



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

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Candidate number

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First name(s)

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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 **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

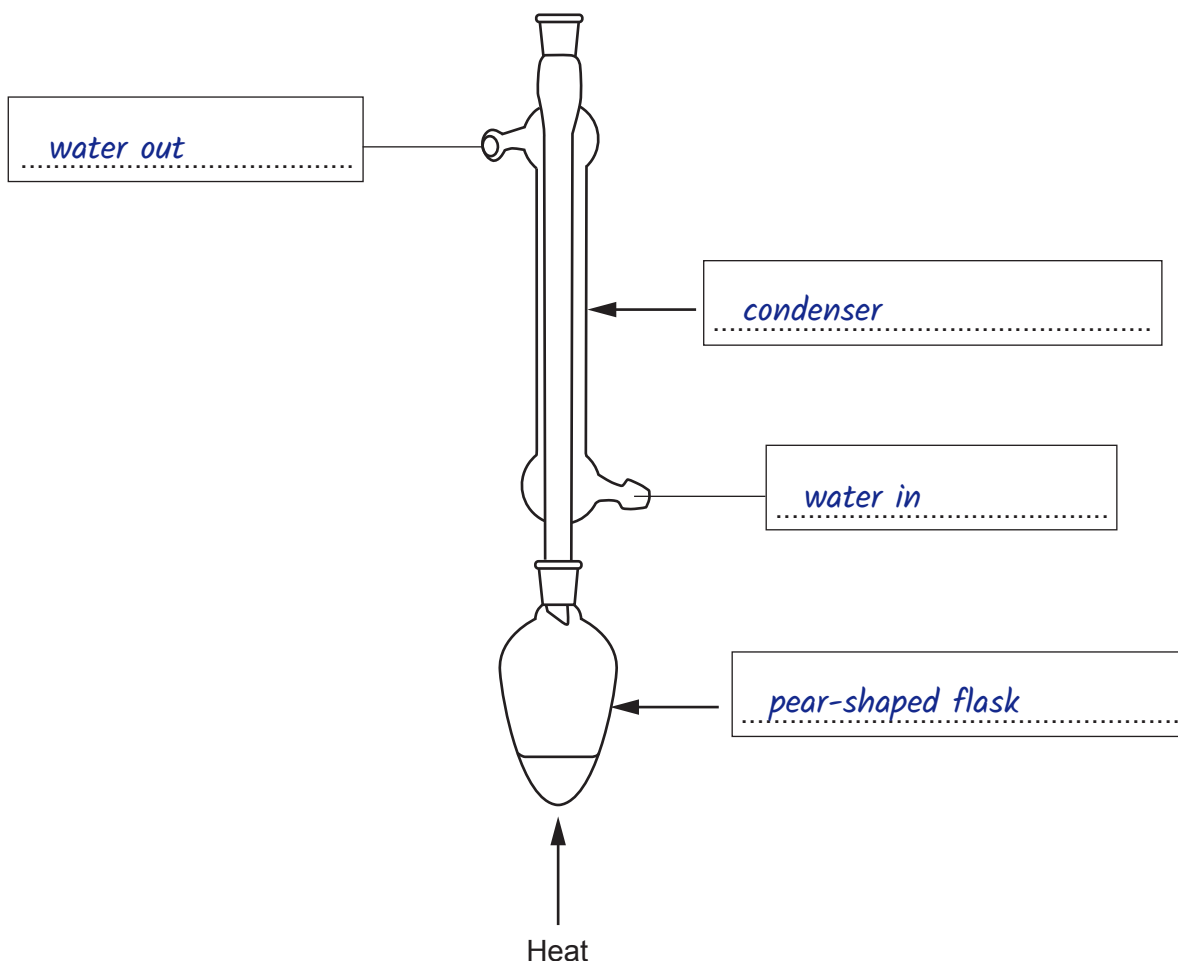
- Read each question carefully before you start your answer.

Answer **all** the questions.

