ROYAL SOCIETY
OF CHEMISTRY

56th INTERNATIONAL

CHEMISTRY OLYMPIAD

2024

UK Round One

STUDENT QUESTION BOOKLET

* * * * *

- **The time allowed is two hours.**
- **Attempt all five questions.**
- **Write your answers in the student answer booklet.**
- **Write only the essential steps of your calculations in the answer booklet.**
- **Always give the appropriate unit and number of significant figures.**
- **A copy of the periodic table and some useful physical constants and formulae are provided as a separate document.**
- **Do *NOT* write anything in the right-hand margin of the answer booklet.**
- **The marks available for each question are shown below. These may be helpful when dividing your time between questions.**

Question	1	2	3	4	5	**Total**
Marks Available	8	15	20	24	15	**82**

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

Q1 This question is about Bronze

The England women's football team achieved success at the 2023 World Cup. One of the players was Lucy Bronze. The metal bronze is an alloy of copper and tin.

The World Cup trophy was made of silver coated with yellow and white gold. It has a mass of 4.60 kg.

(a) Which of the following represents the electronic configuration of a silver atom? Tick the correct answer in the answer booklet.

[Ar]$4d^{10}$ [Ar]$4d^{10}5s^1$ [Kr]$4d^{10}$ [Kr]$4d^{10}5s^1$

(b) Which of the following represents the electronic configuration of a Cu^{2+} ion? Tick the correct answer in the answer booklet.

$1s^22s^22p^63s^23p^63d^{10}4s^1$ $1s^22s^22p^63s^23p^63d^{10}$

$1s^22s^22p^63s^23p^63d^9$ $1s^22s^22p^63s^23p^64s^23d^9$

(c) Calculate the volume of the trophy assuming that it was solid silver. The density of silver is 10.5 g cm^{-3}.

Trophies are often made of bronze instead as it is cheaper.

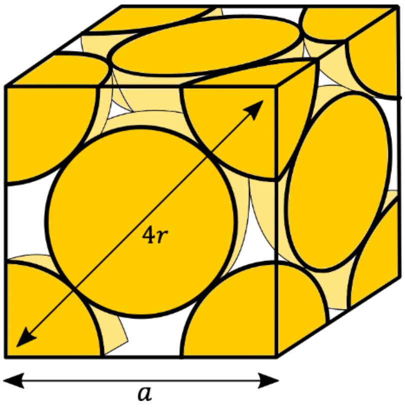
The density of bronze varies depending on the fraction of tin, y, in the alloy. The density of the bronze, in g cm^{-3}, can be calculated by the following equation, where $V = 5.93 \times 10^{-23}$ cm^3 and $M_{(\mathrm{Cu})}$ and $M_{(\mathrm{Sn})}$ are molar masses in g mol^{-1}.

$$\text{density} = \frac{4\left(M_{(\mathrm{Cu})} + y\left(M_{(\mathrm{Sn})} - M_{(\mathrm{Cu})}\right)\right)}{V \times N_\mathrm{A}}$$

(d) Calculate the percentage of tin in a sample of bronze with density 7.85 g cm^{-3}.

Bronze generally has the same structure as pure copper. Copper has a face centred cubic unit cell shown on the right.

The atomic radius of a copper atom, r, is 128 pm. The length of the diagonal across the face is $4r$.



(e) Calculate the length of the side of the unit cell, a, in cm.

(f) Calculate the volume of the unit cell in cm^3.

(g) Calculate the density of copper metal in $g\ cm^{-3}$.

Q2 This question is about iodate salts

Most minerals of iodine contain iodate ions, IO_3^-. One such mineral is called salesite.

A sample of the mineral of salesite

(a) Give the oxidation state of iodine in the iodate ion.

(b) Draw the dot and cross diagram of the iodate ion.

(c) What is the most likely O–I–O bond angle in the iodate ion? Tick the correct answer in the answer booklet.

<109.5°   109.5°   >109.5°

Nuclear disasters can release radioactive isotopes of iodine which are harmful.

A daily dose of the element iodine equivalent to 130 mg of potassium iodide can prevent the absorption of radioactive isotopes.

Potassium iodide can easily degrade. The UK government has a stock of a more stable iodine source, potassium iodate, as a source of the element iodine for this purpose.

(d) Calculate the mass of potassium iodate which contains the same amount of iodine as 130 mg of potassium iodide.

Iodate ions react with iodide ions under acidic conditions to give iodine.

(e) **(i)** Write an ionic equation for the reaction between iodate ions and iodide ions under acidic conditions.

(ii) What type of reaction is this? Tick the correct answer(s) in the answer booklet.

redox   electrophilic substitution   elimination   disproportionation   polymerisation

This reaction is used to determine the amount of iodate ions in a sample. The sample reacts with excess potassium iodide under acidic conditions, and the iodine formed is titrated with a solution of thiosulfate ions ($S_2O_3^{2-}$), giving iodide ions and tetrathionate ions ($S_4O_6^{2-}$).

