51st INTERNATIONAL

CHEMISTRY OLYMPIAD

2019

UK Round One

STUDENT QUESTION BOOKLET

* * * * *

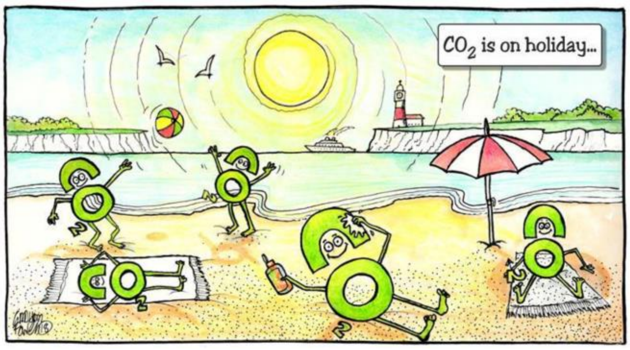
- **The time allowed is two hours.**
- **Attempt all five questions.**
- **Write your answers in the student answer booklet.**
- **Write only the essential steps of your calculations in the answer booklet.**
- **Always give the appropriate unit and number of significant figures.**
- **The final page of this question booklet includes a copy of the periodic table and some useful physical constants and quantities.**
- **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	11	18	11	27	13	**80**

> **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.**

1. This question is about carbon dioxide

The food and drink industries use a lot of carbon dioxide. During summer 2018, a global shortage led to supermarkets limiting frozen food deliveries and rationing beer. This is ironic considering the documented rise of atmospheric CO_2 levels.



(a) **(i)** Draw dot and cross diagrams for carbon dioxide and carbon monoxide.

(ii) Calculate the difference in the oxidation state between the carbons in carbon dioxide and in carbon monoxide.

The English chemist William Henry studied the equilibria when a gas dissolves in a liquid. He proposed that the concentration of a gas dissolved in a liquid is proportional to the gas' partial pressure when in the gas phase. The proportionality factor is called the Henry's law constant. The Henry's law constant for CO_2 is 3.3×10^{-2} mol dm^{-3} atm^{-1}.

Sealed containers of fizzy drinks contain dissolved CO_2. This dissolved CO_2 is in equilibrium with a small quantity of gaseous CO_2 at the top of the container.

(b) **(i)** The partial pressure of CO_2 gas in a 250 cm^3 can of fizzy drink is 3.0 atm at 25 °C. What is the concentration of CO_2 in the fizzy drink?

(ii) What mass of CO_2 is dissolved in a 250 cm^3 can of fizzy drink?

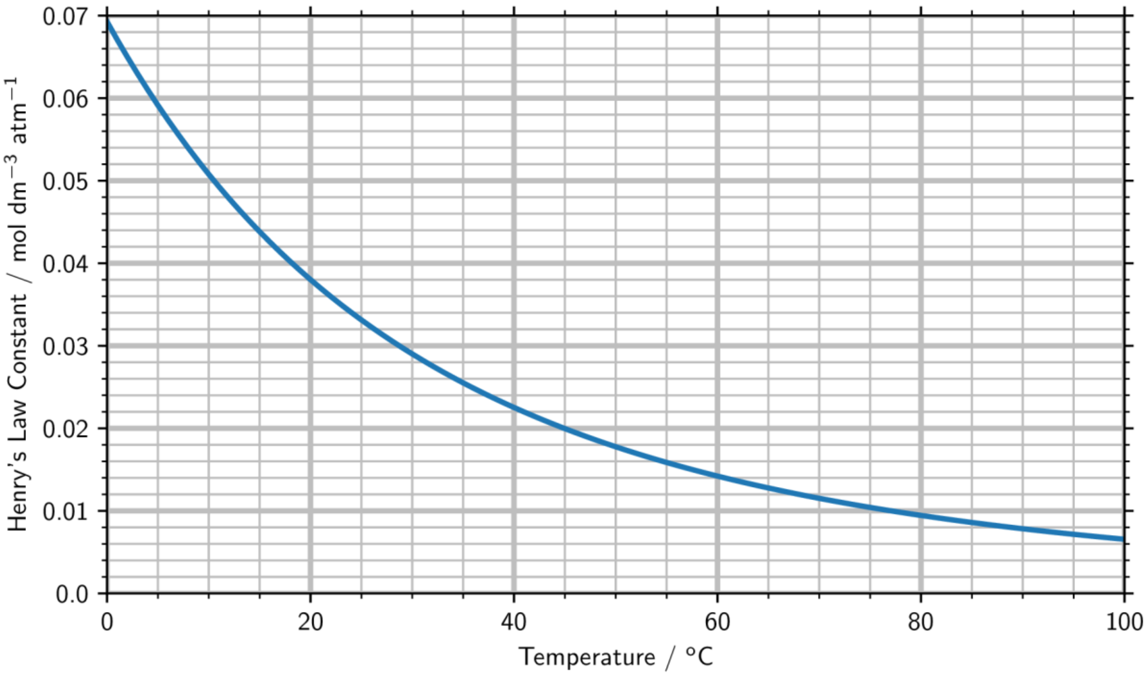
(iii) If the can contained only the mass of CO_2 calculated in *part (ii)* as a gas, calculate the pressure in the can when it is stored at 25 °C.

