50th INTERNATIONAL

CHEMISTRY OLYMPIAD

2018

UK Round One

STUDENT QUESTION BOOKLET

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- **The time allowed is 2 hours.**
- **Attempt all 5 questions.**
- **Write your answers in the student answer booklet.**
- **In your calculations, please write only the essential steps in the answer booklet.**
- **Always give the appropriate units and number of significant figures.**
- **You are provided with a copy of the Periodic Table on page 2.**
- **Some useful physical constants and quantities are listed underneath the Periodic Table on page 2.**
- **Do *NOT* write anything in the right-hand margin of the answer booklet.**
- **The marks available for each question are shown below; this may be helpful when dividing your time between questions.**

Question	1	2	3	4	5	**Total**
Marks Available	10	12	21	25	13	**81**

Some of the questions will contain material you may not be familiar with. However, by logically applying the skills you have learnt as a chemist, you should be able to work through the problems. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may still find subsequent parts straightforward.

1. This question is about the application of some lithium compounds

Lithium-ion batteries are becoming a popular alternative for traditional lead-acid batteries. Recently the safety of lithium-based batteries has attracted media attention. In 2016, a major manufacturer recalled millions of mobile phones due to issues with the batteries catching fire/exploding.

Lithium-ion batteries have intercalated lithium compounds as the electrode material. Intercalation is the reversible inclusion or insertion of a molecule (or ion) into materials with layered structures.

When being discharged, the cathode is cobalt oxide with intercalated lithium ions, and the anode is graphite with intercalated lithium ions. In the process of charging and discharging, lithium ions move from one electrode to the other through an electrolyte. The electrolyte is usually a lithium salt dissolved in an organic solvent.

If the battery is handled according to the manufacturer's instructions, then elemental lithium is never formed in the battery.

(a) When being discharged, the half-reaction at the cathode may be assumed to be

$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$$

(i) What is the oxidation state of cobalt in CoO_2?

(ii) What is the oxidation state of cobalt in $LiCoO_2$?

(b) If the battery is overcharged, Li metal can form on one of the electrodes and this can pose a serious fire risk. At which electrode would Li be formed? Circle the correct answer in the answer booklet.

A At the anode, which is the cobalt oxide electrode.

B At the cathode, which is the cobalt oxide electrode.

C At the anode, which is the graphite electrode.

D At the cathode, which is the graphite electrode.

(c) The most commonly used organic solvent for the electrolyte is called EC. It has the molecular formula $C_3H_4O_3$. One of the products of the hydrolysis of EC is 1,2-ethanediol. Draw the structure of EC.

Lithium burns violently in air producing a mixture of lithium oxide and lithium peroxide (Li_2O_2).

(d) Give the equation for the combustion of lithium in air assuming that the two products form in a 1:1 molar ratio.

Lithium peroxide is used for air purification in confined areas, such as submarines and spacecraft. It removes carbon dioxide from the air and produces oxygen.

(e) Give a balanced equation for the reaction between lithium peroxide and carbon dioxide.

On the International Space Station, compound **A** is used for oxygen storage. Elemental analysis shows that compound **A** contains 6.52% lithium and 33.32% chlorine by mass.

(f) **(i)** Determine the empirical formula of compound **A**.

(ii) Draw a dot and cross diagram for the anion in compound **A**.

(iii) State the shape of the anion in compound **A**.

(iv) Give the equation for the decomposition of compound **A**. Assume that all the oxygen atoms in compound **A** are liberated in the form of molecular oxygen in this process.

The efficiency of a compound to store oxygen is given by its oxygen : volume ratio (*OV*).

$$OV = \frac{\text{Volume of oxygen released}}{\text{Volume of compound that released it}}$$

The density of compound **A** is 2.42 g cm^{-3}.

(g) Calculate the oxygen : volume ratio (*OV*) of compound **A** at room temperature and pressure.

2. This question is about making ammonia

The Haber process is used to make ammonia, the main use of which is in fertilisers that are often sprayed on crops. Around 1% of the entire global energy supply is used in the Haber process and so research groups are looking to find more sustainable methods of producing ammonia.