(f) Write an ionic equation for the reaction between thiosulfate ions and iodine.

The iodate mineral salesite has the molecular formula $\mathbf{M(IO_3)Z}$, where **M** is a metal ion, and **Z** is an anion. The ratio of the three ions in the mineral is 1:1:1. The molar mass of the mineral is 255.46 g mol^{-1}.

1.000 g of the mineral was dissolved in 30 cm^3 of 2 mol dm^{-3} HNO_3. The resulting solution was made up to 100.0 cm^3 with distilled water, forming a stock solution.

10.00 cm^3 of this stock solution reacts with excess potassium iodide. The iodine formed was titrated with 0.1000 mol dm^{-3} sodium thiosulfate solution.

(g) Calculate the volume of sodium thiosulfate solution needed to react with the iodine produced.

Assume that all iodine was formed in the reaction of iodate ions with iodide ions.

However, the metal ion $\mathbf{M^{n+}}$ in this mineral also reacts with iodide ions to form additional iodine. Therefore, the actual volume of sodium thiosulfate solution required in the titration was found to be 27.40 cm^3.

(h) Calculate the number of moles of iodine produced by the reaction of one mole of metal ion $\mathbf{M^{n+}}$ with excess iodide ions.

If you could not get a value in part **(g)**, assume that the answer in part **(g)** was 15.67 cm^3.

(i) The oxidation state of metal ion $\mathbf{M^{n+}}$ in the mineral can be written as +n. Give the oxidation state of the metal ion after it has reacted with iodide ions. Tick the correct answer in the answer booklet.

+(n+3) +(n+2) +(n+1) +(n) +(n−1) +(n−2) +(n−3)

When the mineral was dissolved in nitric acid, no effervescence was observed.

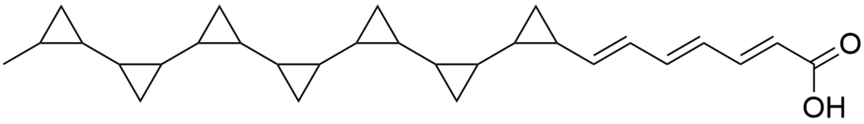
(j) Give the formula of two anions which could not be present in the mineral based on the observation above.

(k) Considering all the information given in the problem, choose from the list of ions below which is metal ion $\mathbf{M^{n+}}$ and anion $\mathbf{Z^{m-}}$.

$\mathbf{M^{n+}}$	Sc^{3+}	Fe^{2+}	Fe^{3+}	Cu^{+}	Cu^{2+}	Mg^{2+}	Ga^{2+}	Zn^{2+}
$\mathbf{Z^{m-}}$	F^{-}	Cl^{-}	Br^{-}	H^{-}	O^{2-}	OH^{-}	PO_4^{3-}	SO_3^{2-}

Q3 This question is about fuel-producing bacteria

Scientists have developed a strain of bacteria that can produce molecules with the energy density of rocket fuels. They have given these molecules the nickname ‘fuelomycins.’



fuelomycin A

Fuelomycins contain multiple cyclopropane rings, which are ‘high energy’ due to a property called ring strain.

cyclopropane

The skeletal formula of cyclopropane is shown above.

(a) Determine the molecular formula of cyclopropane.

To determine how much energy is attributed to ring strain, we can compare cyclopropane to a ring with essentially no ring strain, cyclohexane.

The enthalpy of combustion for cyclopropane is –2091 kJ mol^{-1}; the enthalpy of combustion for cyclohexane is –3951 kJ mol^{-1}.

The enthalpy of formation for water is –285.8 kJ mol^{-1}; the enthalpy of formation for carbon monoxide is –110.5 kJ mol^{-1}; the enthalpy of formation for carbon dioxide is –393.5 kJ mol^{-1}.

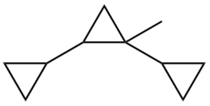
(b) **(i)** Write the equation for combustion of cyclopropane.

(ii) Calculate the enthalpy of formation for cyclopropane.

(iii) Calculate the enthalpy of combustion per mol of carbon atom for cyclopropane.

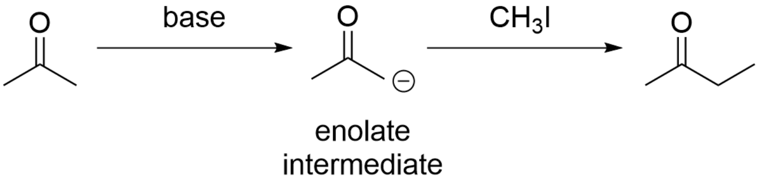
(iv) Calculate the enthalpy of combustion per mol of carbon atom for cyclohexane.

The idea to use cyclopropanes in the structure of a rocket fuel was first developed in 1959 with the molecule syntin.



syntin

The synthesis of syntin relies on enolate chemistry. This is when the carbon next to a carbonyl group (i.e. in the alpha position) is deprotonated. This enolate intermediate can then react with another molecule such as iodomethane to give a final product.

