Oxford Cambridge and RSA

Friday 23 June 2023 – Morning

A Level Chemistry B (Salters)

H433/03 Practical skills in chemistry

Time allowed: 1 hour 30 minutes

You must have:
- the Practical Insert (inside this document)
- the Data Sheet for Chemistry B

You can use:
- a scientific or graphical calculator
- an HB pencil

Please write clearly in black ink. **Do not write in the barcodes.**

Centre number | | | | | | Candidate number | | | | |

First name(s) _____

Last name StemUp Model Solution

INSTRUCTIONS
- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION
- The total mark for this paper is **60**.
- The marks for each question are shown in brackets **[ ]**.
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **16** pages.

ADVICE
- Read each question carefully before you start your answer.

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1 Ozone, O_3, is a serious pollutant when present in the troposphere.

(a) Give **one** polluting effect of ozone in the troposphere.

Photochemical smog, which causes breathing difficulties such as asthma.

..... **[1]**

(b) Tropospheric ozone is produced by the reactions of nitrogen oxides, NO_x, and hydrocarbons. These, together with carbon monoxide, CO, are pollutants produced by motor vehicles.

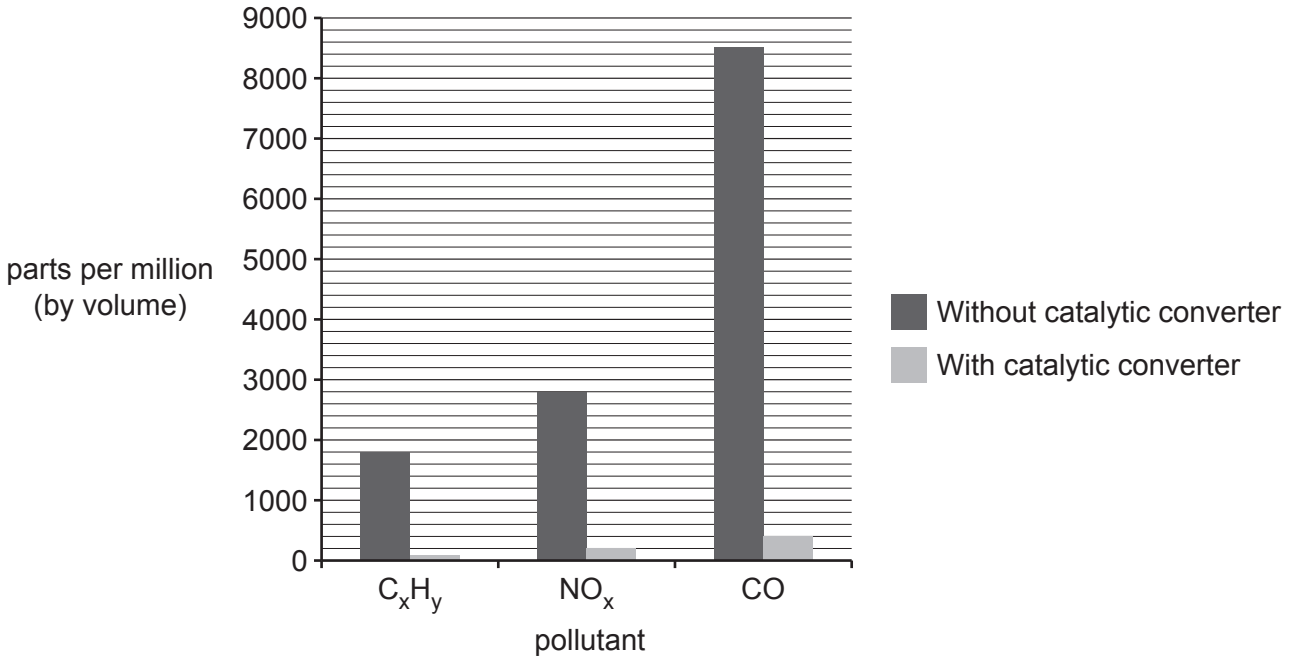
Catalytic converters in vehicle exhausts catalyse the reaction in **Equation 1.1** and also the oxidation of hydrocarbons to carbon dioxide and water.