In answering this question you may need to use the following relationships and constants

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

where:

n is the number of electrons transferred in the equation for the cell reaction

F is Faraday's constant (the charge carried by a mole of electrons), which is equal to 9.65×10^4 C mol^{-1}

$E^{\ominus}_{cell}$ is the electrochemical cell potential, in volts (1 V = 1 J C^{-1})

$Q = It$

where:

Q is the electric charge, in coulombs

I is the current, in amperes

t is the time, in seconds

1 tonne = 1×10^6 g

One recently published approach to making ammonia uses the following three-step method:

Step 1 Electrolysis of molten lithium hydroxide at 750 K to form lithium metal

$$4LiOH \rightarrow 4Li + 2H_2O + O_2$$

Step 2 Reaction of lithium metal with nitrogen to form lithium nitride

Step 3 Reaction of lithium nitride with water to re-form lithium hydroxide and ammonia

Thus the lithium hydroxide formed in **Step 3** can be re-used in **Step 1** and the process can be repeated.

(a) State the two half-equations that combine to give the overall equation in **Step 1**.

The table below gives the thermochemical data (to 3 significant figures) for **Step 1**.

At 750 K	LiOH	Li	H_2O	O_2
$\Delta_f H^\theta$ / kJ mol^{-1}	–446	+15.0	–268	+15.8
S^θ / J K^{-1} mol^{-1}	+128	+63.7	+224	+236

(b) Calculate the following for **Step 1** at 750 K.

(i) ΔH^θ in kJ mol^{-1}

(ii) ΔS^θ in J K^{-1} mol^{-1}

(iii) ΔG^θ in kJ mol^{-1}

The electrolysis will only proceed at an appreciable rate when the applied potential exceeds the electrochemical cell potential by 0.60 V.

(c) Calculate the minimum potential that should be applied in **Step 1**.

(d) Write down the equations for **Step 2** and **Step 3** and hence calculate the stoichiometric ratio between the lithium produced in **Step 1** and the ammonia produced in **Step 3.**

In a small-scale experiment, the researchers applied a current of 0.200 A for 1000 seconds. The yield of lithium production in this process was 88.5%. The yield of **Steps 2** and **3** can be assumed to be 100%.

(e) Calculate the mass of lithium generated in **Step 1**.

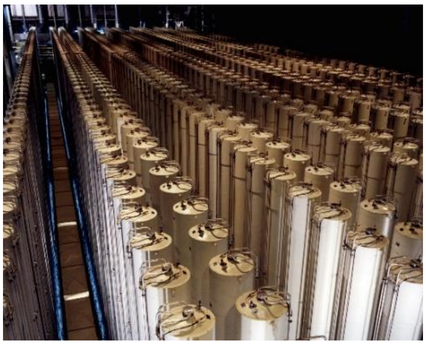
(f) Calculate the volume of ammonia produced in cm^3 at room temperature and pressure.

A potential application of this approach is to use renewable energy sources as the source of electricity for the electrolysis and to produce ammonia at a farm where it can be used straight away. The average size of a UK farm is 130 acres and a farm requires 0.0770 tonnes of ammonia per acre annually.

(g) If the lithium hydroxide was not recycled at the end of the process, calculate the total mass of lithium (in tonnes) that would have to be produced to generate the required mass of ammonia for a year.

3. This question is about the use of enriched uranium

In the news recently there have been reports of several underground nuclear bomb tests. The energy released in these nuclear bombs can come from the nuclear fission of the element uranium. Uranium occurs naturally as two main isotopes: ^{235}U and ^{238}U. However, only ^{235}U can undergo nuclear fission. Naturally occurring uranium requires enrichment (often using gas centrifuges - pictured right) to increase the proportion of ^{235}U in a sample before being used for such purposes.



The energy released (or yield) of a nuclear blast is measured in kilotons (1 kiloton = 4.184×10^{12} J). When 1 pound (0.45 kg) of ^{235}U (accurate relative atomic mass = 235.0439) undergoes complete fission, the yield is 8.0 kilotons.

(a) Calculate the energy released in the fission of ^{235}U in kJ mol^{-1}.

The accurate relative atomic mass of uranium found in the Earth's crust is 238.0289. The accurate relative atomic mass of the ^{238}U isotope is 238.0507.

