Oxford Cambridge and RSA

Monday 19 October 2020 – Morning

A Level Chemistry A

H432/03 Unified chemistry

Time allowed: 1 hour 30 minutes

You must have:
- the Data Sheet for Chemistry A

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 ____________________

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 **70**.
- 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 **20** pages.

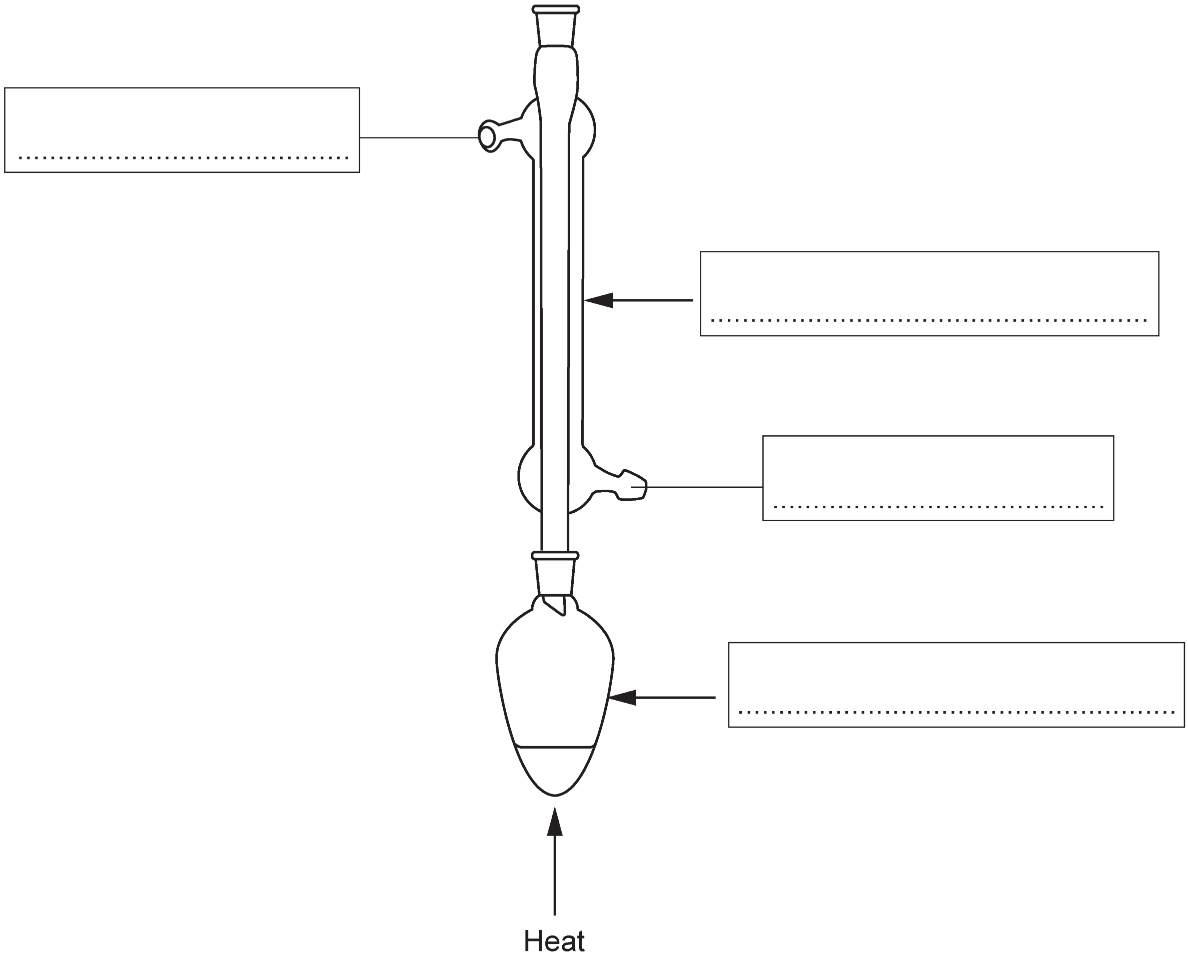
ADVICE
- Read each question carefully before you start your answer.

Answer **all** the questions.

1 This question is about organic chemistry.

(a) This part is about two practical techniques used in organic preparations.

(i) Complete the missing labels on the diagram and name the technique.



