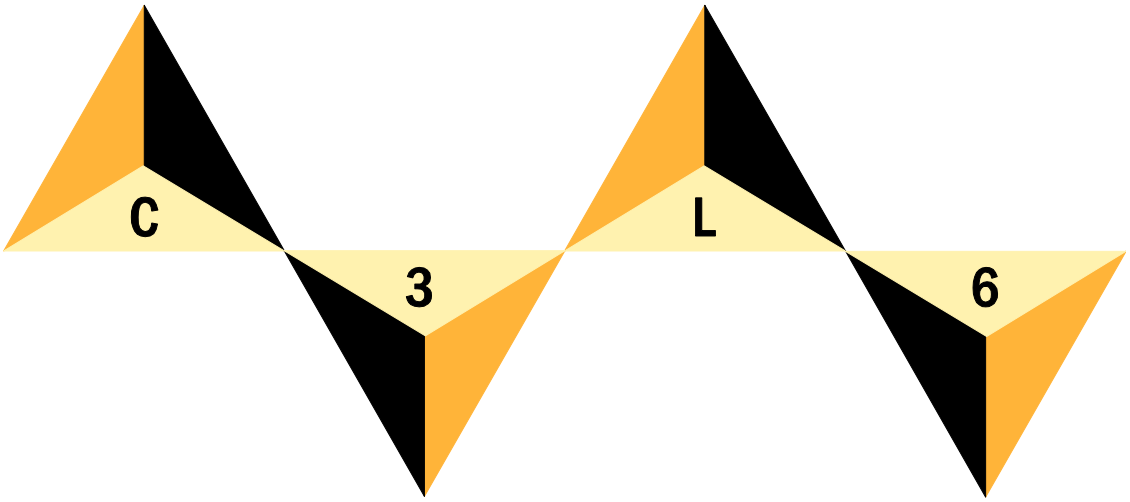



# Cambridge Chemistry Challenge Lower 6th

## June 2020

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 benzene and its isomers

Working out the structure of benzene, $C_6H_6$, was one of the great achievements of 19th century chemists. The carcinogenic hydrocarbon was first discovered by Michael Faraday at the Royal Institution in 1825 during the repeated fractional distillation of some oil residues.

Faraday analysed the pure benzene by passing its vapour over heated copper(II) oxide to produce carbon dioxide, water and copper. He collected and measured the volume of liquid water and gaseous $CO_2$ produced from a given mass of benzene.



**Section I** – the analysis of benzene

**(a)** **(i)** Give the equation for the reaction of copper(II) oxide with benzene gas.

**(ii)** Calculate the relative molar mass of benzene, $C_6H_6$, and hence the number of moles in 1.00 g of benzene.

The amount used by Faraday was tiny, just 0.776 grains – an old unit of mass. This equates to 0.644 mmol. [1 mmol = 1 millimole = 0.001 mol]

**(iii)** Calculate the maximum mass of water that could be formed from 0.644 mmol of benzene using Faraday's method.

**(iv)** Assuming 1.00 mol of a gas occupies 24.0 $dm^3$ at room temperature and pressure, calculate the volume of carbon dioxide that could be produced from 0.644 mmol of benzene. Give your answer in $cm^3$.

**(b)** Faraday confirmed his analysis by a second method – exploding a mixture of benzene vapour with excess oxygen gas and measuring the volume of carbon dioxide produced by absorbing it with potassium hydroxide solution. He took 7.0 'volumes' of the mixture (the precise units are not important) and found that 2.1 volumes of carbon dioxide were produced.

