

OCR

Oxford Cambridge and RSA

A Level Chemistry A

H432/03 Unified chemistry

Tuesday 27 June 2017 – Morning
Time allowed: 1 hour 30 minutes



You must have:

- the Data Sheet for Chemistry A
(sent with general stationery)

You may use:

- a scientific or graphical calculator
- a ruler



First name										
Last name										
Centre number						Candidate number				

INSTRUCTIONS

- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above with your name, centre number and candidate number.
- Answer **all** the questions.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- Do **not** write in the barcodes.

INFORMATION

- The total mark for this paper is **70**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **20** pages.

Answer **all** the questions.

- 1 Within the permafrost in Arctic regions of the Earth, large amounts of methane are trapped within ice as 'methane hydrate', $\text{CH}_4 \cdot x\text{H}_2\text{O}$. Methane makes up about 13.4% of the mass of 'methane hydrate'.

Scientists are concerned that global warming will melt the permafrost, releasing large quantities of methane into the atmosphere.

- (a) The H-O-H bond angle in ice is about 109° but about 105° in gaseous H_2O .

Explain why there is this difference.

Ice can form more hydrogen bonds.....
Water (H_2O) has 2 bonded pairs
and 2 lone pairs:



lone pairs repel more than bonded pairs hence different bond angles. [3]

- (b) Why are scientists concerned about the release of methane into the atmosphere?

Contributes towards global warming

[1]

- (c) Determine the formula of 'methane hydrate', $\text{CH}_4 \cdot x\text{H}_2\text{O}$.

In the formula, show the value of x to two decimal places.

$$\frac{13.4}{(12+4)} = \frac{100}{(12+4)+18x}$$

$$13.4(16+18x) = 100(16)$$

$$214.4 + 241.2x = 1600$$

$$241.2x = 1385.6$$

$$x = 5.74$$

formula = $\text{CH}_4 \cdot 5.74\text{H}_2\text{O}$ [2]

3

- (d) Calculate the volume of methane, in dm^3 , that would be released from the melting of each 1.00 kg of 'methane hydrate' at 101 kPa and 0°C .

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

$$PV = nRT$$

\nearrow Pa \nearrow m^3 \nearrow k \nwarrow

$$\begin{aligned} & \text{moles of } \text{CH}_4 \cdot 5.74\text{H}_2\text{O} \\ & \frac{1 \times 10^3}{12 + 4 + (5.74 \times (2 + 16))} \\ & = 8.38 \text{ mol} \end{aligned}$$

$$V = \frac{nRT}{P}$$

$$V = \frac{8.38 \times 8.314 \times 273}{101 \times 10^3} = 0.188 \text{ m}^3 = 188 \text{ dm}^3$$

volume =188..... dm^3 [4]

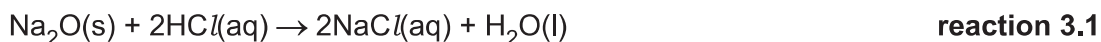
- (e) Suggest why some industries are interested in the presence of 'methane hydrate' in regions of the Earth.

for fuel / energy

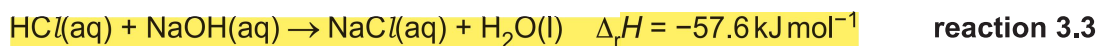
.....
 [1]

4

- 2 A student plans to determine the enthalpy change of **reaction 3.1** shown below.



This enthalpy change can be determined indirectly using Hess' Law from the enthalpy changes of **reaction 3.2** and **reaction 3.3** shown below.



The student will determine the enthalpy change of **reaction 3.2** as outlined below.

- Weigh a bottle containing $\text{Na}_2\text{O(s)}$ and weigh a polystyrene cup.
- Add about 25 cm^3 of water to the polystyrene cup and measure its temperature.
- Add the $\text{Na}_2\text{O(s)}$, stir the mixture, and measure the maximum temperature reached.
- Weigh the empty bottle and weigh the polystyrene cup with the final solution.

Mass readings

Mass of bottle + $\text{Na}_2\text{O(s)}$	= 16.58 g
Mass of empty bottle	= 15.34 g
Mass of empty polystyrene cup	= 21.58 g
Mass of polystyrene cup + final solution	= 47.33 g

Temperature readings

Initial temperature of water	= 20.5°C
Maximum temperature of final solution	= 55.5°C

The density and specific heat capacity, c , of the solution are the same as for water.

$$\Delta H_{3.1} = \Delta H_{3.2} + 2 \times \Delta H_{3.3}$$

5

(a)* Calculate the enthalpy change of reaction 3.2 and the enthalpy change of reaction 3.1.