$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$ **Equation 1.1**

(i) The bar chart below shows the reduction in the various pollutant levels when a suitable catalytic converter is fitted.

Calculate the percentage reduction in **NO_x** levels when a catalytic converter is fitted.

Give your answer to **2** significant figures.



reduction = (2800 − 200) ÷ 2800 × 100 = 92.86 %

= 93 % (to 2 s.f.)

percentage reduction .....*93*..... % **[2]**

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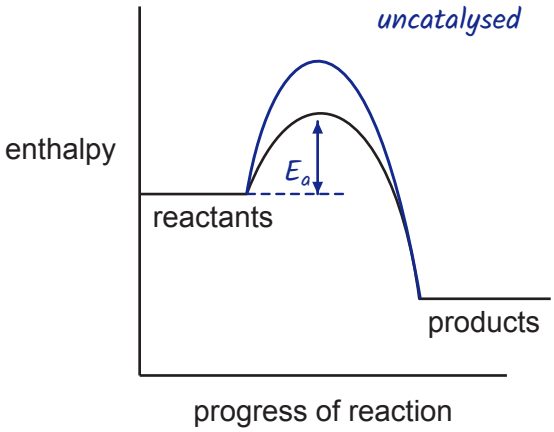
(ii) A student says that the reactions in a catalytic converter decrease car pollution to zero.

Comment on this statement.

The statement is wrong. The converter removes most of the toxic pollutants: NO_x is reduced to N_2, CO is oxidised to CO_2 and hydrocarbons are oxidised to CO_2 and H_2O.

But removal is incomplete; some NO_x, CO and hydrocarbons are still emitted, not zero. Also the CO_2 produced is still a pollutant: a greenhouse gas causing global warming. **[3]**

(iii) The diagram below represents an energy profile for the catalysed reaction in **Equation 1.1**.



On the diagram:

- Indicate the activation enthalpy of the catalysed reaction.
- Draw a progress curve for the uncatalysed reaction.

[1]

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(c) In the stratosphere, nitrogen monoxide removes ozone molecules by the sequence of reactions below.

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ **Reaction 1**

$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$ **Reaction 2**

A student suggests that the NO molecule is behaving as a heterogeneous catalyst.

Use your chemical knowledge to comment on the student's suggestion.

NO is a catalyst; it is used up in Reaction 1 but regenerated in Reaction 2, so it is chemically unchanged at the end. But it is a homogeneous catalyst, not heterogeneous, because NO is in the same state (gas phase) as the reactants O_3 and O. **[2]**

(d) Chlorine atoms also act as catalysts to remove ozone.

The atoms can be formed by the reaction shown below.

$Cl_2 \rightarrow 2Cl$

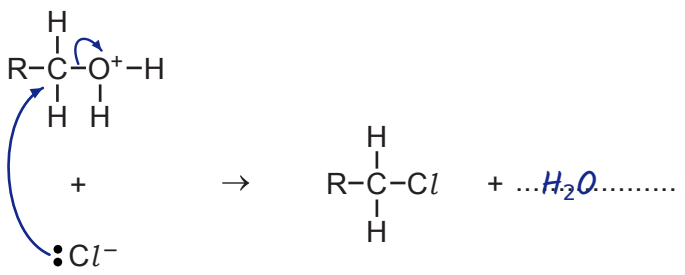
What conditions are needed for this reaction to occur and what **type** of bond fission occurs?

Conditions UV radiation (ultraviolet light)

Type of bond fission homolytic fission **[2]**

(e) By contrast, chloride **ions** react in a different way, for example in the reaction below.

Mark 'curly arrows' on the diagram and give the other product.