1 This question is about organic chemistry.

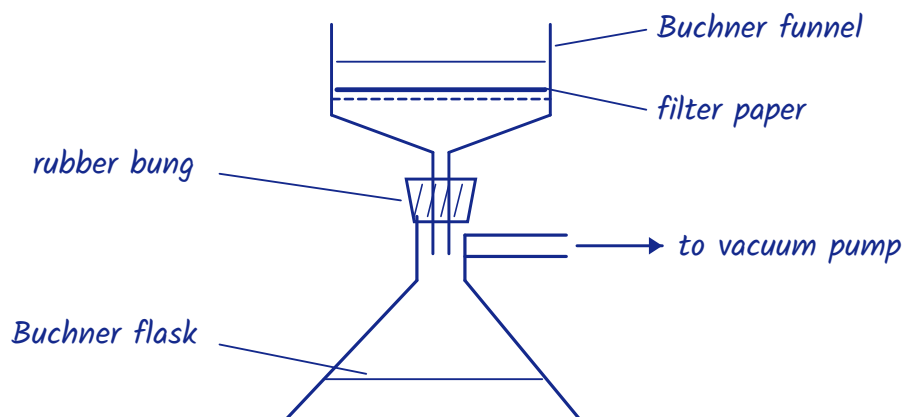
(a) This part is about two practical techniques used in organic preparations.

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



Name of technique: *heating under reflux* [2]

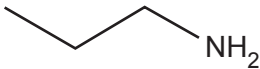
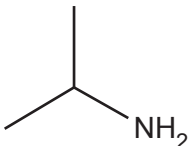
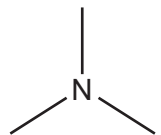
(ii) Draw a labelled diagram to show apparatus set up for filtration under reduced pressure (vacuum filtration).



[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/ $^{\circ}C$	48–49 $^{\circ}C$	33–34 $^{\circ}C$	3–4 $^{\circ}C$

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

$CH_3CH_2CH_2NH_2$ and $(CH_3)_2CHNH_2$ both have an N–H bond, so they form hydrogen bonds between molecules. $(CH_3)_3N$ has no H on the N, so it has no hydrogen bonds, only London forces.

Hydrogen bonds are stronger than London forces, so more energy is needed to break them: $(CH_3)_3N$ has the lowest boiling point.

$CH_3CH_2CH_2NH_2$ has a straight chain (no branches), so more points of contact / surface interaction between molecules than branched $(CH_3)_2CHNH_2$, so stronger London forces and more energy is needed to overcome them.

.....

.....

.....

[4]

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

When vaporised, 0.202 g of the amine produces 72.0 cm³ of gas at 1.00 × 10⁵ Pa and 100 °C. The ¹³C NMR spectrum of amine **A** has 3 peaks.

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

$$n = pV/RT \quad T = 100 + 273 = 373 \text{ K}, \quad V = 72.0 \times 10^{-6} \text{ m}^3$$

$$n = (1.00 \times 10^5 \times 72.0 \times 10^{-6}) \div (8.314 \times 373) = 2.32 \times 10^{-3} \text{ mol}$$

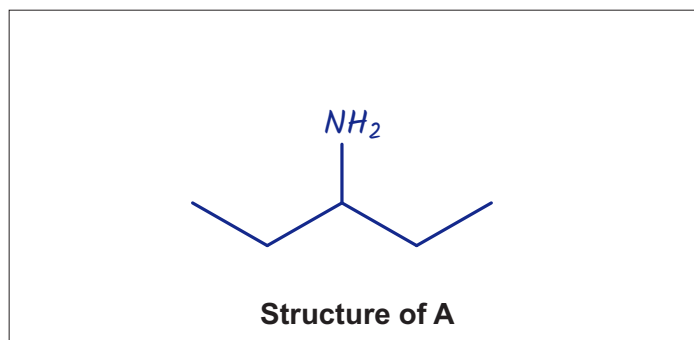
$$M = m/n = 0.202 \div 2.32 \times 10^{-3} = 87.0 \text{ g mol}^{-1}$$

$$\text{amine } C_5H_{13}N: (5 \times 12.0) + (13 \times 1.0) + 14.0 = 87.0$$

3 peaks in ¹³C NMR, so 3 carbon environments:

pentan-3-amine, (CH₃CH₂)₂CHNH₂

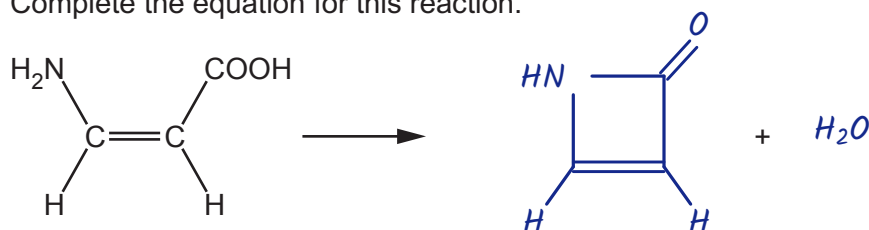
Molecular formula of **A** C₅H₁₃N



[6]