Show all your working.

$$mc\Delta T = E \text{ (joules)}$$

$$\text{mass of Na}_2\text{O} = 16.58 - 15.34 \\ = 1.24 \text{ g}$$

$$\text{mass of solution} = 47.33 - 21.58 \\ = 25.75 \text{ g}$$

$$\Delta T = 55.5 - 20.5 = 35^\circ\text{C}$$

$$25.75 \times 4.18 \times 35 = 3767.225 \text{ J} \\ = 3.767225 \text{ kJ}$$

$$\text{mol} = \frac{1.24}{(23 \times 2) + 16} = 0.02 \text{ mol}$$

exothermic so -ve ΔH values

$$3.767225 \div 0.02 = 188 \text{ kJ mol}^{-1}$$

ΔH 3.2:

$$\Delta H 3.1 = -188 + (-57.6 \times 2) = -303.2 \text{ kJ mol}^{-1} \quad [6]$$

(b) The uncertainty in each temperature reading is $\pm 0.1^\circ\text{C}$.The uncertainty in each mass reading is $\pm 0.005 \text{ g}$.Determine whether the mass of Na_2O or the temperature change has the greater percentage uncertainty.

Show all your working.

$$\text{mass: } \frac{0.005 \times 2}{1.24} \times 100 = 0.81\%$$

number of times readings were used

$$\text{temperature: } \frac{0.1 \times 2}{35} \times 100 = 0.57\%$$

mass has a ³⁵ greater %

uncertainty [2]

6

- (c) Suggest a modification to this experiment, using the **same** apparatus, which would reduce the percentage errors in the measurements.

Explain your reasoning.

larger denominator
smaller % uncertainty

greater mass or greater
temperature change (ΔT)
to reduce % errors

[2]

- (d) Sodium oxide, Na_2O , can be prepared by the redox reaction of NaNO_2 and sodium metal. Nitrogen gas is also formed.

- (i) What is the systematic name for NaNO_2 ?

sodium nitrite [1]

- (ii) Using oxidation numbers, with signs, show the element that is oxidised and the element that is reduced in this reaction.

$2\text{NaNO}_2 + 6\text{Na} \rightarrow 4\text{Na}_2\text{O} + \text{N}_2$

Element oxidised Na +1 +3 -2 0 +1 -2 0

Oxidation number change from 0 to +1

Element reduced N

Oxidation number change from +3 to 0

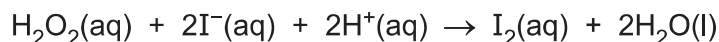
[2]

- (iii) Construct the equation for this reaction.

Equation ... $2\text{NaNO}_2 + 6\text{Na} \rightarrow 4\text{Na}_2\text{O} + \text{N}_2$... [1]

3 This question is about reactions of hydrogen peroxide, H_2O_2 .

(a) Hydrogen peroxide, H_2O_2 , iodide ions, I^- , and acid, H^+ , react as shown in the equation below.



A student carries out several experiments at the same temperature, using the initial rates method, to determine the rate constant, k , for this reaction.

The results are shown below.

Experiment	Initial concentrations			Rate / $10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$
	$[H_2O_2(aq)]$ / mol dm^{-3}	$[I^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	
1	0.0100	0.0100	0.100	2.00
2	0.0100	0.0200	0.100	4.00
3	0.0200	0.0100	0.100	4.00
4	0.0200	0.0100	0.200	4.00

Handwritten notes on the table:
 - Arrows from the concentration columns point to "1st order".
 - An arrow from the rate column points to "0th order".
 - Between experiments 1 and 2: $[H_2O_2]$ is constant (x1), $[I^-]$ doubles (x2), rate doubles (x2).
 - Between experiments 2 and 3: $[H_2O_2]$ doubles (x2), $[I^-]$ is constant (x1), rate is constant (x1).
 - Between experiments 3 and 4: $[H_2O_2]$ is constant (x1), $[I^-]$ is constant (x1), $[H^+]$ doubles (x2), rate is constant (x1).

(i) Determine the rate equation and calculate the rate constant, k , including units.

$$\text{rate} = k [H_2O_2]^1 [I^-]^2 [H^+]^0$$

$$\text{rate} = k [H_2O_2] [I^-]^2$$

$$\frac{2 \times 10^{-6}}{0.01 \times 0.01} = 0.02$$

Handwritten units:
 $\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

$$k = 0.02 \text{ units mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

(ii) The rate constant, k , for this reaction is determined at different temperatures, T .