[2]

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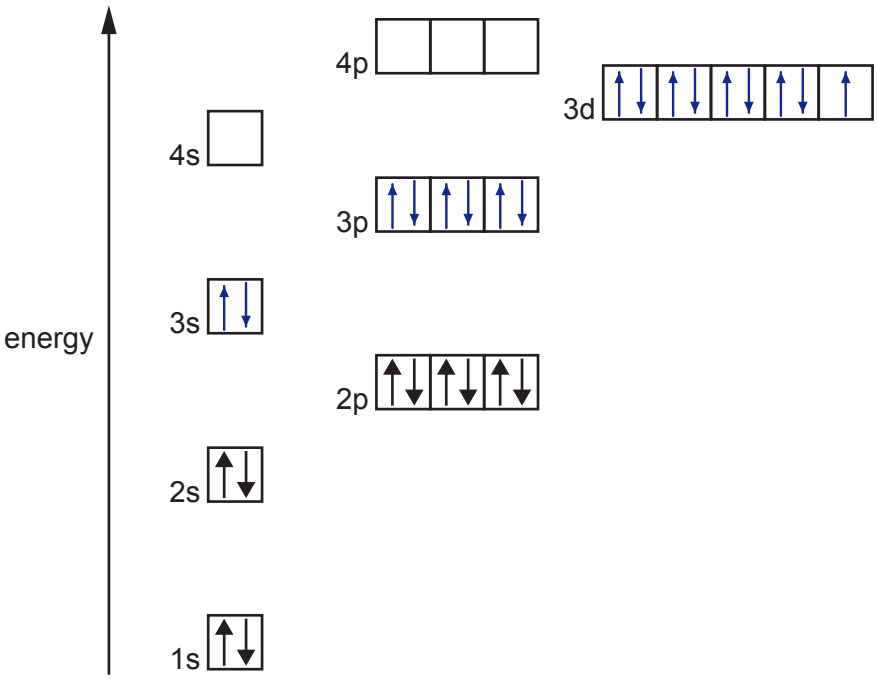
2 Copper is a d-block metal and forms many complexes.

(a) **(i)** Complete the diagram below to show the electronic configuration of a **Cu^{2+} ion**.



[2]

(ii) Explain why copper is classed as a transition metal.

Cu forms an ion, Cu^{2+} ($3d^9$), with an incomplete (partially filled) d subshell. **[1]**

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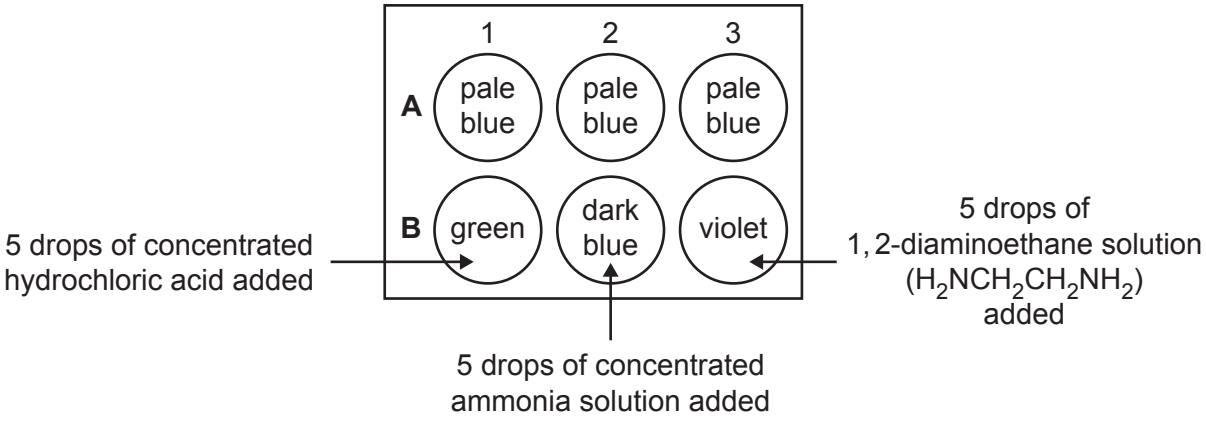
(b)* The Cu^{2+} ion forms several complex ions with different ligands.