- (c) The amino acid Z-H₂NCH=CHCOOH can react to form a cyclic compound with the molecular formula C₃H₃NO 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.

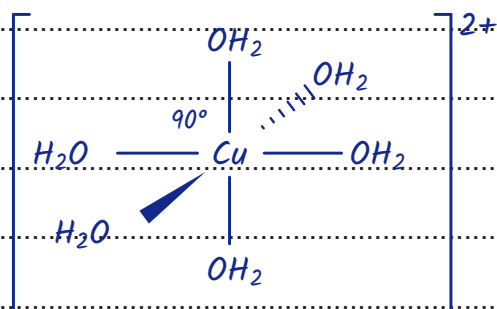
Your answer should include diagrams and equations where appropriate.

[6]

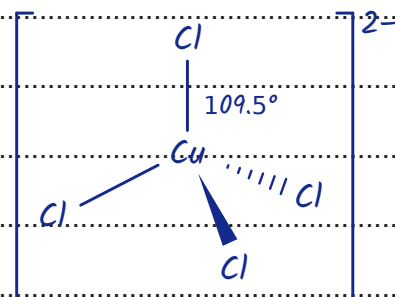
A ligand is a molecule or ion that donates a lone pair of electrons to a central metal ion, forming a coordinate (dative covalent) bond, e.g. H_2O , NH_3 , Cl^- .

The coordination number is the number of coordinate bonds to the central metal ion. With monodentate ligands this equals the number of ligands.

Coordination number 6: octahedral, 90° , e.g. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. Coordination number 4: tetrahedral, 109.5° , e.g. $[\text{CuCl}_4]^{2-}$ or square planar, e.g. $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.



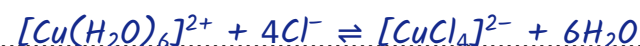
octahedral, coordination no. 6



tetrahedral, coordination no. 4

Additional answer space if required

Ligand substitution is a reaction in which one ligand in a complex ion is replaced by another, e.g. adding conc. HCl to $\text{Cu}^{2+}(\text{aq})$ (blue to yellow):



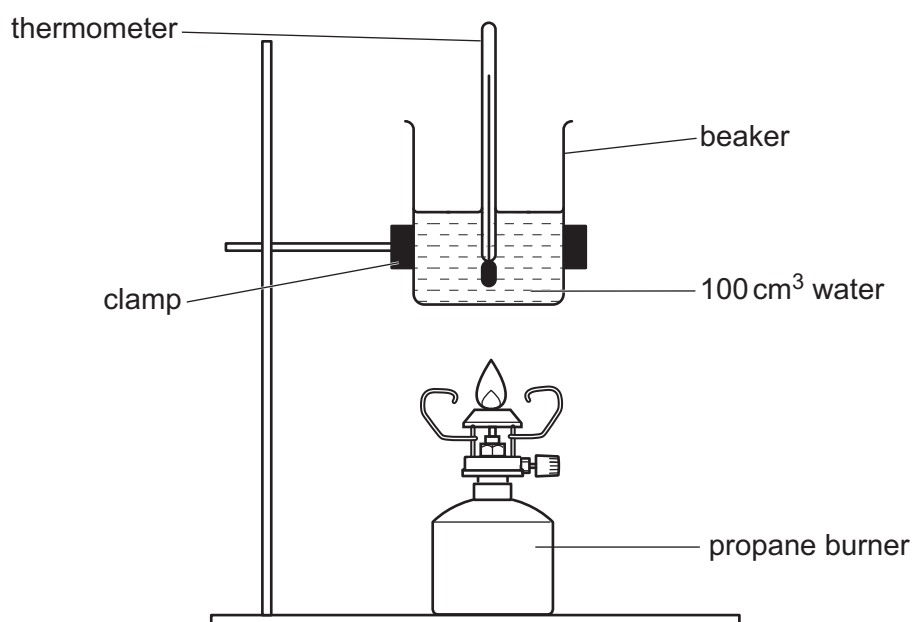
The shape changes from octahedral to tetrahedral as the Cl^- ligands are larger.