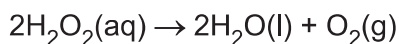
Explain how the student could determine the activation energy, E_a , for the reaction graphically using values of k and T .

plot a graph of $\ln k$ against $1/T$ and measure the gradient.
 $E_a = \text{gradient} \times R$

$$\ln k = -\frac{E_a}{RT} + \ln A \quad [3]$$

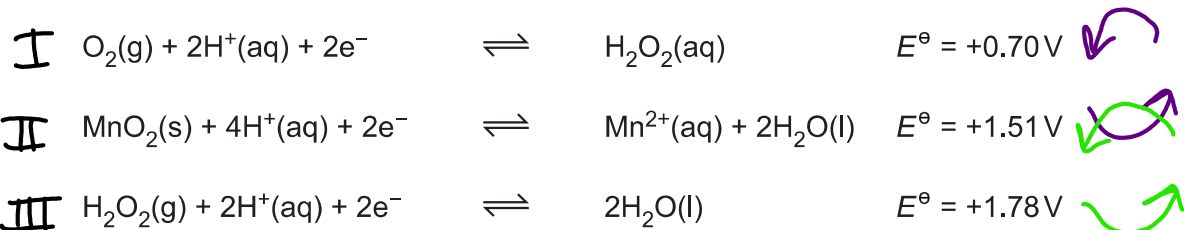
8

(b) Solutions of hydrogen peroxide decompose slowly into water and oxygen:



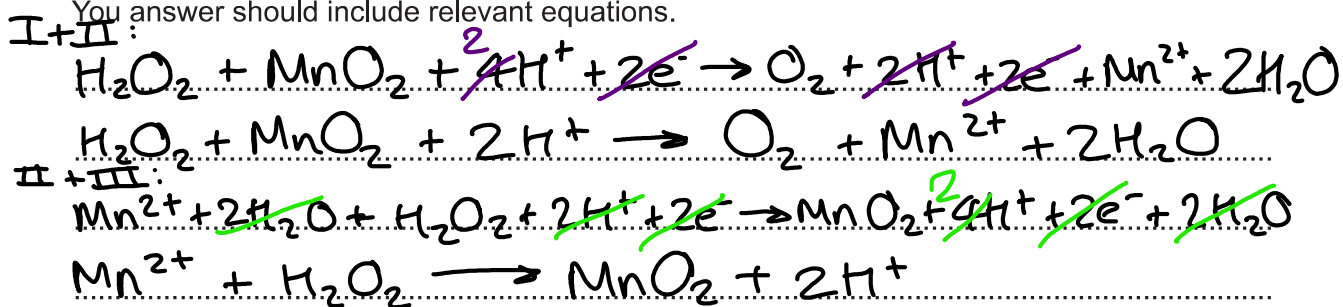
This reaction is catalysed by manganese dioxide, $\text{MnO}_2(\text{s})$.

Standard electrode potentials are shown below.



Using the electrode potentials, explain how MnO_2 is able to act as a catalyst for the decomposition of hydrogen peroxide.

You answer should include relevant equations.



I more -ve E than II so I moves left. II more -ve E than III moves left.

MnO_2 is regenerated so acts as a catalyst.

[4]

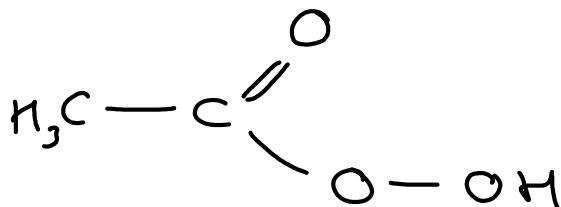
9

(c) Peroxycarboxylic acids are organic compounds with the COOOH functional group.

Peroxyethanoic acid, CH₃COOOH, is used as a disinfectant.

(i) Suggest the structure for CH₃COOOH.

The COOOH functional group must be clearly displayed.



[1]

(ii) Peroxyethanoic acid can be prepared by reacting hydrogen peroxide with ethanoic acid. This is a **heterogeneous** equilibrium.



A 250 cm³ equilibrium mixture contains concentrations of 0.500 mol dm⁻³ H₂O₂(aq) and 0.500 mol dm⁻³ CH₃COOH(aq).

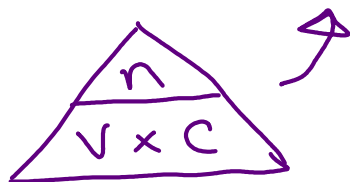
Calculate the amount, in mol, of peroxyethanoic acid in the equilibrium mixture.

squares brackets means concentration

$$0.37 = K_c = \frac{[\text{CH}_3\text{COOOH}]}{[\text{H}_2\text{O}_2][\text{CH}_3\text{COOH}]} = \frac{[\text{CH}_3\text{COOOH}]}{[0.5][0.5]}$$

$$0.37 \times [0.5][0.5] = [\text{CH}_3\text{COOOH}] = 0.0925 \text{ mol dm}^{-3}$$

$$0.0925 \times 250 \times 10^{-3} = 0.023125 \text{ mol}$$



amount = 0.023 mol [3]

This question is about weak acids.