A group of students performs a simple microscale experiment to investigate some copper(II) complexes.

They use a plate with small wells into which drops of solutions can be placed.

Their method and the results are shown below.

- **All** wells have 5 drops of copper(II) sulfate solution added to them.
- Wells **B**1, 2 and 3 have drops of other solutions added as identified in the diagram.



Use the student results to explain the meaning of the term **ligand** and suggest formulae and shapes for the complexes formed.

Use diagrams in your answer. **[6]**

A ligand is a molecule or ion with a lone pair of electrons that it donates to the central metal ion, forming a coordinate (dative covalent) bond.

Wells A: pale blue $[Cu(H_2O)_6]^{2+}$, six H_2O molecule ligands, octahedral.

B1 green: Cl^- ions (ion ligand) replace the water (ligand substitution) to give $[CuCl_4]^{2-}$, tetrahedral, as only four large Cl^- fit around Cu^{2+}.

B2 dark blue: NH_3 molecules (monodentate, lone pair on N) replace four H_2O: $[Cu(NH_3)_4(H_2O)_2]^{2+}$, octahedral (four NH_3 in a square plane).

B3 violet: 1,2-diaminoethane is bidentate: both N atoms donate a lone pair, so it forms two coordinate bonds: $[Cu(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$, octahedral.

Different ligands split the d orbitals by different amounts, so electrons are promoted from lower to higher d levels by different frequencies of light:

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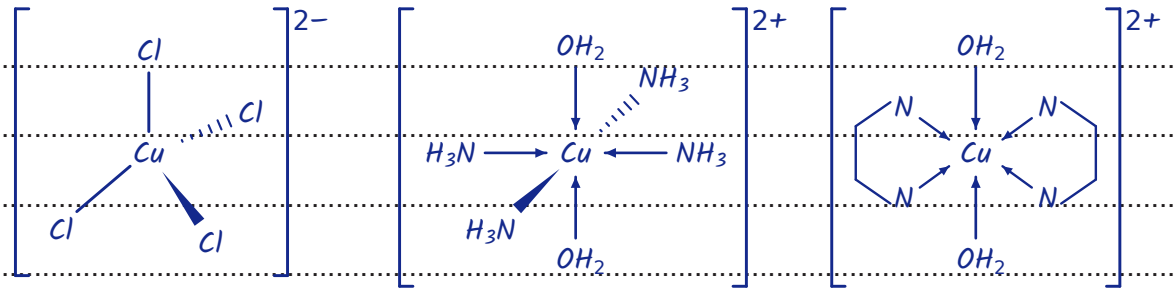
different colours.



$[CuCl_4]^{2-}$ tetrahedral $[Cu(NH_3)_4(H_2O)_2]^{2+}$ octahedral octahedral (bidentate)

(each N–N bridge is one bidentate $H_2N–CH_2–CH_2–NH_2$ ligand)

Additional answer space if required.

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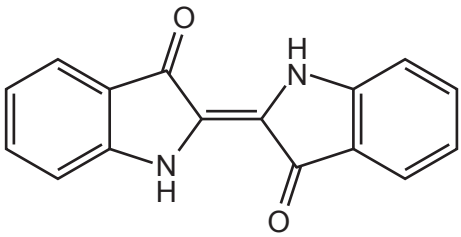
3 Indigo is a natural blue dye that can be extracted from various plants.



Indigo

(a) **(i)** The IR spectrum of indigo has a significant absorption around 3300 cm^{-1}.

Suggest the most likely bond in indigo responsible for this absorption.

N–H bond ..... **[1]**

(ii) Indigo is used to dye cotton. The cotton structure has many –OH groups.

Suggest the strongest type of intermolecular bond that binds indigo to cotton.

hydrogen bonding ..... **[1]**

(b) A frequency of yellow light has a wavelength of 5.90×10^{-7} m.

(i) Calculate the energy (in kJ) associated with one mole of photons of this wavelength.

