



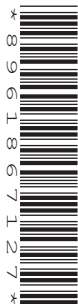
Oxford Cambridge and RSA

Monday 18 October 2021 – 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)

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 These short questions are from different areas of chemistry.

(a) A flask contains 110 g CO₂ and 120 g O₂ at a pressure of 50.0 atm.

What is the partial pressure of the CO₂?

$$n(\text{CO}_2) = 110 \div 44.0 = 2.50 \text{ mol}; \quad n(\text{O}_2) = 120 \div 32.0 = 3.75 \text{ mol}$$

$$\text{total moles} = 2.50 + 3.75 = 6.25 \text{ mol}$$

$$\text{mole fraction of CO}_2 = 2.50 \div 6.25 = 0.400$$

$$p(\text{CO}_2) = 0.400 \times 50.0 = 20.0 \text{ atm}$$

$$\text{partial pressure of CO}_2 = \dots\dots\dots 20.0 \dots\dots\dots \text{ atm [2]}$$

(b) Pure PCl₅ is placed in a sealed container which is heated to 200°C.

An equilibrium is set up: $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

Under these conditions:

- $K_c = 8.00 \times 10^{-3} \text{ mol dm}^{-3}$
- equilibrium concentration of PCl₅ = 0.0500 mol dm⁻³.

Calculate the concentrations of PCl₃ and Cl₂ at equilibrium.

$$K_c = [\text{PCl}_3][\text{Cl}_2] \div [\text{PCl}_5]$$

$$[\text{PCl}_3] = [\text{Cl}_2], \text{ so } [\text{PCl}_3]^2 = K_c \times [\text{PCl}_5]$$

$$[\text{PCl}_3]^2 = 8.00 \times 10^{-3} \times 0.0500 = 4.00 \times 10^{-4}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = \sqrt{(4.00 \times 10^{-4})} = 0.0200 \text{ mol dm}^{-3}$$

$$\text{concentration of PCl}_3 = \dots\dots\dots 0.0200 \dots\dots\dots \text{ mol dm}^{-3}$$

$$\text{concentration of Cl}_2 = \dots\dots\dots 0.0200 \dots\dots\dots \text{ mol dm}^{-3}$$

[2]

- (c) The electronegativities of H, C, N and F, and the boiling points of methane, ammonia and hydrogen fluoride are shown below.

Electronegativity	H: 2.1	C: 2.5	N: 3.0	F: 4.0
-------------------	--------	--------	--------	--------

Compound	CH ₄	NH ₃	HF
Boiling point/°C	-161.5	-33.3	19.5

Explain the difference in the boiling points of CH₄, NH₃ and HF.

Boiling point increases as the electronegativity of the atom bonded to H
(the electronegativity difference) increases: CH₄ < NH₃ < HF.
HF and NH₃ have hydrogen bonding between their molecules, but CH₄ only
has London forces (induced dipole-dipole interactions).
Hydrogen bonding is stronger than London forces, so more energy is needed
to overcome it. HF has stronger hydrogen bonding than NH₃ (F is more
electronegative than N), so HF has the highest boiling point.

[3]

- (d) Compound **A** has the following percentage composition by mass:

Ca, 81.10%; N, 18.90%.

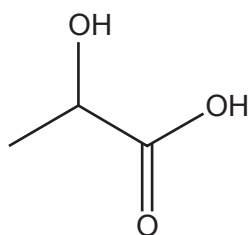
A student reacts compound **A** with water to form alkaline gas **B** and alkali **C**.

Identify **A**, **B** and **C** and write the equation for the reaction of compound **A** with water.

Ca : N = 81.10 ÷ 40.1 : 18.90 ÷ 14.0 = 2.02 : 1.35 = 1.5 : 1 = 3 : 2
A: Ca₃N₂ (calcium nitride)
B: NH₃ (ammonia) C: Ca(OH)₂ (calcium hydroxide)
Ca₃N₂ + 6H₂O → 2NH₃ + 3Ca(OH)₂

[4]

(e) The structure of lactic acid is shown below.