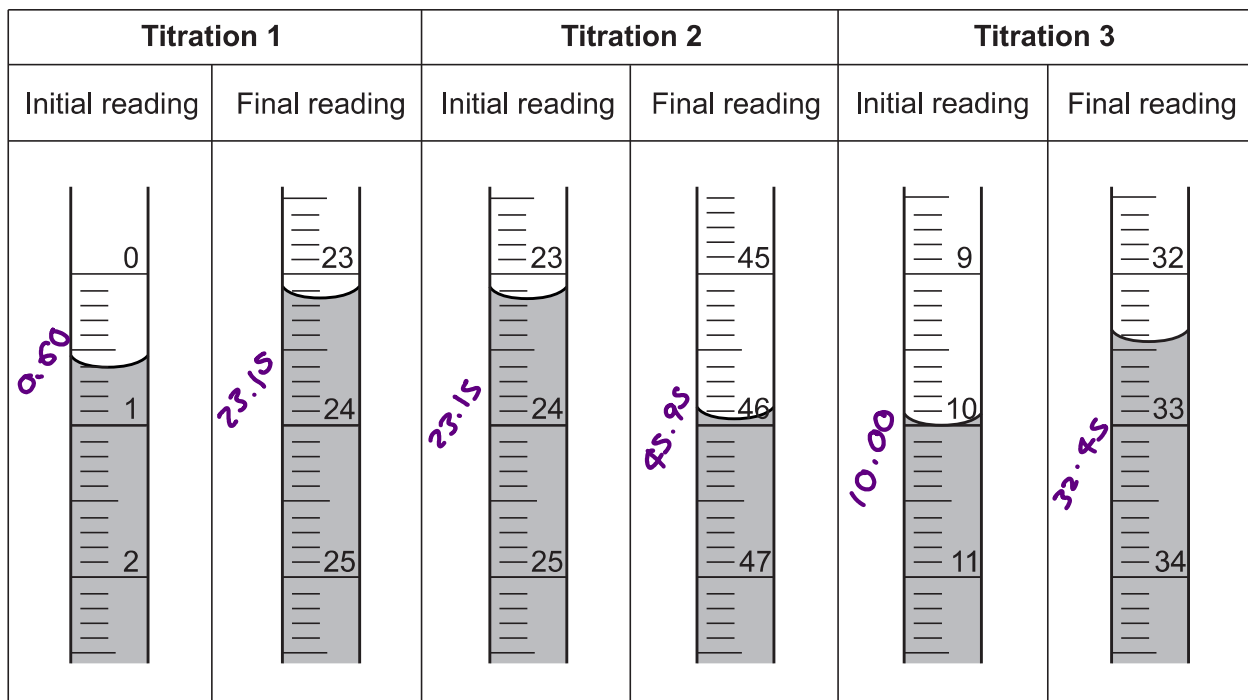
(a) Compound **A** is a weak monobasic acid.

A student is supplied with a 250.0 cm³ solution prepared from 2.495 g of **A**.

The student titrates 25.0 cm³ samples of this solution with 0.0840 mol dm⁻³ NaOH in the burette.

The student carries out a trial, followed by the three further titrations. The diagrams show the initial burette readings and the final burette readings for the student's three **further** titrations.

All burette readings are measured to the nearest 0.05 cm³.



(i) Record the student's readings and the titres in an appropriate format. 2 dp.

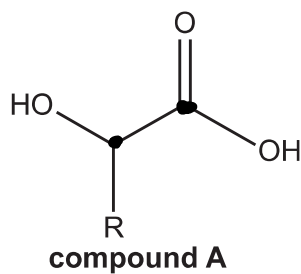
Calculate the mean titre that the student should use for analysing the results.

final (cm ³)	initial (cm ³)	titre (cm ³)
23.15	0.60	22.55
45.95	23.15	22.80
32.45	10.00	22.45

Concordant within ± 0.10 cm³

$$\frac{22.55 + 22.45}{2} = 22.50$$
 mean titre = 22.50 cm³ [4]

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(ii) The structure of compound **A** is shown below.

C: 2

H: 3

O: 3

$$(2 \times 12) + 3 + (16 \times 3) \\ = 75 + R = 131.7$$

Compound **A** has four optical isomers.