$E = hf$ and $f = c \div \lambda$, so $E = hc \div \lambda$

$E = (6.63 \times 10^{-34} \times 3.00 \times 10^{8}) \div (5.90 \times 10^{-7})$

$= 3.37 \times 10^{-19}$ J per photon

per mole: $3.37 \times 10^{-19} \times 6.02 \times 10^{23} \div 1000 = 203$ kJ mol^{-1}

energy = ...203..... kJ **[3]**

(ii) Explain why indigo has a blue colour.

Indigo absorbs light in the visible region: it absorbs the yellow/orange part of the spectrum (around 590 nm).

The energy absorbed promotes delocalised electrons (in the conjugated system) from the ground state to an excited state, a higher energy level.

The remaining light is transmitted/reflected. Blue is the complementary colour of yellow/orange, so indigo appears blue.

..... **[3]**

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(c)* Benzene rings in dyes are usually represented as shown in **Fig. 3.1**. However, benzene rings in other organic molecules are often represented as shown in **Fig. 3.2**.

Fig. 3.1

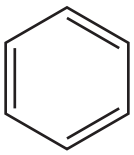

Fig. 3.2

Explain why **Fig. 3.2** is a better match for the actual **structure** and **reactions** of benzene molecules.

Structure: X-ray diffraction (electron density maps) shows benzene is a regular planar hexagon with all six C–C bonds the same length (0.139 nm), between a C–C single bond and a C=C double bond.

Fig. 3.1 (Kekulé) would have three short C=C and three longer C–C bonds, so it would be a distorted hexagon. Fig. 3.2 is a regular hexagon: each C atom gives one p electron and the p orbitals overlap above and below the ring, forming a delocalised ring of six π electrons, shown by the circle.

Kekulé would also give two different 1,2-disubstituted isomers, but only one exists.

Reactions: with three C=C bonds (Fig. 3.1), benzene would readily undergo electrophilic addition and decolorise bromine water, like cyclohexene. Actual benzene does not decolorise bromine water; it only adds under forcing conditions (e.g. H_2, Ni catalyst, high temperature).

Instead benzene mainly undergoes electrophilic substitution, e.g. nitration with conc. HNO_3 and conc. H_2SO_4 to give nitrobenzene, because substitution keeps the stable delocalised ring.

Energetics: hydrogenation of benzene (-208 kJ mol^{-1}) is about 150 kJ mol^{-1} less exothermic than expected for Kekulé ($3 \times -120 = -360$ kJ mol^{-1}), so delocalisation makes benzene more stable than Fig. 3.1.

[6]

Additional answer space if required.

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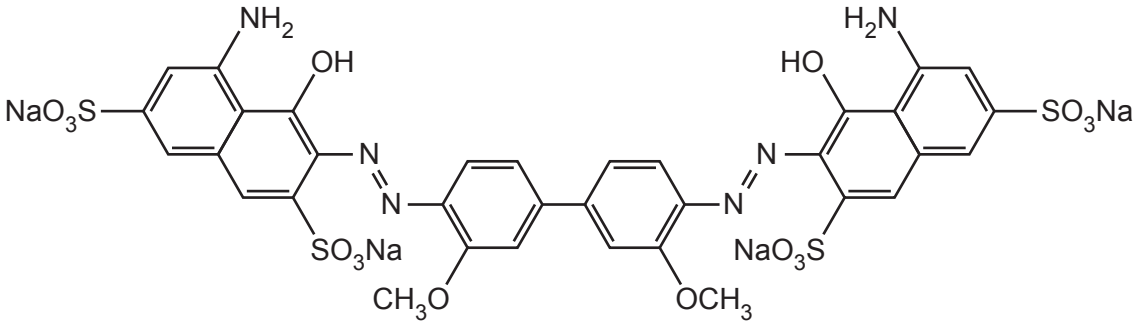
(d) (i) The dye **direct blue 15** does not fade, whereas indigo does.



Direct blue 15

This dye is made by sulfonation.