(iv) Under what conditions would CO_2 gas be most soluble in water?

Tick the correct option in the answer booklet:

- high pressure and low temperature
- high pressure and high temperature
- low pressure and low temperature
- low pressure and high temperature

(c) The maximum pressure that a can of fizzy drink can withstand is 7 atm. Using the graph below, determine the maximum temperature at which a can can be stored safely.



One method of industrially manufacturing CO_2 involves the Haber–Bosch process.

$CH_4 + H_2O \rightleftharpoons CO + 3H_2$ **Step 1**

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ **Step 2**

$CO + H_2O \rightleftharpoons CO_2 + H_2$ **Step 3**

Ammonia (the product of Step 2) is widely used to produce fertiliser. Fertiliser production is often stopped over the summer. Combined with the increase in demand for soft-drinks during the hot summer last year, the halt in fertiliser production contributed to the CO_2 shortage.

In Step 3 an initial mixture of 40 mol of CO, 20 mol of H_2, and 20 mol of CO_2 in contact with 40 mol of steam was allowed to come to equilibrium in a reactor at 1100 K. At 1100 K this reaction has a K_p of 0.64.

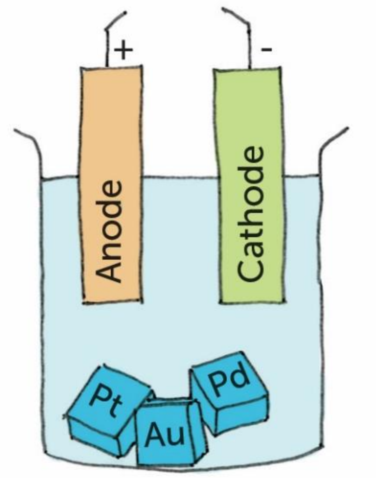
(d) Calculate the number of moles of each gas leaving the reactor after equilibration.

The standard enthalpies of formation of $CO_{(g)}$, $CO_{2(g)}$ and $H_2O_{(g)}$ are −110.5, −393.5 and −241.1 kJ mol^{-1} respectively.

(e) Calculate the enthalpy of reaction for the reaction between CO and steam to form CO_2 and H_2.

2. This question is about the industrial separation of precious metals

When nickel or copper are purified by electrolysis the impurities are deposited below the anode as 'anode sludge'. The impurities include the rare metals ruthenium, osmium, rhodium, iridium, palladium, platinum, silver and gold.



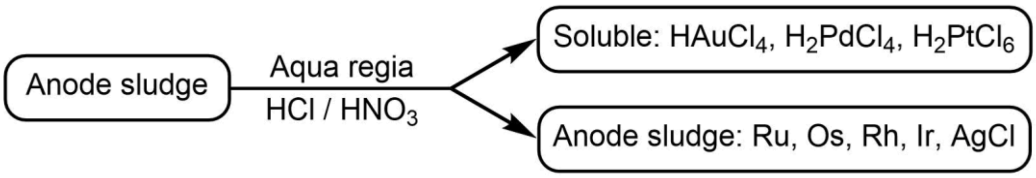
(a) Identify which element is responsible for each of the electronic structures:

(i) [Kr] $4d^{10}$

(ii) [Xe] $4f^{14}5d^{9}6s^{1}$

(iii) [Xe] $4f^{14}5d^{7}6s^{2}$

The metal impurities are initially separated by adding aqua regia (HCl / HNO_3). Gold, palladium and platinum form soluble complexes. Other metals are precipitated as elements and insoluble salts.



The gold and platinum react with the aqua regia to form solutions of chloroauric acid ($HAuCl_4$) and chloroplatinic acid (H_2PtCl_6), as well as nitrogen dioxide.