With excess NH_3 (pale blue to deep blue):



- 3 Propane, C_3H_8 , (boiling point $-42^\circ C$) 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/ $^\circ C$	21.60
Maximum temperature reached/ $^\circ C$	46.10

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

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

$$q = mc\Delta T = 100 \times 4.18 \times (46.10 - 21.60) = 100 \times 4.18 \times 24.5$$

$$q = 10241 \text{ J} = 10.241 \text{ kJ}$$

$$\text{mass of propane} = 99.218 - 98.976 = 0.242 \text{ g}$$

$$n(C_3H_8) = 0.242 \div 44.0 = 0.00550 \text{ mol}$$

$$\Delta_c H = -10.241 \div 0.00550 = -1862 \text{ kJ mol}^{-1}$$

$$\Delta_c H (C_3H_8) = \dots\dots\dots -1860 \dots\dots\dots \text{ kJ mol}^{-1} \text{ [3]}$$

- (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 *heat lost to the surroundings, so not all the heat from burning goes into the water*

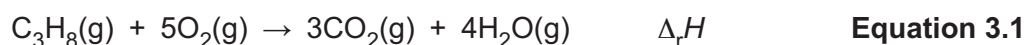
2 *incomplete combustion of the propane (not enough oxygen / air)*

[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**:



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

The standard enthalpy change of vaporisation of water, $\Delta_{\text{vap}} H$, is the enthalpy change for the conversion of 1 mol of $\text{H}_2\text{O}(\text{l})$ into 1 mol of $\text{H}_2\text{O}(\text{g})$ under standard conditions:



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

$$\text{Bonds broken: } 2 \text{ C-C} + 8 \text{ C-H} + 5 \text{ O=O} = (2 \times 347) + (8 \times 413) + (5 \times 498) = 694 + 3304 + 2490 = +6488 \text{ kJ mol}^{-1}$$

$$\text{Bonds made: } 6 \text{ C=O} + 8 \text{ O-H} = (6 \times 805) + (8 \times 464) = 4830 + 3712 = 8542 \text{ kJ mol}^{-1}$$

$$\Delta_r H = \text{bonds broken} - \text{bonds made} = 6488 - 8542 = -2054 \text{ kJ mol}^{-1}$$

Under standard conditions propane is a gas (b.p. -42°C), but water is a liquid, so $\Delta_c H^{\ominus}$ must form $4\text{H}_2\text{O}(\text{l})$, not $4\text{H}_2\text{O}(\text{g})$ as in equation 3.1.

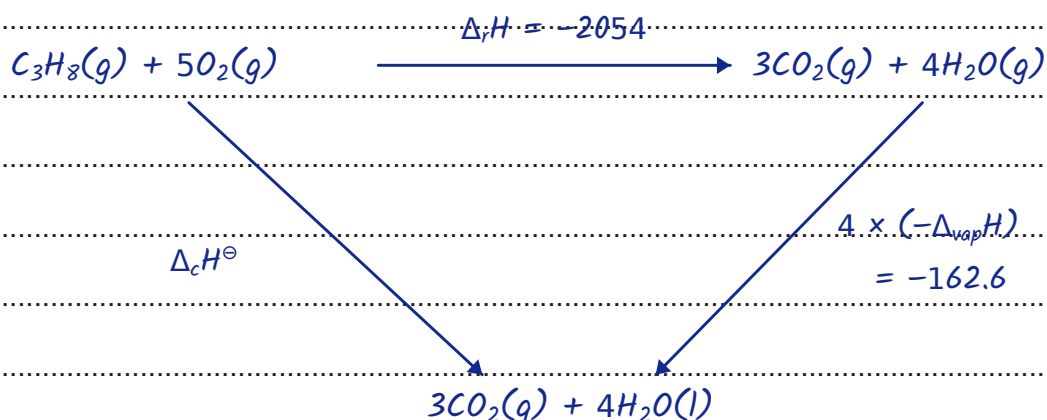
Condensing 4 mol of steam releases energy: $4\text{H}_2\text{O}(\text{g}) \rightarrow 4\text{H}_2\text{O}(\text{l})$