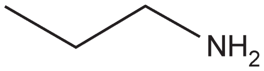
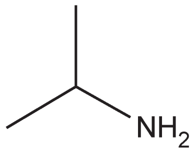
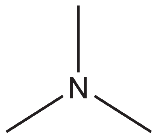
Name of technique: .... **[2]**

(ii) Draw a labelled diagram to show apparatus set up for filtration under reduced pressure (vacuum filtration).

[2]

(b) This part is about amines.

(i) The table shows the structures and boiling points of three amines, which are structural isomers of C_3H_9N.

Amine	$CH_3CH_2CH_2NH_2$	$(CH_3)_2CHNH_2$	$(CH_3)_3N$
Skeletal formula			
Boiling point / °C	48–49 °C	33–34 °C	3–4 °C

Explain the difference in the boiling points of the three amines.

.... **[4]**

(ii) Amine **A** is a liquid at room temperature and pressure.

When vaporised, 0.202 g of the amine produces 72.0 cm^3 of gas at 1.00×10^5 Pa and 100 °C. The ^{13}C NMR spectrum of amine **A** has 3 peaks.

Determine the molecular formula of **A** and suggest a possible structure for amine **A**.

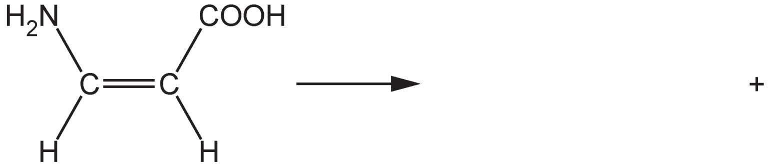
Molecular formula of **A** ....

Structure of A

[6]

(c) The amino acid *Z*−$H_2NCH{=}CHCOOH$ can react to form a cyclic compound with the molecular formula C_3H_3NO and one other product.

Complete the equation for this reaction.



[2]

2* Transition metal ions can bond to ligands to form complex ions with different shapes.

Explain what is meant by the terms **ligand**, **coordination number** and **ligand substitution**, using suitable examples of complex ions with different shapes, limited to monodentate ligands.

Your answer should include diagrams and equations where appropriate. **[6]**

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Additional answer space if required

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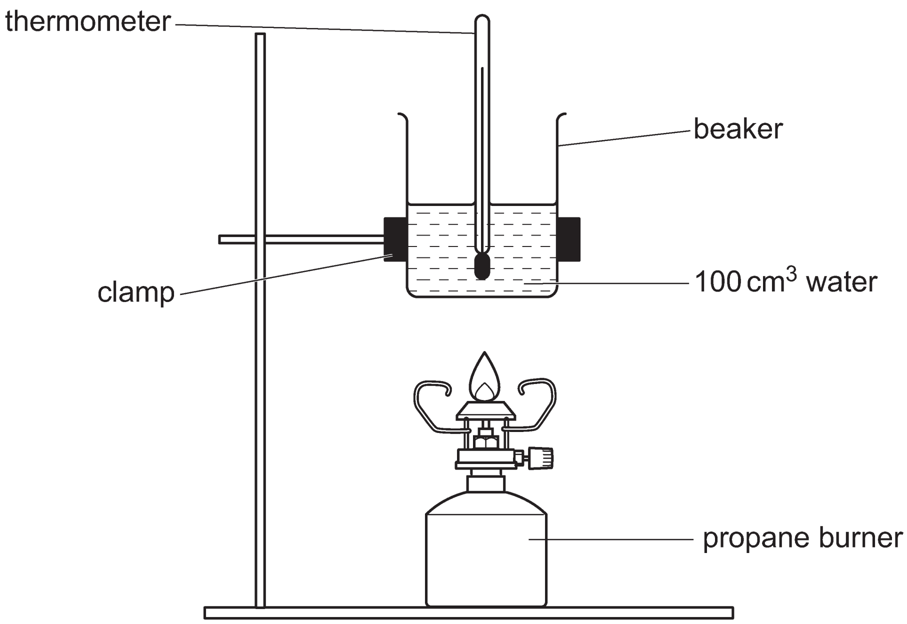
3 Propane, C_3H_8, (boiling point −42 °C) is used as 'camping gas'. A student plans to determine the enthalpy change of combustion of propane, $\Delta_c H$ (C_3H_8), by two methods.

(a) The student first carries out an experiment using the apparatus below.



Results

Mass of propane burner before burning / g	99.218
Mass of propane burner after burning / g	98.976
Initial temperature / °C	21.60
Maximum temperature reached / °C	46.10

(i) Determine the enthalpy change of combustion of propane, in kJ mol^{-1}.