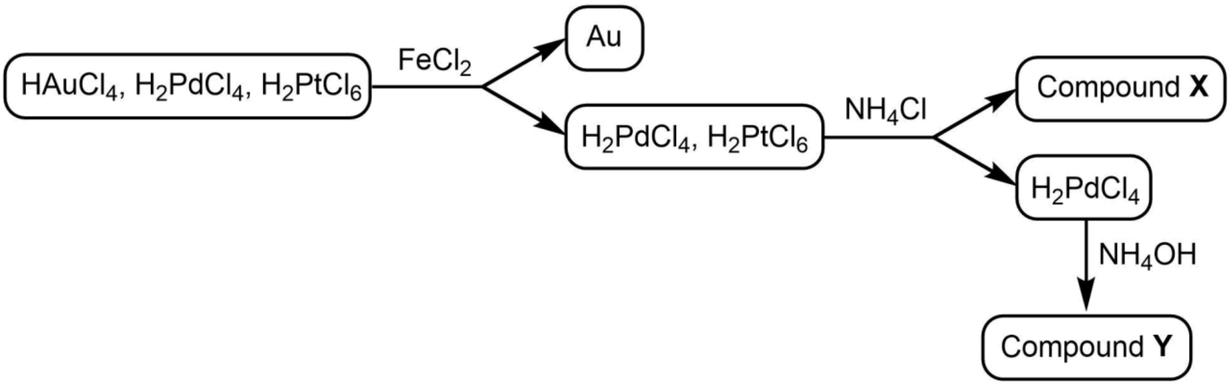
(b) **(i)** Write an equation for the reaction of gold with aqua regia.

(ii) Write an equation for the reaction of platinum with aqua regia.

Mass spectrometry can be used to identify the chloroauric acid. Naturally occurring chlorine exists as two isotopes ^{35}Cl (75% abundance) and ^{37}Cl (25% abundance). ^{197}Au is 100% abundant.

(c) Calculate the m/z values and intensities of the molecular ion peaks for the $AuCl_4^-$ ion as a percentage of the total. Use integer masses in the calculation.

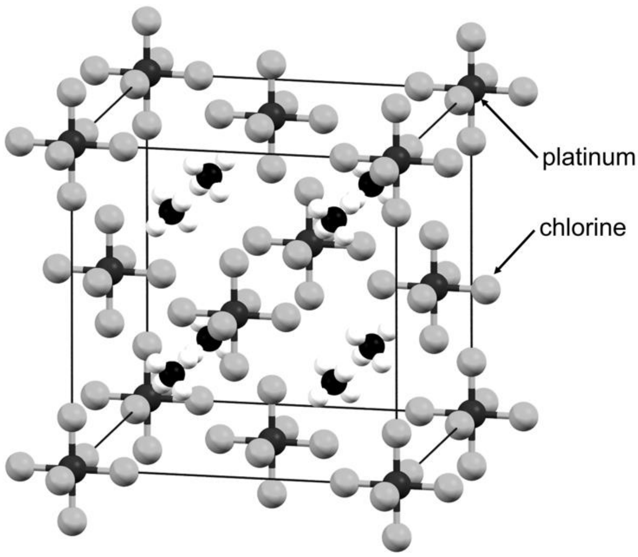
Gold is precipitated out of the mixture by adding iron(II) chloride. This leaves the chloroplatinic acid and chloropalladic acid in solution. The addition of ammonium chloride leads to the precipitation of Compound **X**. Following this, the addition of ammonium hydroxide leads to the precipitation of Compound **Y**.



(d) Write an equation for the reaction of chloroauric acid with iron(II) chloride.

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

The diagram shows the unit cell of complex **X.** Platinum is positioned at the corners and centres of the faces of the unit cell. The NH_4^+ centres are hydrogen-bonded to the chloride ligands. Some of the atoms are completely contained within the boundaries of a single unit cell. Only a fraction of atoms centred on corners, edges, or faces are contained within a single unit cell.



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

Compound **Y** contains Pd in a square planar environment.

Elemental analysis reveals: Pd 50.3%, Cl 33.5%, N 13.3% and H 2.9%.

(f) Draw the possible structures of compound **Y**.

(g) Write an equation for the formation of compound **Y** from H_2PdCl_4.

Transition metal complexes can be identified using a range of spectroscopic techniques, one of which is nuclear magnetic resonance (NMR). Just as ^{1}H and ^{13}C nuclei can be excited in an NMR experiment, so can transition metal nuclei. An NMR spectrum can be run if the spin (I) is not zero. Nuclei such as ^{195}Pt and ^{103}Rh give useful spectra, however, other nuclei such as ^{105}Pd lead to very broad lines and are unsuitable for NMR experiments.

Coupling of transition metal nuclei to other nuclei can cause signals to split, similar to the doublets, triplets and quartets seen in ^{1}H NMR.

$$\text{Number of peaks into which the resonance is split} = (2N \times I) + 1$$

where N = number of equivalent nuclei

I = spin of nuclei coupled to

^{195}Pt has spin $I = ½$. ^{1}H can be considered as 100% abundant and has spin $I = ½$. ^{16}O can be considered as 100% abundant and has spin $I = 0$. ^{1}H nuclei are not seen to couple to the platinum in ^{195}Pt NMR.

Platinum complexes, such as $[Pt(NH_3)_4]^{2+}$ and *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$, can be formed in electroplating baths. A ^{195}Pt NMR of a mixture of the two complexes exhibits signals at $\delta = -2576$ and -1555 ppm. These signals are split because the platinum nuclei couple to either ^{14}N ($I = 1$) or ^{15}N ($I = {}^{1}/_{2}$). The signals can be assigned from their splitting pattern.