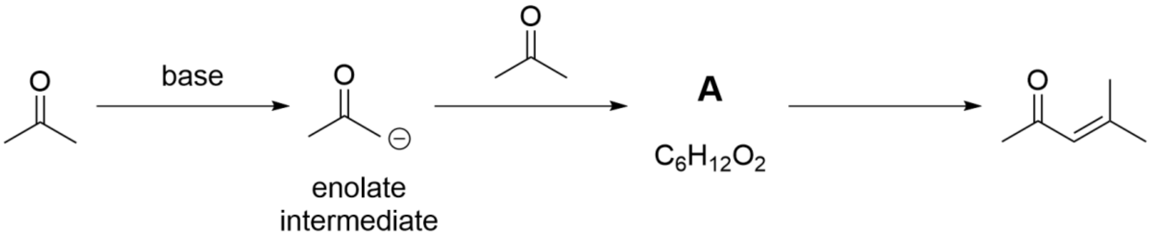


(c) Draw a resonance form of the enolate intermediate.

(d) In the answer booklet, tick the correct statement(s) about the reaction between iodomethane and the enolate intermediate:

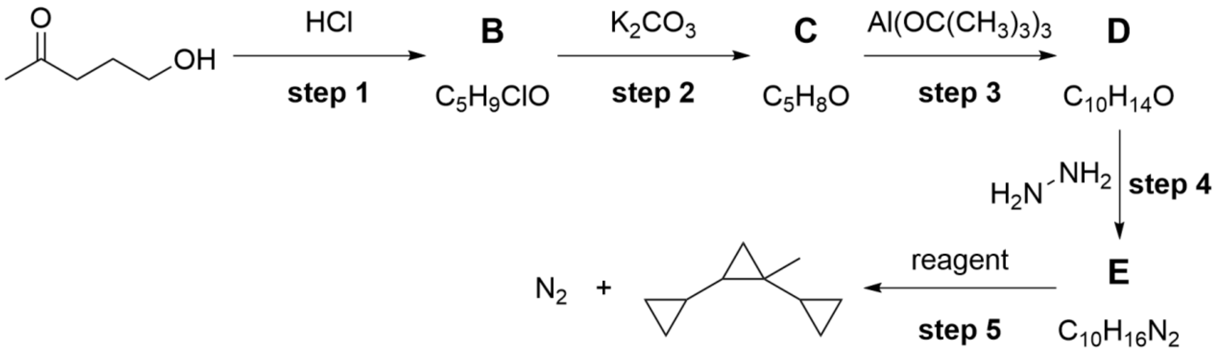
- The enolate intermediate acts a reducing agent; the iodomethane acts an oxidising agent.
- The enolate intermediate acts an oxidising agent; the iodomethane acts a reducing agent.
- The enolate intermediate acts an electrophile; the iodomethane acts a nucleophile.
- The enolate intermediate acts a nucleophile; the iodomethane acts an electrophile.
- The enolate intermediate acts an acid; the iodomethane acts a base.
- The enolate intermediate acts a base; the iodomethane acts an acid.

Enolates can also react with a carbonyl compound as shown below.



(e) Draw the structure of compound **A** which is formed as an intermediate in this reaction.

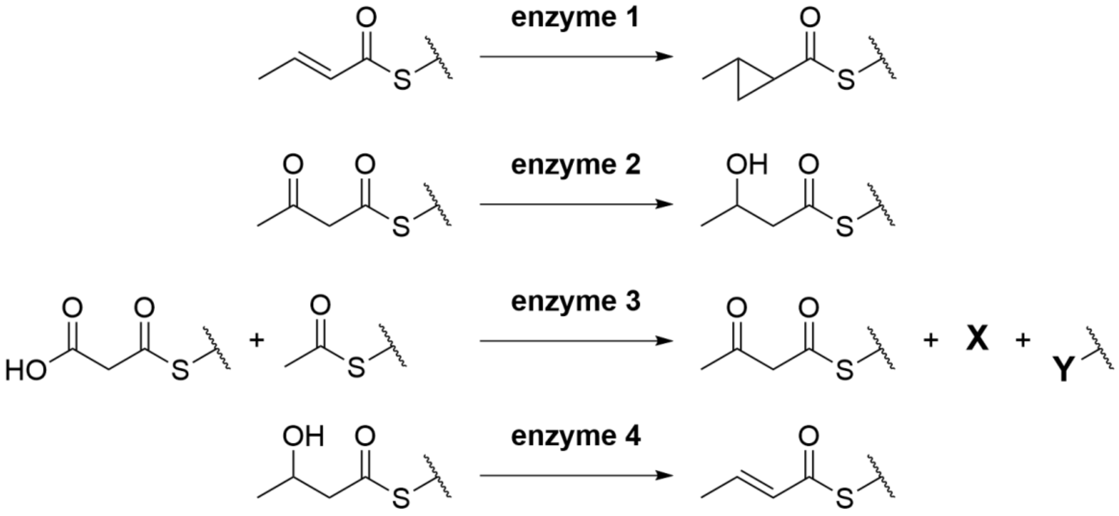
Syntin was synthesised on industrial scale according to the scheme below.