(b) Assuming only ^{235}U and ^{238}U are present, calculate the percentage abundance in the Earth's crust of:

(i) ^{235}U

(ii) ^{238}U

For use in nuclear weapons, a sample of uranium must contain at least 80% of the ^{235}U isotope. As this is a much higher percentage of ^{235}U than found in the crust, the amount of ^{235}U must be enriched artificially. The enrichment of the ^{235}U isotope is performed by converting the uranium to uranium hexafluoride (UF_6), which is a gas above 57 °C. The two different isotopic forms of uranium hexafluoride gas ($^{235}UF_6$ and $^{238}UF_6$) can be separated in a centrifuge.

(c) Which property of fluorine is essential for the successful separation of $^{235}UF_6$ and $^{238}UF_6$ in a gas centrifuge? Circle the correct answer in the answer booklet.

A Elemental fluorine exists as diatomic molecules.

B Fluorine has only one naturally occurring isotope.

C Fluorine has the highest electronegativity of all elements.

D Fluorine is a gas at room temperature and pressure.

E Fluorine reacts vigorously with most metals.

UF_6 is octahedral in shape.

(d) Is UF_6 a polar molecule? Circle the correct answer in the answer booklet.

(e) Calculate how much heavier $^{238}UF_6$ is than $^{235}UF_6$. Give your answer as a percentage of the mass of $^{235}UF_6$. Use integer relative atomic masses for this part of the problem.

Once the sample of UF_6 has been enriched to contain sufficiently high amounts of the ^{235}U isotope, it must be converted back to uranium metal. Firstly, UF_6 is treated with hydrogen gas to form uranium tetrafluoride. Uranium tetrafluoride is then heated with magnesium to give uranium metal.

(f) Write equations for:

(i) the reaction of uranium hexafluoride with hydrogen.

(ii) the reaction of uranium tetrafluoride with magnesium.

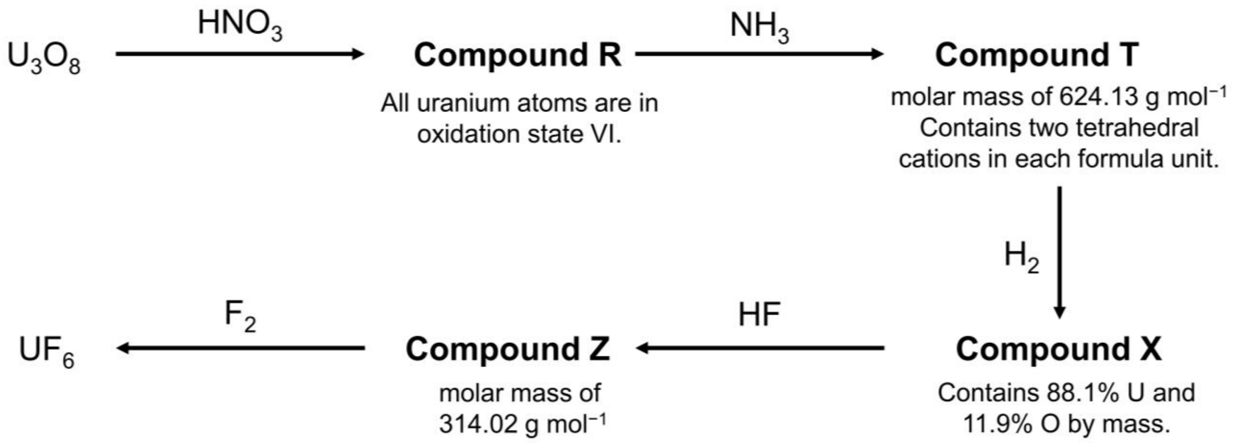
Conversion of uranium ore into UF_6 is a more complicated process. Uranium can be found in nature as the oxide U_3O_8. There are several crystal structures of U_3O_8 which all contain atoms of uranium in two different oxidation states.

(g) Give the oxidation states of uranium in U_3O_8 if the oxidation states of the uranium atoms in U_3O_8 differ by:

(i) One

(ii) Two

The conversion of U_3O_8 to UF_6 is shown in the scheme below (not all reaction by-products are shown).



(h) **(i)** Compound **R** is composed of a linear cation of charge +2 and a trigonal planar anion of charge −1. Draw the structure of both the cation and the anion present in compound **R**, showing the bonding in each structure.

(ii) Compound **T** has a complex structure. It may be considered to consist of two identical tetrahedral cations and an anionic part. Draw the structure of the tetrahedral cation and give the formula of the anionic part.