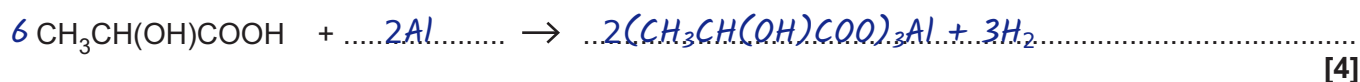
lactic acid

Complete and balance the equations for two reactions of lactic acid.

Reaction with sodium carbonate



Reaction with aluminium

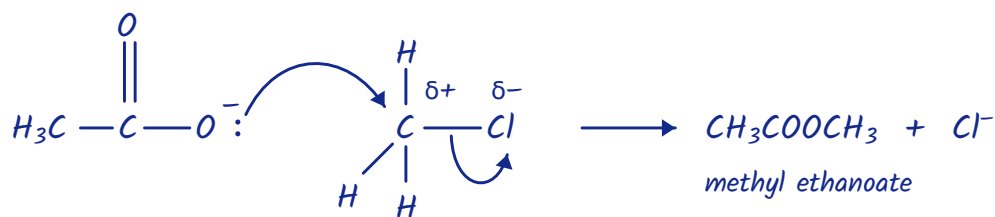


[4]

(f) The ester, methyl ethanoate, can be synthesised by reacting a haloalkane with a carboxylate ion.

The mechanism is nucleophilic substitution.

Outline the mechanism for this reaction.



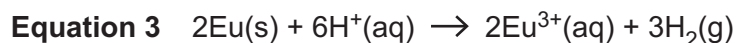
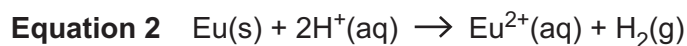
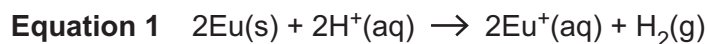
[3]

5
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- 2 Europium ($A_r = 152.0$) reacts with dilute aqueous acid in a redox reaction, forming a solution and hydrogen gas.

A student proposed three possible ionic equations for this reaction, forming europium ions with different charges:



The student plans to carry out an investigation to determine which equation is correct. Hydrochloric acid is used as the source of $\text{H}^+(\text{aq})$ ions.

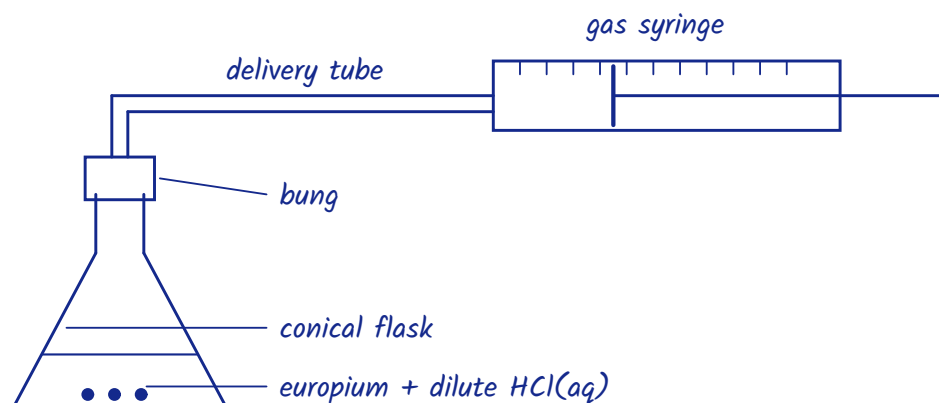
The student's method is outlined below.

- Step 1** Using a 3 decimal place balance, weigh a suitable container for the reaction. Add **about** 1 g of europium to the container and reweigh.
- Step 2** Set up apparatus for gas collection. Add an excess of dilute hydrochloric acid to the europium.
- Step 3** Measure the volume of gas produced.

Results

Mass of container	= 32.795 g
Mass of container + europium	= 33.783 g
Volume of gas collected	= 152 cm ³

- (a) Draw a labelled diagram of suitable apparatus for this investigation.