(h) Calculate the number of lines the ^{195}Pt signal is split into by nitrogen in the ^{195}Pt NMR of:

(i) *cis*-$[Pt(^{14}NH_3)_2(H_2O)_2]^{2+}$

(ii) $[Pt(^{14}NH_3)_4]^{2+}$

(iii) $[Pt(^{15}NH_3)_4]^{2+}$

The line intensities for ^{195}Pt NMR resonances split by nuclei with $I = 1$ can be derived from the coefficients in the expansion of the polynomial $(x^2 + xy + y^2)^n$, where n is the number of equivalent coupling ^{14}N atoms.

Therefore:

n = 1 $(x^2 + xy + y^2)^1 = x^2 + xy + y^2$

n = 2 $(x^2 + xy + y^2)^2 = x^4 + 2x^3y + 3x^2y^2 + 2xy^3 + y^4$

n = 3 $(x^2 + xy + y^2)^3 = x^6 + 3x^5y + 6x^4y^2 + 7x^3y^3 + 6x^2y^4 + 3xy^5 + y^6$

This leads to a Pascal-like triangle

n = 0				1			
n = 1			1	1	1		
n = 2		1	2	3	2	1	
n = 3	1	3	6	7	6	3	1

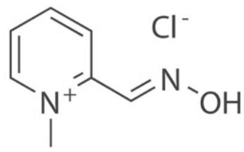
(i) Calculate the intensities of the splitting pattern in the ^{195}Pt NMR of

(i) *cis*-$[Pt(^{14}NH_3)_2(H_2O)_2]^{2+}$

(ii) $[Pt(^{14}NH_3)_4]^{2+}$

3. This question is about treating nerve agent poisoning

Nerve agents bind to and inhibit an enzyme called acetylcholinesterase (AChE). The inhibited AChE can no longer hydrolyse a key neurotransmitter, which leads to paralysis and ultimately death.



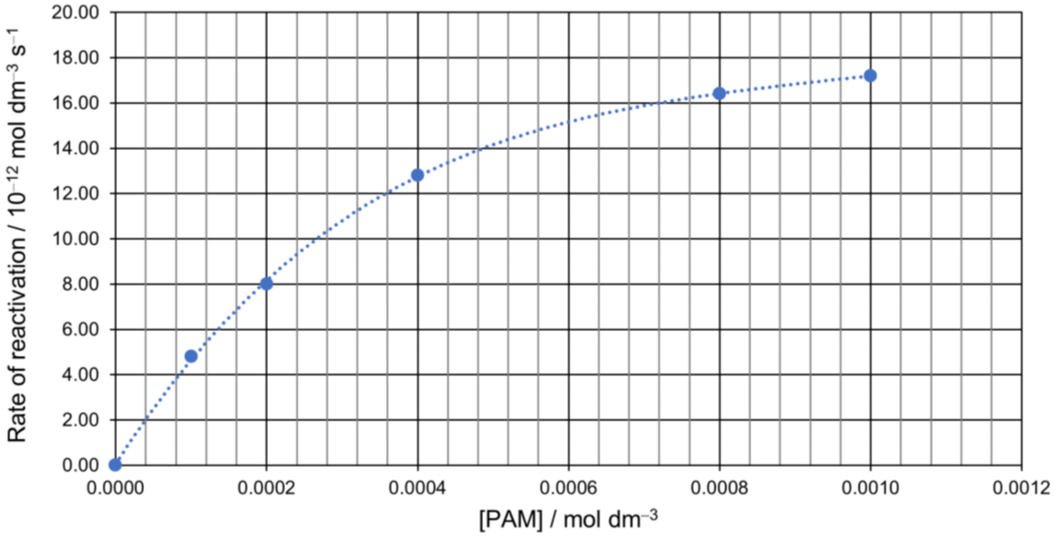
PAM

One of the main treatments for nerve agent poisoning is a group of chemicals containing the oxime functional group (C=NOH). These reactivate the inhibited AChE by removing the bound nerve agent. An important reactivator is the salt 2-pyridine aldoxime methyl chloride (PAM).

(a) **(i)** Calculate the molar mass of PAM.

(ii) An adult poisoned by a nerve agent requires an hourly dose of 3.00 mmol of PAM for every kilogram of body mass. Calculate the mass of PAM required for an 80 kg person over a 24-hour treatment period.

Nerve agents work very quickly. Kinetic studies of oximes treatments are an important area of study. The rate of reactivation of inhibited AChE by PAM is shown below.



(b) **(i)** Give the approximate order of reaction with respect to PAM at concentrations of PAM below 0.0002 mol dm^{-3}.