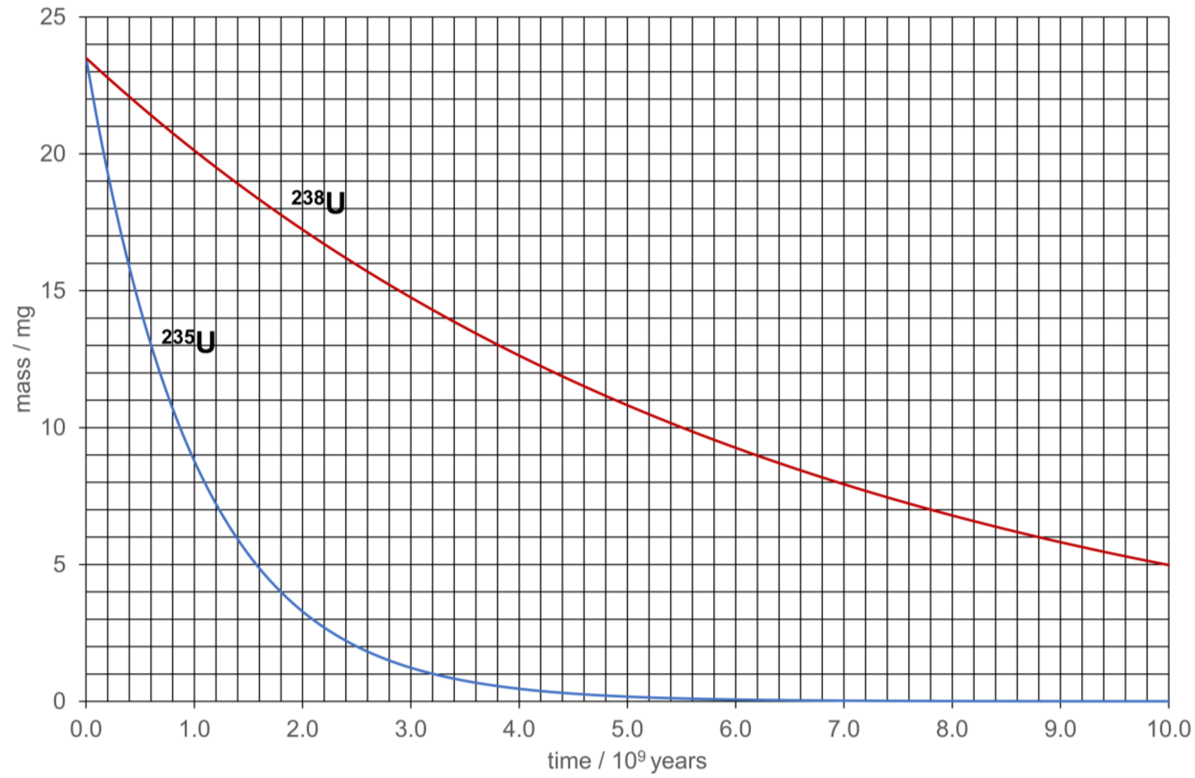
(iii) Give the formulae of compound **X** and compound **Z**.

Uranium is a radioactive element. Both ^{235}U and ^{238}U isotopes undergo alpha decay. The uranium atom is converted into an atom of a different element with the loss of an alpha particle. An alpha particle is the nucleus of a helium atom.

(i) Write radioactive decay equations for the radioactive decays of ^{235}U and ^{238}U, giving the mass number of any new element formed.

^{235}U decays much faster than ^{238}U. This means that a naturally occurring sample of uranium cannot be used to make a bomb without enriching it first.

The rate of radioactive decay of an isotope can be measured in terms of the radioactive half-life, $t_{½}$. The graph below shows how the amount of the two isotopes of uranium falls over time.



(j) Using the graph, give the half-life in years of

(i) ^{235}U

(ii) ^{238}U

The following equation relates the number of radioactive atoms, N, remaining after a time t, to the number initially present, N_0.

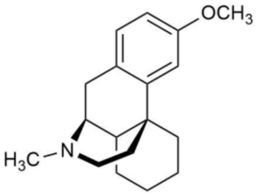
$$N = N_0 e^{-\lambda t} \quad \text{where} \quad \lambda = \frac{\ln 2}{t_{½}}$$

It is assumed that when the Earth was formed, the number of atoms of ^{235}U and ^{238}U was the same.