Give your answer to **3** significant figures.

$\Delta_c H$ (C_3H_8) = ... kJ mol^{-1} **[3]**

(ii) The student finds that the experimental enthalpy change $\Delta_c H$ (C_3H_8) is much less exothermic than the accurate standard enthalpy change $\Delta_c H$ (C_3H_8) in databases.

One reason could be that the student's experiment had not been carried out under standard conditions.

Suggest **two** other reasons for this difference in enthalpy change.

1 ....

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2 ....

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[1]

(b)* The student determines the standard enthalpy change of combustion of propane using the bond enthalpies in the table. An experiment is not needed.

Bond	**Bond enthalpy / $kJ\,mol^{-1}$**
C−H	+413
C−C	+347
C=O	+805
O=O	+498
O−H	+464

The bond enthalpies can be used to determine the standard enthalpy change of reaction, $\Delta_r H$, for **equation 3.1**:

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta_r H$ **Equation 3.1**

Enthalpy change of vaporisation, $\Delta_{vap}H$

The standard enthalpy change of vaporisation of water, $\Delta_{vap}H$, is the enthalpy change for the conversion of 1 mol of $H_2O(l)$ into 1 mol of $H_2O(g)$ under standard conditions:

$H_2O(l) \rightarrow H_2O(g)$ $\Delta_{vap}H = +40.65\,kJ\,mol^{-1}$

Determine the standard enthalpy change of combustion of propane (boiling point −42 °C) using the $\Delta_r H$ value for **equation 3.1** and $\Delta_{vap} H$ for water. **[6]**

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4 A student carries out an investigation to identify two metals, **M** and **X**, by two different methods.

(a) The student is provided with a sample of metal **M**.

The student analyses metal **M** using a 'back-titration' technique:

- The metal is reacted with excess acid.
- The resulting solution is titrated to determine the amount of acid remaining after the reaction.

Stage 1
The student adds 100 cm^3 of 2.10 mol dm^{-3} $HCl(aq)$ to 6.90 g of **M**.
An excess of $HCl(aq)$ has been used to ensure that all of metal **M** reacts.

A redox reaction occurs, forming a solution containing **M** in the +2 oxidation state.

Stage 2
The resulting solution from **Stage 1** is made up to 250.0 cm^3 with distilled water.

Stage 3
A 25.00 cm^3 sample of the diluted solution from **Stage 2** is titrated with 0.320 mol dm^{-3} NaOH(aq).

The NaOH(aq) reacts with excess $HCl(aq)$ that remains in **Stage 1**:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

The student repeats the titration to obtain concordant titres.

Titration results (The trial titre has been omitted.)
The burette readings have been recorded to the nearest 0.05 cm^3.

	1	**2**	**3**
Final reading / cm^3	27.80	37.55	32.20
Initial reading / cm^3	0.50	10.00	5.00

(i) In **Stage 1**, a redox reaction takes place between **M** and $HCl(aq)$, forming hydrogen and a solution containing **M** in the +2 oxidation state.

Write an overall equation, with state symbols, for this reaction. Write half-equations for the oxidation and reduction processes.

Overall equation ....

Oxidation half-equation ....

Reduction half-equation ....

[3]

(ii) In **Stage 1**, suggest **two** observations that would confirm that all of metal **M** has reacted.

1 ....

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2 ....

.... **[2]**

(iii) In **Stage 3**, write the ionic equation for the reaction taking place in the titration.

.... **[1]**

(iv) Metal **M** can be identified following the steps below.

1. The amount, in mol, of excess HCl(aq) that remains after the reaction of **M** with HCl(aq).
2. The amount, in mol, of HCl(aq) that reacted with **M**.
3. The identity of metal **M**.

Analyse the results to identify metal **M**.

Metal **M** = ... **[6]**

(b) The student is provided with the carbonate of an unknown metal, $\mathbf{X}_2CO_3$.

The student measures the mass loss when the $\mathbf{X}_2CO_3$ is reacted with an **excess** of hydrochloric acid. The equation is shown below.

$$\mathbf{X}_2CO_3(s) + 2HCl(aq) \rightarrow 2\mathbf{X}Cl(aq) + CO_2(g) + H_2O(l)$$

The reaction is carried out using this method:

Step 1 Add 100 cm^3 HCl(aq) to a conical flask and weigh.