(ii) Give the approximate order of reaction with respect to PAM at concentrations of PAM above 0.0008 mol dm^{-3}.

The following two-step mechanism was proposed to explain these results:

$$\text{AChE-I} + \text{PAM} \xrightleftharpoons{K_c} \text{AChE-I-PAM} \xrightarrow{k_2} \text{AChE} + \text{I-PAM}$$

where AChE-I is the inhibited AChE, AChE-I-PAM is a complex of the inhibited AChE and PAM, and I-PAM is PAM with the nerve agent attached.

(c) K_c is the equilibrium constant for the the first step. Write an expression for K_c.

Based on this model, the following expression can be derived for the observed first-order rate constant with respect to the concentration of inhibited AChE (k_{obs}):

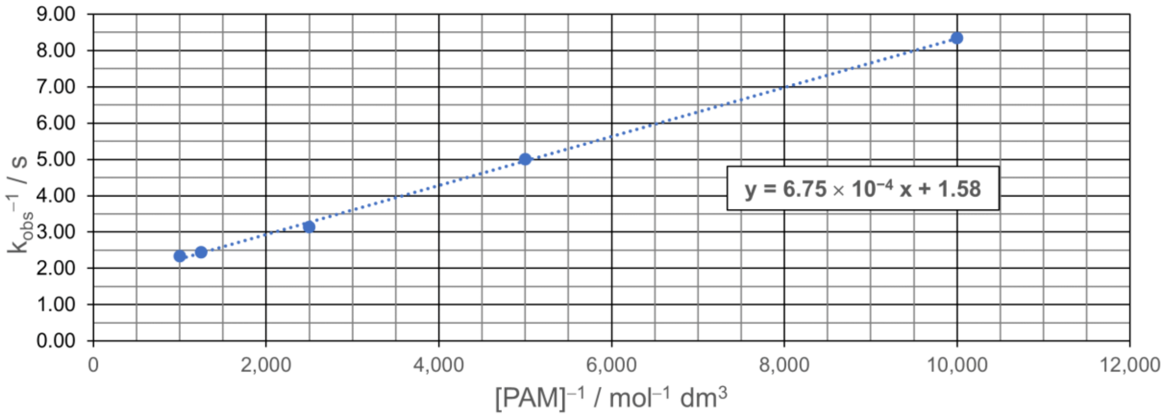
$$k_{obs} = \frac{k_2[PAM]}{[PAM] + \frac{1}{K_c}}$$

k_{obs} is the observed rate constant

K_c is the equilibrium constant for the the first step

k_2 is the rate constant for the second step

A graph of $\frac{1}{k_{obs}}$ was plotted against $\frac{1}{[PAM]}$:



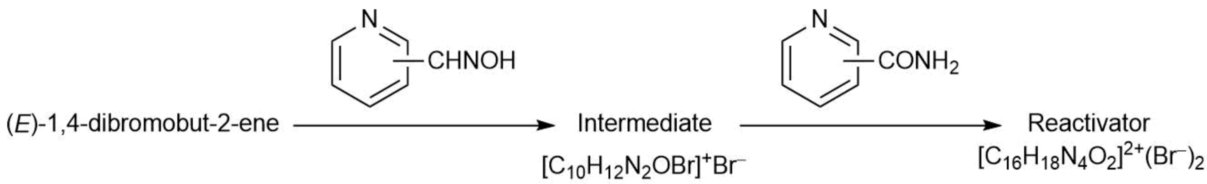
(d) **(i)** Calculate k_2.

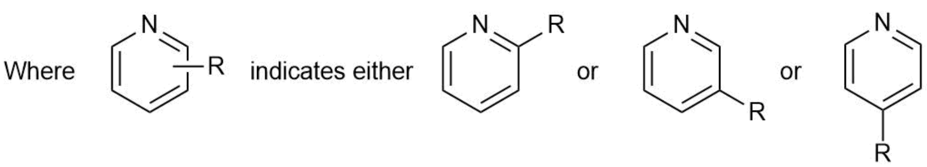
(ii) Calculate K_c.

Another important research area is developing more effective AChE reactivators for treating nerve agent poisoning. One new group of reactivators was developed using (*E*)-1,4-dibromobut-2-ene as a starting material.

(e) Draw the structure of (*E*)-1,4-dibromobut-2-ene.

This group of reactivators was synthesised via a 2-step pathway, using a series of related reagents:





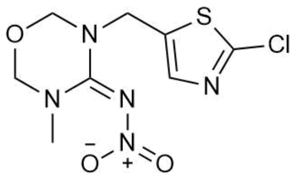
(f) How many different reactivators could be made with the above set of reagents?

The most potent reactivator **Y** had 12 signals in its ^{13}C NMR and was obtained from intermediate **X** that had 8 signals in its ^{13}C NMR.

(g) Draw the structures of **X** and **Y**.