(f) **(i)** Determine the structure of compounds **B – E**.

(ii) Tick which step(s) involve enolate chemistry in the answer booklet.

The production of syntin was halted due to high expense. For this reason, bacteria that produce a rocket fuel are a huge advantage as they can produce the molecules more economically. The bacteria developed to make fuelomycins require enzymes that can catalyse four types of reactions.

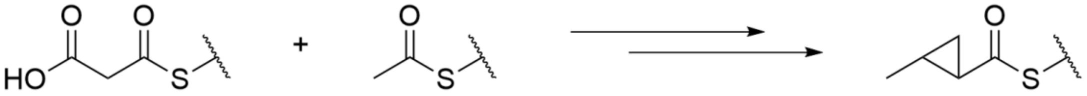


(g) Tick the reaction type catalysed by enzyme 2 in the answer booklet.

oxidation reduction condensation hydrolysis isomerisation elimination

(h) Identify the other products **X** and **Y** of enzyme 3.

The synthesis of fuelomycin A begins in the following way. For this sequence, each enzyme is required exactly once.



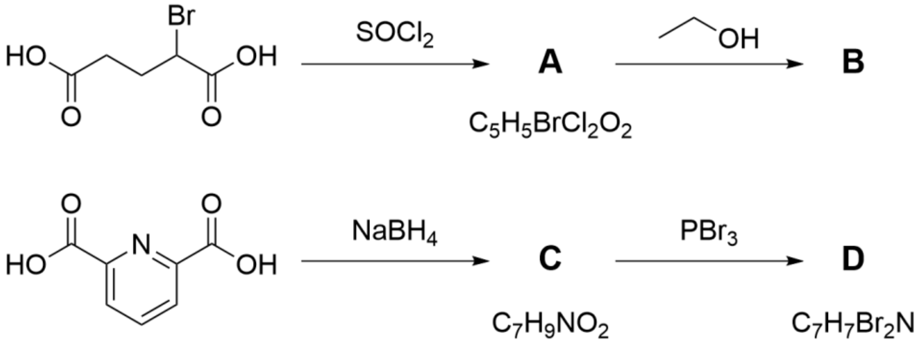
(i) Complete the table in the answer booklet to give the order of the enzymes required for this process.

Q4 This question is about the MRI contrast agent gadopiclenol

Due to shortages in the NHS, there was no hospital gown to fit UK Team Mascot Paddington after he had taken his clothes off ready for a magnetic resonance imaging (MRI) scan.

MRI uses the same technology as NMR. To enhance the image, patients are often given a contrast agent containing gadolinium(III) ions. In 2022 the US government approved the use of a new contrast agent, gadopiclenol ($C_{35}H_{54}GdN_7O_{15}$).

The synthesis of gadopiclenol starts with the synthesis of compounds **B** and **D**.