Using this information and the student's results, answer the following.

- Determine the molar mass of **A** and the formula of the alkyl group R.
- Draw the structure of compound **A** and label any chiral carbon atoms with an asterisk*.

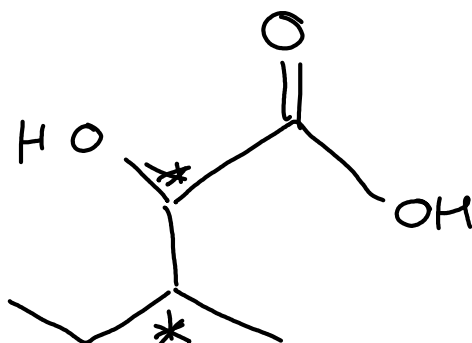
Show all your working.

$$\text{mol of NaOH} : 0.084 \times 72.5 \times 10^{-3} = 1.89 \times 10^{-3} \text{ mol}$$

$$250 \text{ cm}^3 : 1.89 \times 10^{-3} \times 10 = 1.89 \times 10^{-2} \text{ mol}$$

$$\frac{2.495}{1.89 \times 10^{-2}} = 131.7$$

$$131.7 - 75 = 56.7 = 57 = \text{C}_4\text{H}_9$$

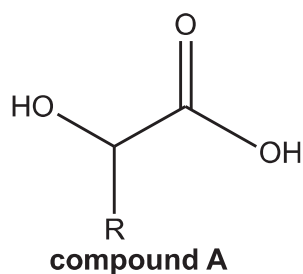


[6]

Turn over

12

(b) The structural formula of compound **A** is repeated below.



Two reactions of compound **A** are carried out.

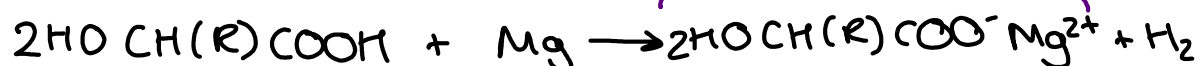
Suggest an equation for each reaction and state the type of reaction.

In your equations, draw structures for organic compounds.

You can use R for the alkyl group.

- (i) Magnesium ribbon is added to a solution of compound **A**.
Gas bubbles are seen and the magnesium slowly dissolves.

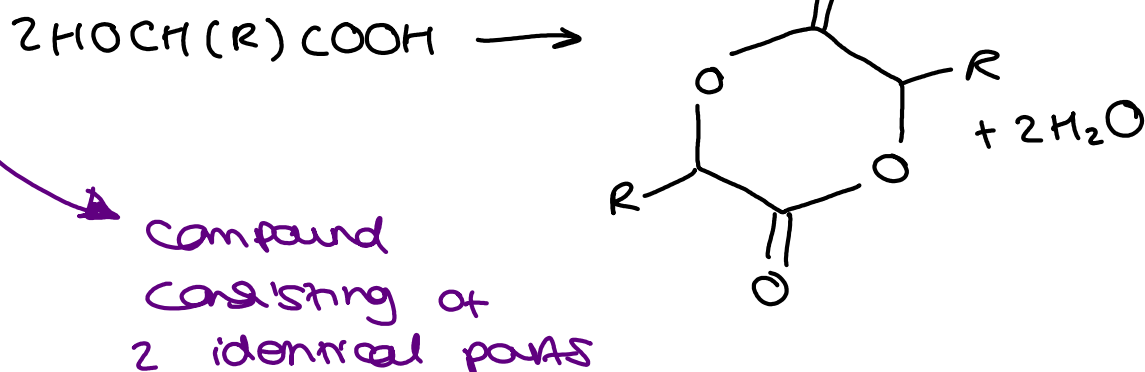
Equation



Type of reaction redox [3]