[2]

- (b) Analyse the student's results to conclude which of **Equation 1** or **2** or **3**, is supported by the experimental results.

Assume that the conditions in the laboratory are 'room temperature and pressure' (RTP).

$$\text{mass of Eu} = 33.783 - 32.795 = 0.988 \text{ g}$$

$$n(\text{Eu}) = 0.988 \div 152.0 = 6.50 \times 10^{-3} \text{ mol}$$

$$n(\text{H}_2) = 152 \div 24000 = 6.33 \times 10^{-3} \text{ mol}$$

$$\text{ratio } \text{H}_2 : \text{Eu} = 6.33 \times 10^{-3} : 6.50 \times 10^{-3} = 0.974 : 1, \text{ so } 1 : 1$$

Equation 2 has $\text{H}_2 : \text{Eu} = 1 : 1$ (Equation 1 is $1 : 2$,

Equation 3 is $3 : 2$), so Equation 2 is supported.

correct equation (1, 2, or 3) = ...2..... [3]

- (c) The student repeats the experiment but adds concentrated hydrochloric acid instead of dilute hydrochloric acid. The apparatus gets hot during the reaction.

Predict how the hot apparatus would change the student's results and the conclusion in (b).

Explain your answer.

The hot gas expands, so the volume of gas collected would be larger than it would be at RTP.
So the calculated $n(\text{H}_2)$ and the ratio $\text{H}_2 : \text{Eu}$ would be larger than $1 : 1$, which could wrongly support Equation 3 ($\text{H}_2 : \text{Eu} = 1.5 : 1$). [2]

- (d) The student modifies their method as outlined below:

- 1.52 g (0.01 mol) of europium is reacted with an excess of dilute hydrochloric acid.
- An excess of aqueous sodium hydroxide is added to the reaction mixture.
- A precipitate forms which is collected, dried and weighed.

Explain how the mass of precipitate formed would allow the student to conclude which of **Equation 1** or **2** or **3** is correct.

The precipitates have different formulae and molar masses: EuOH ($M = 169$), Eu(OH)_2 ($M = 186$), Eu(OH)_3 ($M = 203$).
0.01 mol Eu forms 0.01 mol precipitate, so $M = \text{mass} \div 0.01$. Equation 2 would form 1.86 g of Eu(OH)_2 (Equation 1 gives 1.69 g, Equation 3 gives 2.03 g). [2]

3 This question is about carboxylic acids.

Compound **D** is a *cis* stereoisomer of an unsaturated organic acid with the general formula $C_nH_{2n-1}COOH$.

A student plans to analyse acid **D** by carrying out a titration.

- (a) A student first prepares 250.0 cm^3 of a standard solution of 0.150 mol dm^{-3} $Ba(OH)_2$ for the titration.

The student is provided with solid $Ba(OH)_2$ and usual laboratory apparatus and equipment.

Describe how the student would prepare the standard solution, giving full details of quantities, apparatus and method.

$$n(Ba(OH)_2) = 0.150 \times 250.0 \div 1000 = 0.0375 \text{ mol}$$

$$\text{mass of } Ba(OH)_2 = 0.0375 \times 171.3 = 6.42 \text{ g}$$

Weigh 6.42 g of solid $Ba(OH)_2$ accurately on a balance. Dissolve the solid

in about 150 cm^3 of distilled water in a beaker, stirring with a glass rod.

Transfer the solution to a 250.0 cm^3 volumetric flask using a funnel. Rinse

the beaker, glass rod and funnel with distilled water and transfer all the

washings into the flask.

Make up to the graduation mark (250.0 cm^3) with distilled water, adding

the last drops with a dropping pipette until the bottom of the meniscus is

on the mark.

Stopper the flask and invert it several times to mix thoroughly.

[5]

- (b) The student prepares a 100.0 cm^3 solution containing 3.215 g of acid **D**.

The student titrates 25.0 cm^3 samples of the solution of **D** with 0.150 mol dm^{-3} $\text{Ba(OH)}_2(\text{aq})$ in the burette.