Step 2 Add $\mathbf{X}_2CO_3$ to the conical flask and immediately reweigh.

Step 3 After 5 minutes, reweigh the conical flask and contents.

Results

Mass of conical flask + HCl(aq)	172.93 g
Mass of conical flask + $\mathbf{X}_2CO_3$ + HCl(aq) before reaction	187.50 g
Mass of conical flask + contents after 5 minutes	184.75 g

(i) Calculate the amount, in mol, of CO_2 released in the reaction.

Amount of CO_2 = ... mol **[1]**

(ii) Calculate the molar mass of $\mathbf{X}_2CO_3$ and identify metal **X**.

Molar mass of $\mathbf{X}_2CO_3$ = ... g mol^{-1} Metal **X** = ...**[3]**

(c) After analysing the results, the student was told that their molar mass of $\mathbf{X}_2CO_3$ was incorrect.

The student evaluated the experiment for possible reasons for the incorrect result.

(i) The student wondered whether the reaction was complete when the mass was recorded after 5 minutes (**Step 3**).

How could the student modify the experimental procedure to be confident that the reaction was complete?

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.... **[1]**

(ii) The student finds out that carbon dioxide is slightly soluble in water.

State and explain how the solubility of CO_2 would affect the calculated molar mass of $\mathbf{X}_2CO_3$.

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.... **[2]**

5 The equilibrium constant K_p and temperature T (in K) are linked by the mathematical relationship shown in **equation 5.1** (R = Gas constant in J mol^{-1} K^{-1} and ΔH is enthalpy change in J mol^{-1}).

$$\ln K_p = -\frac{\Delta H}{R} \times \frac{1}{T} + \frac{\Delta S}{R}$$ **Equation 5.1**

(a) The table shows the values of K_p at different temperatures for an equilibrium.

Complete the table by adding the missing values of $\frac{1}{T}$ and $\ln K_p$.

Temperature, *T* / K	400	500	600	700	800
K_p	3.00×10^{58}	5.86×10^{45}	1.83×10^{37}	1.46×10^{31}	1.14×10^{26}
$\frac{1}{T}$ / K^{-1}	2.50×10^{-3}	....	....	....	....
$\ln K_p$	135	....	....	....	....

[2]

(b) State and explain how increasing the temperature affects the position of this equilibrium and whether the forward reaction is exothermic or endothermic.

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.... **[1]**

(c) Plot a graph of $\ln K_p$ against $\frac{1}{T}$ using the axes provided on the opposite page.

Use your graph and **equation 5.1** to determine ΔH, in kJ mol^{-1}, for this equilibrium.

Give your answer to **3** significant figures.

ΔH = ... kJ mol^{-1} **[4]**

(d) Explain how ΔS could be calculated from a graph of $\ln K_p$ against $\frac{1}{T}$.