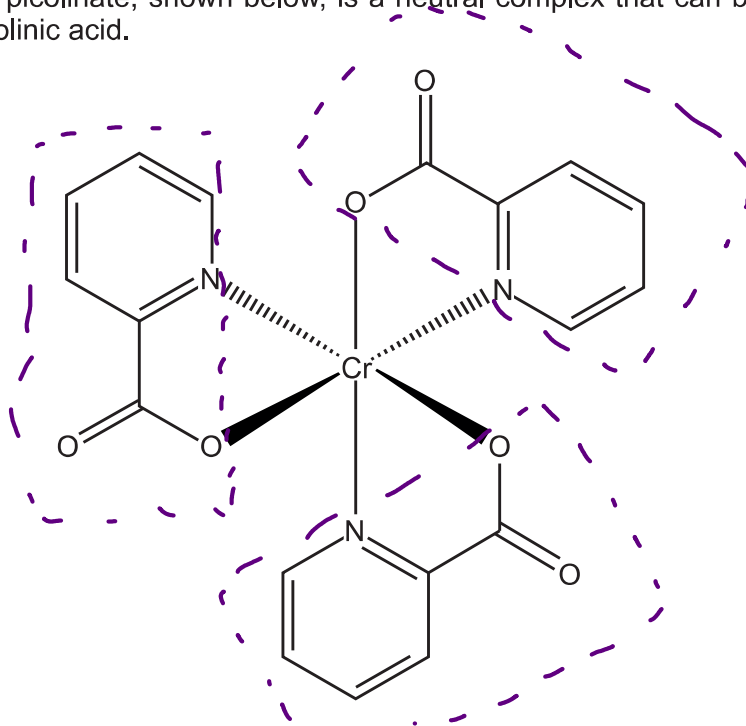
- (ii) Compound **A** is heated with a few drops of concentrated sulfuric acid as a catalyst.
A cyclic **dimer** of compound **A** forms.

Equation



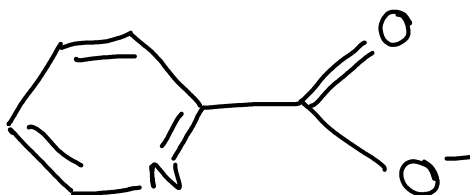
Type of reaction esterification [3]

- (c) Chromium(III) picolinate, shown below, is a neutral complex that can be prepared from the weak acid, picolinic acid.



Chromium(III) picolinate is used in tablets as a nutritional supplement for chromium.

- (i) Draw the structure of the ligand in chromium(III) picolinate.



[1]

- (ii) A typical tablet of chromium(III) picolinate contains 200 μg of chromium.

Calculate the mass, in g, of chromium(III) picolinate in a typical tablet.

$1 \mu\text{g} = 10^{-6}\text{g}$.

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

$$\begin{array}{l}
 \text{C: } 6 \\
 \text{H: } 4 \\
 \text{O: } 2 \\
 \text{N: } 1
 \end{array}
 \left. \vphantom{\begin{array}{l} \text{C: } 6 \\ \text{H: } 4 \\ \text{O: } 2 \\ \text{N: } 1 \end{array}} \right\} \text{RFM} = (12 \times 6) + 4 + 14 + (16 \times 2) = 122$$

$$(122 \times 3) + 52 = 418 \text{ RFM of Chromium(III) picolinate}$$

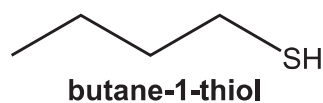
$$\frac{200 \times 10^{-6}}{52} = 3.85 \times 10^{-6}$$

$$3.85 \times 10^{-6} \times 418 = 1.6 \times 10^{-3} \text{ g [2]}$$

5 This question is about organic molecules that have a strong smell.

(a) Thiols are foul-smelling, organic sulfur compounds with the functional group $-SH$.

Butane-1-thiol, shown below, contributes to the strong smell of skunks.



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

(i) Thiols are weak acids.

Write the expression for the acid dissociation constant, K_a , for butane-1-thiol.

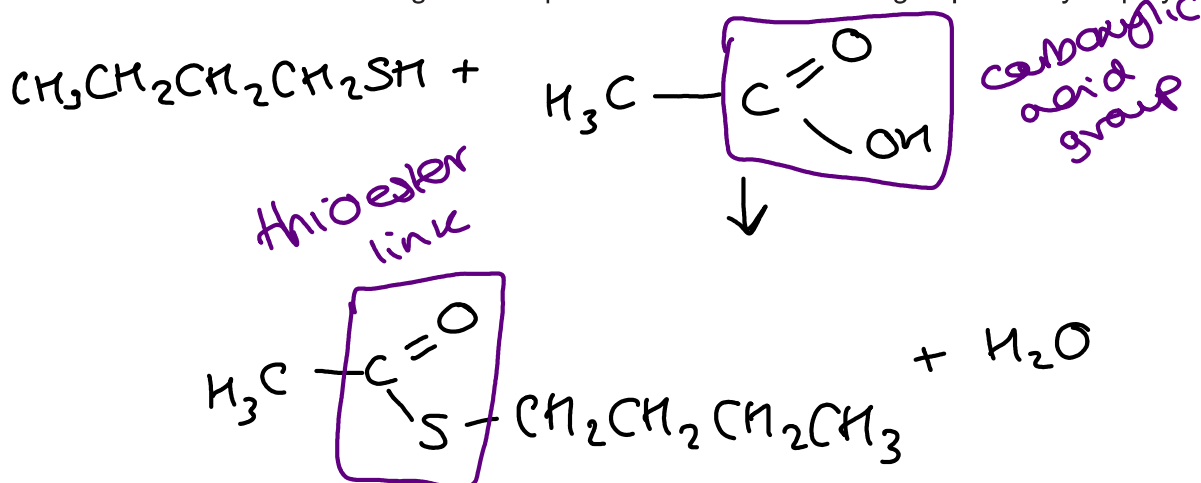
$$K_a = \frac{[H^+][C_4H_9S^-]}{[C_4H_9SH]}$$

[1]

(ii) Thiols react with carboxylic acids to form thioesters.