**(i)** Give the equation for the complete combustion of benzene.

**(ii)** Give the equation for the reaction of potassium hydroxide solution with carbon dioxide.

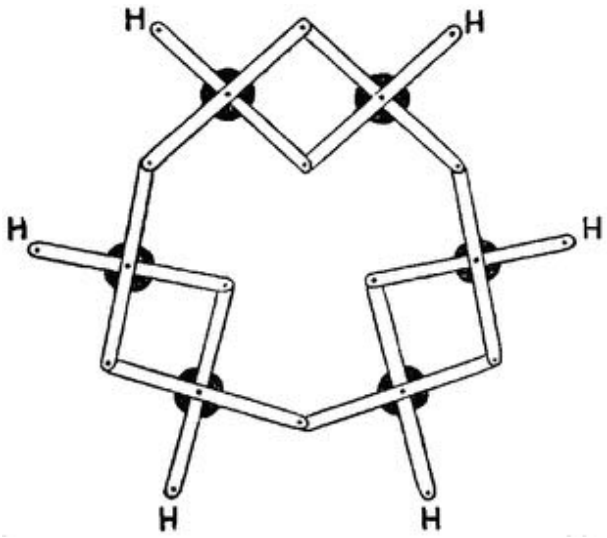
**(iii)** Assuming that all volumes of gases & vapours were measured at the same temperature and pressure, calculate how many volumes of benzene vapour were contained in the original mixture.

**(iv)** Calculate how many volumes of oxygen gas were left after the combustion had taken place and the carbon dioxide and water had been removed.

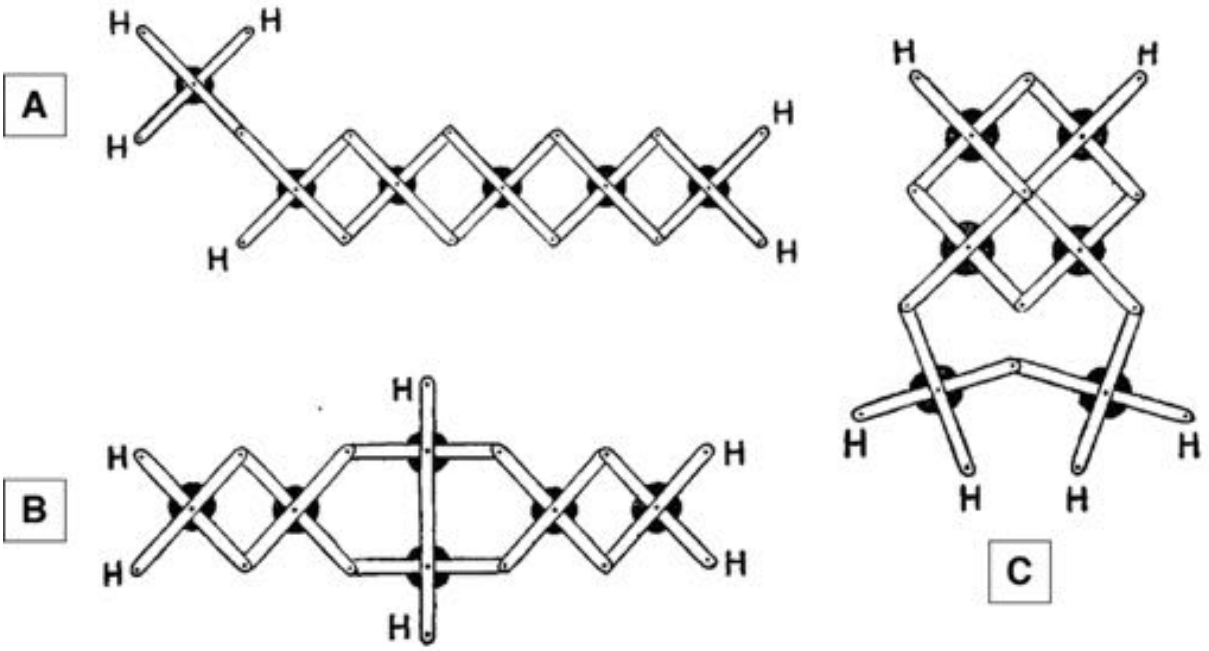
**Section II** – isomers of benzene

It took several decades after the initial discovery of benzene before people understood that its molecular formula was $C_6H_6$. Once this was known, the next problem was working out the arrangement of the atoms. Several different possible structures were suggested.