$$\Delta H = -4 \times \Delta_{\text{vap}} H = -4 \times 40.65 = -162.6 \text{ kJ mol}^{-1} \text{ (energy cycle below)}$$

$$\Delta_c H^{\ominus}(\text{C}_3\text{H}_8) = \Delta_r H - 4\Delta_{\text{vap}} H = -2054 - 162.6 = -2216.6 \text{ kJ mol}^{-1}$$

$$\Delta_c H^{\ominus}(\text{C}_3\text{H}_8) = -2217 \text{ kJ mol}^{-1}$$

Additional answer space if required



- 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 cm³ 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.

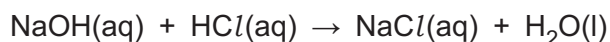
Stage 2

The resulting solution from **Stage 1** is made up to 250.0 cm³ with distilled water.

Stage 3

A 25.00 cm³ 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**:



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 cm³.

	1	2	3
Final reading / cm³	27.80	37.55	32.20
Initial reading / cm³	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 $M(s) + 2HCl(aq) \rightarrow MCl_2(aq) + H_2(g)$

Oxidation half-equation $M \rightarrow M^{2+} + 2e^{-}$

Reduction half-equation $2H^{+} + 2e^{-} \rightarrow H_2$

[3]

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

1 *all bubbles (effervescence / fizzing) stop*.....

2 *all of the metal (solid) has disappeared / dissolved*.....

[2]

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

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ [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**.

titres: 27.30, 27.55, 27.20 cm³; concordant: 27.30 and 27.20 cm³

mean titre = $(27.30 + 27.20) \div 2 = 27.25 \text{ cm}^3$

$n(NaOH) = 0.320 \times 27.25 \div 1000 = 8.72 \times 10^{-3} \text{ mol}$

1. $n(HCl) \text{ in } 25.00 \text{ cm}^3 = n(NaOH) = 8.72 \times 10^{-3} \text{ mol}$

$n(HCl) \text{ excess in } 250.0 \text{ cm}^3 = 8.72 \times 10^{-3} \times 10 = 8.72 \times 10^{-2} \text{ mol}$

$n(HCl) \text{ added} = 2.10 \times 100 \div 1000 = 0.210 \text{ mol}$

2. $n(HCl) \text{ reacted with M} = 0.210 - 0.0872 = 0.1228 \text{ mol}$

$n(M) = 0.1228 \div 2 = 0.0614 \text{ mol} \quad (M + 2HCl)$

3. $A_r(M) = 6.90 \div 0.0614 = 112.4$

$A_r = 112.4$ matches cadmium, Cd (forms Cd^{2+})

Metal **M** = ...*cadmium, Cd*..... [6]

- (b) The student is provided with the carbonate of an unknown metal, X_2CO_3 .

The student measures the mass loss when the X_2CO_3 is reacted with an **excess** of hydrochloric acid. The equation is shown below.



The reaction is carried out using this method:

- Step 1** Add 100 cm³ HCl(aq) to a conical flask and weigh.
- Step 2** Add 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 + 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.

$$\text{mass of } CO_2 \text{ lost} = 187.50 - 184.75 = 2.75 \text{ g}; \quad n = 2.75 \div 44.0$$

$$\text{Amount of } CO_2 = \dots\dots\dots 0.0625 \dots\dots\dots \text{ mol [1]}$$

- (ii) Calculate the molar mass of X_2CO_3 and identify metal X.

$$n(X_2CO_3) = n(CO_2) = 0.0625 \text{ mol}$$

$$\text{mass of } X_2CO_3 = 187.50 - 172.93 = 14.57 \text{ g}$$

$$M(X_2CO_3) = 14.57 \div 0.0625 = 233.1 \text{ g mol}^{-1}$$

$$2A_r(X) = 233.1 - 60.0 = 173.1, \text{ so } A_r(X) = 86.6$$

$$\text{closest Group 1 metal is rubidium, Rb } (A_r = 85.5)$$

$$\text{Molar mass of } X_2CO_3 = \dots\dots\dots 233.1 \dots\dots\dots \text{ g mol}^{-1} \quad \text{Metal X} = \dots\dots\dots \text{Rb} \dots\dots\dots [3]$$

- (c) After analysing the results, the student was told that their molar mass of 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?