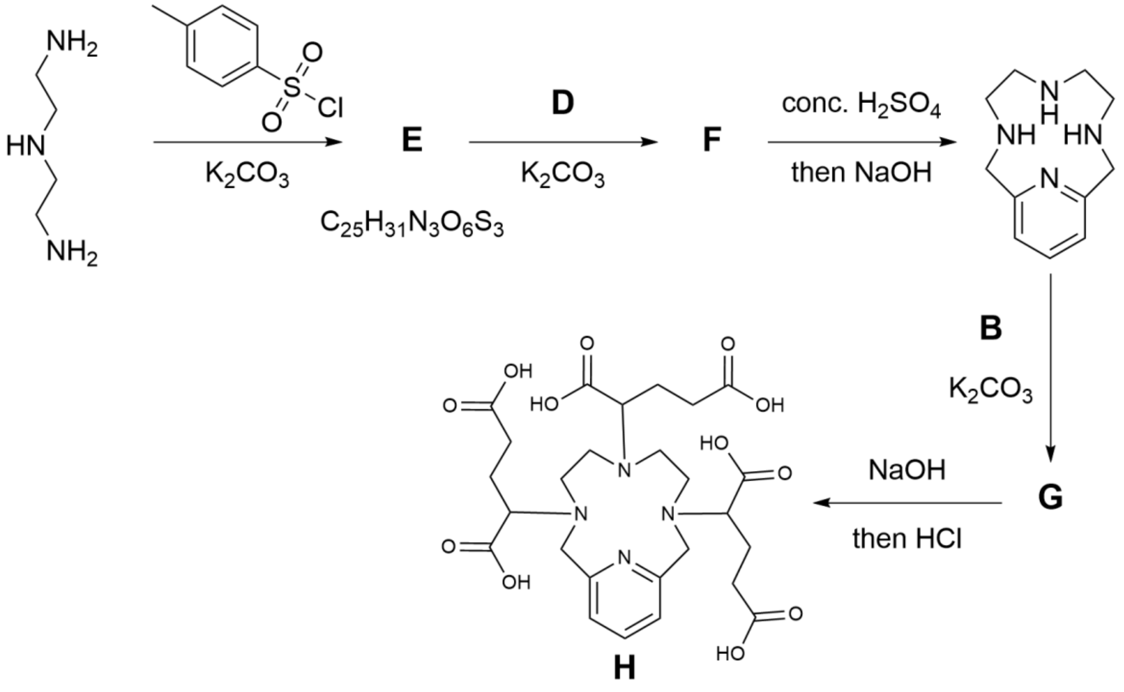


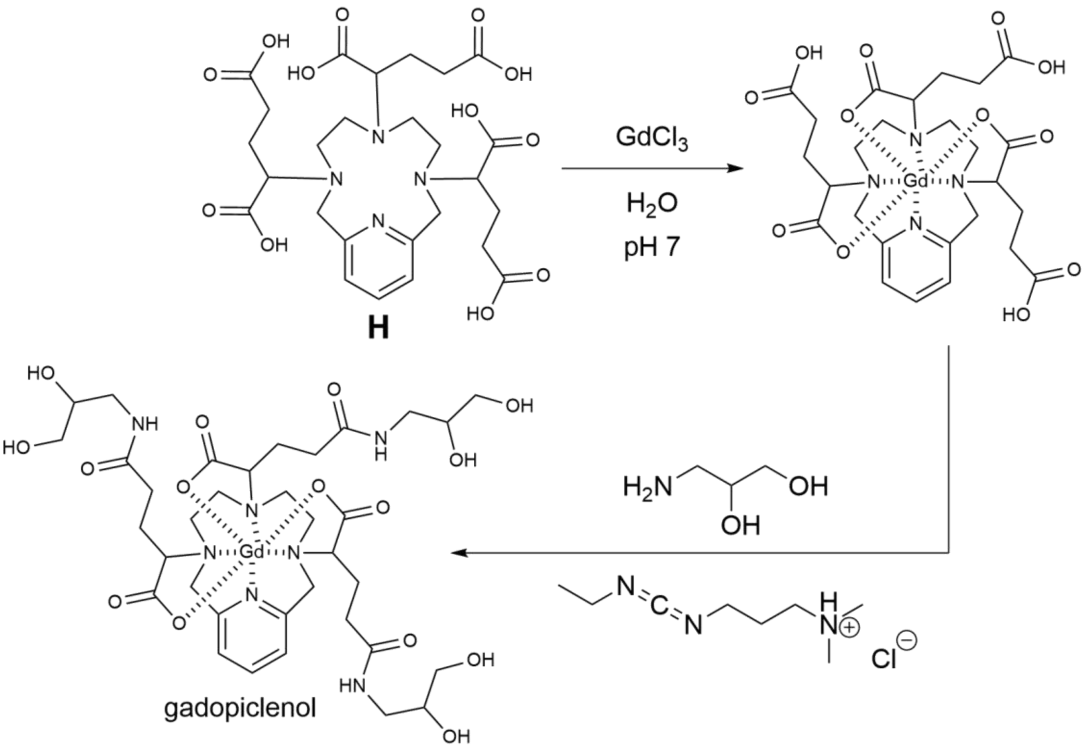
(a) Draw the structures of compounds **A** – **D**.

The synthesis continues with the construction of hexacarboxylic acid compound **H**.

(b) Circle the stereocentres on the structure of compound **H** in the answer booklet.

(c) Draw the structures of compounds **E** – **G**.



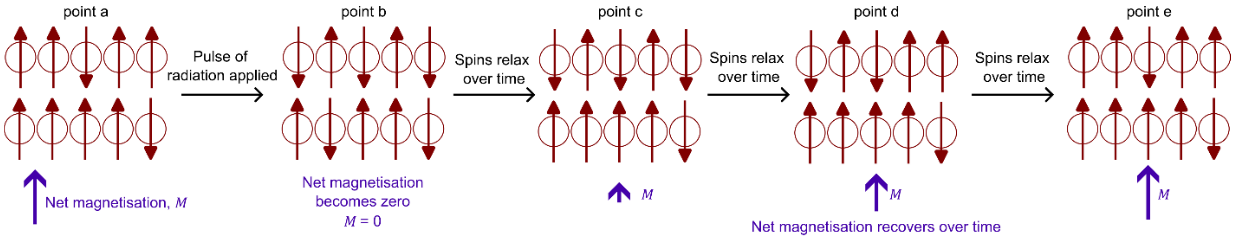


Compound **H** is converted into gadopiclenol in two steps. Since gadolinium is toxic, gadopiclenol has the benefit that less gadolinium is required per dose. The average dose of gadopiclenol is 6.00 cm^3 of an aqueous solution of concentration 485.05 g dm^{-3}.

(d) Calculate the mass of the element gadolinium required per dose, in mg.