(k) Estimate the age of the Earth using your answers to earlier parts of the question.

4. This question is about cough suppressants

In September 2017, the UK Prime Minister, Theresa May, had a bad cough during her speech at the Conservative Party Conference. The cough suppressant drug dextromethorphan, which is present in cough remedies such as Benylin®, could have helped her out. This question is about the synthesis of dextromethorphan. The synthesis involves the formation of some strong bonds and some stable carbocations.



dextromethorphan

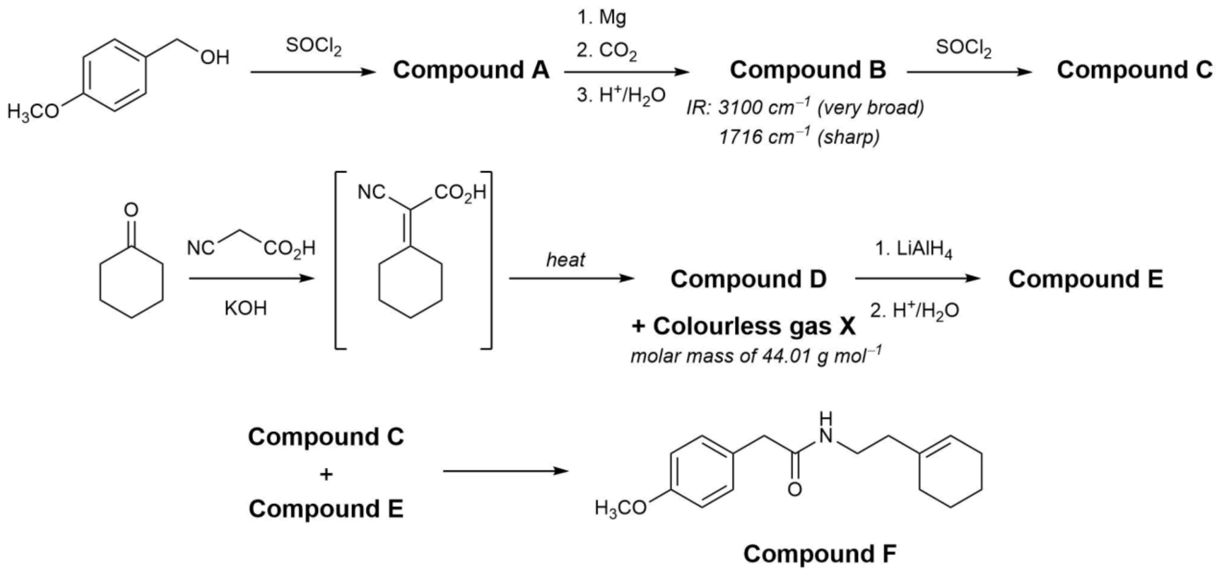
Dextromethorphan is often administered as the hydrobromide monohydrate salt.

(a) In the answer book, circle the atom in dextromethorphan that is protonated in the salt.

(b) Determine the molecular formula of dextromethorphan and hence calculate the molar mass of the dextromethorphan hydrobromide monohydrate salt.

The synthesis of dextromethorphan takes a number of steps. Please note that in the schemes describing the synthesis, by-products of the reactions are not always shown.

The synthesis of dextromethorphan begins with the synthesis of compound **F**.



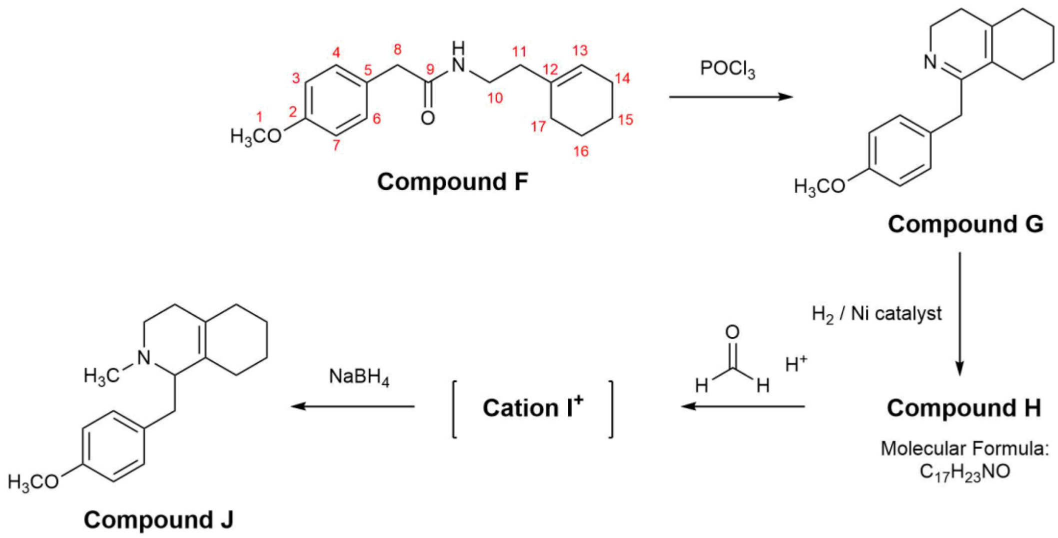
(c) Draw the stuctures of compounds **A**, **B**, **C**, **D**, **E** and gas **X**.