Reweigh the flask and contents at intervals (e.g. every minute) until the mass stays constant, i.e. reweigh to constant mass.

[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 X_2CO_3 .

Some CO_2 stays dissolved, so the mass loss of CO_2 is smaller and $n(X_2CO_3)$ calculated is smaller. So the calculated molar mass ($mass \div n$) would be greater.

[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 $\text{J mol}^{-1} \text{K}^{-1}$ and ΔH is enthalpy change in J mol^{-1}).

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

- (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}
$\frac{1}{T} / \text{K}^{-1}$	2.50×10^{-3}	2.00×10^{-3}	1.67×10^{-3}	1.43×10^{-3}	1.25×10^{-3}
$\ln K_p$	135	105.4	85.8	71.8	60.0

[2]

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

Increasing the temperature decreases K_p , so the equilibrium position shifts to the left (favours the reverse reaction), so the forward reaction is exothermic. [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.

$$\text{gradient} = (135 - 45) \div (2.50 \times 10^{-3} - 1.00 \times 10^{-3}) = +6.00 \times 10^4$$

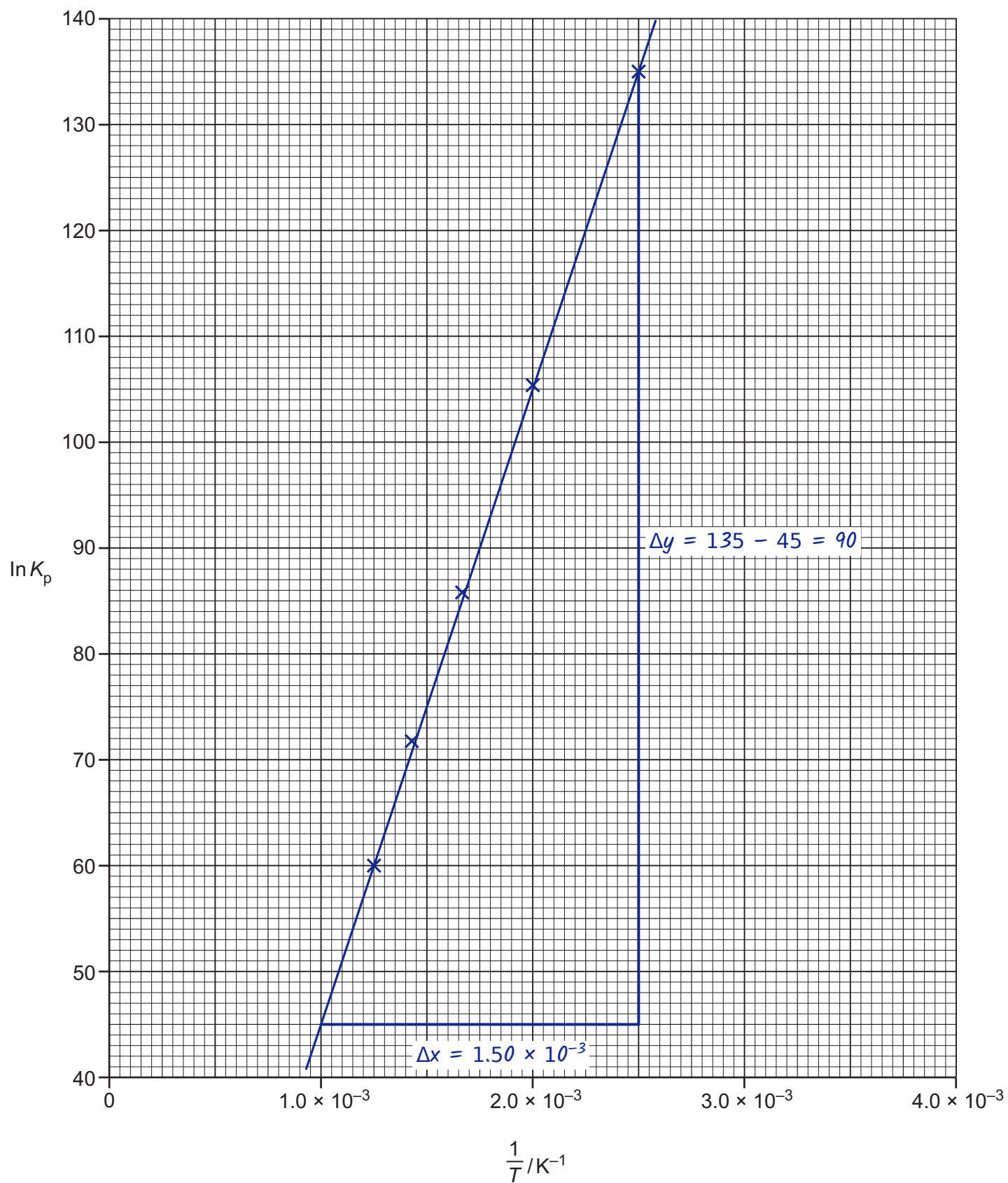
$$\text{gradient} = -\Delta H/R, \text{ so } \Delta H = -\text{gradient} \times R = -60000 \times 8.314$$