Write an equation for the reaction of butane-1-thiol with ethanoic acid.

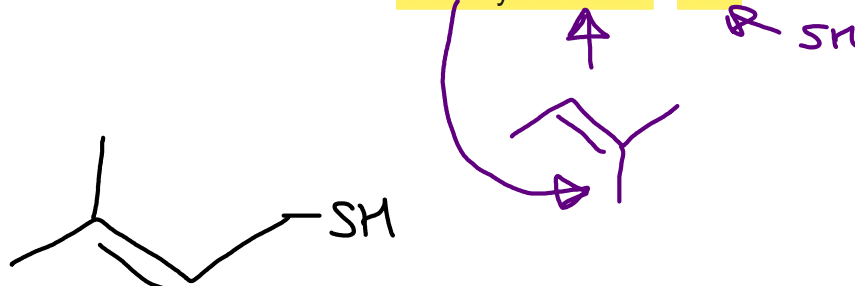
Use structures for all organic compounds with the functional groups clearly displayed.



[2]

(iii) When beer is exposed to light, 3-methylbut-2-ene-1-thiol is formed, which gives an unpleasant smell and flavour to the beer.

Draw the **skeletal** formula for 3-methylbut-2-ene-1-thiol.



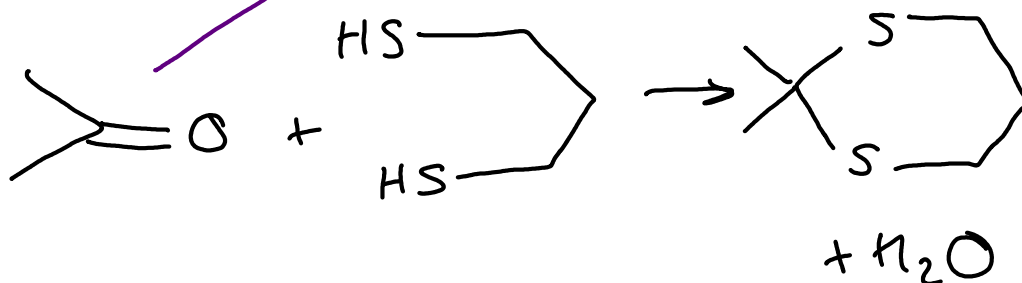
[1]

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- (iv) Propane-1,3-dithiol reacts with **carbonyl** compounds in a **condensation** reaction to form a **cyclic** organic sulfur product.

Write an equation for the reaction of propane-1,3-dithiol with propanone.