1 mol Ba(OH)_2 reacts with 2 mol of **D**.

The mean titre of $\text{Ba(OH)}_2(\text{aq})$ is 23.50 cm^3 .

Analyse the titration results to determine **two** possible structures for the *cis* stereoisomer of organic acid **D**.

$$n(\text{Ba(OH)}_2) = 0.150 \times 23.50 \div 1000 = 3.525 \times 10^{-3} \text{ mol}$$

$$n(\text{D}) \text{ in } 25.0 \text{ cm}^3 = 2 \times 3.525 \times 10^{-3} = 7.05 \times 10^{-3} \text{ mol}$$

$$n(\text{D}) \text{ in } 100.0 \text{ cm}^3 = 7.05 \times 10^{-3} \times 100.0 \div 25.0 = 0.0282 \text{ mol}$$

$$\text{molar mass of D} = 3.215 \div 0.0282 = 114 \text{ g mol}^{-1}$$

$$\text{C}_n\text{H}_{2n-1}\text{COOH: } M(\text{COOH}) = 45.0, \text{ so } M(\text{C}_n\text{H}_{2n-1}) = 114 - 45 = 69$$

$$12n + 2n - 1 = 69, \text{ so } n = 5: \text{ the alkenyl group is } \text{C}_5\text{H}_9$$

$$\text{Acid D is } \text{C}_5\text{H}_9\text{COOH (C}_6\text{H}_{10}\text{O}_2\text{)}$$

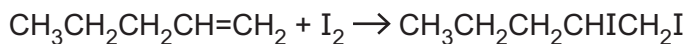
For a *cis* isomer, each C of the $\text{C}=\text{C}$ must have two different groups, with the same group (H) on the same side of the double bond.

Structures of 2 possible *cis* stereoisomers of acid D



[7]

- 4 Pent-1-ene and iodine react as shown in the equation below.