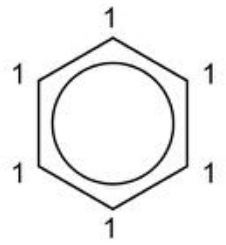
In one paper on benzene, British scientist James Dewar suggested constructing models using thin strips of brass to show the arrangement of bonds, and black discs to represent the carbon atoms. His representation of the correct structure of benzene is shown on the right.



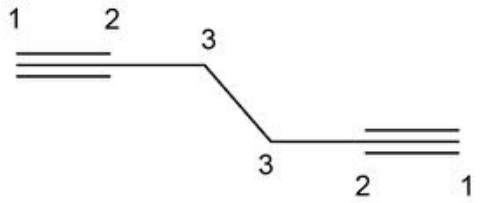

**(c)** Draw a skeletal structural formula for each of the three isomers represented by the models **A**, **B**, and **C** shown below.



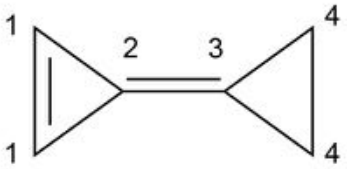
One of the key features of benzene is that all the C—C bond lengths are exactly the same with all the carbon atoms in exactly the same environment. This is instantly revealed using the modern technique of $^{13}C$ *nuclear magnetic resonance spectroscopy*, or $^{13}C$ NMR. The $^{13}C$ NMR spectrum of benzene shows one peak since there is only one unique carbon environment. In contrast, in the isomers of $C_6H_6$ shown below, some of the carbon atoms are in equivalent environments, others are not. In each structure, the different carbon environments are numbered; atoms with the same number are in the same environment. The number of peaks in the $^{13}C$ NMR spectrum corresponds to the number of different carbon environments in a given molecule.




just **one** peak in the $^{13}C$ NMR spectrum




**three** peaks in the $^{13}C$ NMR spectrum

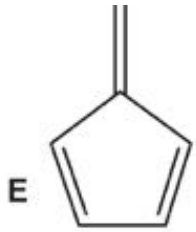



**four** peaks in the $^{13}C$ NMR spectrum

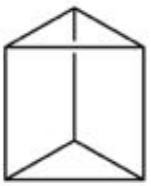
**(d)** Copy each of the structures shown below into your answer booklet. For each structure, label each unique carbon environment using the same label for equivalent atoms. Hence predict how many peaks would be seen for each compound in the $^{13}C$ NMR spectrum.



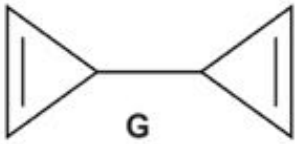
**D**



**E**



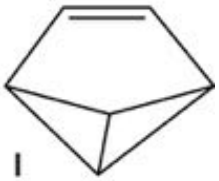
**F**



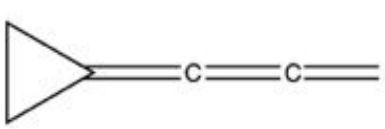
**G**



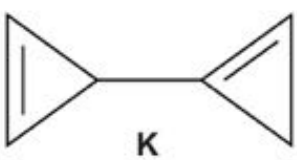
**H**



**I**

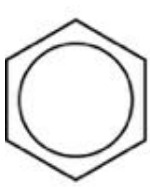



**J**

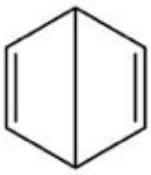


**K**

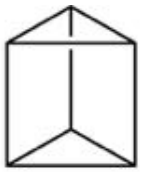
**Section III** – historic structures



benzene



Dewar benzene



Ladenburg benzene
or 'prismane'

The correct structure of benzene and two other structures which were considered are shown above. So-called 'Dewar benzene' is 252 kJ mol$^{-1}$ higher in energy than normal benzene (both species in the gas phase). Prismane is even higher in energy and is explosive.