Give the reagents and conditions used in the sulfonation of **benzene**, the name of the mechanism of the reaction and a property of **direct blue 15** that is caused by the sulfonation.

Reagents and conditions *concentrated sulfuric acid, H_2SO_4*

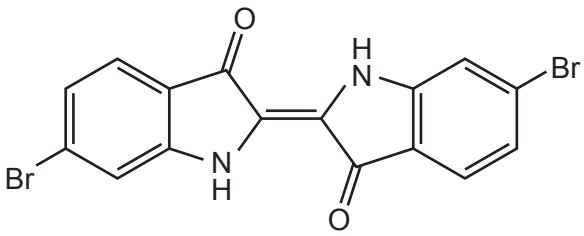
heat under reflux

Name of mechanism *electrophilic substitution*

Property of **direct blue 15** *it is soluble in water (the ionic $-SO_3^-Na^+$ groups*

increase its solubility in water). **[4]**

(ii) Dibromoindigo can be prepared synthetically by reacting indigo with bromine, using an iron catalyst.



Dibromoindigo

The reaction has the same type of mechanism as sulfonation.

Explain the role of the iron in forming Br^+.

Iron reacts with bromine to form iron(III) bromide, the halogen carrier:

$2Fe + 3Br_2 \rightarrow 2FeBr_3$.

$FeBr_3$ then reacts with Br_2: $FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$, forming the

Br^+ electrophile. **[2]**

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4 This question refers to the **Practical Insert** that is provided as an insert to this paper.

(a) **(i)** Explain why the results of **Experiment 1** show that the rate of reaction does **not** vary with the iodine concentration.

The titre is proportional to $[I_2]$ left, and the graph of titre against time is a straight line with a constant gradient. The gradient (slope) is the rate, so the rate does not change as $[I_2]$ decreases: zero order with respect to iodine. **[2]**

(ii) During **Experiment 1**, the students ensured the concentration of propanone remained virtually constant.

How did they do this?

They used a large excess of propanone (2.0 mol dm^{-3} compared with 0.010 mol dm^{-3} iodine). **[1]**

(b) Suggest why the total volume is kept constant in **Experiment 2**.

So that the concentration of each reactant is proportional to the volume of its solution added, so concentration is the only variable changed. **[1]**

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(c) **(i)** An extended version of **Table 4.1** from the Insert is given below.

Use the data in this table to calculate the rates of reaction (in cm^3 of iodine solution decolorised per second) in **Run B** and **Run C**.

Give your answers to **2** significant figures and write your values in the appropriate blank boxes in the table.

Table 4.1

	Run A	**Run B**	**Run C**
Volume of 2.0 mol dm^{-3} HC*l* / cm^3	20.0	10.0	20.0
Volume of 2.0 mol dm^{-3} propanone / cm^3	8.0	8.0	4.0
Volume of water / cm^3	0	10.0	4.0
Volume of 0.010 mol dm^{-3} iodine / cm^3	4.0	4.0	4.0
Total volume in flask / cm^3	32.0	32.0	32.0
Time for colour to disappear	115	234	240
Rate of reaction of iodine / $cm^3 s^{-1}$	0.035	0.017	0.017
Rate of reaction of iodine / mol $dm^{-3} s^{-1}$	1.1×10^{-5}		

[1]

(ii) The students do a text book search and find that the rate equation for the reaction is:

Rate = k [propanone][H^+]

Explain whether the results of **Experiment 1** and **Experiment 2** support this rate equation.

Yes. Experiment 1 shows zero order with respect to iodine, so I_2 is not in the rate equation.

Runs A and B: [HCl] is halved, [propanone] constant, and the rate halves (0.035 to 0.017), so first order with respect to H^+.

Runs A and C: [propanone] is halved, [HCl] constant, and the rate halves, so first order with respect to propanone. **[3]**

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(d) **(i)** Show why the rate of reaction of iodine in **Run A** is 1.1×10^{-5} mol dm^{-3} s^{-1}.