In the reaction to make compound **D**, the cyanoacetic acid can be deprotonated twice by the potassium hydroxide.

(d) **(i)** Draw a structure for anion **Z⁻**.

(ii) Draw a structure for dianion $\mathbf{Z^{2-}}$.

The synthesis continues with the conversion of compound **F** to compound **J**.



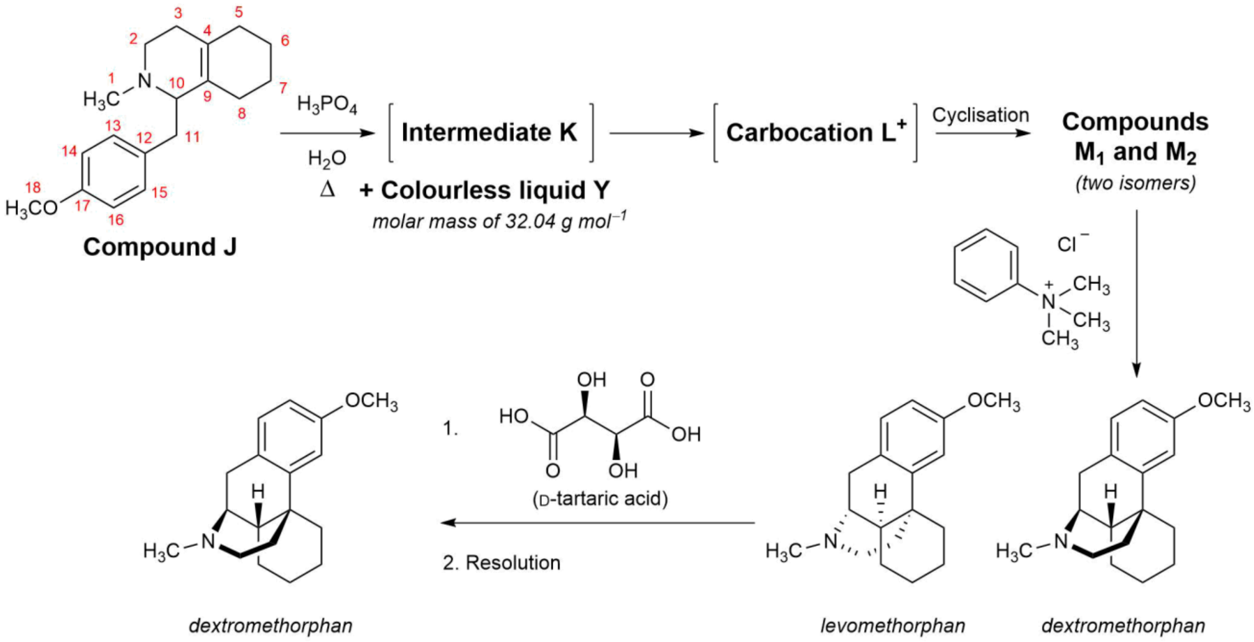
(e) Write down the numbers of the two carbon atoms in compound **F** that are connected in the reaction to synthesise compound **G**.

(f) Draw the structures of compound **H** and cation $\mathbf{I^+}$.

The synthesis continues with the conversion of compound **J** to compounds **M_1 and M_2** in one step. Upon heating with aqueous phosphoric acid, compound **J** is first converted into intermediate **K** and a colourless liquid **Y**. Intermediate **K** is then converted to carbocation **L^+**, which undergoes cyclisation to give the mixture of the two isomers **M_1** and **M_2**.