4. This question is about bees and Brexit

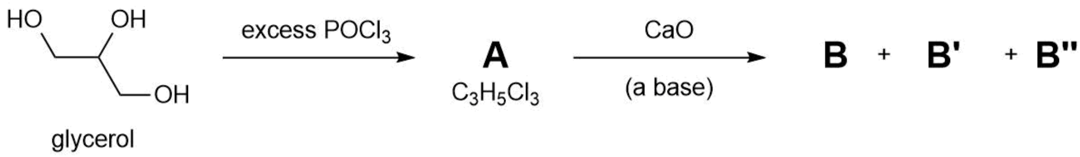
There is concern that neonicotinoid pesticides are harmful to bees. Thiamethoxam is one of three neonicotinoids that the European Union (EU) banned from all outdoor uses in April 2018. When Britain leaves the EU, this pesticide may become available for use in the UK again. People are worried this will harm our bee population.



thiamethoxam

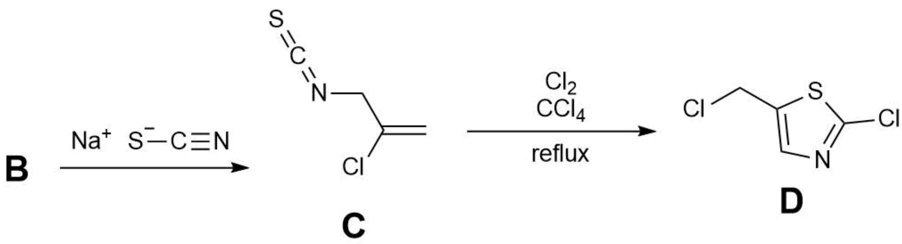
(a) What is the molecular formula of thiamethoxam?

The synthesis of thiamethoxam begins with glycerol. In the conversion of **A** to **B**, two other side products (**B'** and **B''**) can also be formed. **B**, **B'** and **B''** are isomers. **B'** and **B''** are geometric isomers. Much less **B''** is formed than **B'**.



(b) Draw the structures of **A**, **B**, **B'** and **B''**.

B reacts with sodium thiocyanate (NaSCN) to form **C**, which can be converted into **D** upon treatment with chlorine and carbon tetrachloride.

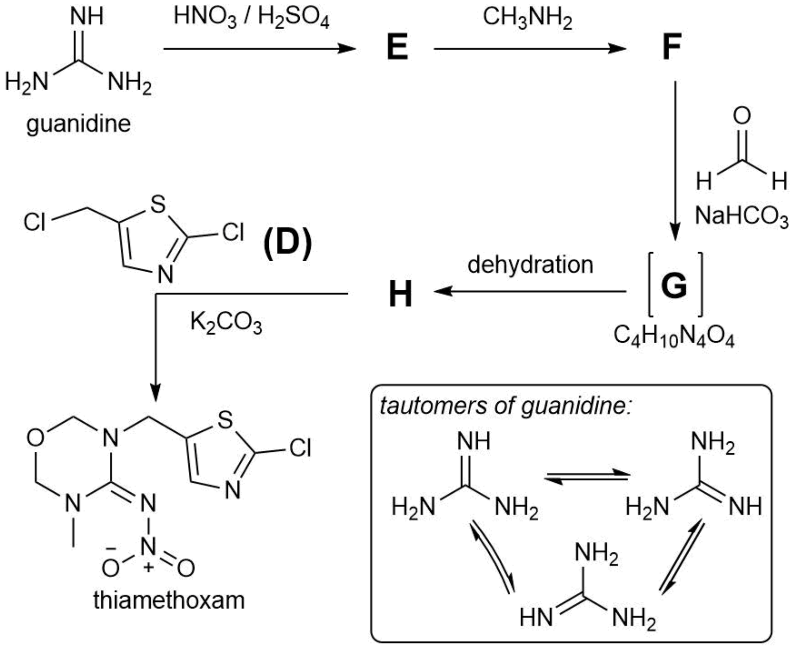


(c) Draw a resonance structure of the thiocyanate ion that explains the formation of **C**.

The remainder of the synthesis begins with guanidine.

Guanidine exists as one of three equivalent tautomers, which are all in rapid equilibrium with each other. Tautomers are isomers that only differ in the position of hydrogen atoms and double bonds.