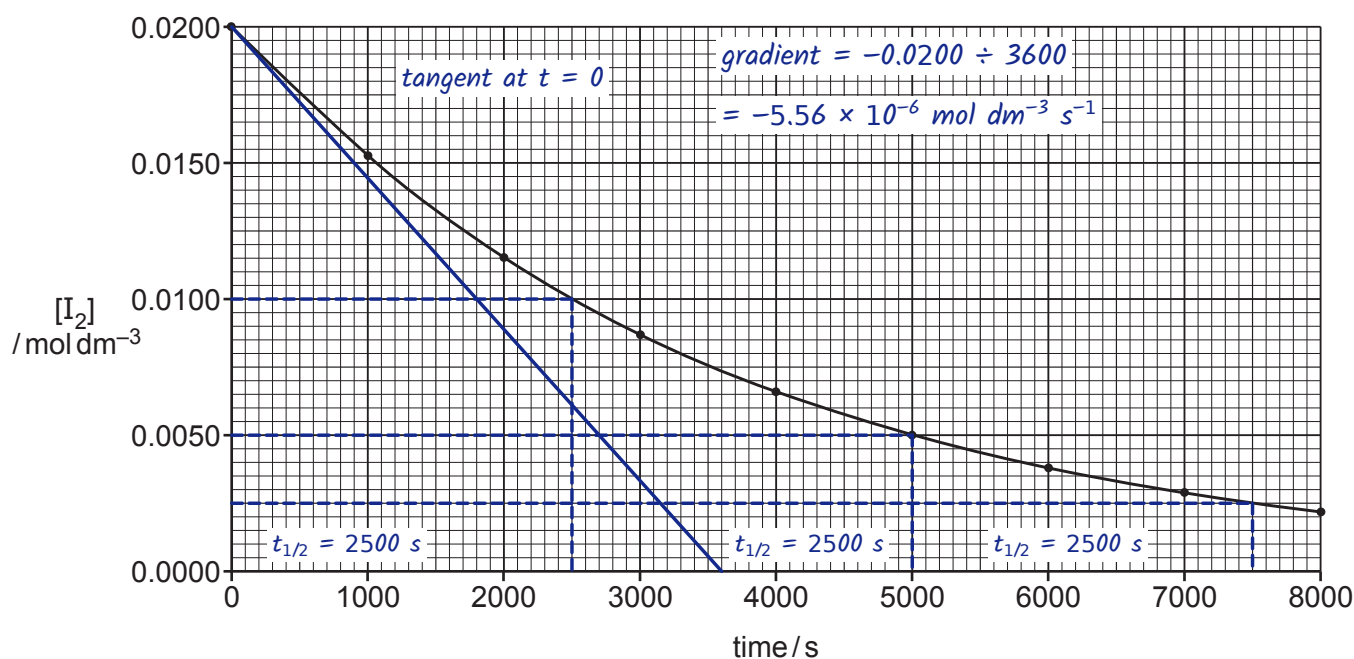


A student investigates the rate of this reaction by monitoring the concentration of iodine over time. The initial concentrations are shown in the table.

	Concentration / mol dm^{-3}
I_2	0.0200
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	2.0000

In this investigation, the order with respect to pent-1-ene can be assumed to be zero.

The student plots the graph below from the experimental results.



- (a) Why can the order with respect to pent-1-ene be assumed to be zero in this investigation?

Pent-1-ene is in large excess ($2.0000 \text{ mol dm}^{-3}$ compared with $0.0200 \text{ mol dm}^{-3} \text{ I}_2$), so its concentration stays effectively constant.

[1]

- (b)* The student's experimental procedure shows that the reaction is first order with respect to iodine.

Show that this statement is true and determine the initial rate of reaction and rate constant.

Assume that the reaction is zero order with respect to pent-1-ene. Show your working on the graph on page 10 and the lines below as appropriate. [6]

Initial rate: a tangent is drawn to the curve at $t = 0$ s (on the graph).

gradient = $-0.0200 \div 3600 = -5.56 \times 10^{-6}$, so initial rate = 5.56×10^{-6}

mol dm⁻³ s⁻¹

Order: half-lives measured on the graph: $[I_2]$ falls from 0.0200 to 0.0100

mol dm⁻³ in 2500 s, from 0.0100 to 0.0050 in $5000 - 2500 = 2500$ s,

and from 0.0050 to 0.0025 in $7500 - 5000 = 2500$ s.

The half-life is constant at 2500 s, so the reaction is first order with

respect to I_2 . Rate equation: rate = $k[I_2]$

Rate constant: $k = \text{initial rate} \div [I_2] = 5.56 \times 10^{-6} \div 0.0200$

$k = 2.78 \times 10^{-4} \text{ s}^{-1}$

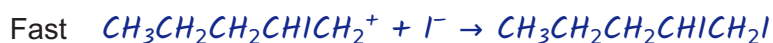
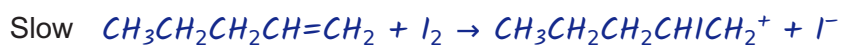
Check using the half-life: $k = \ln 2 \div t_{1/2} = 0.693 \div 2500 = 2.77 \times 10^{-4}$

s⁻¹, which agrees.

Additional answer space if required.

- (c) Further experiments provide evidence that the reaction is first order with respect to **both** $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ **AND** I_2 .

- (i) Write equations to suggest a two-step mechanism for the reaction.



[2]

- (ii) Suggest how the investigation could be modified to show that the reaction is first order with respect to pent-1-ene.

Repeat with I_2 in large excess (e.g. $2.00 \text{ mol dm}^{-3} \text{I}_2$ and $0.0200 \text{ mol dm}^{-3}$ pent-1-ene), so $[\text{I}_2]$ stays constant.

Monitor [pent-1-ene] over time and plot a graph: a constant half-life shows first order with respect to pent-1-ene.

[2]

13
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5 This question is about nitrogen and its compounds.

(a) Sodium azide, NaN_3 , has been used in car airbags.

The airbag inflates when the NaN_3 decomposes to form nitrogen gas:



(i) This is a redox reaction.