Treatment of the mixture of **M_1** and **M_2** with trimethylphenylammonium chloride (a methylating agent) gives a mixture of levomethorphan and dextromethorphan.

The addition of D-tartaric acid to this mixture allows the desired dextromethorphan to be separated from the undesired levomethorphan. This process is called resolution.



In the conversion of compound **J** to compounds **M_1** and **M_2** it is possible for different pairs of carbon atoms to become connected.

(g) Indicate all pairs of carbon atoms that can be connected in this reaction.

(h) Draw the structures of intermediate **K**, carbocation **L^+** and liquid **Y**.

(i) Complete the structures of the two isomers **M_1** and **M_2** indicating clearly any atoms other than hydrogen that come out of the plane of the paper (with wedged lines) and go into the plane of the paper (with dashed lines).

State what type of isomers **M_1** and **M_2** are.

5. This question is about the 'inert' gas helium

In 2013 newspapers reported that scientists were asking the government to ban the sale of party balloons filled with helium, as its use in scientific applications such as superconducting magnets meant it was far too valuable to squander on children's parties.

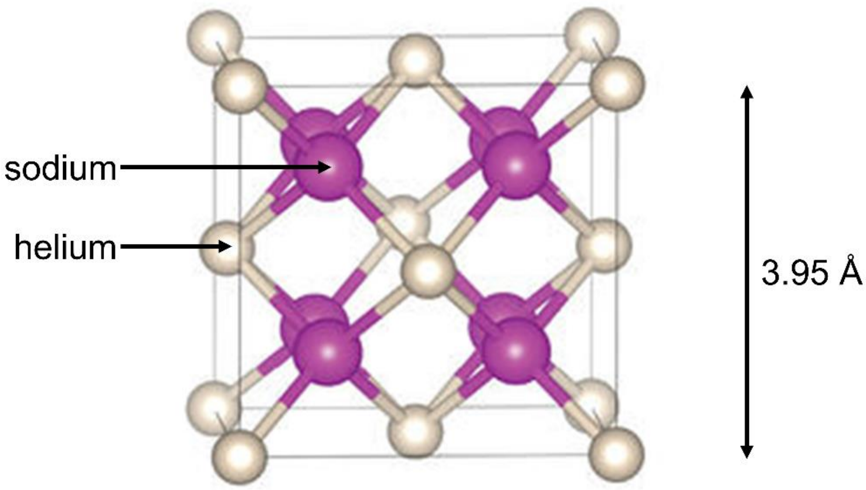
Helium is present in the Earth's atmosphere at an average concentration of 0.916 mg m^{-3} and the volume of the Earth's atmosphere is approximately 4.2×10^9 km^3.

(a) Calculate the number of moles of helium in the Earth's atmosphere.

(b) The volume of a sphere of radius r is $^4/_3\pi r^3$. Assuming party balloons are spherical and have a radius of 14 cm, calculate the number of balloons that can be filled with helium from the Earth's atmosphere at room temperature and pressure.

Helium is very unreactive, with a full outer shell and the highest ionisation energy of any element. Last year a collaboration between 17 researchers across the globe suggested that compound **X** (a compound of helium and sodium) had been formed under an extreme pressure of 300 GPa.

The unit cell of a crystal is determined by X-ray crystallography and shows the arrangement of the atoms in the crystal. Stacking the unit cells together generates the bulk structure.



The unit cell of compound **X** is represented in the diagram above, with helium atoms positioned at the corners and at the centres of the faces of the unit cell, and sodium atoms positioned cubically within the unit cell. Some of the atoms are contained completely within the boundaries of a single unit cell, whilst for atoms centred on the corners, edges or faces, only a fraction of the atom is contained within a single unit cell.

(c) By considering the number of fractions of atoms within one unit cell, count the total numbers of sodium and helium atoms within one unit cell.

(d) What is the formula of compound **X**?

(e) Use your answer in part **(c)** and the dimensions of the unit cell to calculate the density of compound **X** in g cm^{-3}.

Calculations on compound **X** have shown that the sodium atoms in compound **X** are present as Na^+ ions. The valence electrons of the sodium atoms have formed pairs and are localised in the gaps of the crystal structure.