$$\Delta H = -498840 \text{ J mol}^{-1} = -499 \text{ kJ mol}^{-1}$$

$$\Delta H = -499 \text{ kJ mol}^{-1} \quad [4]$$

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

Extrapolate the line to the y-intercept ($1/T = 0$): intercept = $\Delta S/R$, so $\Delta S = R \times \text{intercept} = 8.314 \times (135 - 60000 \times 2.50 \times 10^{-3}) = 8.314 \times (-15) = -125 \text{ J K}^{-1} \text{ mol}^{-1}$ [2]



- 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**.

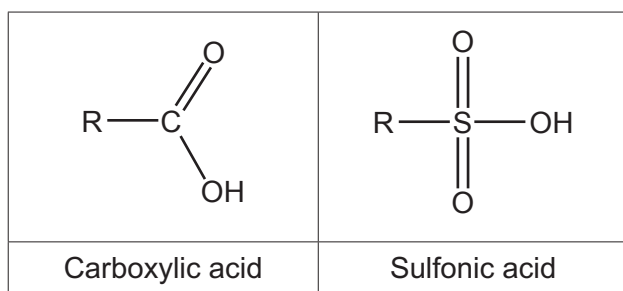


Fig. 6.1

- (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.

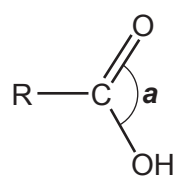
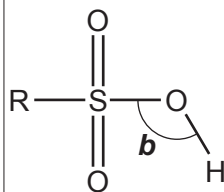
Type of acid	Acid	Bond angle	Name of shape
Carboxylic acid		120°.....	trigonal planar.....
Sulfonic acid		104.5°.....	non-linear (bent).....

Table 6.1

[2]

- (b) Ethanoic acid, CH_3COOH , and methanesulfonic acid, $\text{CH}_3\text{SO}_2\text{OH}$, are both monobasic acids. The $\text{p}K_a$ values are shown in the table.

Acid		$\text{p}K_a$
Ethanoic acid	CH_3COOH	4.76
Methanesulfonic acid	$\text{CH}_3\text{SO}_2\text{OH}$	-1.90

A student suggests that 1.0mol dm^{-3} $\text{CH}_3\text{SO}_2\text{OH}$ should have a lower pH value than 1.0mol dm^{-3} CH_3COOH .

Write an equation, showing conjugate acid–base pairs, for the equilibrium of $\text{CH}_3\text{SO}_2\text{OH}$ with water and explain, with reasons, whether the student is correct.

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



A1 B2 B1 A2

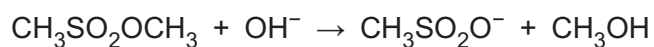
The student is correct. $\text{CH}_3\text{SO}_2\text{OH}$ has a lower $\text{p}K_a$ (higher K_a) so it is a much stronger acid and dissociates more than CH_3COOH , giving a greater $[\text{H}^+]$, so a lower pH ($\text{pH} \approx -0.95$ compared with 2.38).