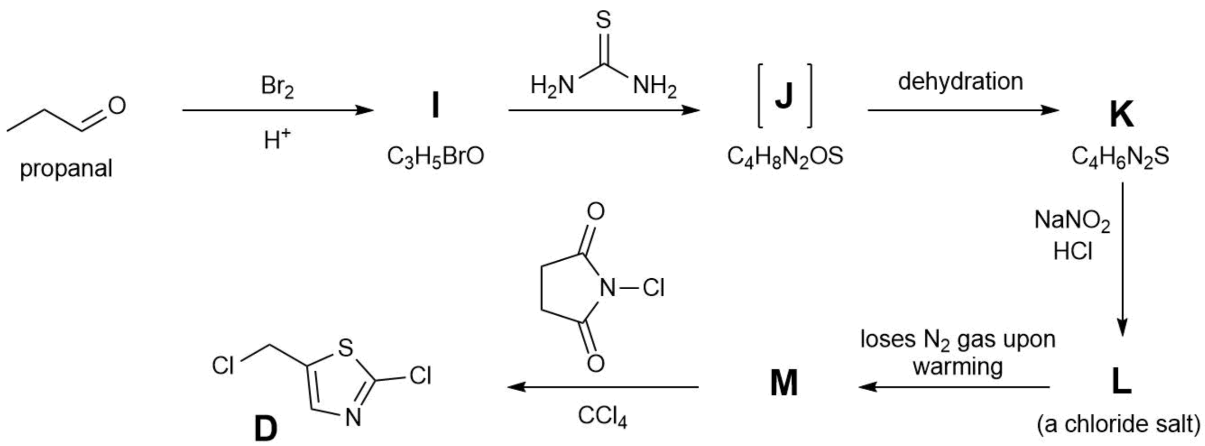
Each intermediate (**E**, **F**, **G** and **H**) can also exist as different tautomers.



(d) Draw the electrophile that reacts with guanidine to form **E**, clearly indicating its shape.

(e) Draw the structures of **E**, **F**, **G** and **H**. You only need to draw one tautomer for each compound.

In an alternative synthesis of thiamethoxam, compound **D** can also be synthesised from propanal.



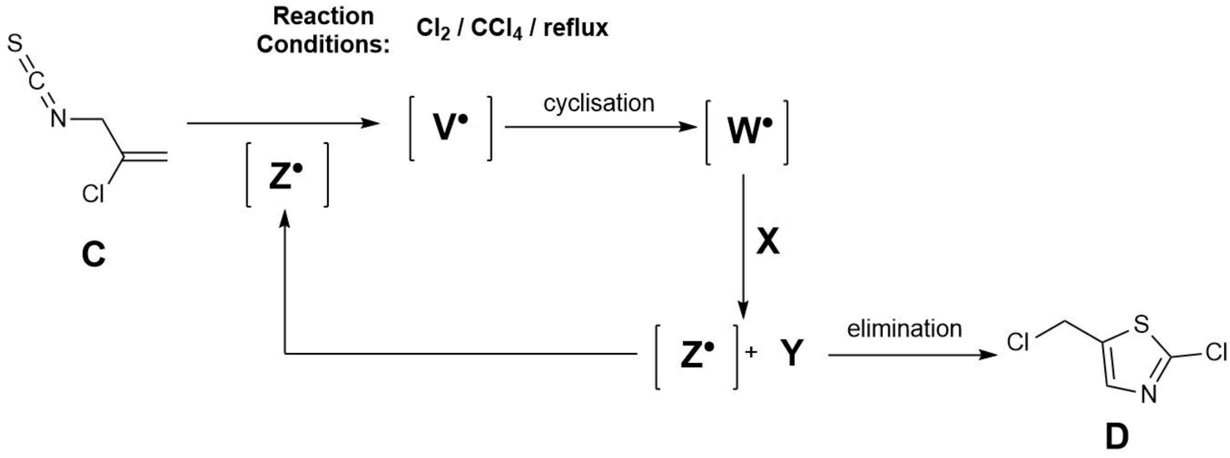
(f) Draw the structures of **I** and intermediate **J**.

Intermediate **J** undergoes dehydration to form **K**. There are three possible tautomers of **K**. However, as one tautomer is aromatic (as it has six π electrons in a ring like benzene), this tautomer is far lower in energy than the other two. Hence, at equilibrium this lowest energy tautomer predominates.

(g) Draw the structure of the lowest energy tautomer of **K** (showing the π electrons as double bonds rather than as a circle).

(h) Draw the structures of **L** and **M**.

The conversion of **C** to **D** occurs via a free radical chain reaction, followed by an elimination. The chain-carrying radical **Z·** adds to the thiocyanate in **C** to give radical intermediate **V·**. Intermediate **V·** undergoes cyclisation to give radical intermediate **W·**, which reacts with reagent **X** to form **Y** and regenerate the chain-carrying radical **Z·**. **Y** then undergoes an elimination to form **D**.



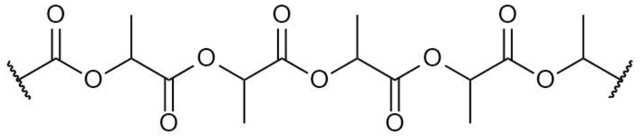
(i) Draw the structures of radical intermediates **V·** and **W·**, and intermediate **Y**.

(j) Identify reagent **X** and chain-carrying radical **Z·**.