**(e)** Use the thermodynamic data given to calculate:

**(i)** the standard enthalpy change of formation, $\Delta_f H°$, of benzene (g)

**(ii)** the standard enthalpy change of combustion, $\Delta_C H°$, of Dewar benzene (g).

| | value / kJ mol$^{-1}$ |
|---|---|
| $\Delta_C H°$ of benzene (g) | –3301 |
| $\Delta_f H°$ $CO_2$ (g) | –393.5 |
| $\Delta_f H°$ $H_2O$ (l) | –285.8 |

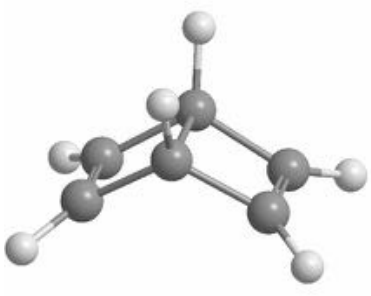
We now know that the correct structure of benzene is a regular hexagon with all the C-C bond lengths being exactly the same. One of the crucial clues in helping to deduce this correct structure, was how many different substituted structures it forms. With one substituent, only one positional isomer is formed, but with two of the same substituents, three positional isomers may be formed.

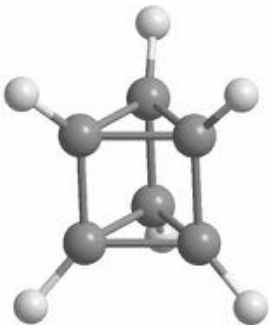
**(f)** **(i)** Draw the three positional isomers of dichlorobenzene.

**(ii)** Draw all the positional isomers of trichlorobenzene

**(iii)** Initially Dewar benzene was considered as a planar structure. Draw all the positional isomers for *planar* dichloro-Dewar benzene.

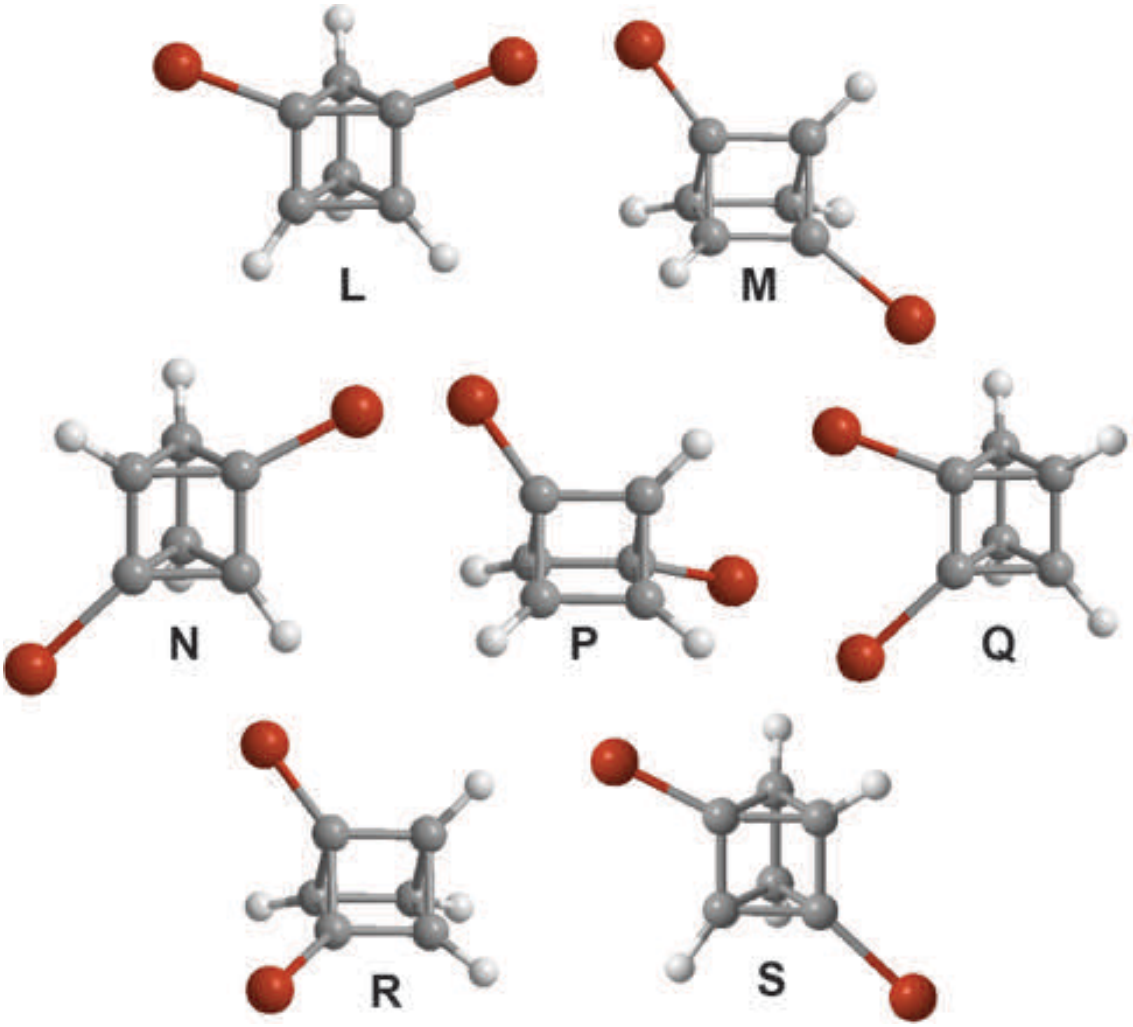
Modern chemists have now synthesised both Dewar benzene and prismane and they are found to have the three-dimensional structures shown below.