Write half-equations for the reduction and oxidation processes that take place.

Reduction ... $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

Oxidation ... $2\text{N}_3^- \rightarrow 3\text{N}_2 + 2\text{e}^-$ [2]

(ii) A 16.0 dm^3 airbag is inflated at 17.0°C .
The pressure in the inflated airbag is $1.20 \times 10^5 \text{ Pa}$.

Calculate the mass of NaN_3 that has decomposed.

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

$$n(\text{N}_2) = pV \div RT$$

$$T = 17.0 + 273 = 290 \text{ K}; \quad V = 16.0 \text{ dm}^3 = 16.0 \times 10^{-3} \text{ m}^3$$

$$n(\text{N}_2) = (1.20 \times 10^5 \times 16.0 \times 10^{-3}) \div (8.314 \times 290)$$

$$n(\text{N}_2) = 1920 \div 2411.06 = 0.796 \text{ mol}$$

$$n(\text{NaN}_3) = 2/3 \times 0.796 = 0.531 \text{ mol}$$

$$M(\text{NaN}_3) = 23.0 + (3 \times 14.0) = 65.0 \text{ g mol}^{-1}$$

$$\text{mass of NaN}_3 = 0.531 \times 65.0 = 34.5 \text{ g (3 s.f.)}$$

mass of NaN_3 = ... **34.5** g [5]

(b) Hydrazoic acid, HN_3 , is a weak acid ($K_a = 2.51 \times 10^{-5} \text{ mol dm}^{-3}$).

(i) Calculate the pH of $0.125 \text{ mol dm}^{-3}$ hydrazoic acid.

Give your answer to **2** decimal places.

$$[H^+] = \sqrt{(K_a \times [HN_3])} = \sqrt{(2.51 \times 10^{-5} \times 0.125)}$$

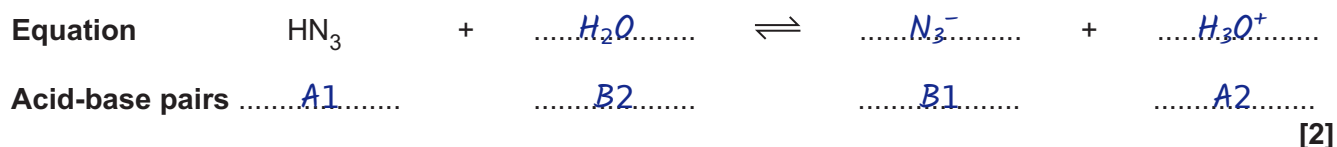
$$[H^+] = 1.77 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.77 \times 10^{-3}) = 2.75$$

$$\text{pH} = \dots\dots\dots 2.75 \dots\dots\dots [2]$$

(ii) When added to water, hydrazoic acid forms an equilibrium mixture containing conjugate acid–base pairs.

Complete the equation for this equilibrium and label the conjugate acid–base pairs as: **A1**, **B1** and **A2**, **B2**.

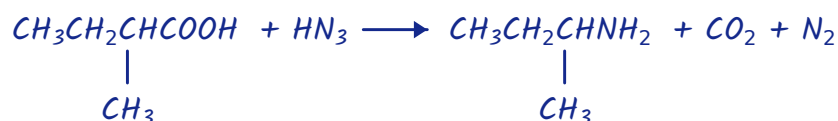


(iii) In the Schmidt reaction, hydrazoic acid, HN_3 , reacts with carboxylic acids to form primary amines.

For example, HN_3 reacts with RCOOH to form RNH_2 and two gases that are found in the atmosphere.

Write the equation for the reaction of HN_3 with 2-methylbutanoic acid.

Show structures for organic compounds.



[3]

(c)* This question is about two reactions of ammonia.