In a magnetic field, hydrogen nuclei can be "spin up" (↑) or "spin down" (↓). Each spin acts as a small magnet. We can sum all the spins together to get a value called the net magnetisation, M. More nuclei will initially be spin up as this is lower in energy (point a).

A pulse of electromagnetic radiation is applied that corresponds to the difference in energy between the spin up and the spin down state, and this flips just enough spins to reduce M to zero (point b).



(e) What type of electromagnetic radiation would be required to do this? Tick the correct answer in the answer booklet.

radiowave   microwave   IR   visible   UV   X-ray   gamma ray

Over time (between point b and point e), some higher energy spin down protons flip back to being spin up. We call this relaxation. We can detect this, and this gives us our MRI data. The whole process (point a to point e) is one scan.

An MRI machine needs to run multiple scans to make a clear image. However, it can only run the next scan once the hydrogen nuclei have fully relaxed to their starting arrangement.

The value of the net magnetisation, M, at time, t, after the pulse is given by the following equation, where M_0 is the value of the net magnetisation before the pulse and τ is a constant called the relaxation time.

$$M = M_0\left(1 - e^{-\frac{t}{\tau}}\right)$$

(f) Calculate the net magnetisation as a percentage of M_0 at a time of 3τ after the pulse of radiation has been applied.

Gadolinium contrast agents are used to decrease the value of τ so the next scan can be taken sooner. Proton spins relax faster when they are close to unpaired electrons. As the gadolinium(III) ion is large, there is space for water molecules to coordinate to the gadolinium in addition to the seven coordinating atoms from the ligand. This allows their protons to relax more quickly. The water molecules which coordinate to the gadolinium are constantly exchanging with other water molecules in the solvent, allowing many protons to be relaxed in a short amount of time.

The quality of a contrast agent is therefore determined by:

- The number of unpaired electrons on the metal ion (seven in gadolinium(III))
- The average number of coordinated water molecules
- The rate at which the coordinated water is exchanged with the solvent

We can define a molar fraction, χ, as the ratio of the number of moles of gadopiclenol to the number of moles of water at the site being imaged.

$$\chi = \frac{n(\text{gadopiclenol})}{n(\text{H}_2\text{O})}$$

(g) Calculate χ if the molar concentration of gadopiclenol at the image site is 0.0500 mol dm^{-3}. Assume the density of water in the tissue is 1.00 kg dm^{-3}.

Assume that the overall relaxation time, τ, is described by:

$$\tau = \tau_c + \tau_e$$

The relaxation time, τ_c, does not depend on the magnetic field of the MRI machine, B, whereas the relaxation time, τ_e, has the following dependence:

$$\tau_e \propto \frac{1}{B^2}$$

We can determine τ_c by measuring the overall relaxation times τ_1 and τ_2 at two different magnetic field strengths, B_1 and B_2, respectively.

(h) Express the field independent relaxation time, τ_c, in terms of B_1, B_2, τ_1 and τ_2.

At low temperature,

$$\tau_c = \frac{1}{q\chi r_c}$$

where q is the number of water molecules coordinated to gadolinium and r_c is the rate at which the coordinated water is exchanged with the solvent.

The exchange rate, r_c, depends on the temperature in Kelvin, T, as follows:

$$r_c = ATe^{-\frac{\Delta H}{RT}}$$

where ΔH is the activation enthalpy and A is a constant.

(i) Rearrange the expression for τ_c into the form:

$$y = \frac{a}{T} + b$$

expressing y as a function of τ_c and T, and the coefficients a and b in terms of q, χ, A, ΔH and R.

(j) Some low temperature values of τ_c are given in the table below. Using the result of part **(i)**, or by any other means, calculate the value of $Aq\chi$ in K^{-1} s^{-1}.

T / K	275	280
τ_c / s	4.775×10^{-4}	3.326×10^{-4}

(k) Applying a similar approach to exchange rates at high temperature, it has been calculated that:

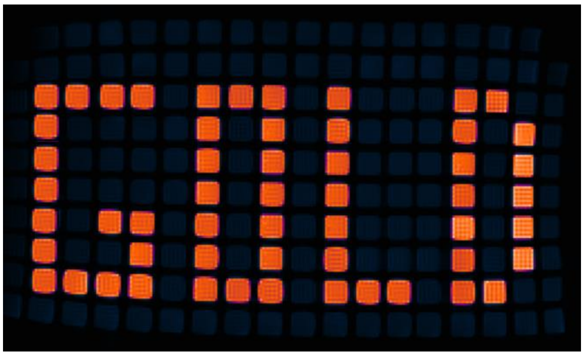
$$\frac{A}{q\chi} = 6.618 \times 10^{14}\ \mathrm{K^{-1}\ s^{-1}}$$

Use this information and your previous results to calculate q (the average number of water molecules coordinated to gadopiclenol).

If values from previous calculations are not available, use:

$\chi = 0.00100$ and $Aq\chi = 2.00 \times 10^{9}\ \mathrm{K^{-1}\ s^{-1}}$.