5. This question is about a biodegradable plastic

The recent campaign to end the use of plastic straws has turned attention to biodegradable plastics and paper as alternative straw materials.

Poly(lactic acid), (PLA), was initially developed for use in biomedical implants. PLA can be used as biodegradable packaging. A section of PLA is shown below.



Note: no stereochemistry is required in skeletal formulae of organic structures in your answers to this question.

(a) Draw the structure of lactic acid (the monomer that forms PLA). It has the molecular formula $C_3H_6O_3$. Mark any chiral centres on the structure you have drawn with an asterisk (*).

(b) Which term(s) describe the polymerisation reaction of the monomer to form PLA?

Tick the correct option in the answer booklet:

- addition
- condensation
- neutralisation
- oxidation
- reduction

PLA can also be formed from compound **A**, which has the molecular formula $C_6H_8O_4$.

(c) Draw the structure of compound **A**.

The average number of lactic acid monomers per polymer chain in a sample of PLA can be determined using end-group analysis. End-group analysis is a procedure whereby reactive end groups of the polymer are used to determine the polymer's molecular weight.

0.1619 g of PLA was dissolved in 25 cm^3 of benzyl alcohol. The mixture was titrated with 0.0400 mol dm^{-3} KOH solution. The titre was 6.81 cm^3.

(d) Calculate the average molar mass of polymer chains in this sample of PLA.

(e) Calculate the average number of monomer units in each polymer chain of this sample.

If you did not get an answer to *part (d)*, use the incorrect value of 306 g mol^{-1} as the average molar mass.

286,000 tonnes of PLA are manufactured each year.

(f) Calculate the mass of NaOH needed to completely degrade all the PLA manufactured in one year to sodium lactate. Assume the PLA is pure and ignore the contribution from any end groups.

In fact, PLA can be broken down by enzyme degradation. Assume an enzyme degrades PLA into a mixture of the lactic acid monomer and compound **B** (a dimer of lactic acid). Commercial plastics actually contain other compounds in addition to PLA. Assume these other compounds in the plastic are unreactive.

A plastic was degraded, resulting in a sample of mass 1.044 g, and titrations were used to determine the composition of this sample. The sample was dissolved in 100 cm^3 of water to make a stock solution. 19.40 cm^3 of 0.100 mol dm^{-3} NaOH solution was needed to neutralise 20.00 cm^3 of this stock solution.

(g) Calculate the amount of acid in the sample (in moles).

Compound **B** was hydrolysed by boiling in NaOH solution to help determine the masses of lactic acid and compound **B**.

This was done by taking a further 20.00 cm^3 of the stock solution and mixing it with 40.00 cm^3 of 0.100 mol dm^{-3} NaOH solution. This was boiled for 1 h under reflux. The remaining NaOH was titrated with 0.100 mol dm^{-3} HCl. The titre was 18.50 cm^3.

(h) Draw the structure of compound **B**.

(i) Calculate the mass of lactic acid and the mass of compound **B** in the sample.

If you did not get an answer to *part (g)*, use the incorrect value of 8.60×10^{-3} mol as the amount of acid in the sample.

Acknowledgements & References

Q1 The image is © 'The Hitman'.

Q2 The image is © Matt Baldwin/Royal Society of Chemistry.

Q3

An In Vitro Comparative Study on the Reactivation of Nerve Agent-Inhibited Guinea Pig and Human Acetylcholinesterases by Oximes *Biochemistry*, **2007**, *46*, 11771-11779.

Synthesis of monooxime-monocarbamoyl bispyridinium compounds bearing (*E*)-but-2-ene linker and evaluation of their reactivation activity against tabun- and paraoxon-inhibited acetylcholinesterase *Journal of Enzyme Inhibition and Medicinal Chemistry*, **2008**, *23*, 70-76.

Q4 The image is © Matt Baldwin/Royal Society of Chemistry.
Thieme Pharmaceutical Substances

Q5 The image is © Shutterstock.

Authors of 2019 UK Round One Paper (listed alphabetically)

Mr Peter Bolgar (St Catharine's College, University of Cambridge)
Mr Mark Jordan (Royal Society of Chemistry)
Dr JL Kiappes (Corpus Christi College, University of Oxford)
Dr Ben Pilgrim (Corpus Christi College, University of Cambridge)
Dr Penny Robotham (The National Mathematics and Science College)
Ms Holly Salisbury (Royal Society of Chemistry)
Mr David Schofield (Hampton School)
Mr Richard Simon (A Welsh Farm)
Dr Andy Taylor (King Edward VI Camp Hill School for Boys)
Dr Alex Thom (Magdalene College, University of Cambridge)

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.102	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

$N_A = 6.02 \times 10^{23}\ mol^{-1}$ molar gas constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$ $0\ °C = 273\ K$ molar gas volume at RTP = $24\ dm^3$