The three-dimensional structure means that it now possible to get optical isomers of both disubstituted Dewar benzene, and of disubstituted prismane. Optical isomers are mirror images, but are non-superimposable; that means one optical isomer cannot fit exactly into the space occupied by the other. (Your hands are also non-superimposable mirror images – if you made a mould of your right hand, your left hand could not fit exactly into this space.)

Shown below are some structures of dichloro-prismane. Some of the structures are the same molecule rotated, others are optical isomers.




**(g)** **(i)** Which of the structures **L**-**S** shown above represent the same molecule rotated?

**(ii)** Which of the structures **L**-**S** shown above are optical isomers?

**(iii)** Including optical isomers, how many different dichloro-prismane structures are there in total?

**(iv)** How many pairs of optical isomers exist for three-dimensional dichloro-DEWAR benzene?

A solution of Dewar-benzene at room temperature spontaneously converts into normal benzene with a half-life of about 2 days. This means every two days, half of whatever Dewar-benzene is left has been converted to normal benzene.

**(h)** Taking the half-life to be exactly 2 days, how many days would it take a sample of Dewar-benzene to convert to 99% normal benzene?

## 2. This question is about the chlorides of a mythical metal



The mythical metal *stuck-at-homium*, symbol Sk, forms just two chlorides – $SkCl_2$ which is a white solid, and $SkCl_4$, a colourless volatile oily liquid which fumes on contact with air. The preparation of $SkCl_4$ was first described over four hundred years ago, but its formation may well have been described earlier and may have been one of the winged dragons referred to by the alchemists.

Aqueous $SkCl_2$ is easily prepared by dissolving metallic stuck-at-homium in dilute hydrochloric acid. On evaporation, the dihydrate is produced, $SkCl_2 \cdot 2H_2O$. This can be dehydrated to give anhydrous $SkCl_2$ using ethanoic anhydride, $(CH_3CO)_2O$. The structure of solid anhydrous $SkCl_2$ consists of chains of $SkCl_2$ units in which there are two different Sk—Cl bond lengths and two different chlorine environments. The anhydrous solid melts and then boils at a temperature less than 700 ºC.