Whilst you have been working on this question, the MRI scan of Paddington's brain was completed. Paddington was thinking about the medals the UK Team would win at the time.

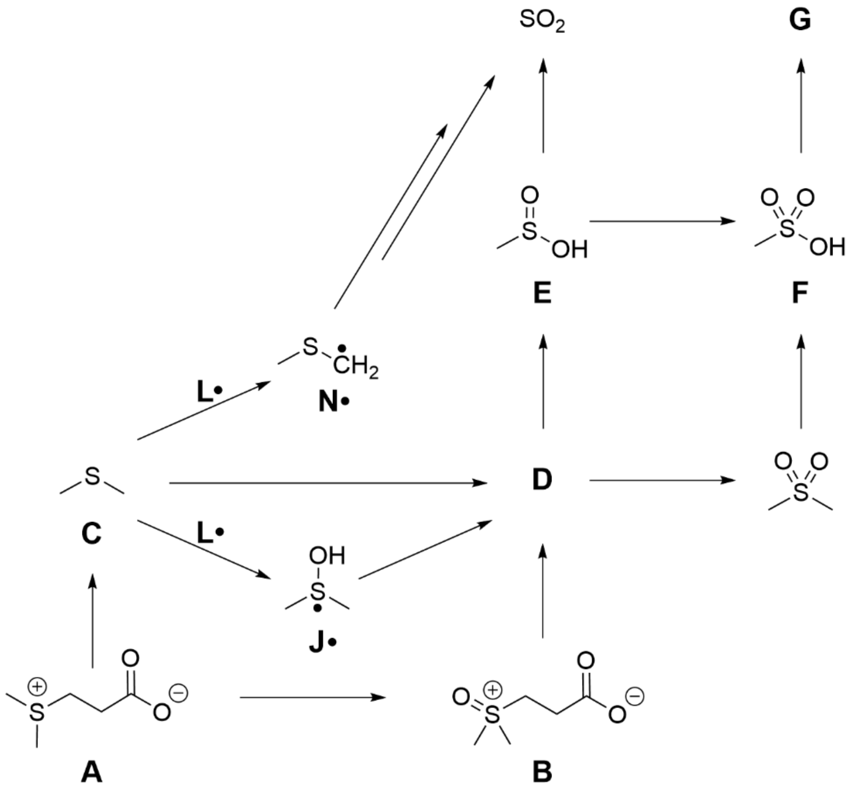


Q5 This question is about sulfur-containing molecules in the atmosphere

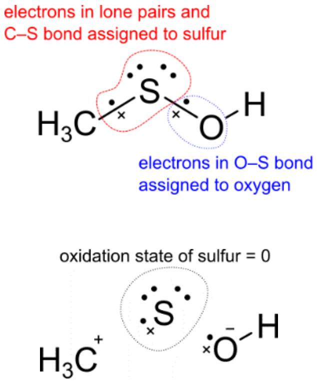
In September 2023, NASA published spectroscopy from the James Webb space telescope indicating the presence of methane and water in the atmosphere of exoplanet K2-18b. They also found possible evidence of dimethylsulfide, which is produced on earth by marine microorganisms and is a possible signature of life.

Dimethylsulfide is a volatile liquid with a disagreeable odour that occurs naturally in foods such as cabbage.

On Earth, organic sulfur-containing molecules are quickly broken down by oxidation the atmosphere. The sulfur species are shown in the scheme below.



The oxidation state of sulfur changes during the cycle. An example of determining the oxidation state of sulfur in a molecule is shown on the right.



For each covalent bond made by sulfur, assign the shared electron pair(s) to the more electronegative atom.

Electronegativities: H = 2.20, C = 2.55, S = 2.58, O = 3.44

Determine the resulting charge on the sulfur atom by comparing the number of electrons allocated to the sulfur atom to the number in a neutral sulfur atom. The resulting charge is the oxidation state of the sulfur.

(a) Determine the oxidation states of sulfur in compounds **B**, **C** and **E**.

Compound **D** can be formed from the reaction of compound **C** with oxygen.

(b) **(i)** Write an equation for the reaction of compound **C** with oxygen to form compound **D**.

(ii) Draw the structure of compound **D**.

Compound **G** is highly soluble in water, dissolving to form a diprotic acid.

(c) Give the formula of compound **G**.

Assume at 323 K compound **G** behaves as an ideal gas. 13.4 cm^3 of gas **G** at 100 kPa is dissolved in 1.000 dm^3 of water.

(d) Calculate the pH of the resulting solution to the nearest whole number. Assume that the acid fully dissociates.

The direct reaction of compound **C** with oxygen to form compound **D** is very slow. In the atmosphere compound **D** is formed by a reaction with a radical **L**$^\bullet$.

Radical **L**$^\bullet$ can react with compound **C** in two different ways, producing intermediates **J**$^\bullet$ and **N**$^\bullet$.