..... [4]

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

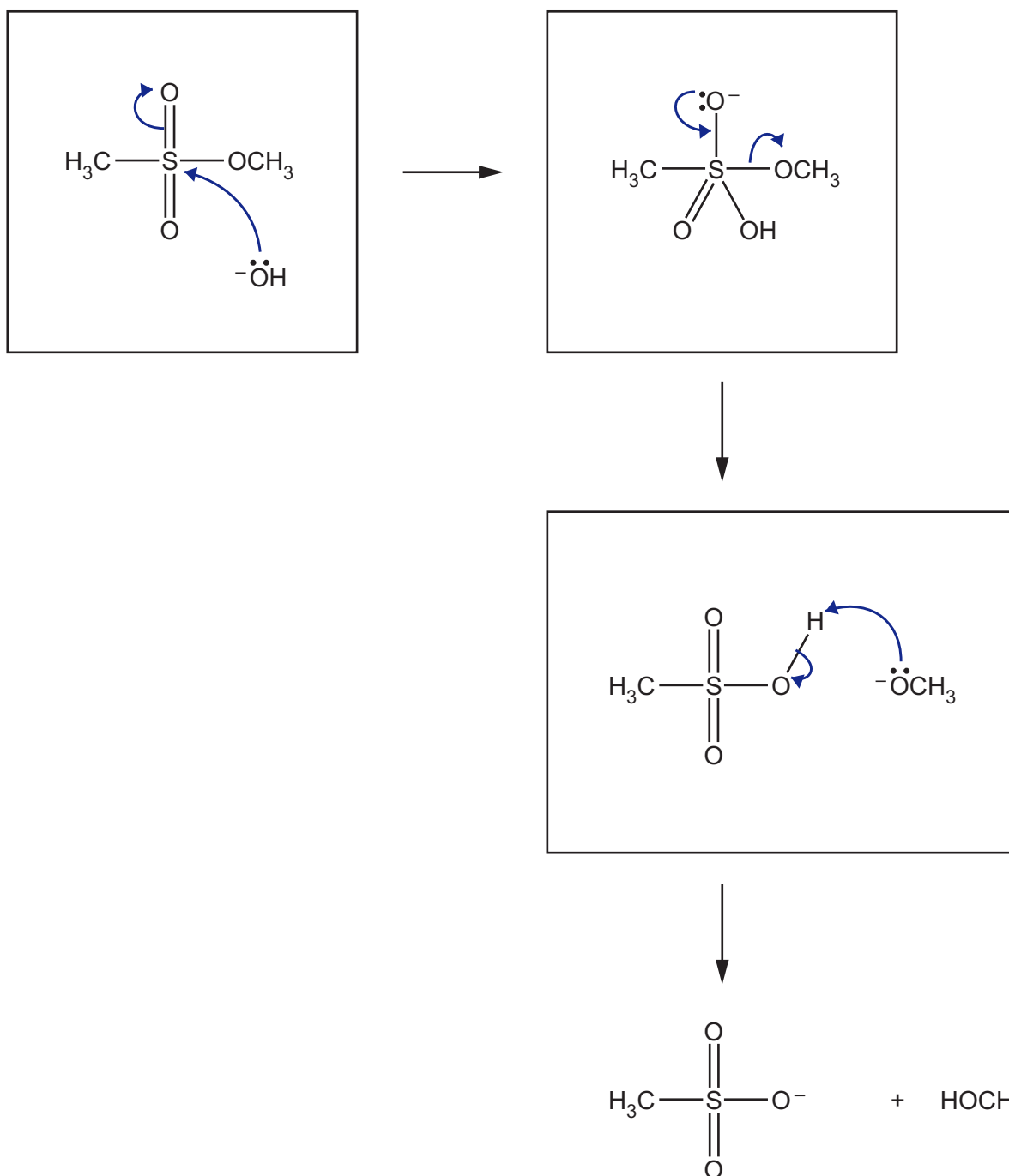
Sulfonic acid esters can be hydrolysed by aqueous alkali.

The equation shows the alkaline hydrolysis of a sulfonic acid ester.



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

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