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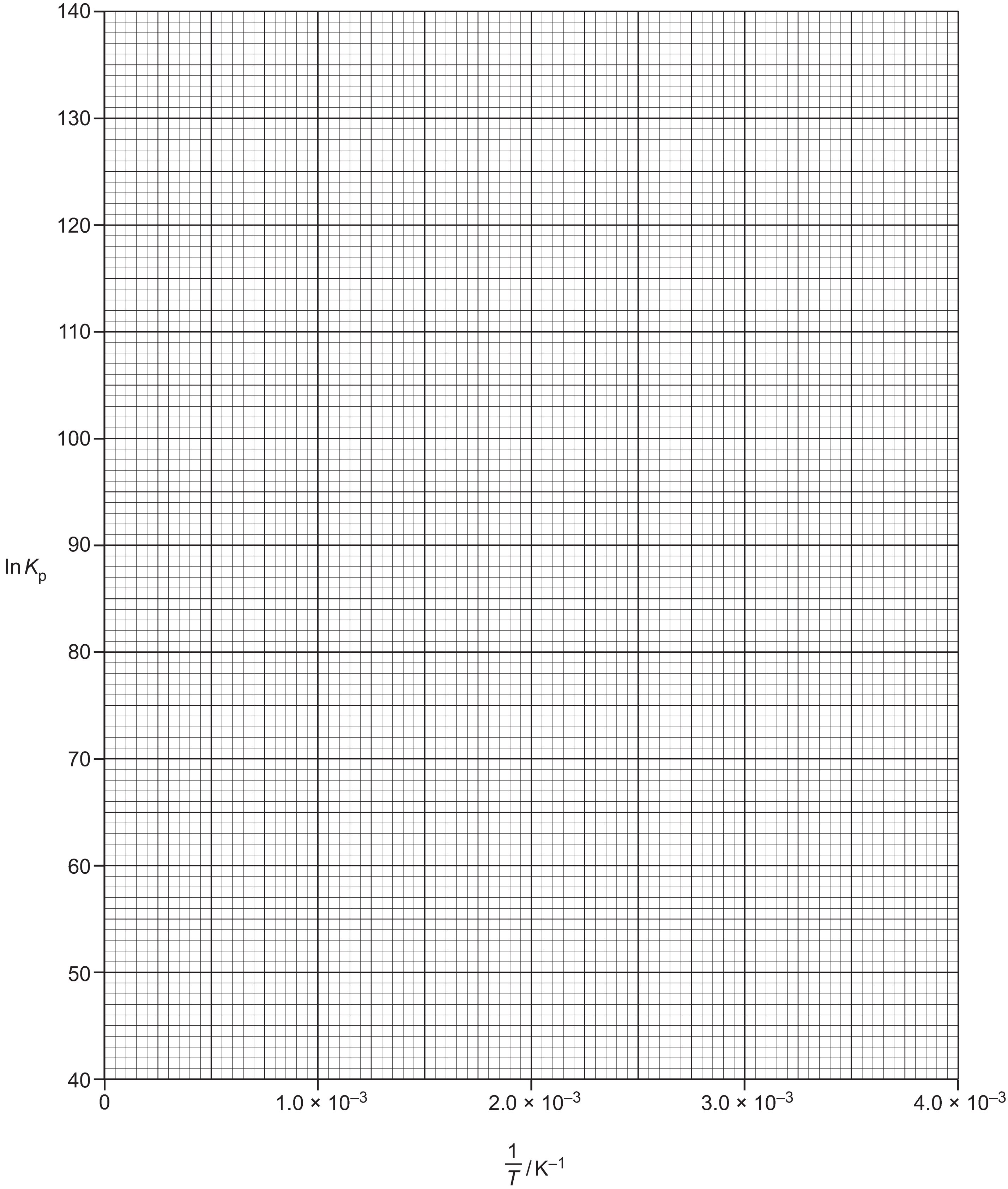
.... **[2]**



140
130
120
110
100
90
80
70
60
50
40
ln K_p
0
1.0×10^{-3}
2.0×10^{-3}
3.0×10^{-3}
4.0×10^{-3}
$\frac{1}{T}$ / K^{-1}

6 This question is about two different types of acid found in organic compounds, carboxylic acids and sulfonic acids, as shown in **Fig. 6.1**.

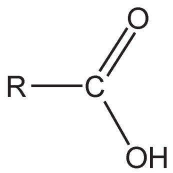
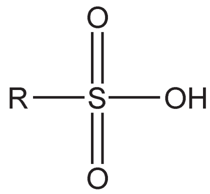
	
Carboxylic acid	Sulfonic acid

Fig. 6.1

(a) Complete **Table 6.1** to predict bond angles ***a*** and ***b*** and name the shapes which makes these bond angles in the functional groups of carboxylic acids and sulfonic acids.

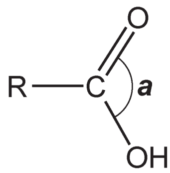
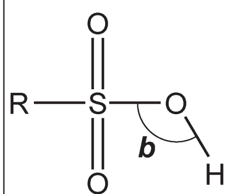
Type of acid	Acid	Bond angle	Name of shape
Carboxylic acid		....	....
Sulfonic acid		....	....

Table 6.1

[2]

(b) Ethanoic acid, CH_3COOH, and methanesulfonic acid, CH_3SO_2OH, are both monobasic acids. The pK_a values are shown in the table.

Acid		**pK_a**
Ethanoic acid	CH_3COOH	4.76
Methanesulfonic acid	CH_3SO_2OH	–1.90

A student suggests that 1.0 mol dm^{-3} CH_3SO_2OH should have a lower pH value than 1.0 mol dm^{-3} CH_3COOH.

Write an equation, showing conjugate acid–base pairs, for the equilibrium of CH_3SO_2OH with water and explain, with reasons, whether the student is correct.

Label the conjugate acid–base pairs: **A1**, **B1** and **A2**, **B2**.

