

Monday 19 October 2020 – Morning

A Level Chemistry A

H432/03 Unified chemistry

Time allowed: 1 hour 30 minutes





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.



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

- (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) ₂ CHNH ₂	(CH ₃) ₃ N
Skeletal formula	NH ₂	NH ₂	│ ╱ ^N ∕
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, 0.202g of the amine produces 72.0 cm^3 of gas at $1.00 \times 10^5 \text{ Pa}$ and $100 \,^\circ\text{C}$. The ¹³C NMR spectrum of amine **A** has 3 peaks.

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

Molecular formula 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]
Additional answer space if required	

- **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.

(ii) The student finds that the experimental enthalpy change $\Delta_c H$ (C₃H₈) is much less exothermic than the accurate standard enthalpy change $\Delta_c H$ (C₃H₈) 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 2 [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=0	+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**:

 $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g) \qquad \Delta_r H$ 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 H₂O(I) into 1 mol of H₂O(g) under standard conditions:

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

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] Additional answer space if required

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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 \mathbf{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 $0.320 \text{ mol dm}^{-3}$ NaOH(aq).

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

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

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/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 HC*l*(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]
	1.71

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

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

Turn over

(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.

 $\textbf{X}_2\text{CO}_3(s) \ \textbf{+} \ 2\text{HC}\textit{l}(\text{aq}) \ \rightarrow \ 2\textbf{X}\text{C}\textit{l}(\text{aq}) \ \textbf{+} \ \text{CO}_2(g) \ \textbf{+} \ \text{H}_2\text{O}(\textbf{I})$

The reaction is carried out using this method:

- **Step 1** Add $100 \text{ cm}^3 \text{ HC}l(\text{aq})$ 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)	172.93g
Mass of conical flask + X_2CO_3 + HCl(aq) before reaction	187.50 g
Mass of conical flask + contents after 5 minutes	184.75g

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

Amount of CO₂ = mol [1]

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

Molar mass of $X_2CO_3 = \dots g mol^{-1}$ Metal $X = \dots$ [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?

(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 .

 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).

$$\ln K_{\rm p} = -\frac{\Delta H}{R} \times \frac{1}{T} + \frac{\Delta S}{R}$$
 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 $\frac{1}{\tau}$ and $\ln K_{\rm p}$.

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				
In K _p	135				
	1	I	I	I	[2]

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

......[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.

 $\Delta H = \dots KJ \text{ mol}^{-1} [4]$ (d) Explain how ΔS could be calculated from a graph of $\ln K_p$ against $\frac{1}{T}$.



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**.





(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	R-C OH		
Sulfonic acid			

Table 6.1

[2]

- 17
- (b) Ethanoic acid, CH_3COOH , and methanesulfonic acid, CH_3SO_2OH , are both monobasic acids. The p K_a values are shown in the table.

Ac	р <i>К</i> _а	
Ethanoic acid CH ₃ COOH		4.76
Methanesulfonic acid	CH ₃ SO ₂ OH	-1.90

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

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.

 (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.

 $\mathsf{CH}_3\mathsf{SO}_2\mathsf{OCH}_3\ +\ \mathsf{OH}^- \rightarrow \ \mathsf{CH}_3\mathsf{SO}_2\mathsf{O}^-\ +\ \mathsf{CH}_3\mathsf{OH}$

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.



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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