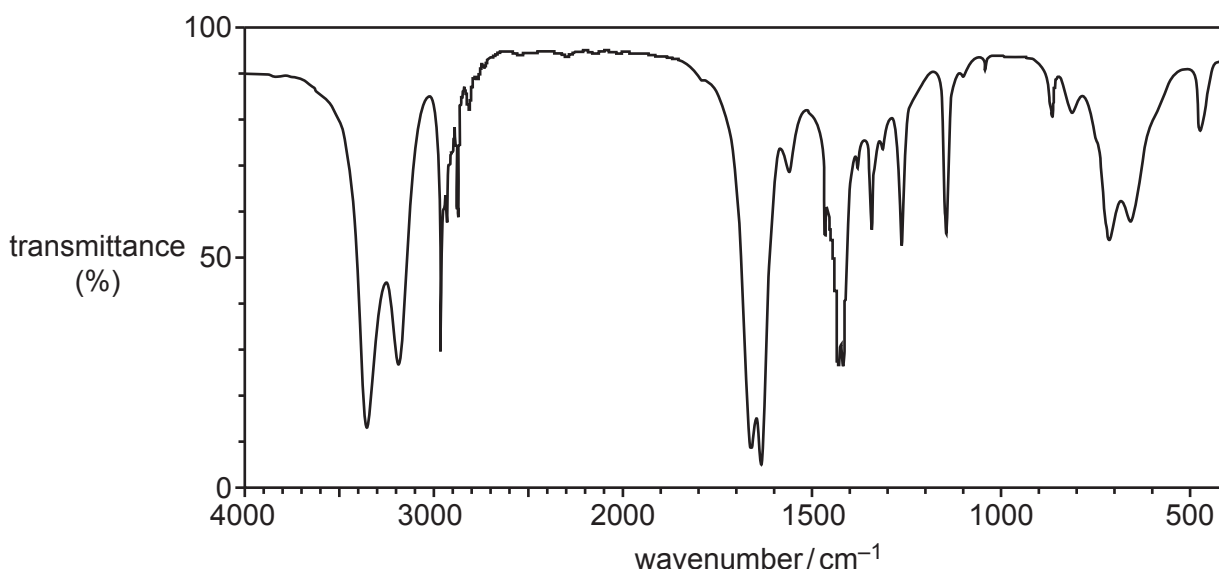
Reaction 1

Excess ammonia is reacted with 4.77 g of copper(II) oxide. The reaction produces 3.81 g of solid **E**, liquid **F** and 0.560 g of gas **G**, which has a volume of 480 cm³ at RTP.

Reaction 2

Ammonia reacts with compound **H** to form compound **I**, C₂H₅NO, and chloride salt **J**.

The IR spectrum of **I** is shown below.



Identify **E**, **F**, **G**, **H**, **I** and **J**, and write equations for the **two** reactions.

Show your reasoning.

[6]

Reaction 1: $n(\text{CuO}) = 4.77 \div 79.5 = 0.0600 \text{ mol}$

$M(\text{E}) = 3.81 \div 0.0600 = 63.5 \text{ g mol}^{-1}$, so solid E is copper, Cu (CuO is reduced).

$n(\text{G}) = 480 \div 24000 = 0.0200 \text{ mol}$; $M(\text{G}) = 0.560 \div 0.0200 = 28.0 \text{ g mol}^{-1}$, so gas G is nitrogen, N₂ (NH₃ is oxidised).

The H atoms from NH₃ combine with the O atoms from CuO, so liquid F is water, H₂O.

$\text{CuO} : \text{N}_2 = 0.0600 : 0.0200 = 3 : 1$, so the equation is:



Reaction 2: in the IR spectrum of I, the strong absorption at about 1650

to 1700 cm^{-1} shows a C=O bond, and the two absorptions at about 3200

to 3400 cm^{-1} show N-H bonds of an NH_2 group. There is no broad O-H absorption (2500 to 3300 cm^{-1}).

So I, $\text{C}_2\text{H}_5\text{NO}$, is the primary amide ethanamide, CH_3CONH_2 .

An amide forms when ammonia reacts with an acyl chloride, so H is ethanoyl chloride, CH_3COCl . The HCl formed reacts with the excess NH_3 , so the chloride salt J is ammonium chloride, NH_4Cl .



Additional answer space if required.

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