mole of oxide **C** forms chloride **B**.

$\Delta_f H^\circ$ (chloride **B**)	–403 kJ mol^{-1}
$\Delta_f H^\circ$ (carbon monoxide)	–110 kJ mol^{-1}
$\Delta_c H^\circ$ (boron)	–636.5 kJ mol^{-1}

In the solvent $CFCl_3$, fluoride **A** shows a signal at 10.8 ppm in the ^{11}B NMR spectrum; in the same solvent, chloride **B** shows a signal at 47.1 ppm. When the solutions are mixed, some molecules react to form a short-lived species **D** (no signals are seen in the NMR spectrum for this since it is so short-lived) then signals also appear at 33.7 ppm and 20.7 ppm.

(d) (i) Suggest a structure for the species which gives rise to the signal at 33.7 ppm in the ^{11}B NMR spectrum.

(ii) Suggest a structure for the species which gives rise to the signal at 20.7 ppm in the ^{11}B NMR spectrum.

(iii) Suggest a structure for the short-lived species **D**.

(iv) How would you expect the geometry around the boron to change in forming short-lived species **D**? (Circle one answer in your answer booklet.)

1 tetrahedral to trigonal planar

2 trigonal planar to tetrahedral

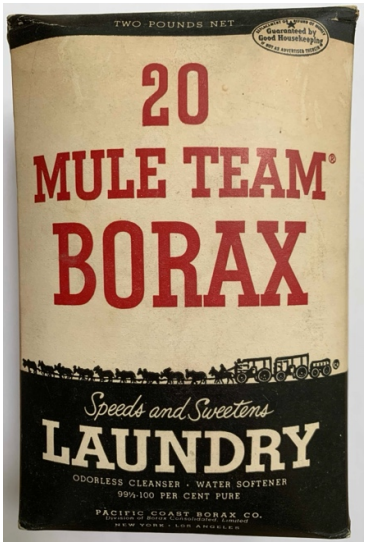
3 trigonal planar to square planar

4 tetrahedral to spare planar.

Boron is almost entirely found on Earth bound to oxygen atoms. The boron mine in Boron produces 30% of the world demand for refined borax mineral and used to use teams of horses / mules to transport the borax out of the town. Borax is a compound of sodium, boron, oxygen and hydrogen. One form that is mined has the following composition by mass:

Na: 12.06% B: 11.34%

O: 71.32% H: 5.29%



(e) **(i)** Calculate the empirical formula of borax.

(ii) Assuming that all hydrogen atoms are contained within water of crystallisation molecules, re-write this formula in the form $Na_aB_bO_c \bullet dH_2O$, where a, b, c, and d are integers.

When borax crystals are examined by X-ray crystallography, it is found that there are actually eight water molecules per mole of borax

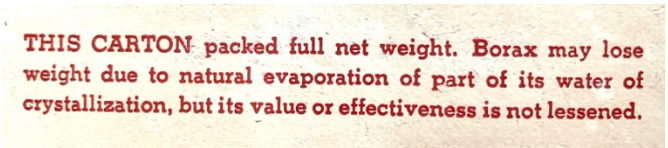
(iii) Assuming that the sodium is all present as sodium ions in the crystal structure, give the formula of the remaining, single ion (taking into account the correct number of water molecules present).

Further analysis of the structure of this ion shows that each boron has one -OH group attached. Half of the boron atoms form 4 bonds to oxygen, while the other half form 3 bonds to oxygen. The structure of the ion has two planes of symmetry.

(iv) Re-write the formula of the boron-containing ion in the form $B_wO_x(OH)_y^{z-}$, where w, x, y, and z are integers.

(v) Suggest a structure for the boron-containing ion in borax.

When borax is heated, it loses water.
The amount of mass that it loses depends on the temperature at which it is heated.



Borax $\xrightarrow{334\ K}$ **K** $\xrightarrow{393\ K}$ **L** $\xrightarrow{573K}$ **M** $\xrightarrow{>573K}$ **N**

When each of compounds **K**, **L**, **M** and **N** are analysed it is possible to determine by titration the percentage by mass of $Na_aB_bO_c$ [as determined in part **(e)(ii)**]. The results are as follows:

K: 70.0% **L**: 79.9% **M**: 91.7% **N**: 100%

(Note: this is real, experimental data and as such is subject to uncertainty.)

(f) **(i)** Calculate the formula of compounds **K**, **L**, **M** & **N**, expressing them in the form $Na_aB_bO_c \bullet dH_2O$.

(ii) Compound **N** reacts with concentrated sulphuric acid to produce boron oxide **C** (from earlier) together with water and sodium sulphate. Give the equation for this reaction.

Acknowledgements

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