(e) In the answer booklet, tick which of the following descriptions are correct about what happens to compound **C** during the formation of intermediates **J**$^\bullet$ and **N**$^\bullet$.

	Forming **J**$^\bullet$	Forming **N**$^\bullet$
Loss of a H$^+$		
Loss of a H$^\bullet$		
Loss of a H$^-$		
Reduction of sulfur		
Oxidation of sulfur		
Atomisation		
Radical substitution		
Radical addition		

(f) Give the formula of radical **L**$^\bullet$.

The rate law for the formation of $\mathbf{J}^{\bullet}$ is:

$$\text{rate} = k_1[\mathbf{C}]^a[\mathbf{L}^{\bullet}]^b$$

The progress of the reaction was studied in the gas phase at 298 K for two different initial concentrations with an inert gas making up the remaining composition. The pressure was fixed at 100 kPa, and the concentrations as a function of time are given below.

	Experiment 1			Experiment 2		
Time / s	0	10	20	0	10	20
[**C**] / µmol dm^{-3}	1000.00	999.50	999.25	500.00	499.42	499.00
[$\mathbf{L}^{\bullet}$] / µmol dm^{-3}	1.00	0.50	0.25	2.00	1.42	1.00
[$\mathbf{J}^{\bullet}$] / µmol dm^{-3}	0.00	0.50	0.75	0.00	0.58	1.00

The concentration of an ideal gas at 298 K at 100 kPa is 40.4 mmol dm^{-3}.

(g) Determine the values of a and b.

In gas phase reactions, a collision with an additional molecule, X, is sometimes required to provide or remove energy. Any gas present in the mixture can play the role of X (it could be any of the molecules reacting or another unreactive species).

The formation of SO_2 from compound $\mathbf{N}^{\bullet}$ is an example of such a reaction. The overall equation is:

$$\mathbf{N}^{\bullet} + O_2 + X \rightarrow SO_2 + X + \text{other products}$$

When [$\mathbf{N}^{\bullet}$] and [O_2] are low, this reaction appears to have the following rate law:

$$rate = k_2[\mathbf{N}^{\bullet}][O_2]$$

where rate constant, $k_2 = 5.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and 100 kPa.

The actual rate law for this reaction involves all three species:

$$rate = k_3[\mathbf{N}^{\bullet}][O_2][X]$$

(h) Calculate the value of k_3 at 298 K with units in terms of molecules cm^{-3} rather than mol dm^{-3}. Hint: the concentration of X is only determined by the total pressure.

Acknowledgements & References

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Q3 The images are © David Scharf/Science Photo Library and © The Regents of the University of California, Lawrence Berkeley National Laboratory / Jenny Nuss.
Biosynthesis of polycyclopropanated high energy biofuels *Joule*, **2022**, *6*, 1590-1605.
https://doi.org/10.1016/j.joule.2022.05.011
Combustion and Thermal Decomposition Research on 1,2- Dicyclopropyl-1-Methyl Cyclopropane (DMCP) as High Energy Fuel for Liquid Rocket Propellants *Propellants, Explosives, Pyrotechnics* **2022**, *47*, e202200018, 1-9.
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Synthesis of 1,3-dicyclopropyl-2-buten-1-one *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, **1962**, 176-178.

Q4 The images are © Dr Ben Pilgrim and Dr Pete Harvey. The University of Nottingham and Dr Pete Harvey are thanked for the use of their preclinical MRI scanner. The image of the word GOLD was taken in an MRI scanner using a multi-well plate containing a 2 mM solution of Gd-DTPA in the bright cells. This image has been digitally processed.
^{17}O NMR Study of Water Exchange on $[Gd(DTPA)(H_2O)]^{2-}$ and $[Gd(DOTA)(H_2O)]^{-}$ Related to NMR Imaging *Inorganic Chemistry*, **1993**, *32*, 3844-3850.
https://pubs.acs.org/doi/10.1021/ic00070a013
NMR relaxometric studies of Gd(III) complexes with heptadentate macrocyclic ligands *Magnetic Resonance in Chemistry*, **1998**, *36*, S200-S208.
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Q5 The image is © Dr Penny Robothom and was generated by DALL.E 3.
Dimethyl Sulfide and Dimethyl Sulfoxide and Their Oxidation in the Atmosphere *Chemical Reviews* **2006**, *106*, 940-975.
https://pubs.acs.org/doi/abs/10.1021/cr020529%2B
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https://www.chemistryworld.com/features/the-secrets-of-the-sulfur-cycle/4015331.article

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Dr Ryan Beattie (Bradley Stoke Community School, Olympus Academy Trust)
Dr Peter Bolgar (University College London)
Richard Danylyuk (University of Cambridge)
Oliver Evans (University of Cambridge)
Sky Kang (Up Learn)
Dr JL Kiappes (University College London)
Anamaria Leonescu (University College London)
Dr Ben Pilgrim (University of Nottingham)
Sophie Redman (Royal Society of Chemistry)
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