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.... **[4]**

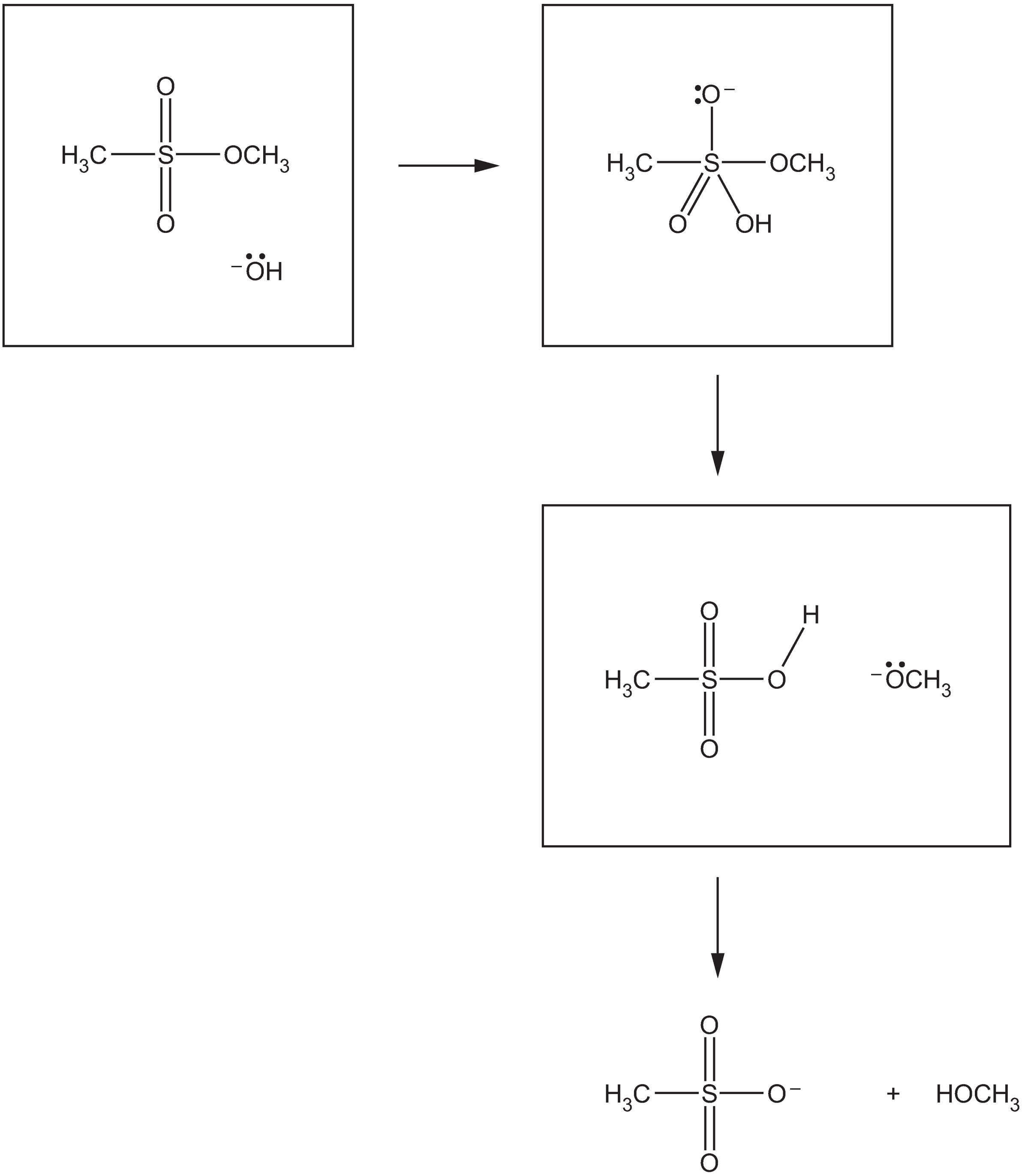
(c) Carboxylic acids and sulfonic acids both form esters.

Sulfonic acid esters can be hydrolysed by aqueous alkali.
The equation shows the alkaline hydrolysis of a sulfonic acid ester.

$CH_3SO_2OCH_3 + OH^- \rightarrow CH_3SO_2O^- + CH_3OH$

In the **3 boxes below**, add curly arrows to show the mechanism for this reaction.

In the first box, the hydroxide ion acts as a nucleophile.



[4]

END OF QUESTION PAPER

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).