(f) Which of the following do you expect compound **X** to be? Circle all correct answers in the answer booklet.

A A metallic solid

B A covalent solid

C An ionic solid

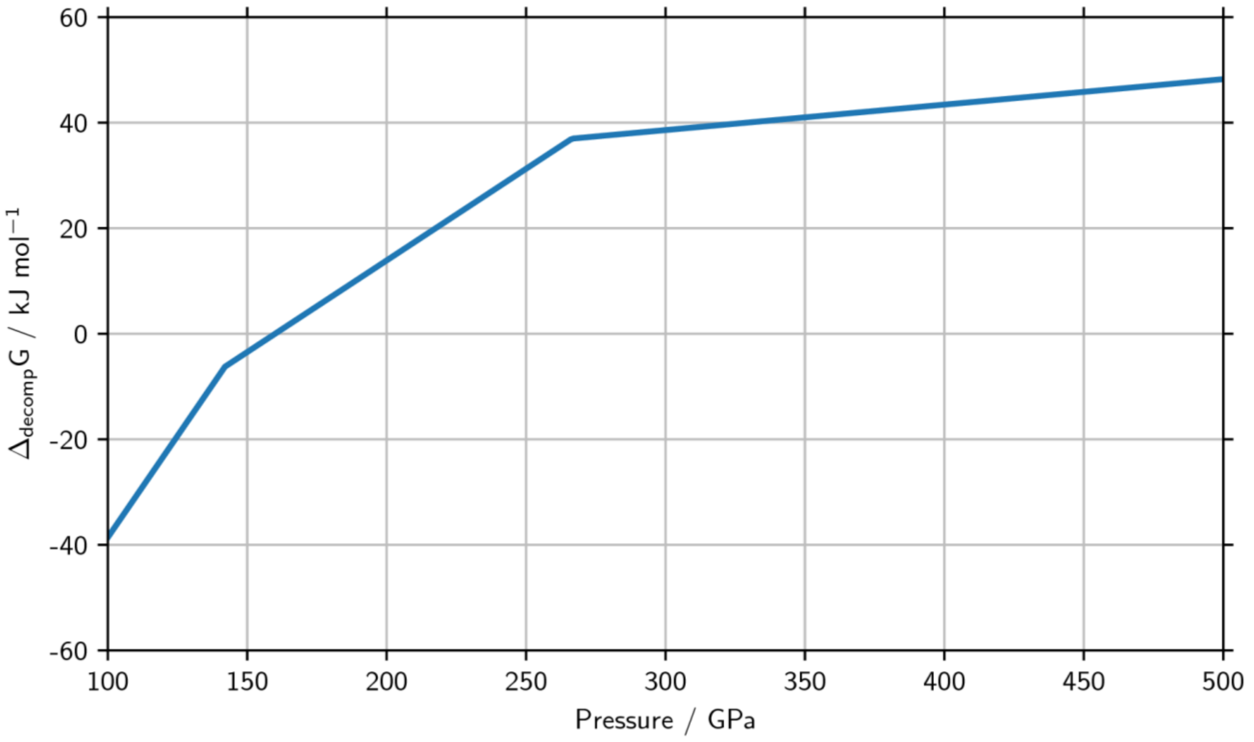
D A conductor

E An insulator

At atmospheric pressure, compound **X** is not stable; it decomposes into a mixture of sodium and helium.

(g) Write an equation for the decomposition of compound **X**.

The graph below shows how the free energy change of decomposition, $\Delta_{decomp}G$, changes as a function of pressure.



(h) What is the minimum pressure at which the formation of compound **X** becomes thermodynamically favourable?

Acknowledgements & References

Q1 Image credit: wk1003mike / shutterstock.com

Q2 Ammonia Synthesis from N_2 and H_2O using a lithium cycling electrification strategy at atmospheric pressure *Energy & Environmental Science*, **2017**, *10*, 1621–1630.
Image credit: Todd Klassy / shutterstock.com Link

Q3 Image credit: Photo courtesy of U.S. Photonics, Inc., authored by Nuclear Regulatory Commission, under the Creative Commons Attribution 2.0 Generic license

Q4 *Thieme Pharmaceutical Substances.*
Image credit: Carl Court / Getty Images News

Q5 A stable compound of helium and sodium at high pressure *Nature Chemistry*, **2017**, *9,* 440–445.
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