$[I_2]$ in flask = $0.010 \times 4.0 \div 32.0 = 1.25 \times 10^{-3}$ mol dm^{-3}

rate = $1.25 \times 10^{-3} \div 115 = 1.09 \times 10^{-5}$

$= 1.1 \times 10^{-5}$ mol dm^{-3} s^{-1}

[1]

(ii) Using the data in **Table 4.1** for **Experiment 2 Run A**, calculate the initial concentrations of hydrochloric acid and propanone in the flask.

Use these values, along with the rate from **(d)(i)**, to calculate the value of the rate constant, *k*, with its units.

[HCl] = $2.0 \times 20.0 \div 32.0$

[HC*l*] = ...1.25..... mol dm^{-3}

[propanone] = $2.0 \times 8.0 \div 32.0$

[propanone] = ...0.50..... mol dm^{-3}

k = rate ÷ ([propanone][H^+])

$= 1.1 \times 10^{-5} \div (0.50 \times 1.25)$

$= 1.76 \times 10^{-5}$

units: mol dm^{-3} s^{-1} ÷ (mol dm^{-3})^2 = dm^3 mol^{-1} s^{-1}

k = ..1.76×10^{-5}..... units ..dm^3 mol^{-1} s^{-1}.. **[4]**

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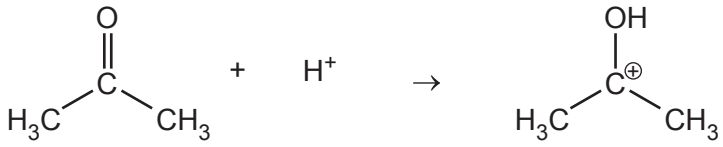
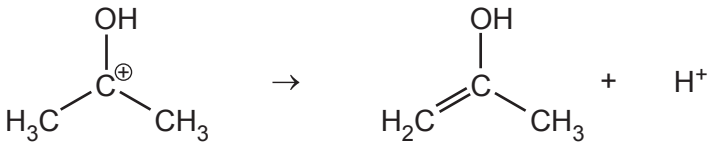
(e) A student proposes the reaction mechanism below for the iodination of propanone.

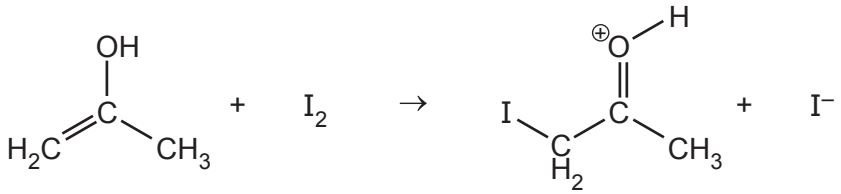
Step 1



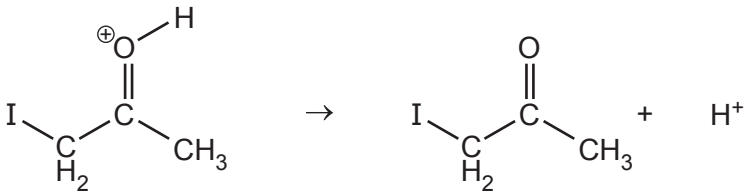
Step 2



Step 3



Step 4



Assuming the rate equation below to be correct, identify and explain the **rate determining step** in the student's mechanism.

Explain why the reactant iodine does not feature in the rate equation.

Rate = k [propanone][H^+]

The rate-determining step is the slowest step in the mechanism. The rate equation contains propanone and H^+, each first order, so the rds involves one propanone molecule and one H^+ ion: this is Step 1, where propanone reacts with H^+.

Iodine is zero order, so it is not involved in the rds: it only reacts in a later, fast step (Step 3), so changing $[I_2]$ does not affect the rate.

..... **[4]**

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(f) The students wear safety goggles and protective gloves when carrying out the experiments.

Using the information from the insert, suggest **one other** necessary health and safety measure.

Work in a fume cupboard (well-ventilated lab) and keep away from naked flames, as propanone is highly flammable. **[1]**

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

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