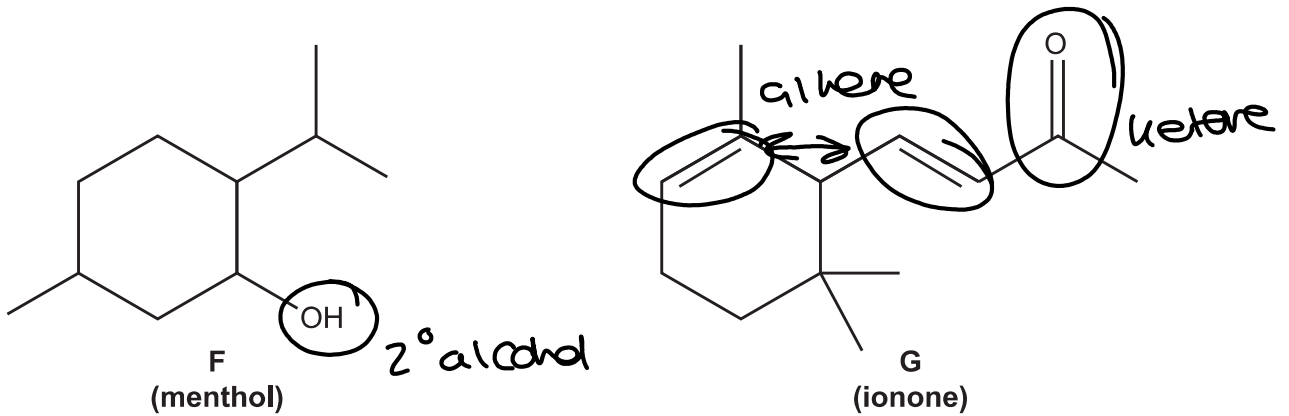
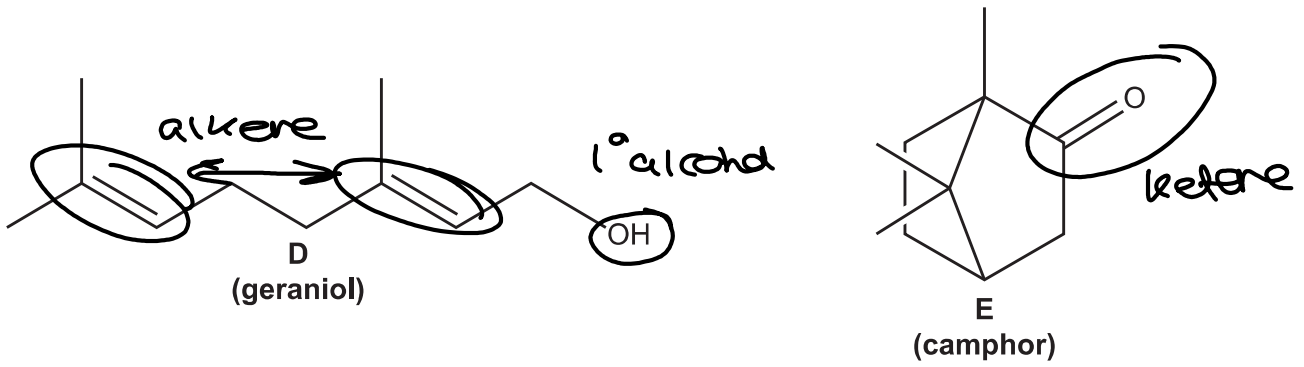
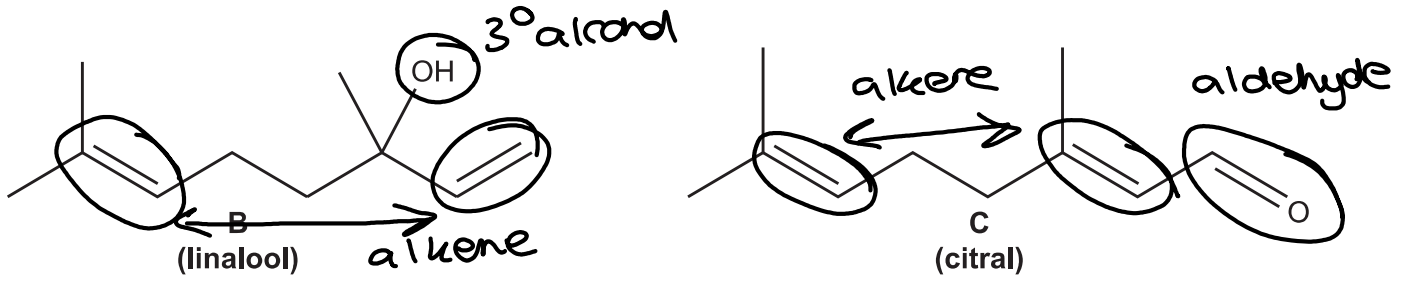
Use structures for organic compounds.



[2]

16

(b)* The structures for six naturally occurring organic compounds with pleasant smells, B–G, are shown below. The common names in brackets relate to their source and smell.



Explain how chemical tests would allow each compound to be distinguished from the other compounds.

In your answer, include essential details for all test procedures and observations.

Details of apparatus and quantities are **not** required.

	B	C	D	E	F	G
decolorizes bromine water alkene	✓	✓	✓			✓
$H^+/Cr_2O_7^{2-}$ orange \rightarrow green 1 ^o , 2 ^o alcohol, aldehyde		✓	✓		✓	
2,4 DNP orange ppt. C=O		✓		✓		✓
Tollens reagent silver mirror aldehyde		✓				

[6]

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).

A large area of lined paper for writing answers. It features a vertical solid line on the left side, creating a margin. The rest of the page is filled with horizontal dotted lines, providing space for writing. The lines are evenly spaced and extend across the width of the page.

A large grid of dotted lines for writing, consisting of 20 horizontal rows and a vertical margin line on the left side.

A large area of the page is filled with horizontal dotted lines, providing a space for students to write their answers. A solid vertical line runs down the left side of this area, creating a margin.



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