**(a) (i)** Give the equation for the reaction of stuck-at-homium with aqueous hydrochloric acid.

**(ii)** In this reaction, which element is oxidised, and which element is reduced?

**(iii)** Draw the structure of ethanoic anhydride.

**(iv)** Give the name of the other by-product formed when $SkCl_2 \cdot 2H_2O$ reacts with ethanoic anhydride.

**(v)** Assuming that gaseous $SkCl_2$ has one lone pair on the stuck-at-homium, predict the bond angle around the central metal.

**(vi)** What would you expect the Cl–Sk–Cl bond angle to be in a molecule of $SkCl_2$ if the bonding were covalent and the stuck-at-homium *only* formed bonds using its outermost valence p orbitals?

**(vii)** Assuming once again there is one lone pair on the stuck-at-homium, show the repeating structure in solid $SkCl_2$ (show three $SkCl_2$ units in your structure).

To prepare $SkCl_4$ from $SkCl_2$, an oxidising agent must be used. One preparation uses $HgCl_2$. Mercury forms two chlorides: $HgCl_2$ and $Hg_2Cl_2$.

**(b) (i)** Give the oxidation state of mercury in $HgCl_2$ and in $Hg_2Cl_2$.

**(ii)** Give TWO different equations for the preparation of $SkCl_4$ from $SkCl_2$ and $HgCl_2$.

**(iii)** $SkCl_4$ smokes in air because it reacts with water vapour. In the simplest equation for this reaction, an oxide of stuck-at-homium is formed and one other product. Give an equation for this reaction.

$SkCl_4$ reacts with lithium aluminium hydride $LiAlH_4$ (a source of hydride ions) to form three products. Two of these are salts the third is a colourless gas, **Z**. If a sample of gas **Z** is kept in a container over time it is found that the pressure inside the container doubles, and a metallic residue is deposited.

**(c)** **(i)** Give an equation for the reaction of $SkCl_4$ with $LiAlH_4$.

**(ii)** Draw the structure of gas **Z** and predict the bond angles.

**(iii)** Give an equation for change that **Z** undergoes on standing.

One of the most important commercial uses of $SkCl_4$ is the preparation of *organo-stuck-at-homium compounds* which are heavily used in the plastics industry. These may be prepared using so-called Grignard reagents, RMgCl, where R is some alkyl group. Different products may be formed depending on the proportions of the Grignard reagent used. A (partial) generalised equation where 1 mol of $SkCl_4$ reacts with $x$ moles of RMgCl may be written:

$$SkCl_4 + x\,RMgCl \longrightarrow _____ + x\,MgCl_2$$

**(d)** By balancing the above equation, give the generalised formula (using $x$) for the organo-stuck-at-homium compounds that can be formed.

One compound that may be produced by this method is methylstuck-at-homium trichloride. One mole of this reacts with four moles of sodium hydroxide to produce the salt sodium methylstuck-at-homanoate (a salt of methylstuck-at-homanoic acid) and two other by-products.

**(e)** **(i)** Draw the structure of methylstuck-at-homium trichloride.

**(ii)** Give the equation for the reaction of methylstuck-at-homium trichloride with sodium hydroxide.

**(iii)** Suggest a structure for methylstuck-at-homanoic acid.

Another organo-stuck-at-homium compound is tributyl-stuck-at-homium chloride. This reacts with water to form a compound with the formula $C_{24}H_{54}OSk_2$. This compound has been widely used in *bottom painting* – which, of course, is where the hulls of boats are painted to prevent biofouling.

**(f)** **(i)** Draw the structure of tributylstuck-at-homium chloride.

**(ii)** Suggest a structure for the compound $C_{24}H_{54}OSk_2$.

## Acknowledgements

We would like to thank those who support C3L6:

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St Catharine's College, Cambridge

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