



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	StemUp Model Solution									
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.

In gaseous H_2O the O atom has 2 bonded pairs and 2 lone pairs. Lone pairs repel more than bonded pairs, so the H–O–H angle is squeezed to about 105° .

In ice, each O also forms hydrogen bonds to other molecules using its lone pairs, so all four pairs act like bonded pairs and repel equally, giving about 109° .

[3]

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

Methane is a greenhouse gas: its C–H bonds absorb infrared radiation, so its release would increase 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.

$$\begin{aligned} n(\text{CH}_4) : n(\text{H}_2\text{O}) &= 13.4/16.0 : 86.6/18.0 \\ &= 0.8375 : 4.811 \end{aligned}$$

$$x = 4.811 \div 0.8375 = 5.74$$

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

- (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.

$$\text{mass of CH}_4 \text{ in 1.00 kg} = 0.134 \times 1000 = 134 \text{ g}$$

$$n(\text{CH}_4) = 134 \div 16.0 = 8.375 \text{ mol}$$

$$pV = nRT, \text{ so } V = nRT \div p$$

$$T = 0 + 273 = 273 \text{ K}, \quad p = 101 \times 10^3 \text{ Pa}$$

$$V = (8.375 \times 8.314 \times 273) \div (101 \times 10^3)$$

$$= 0.188 \text{ m}^3 = 188 \text{ dm}^3$$

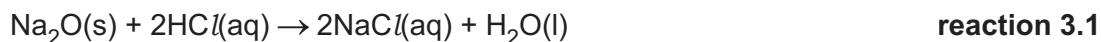
volume = ...188..... dm^3 [4]

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

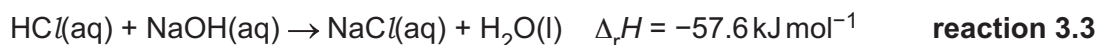
.....It can be used as a fuel (energy source), e.g. burned to generate electricity,.....
or as a chemical feedstock.

..... [1]

- 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.

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

Show all your working.

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

$$\text{Mass of solution} = 47.33 - 21.58 = 25.75 \text{ g}; \quad \Delta T = 55.5 - 20.5 = 35.0 \text{ }^\circ\text{C}$$

$$\text{Energy released, } q = mc\Delta T = 25.75 \times 4.18 \times 35.0 = 3767 \text{ J} = 3.767 \text{ kJ}$$

$$n(\text{Na}_2\text{O}) = 1.24 \div 62.0 = 0.0200 \text{ mol}$$

$$\text{Reaction 3.2: } \Delta_r H = -q \div n = -3.767 \div 0.0200 = -188 \text{ kJ mol}^{-1}$$

(negative because the temperature rose, so the reaction is exothermic)

Hess' Law: reaction 3.1 = reaction 3.2 + 2 × reaction 3.3, as adding these equations and cancelling 2NaOH and H₂O gives Na₂O + 2HCl → 2NaCl + H₂O

$$\Delta_r H(3.1) = \Delta_r H(3.2) + 2\Delta_r H(3.3)$$

$$= -188 + (2 \times -57.6) = -188 - 115.2 = -303 \text{ kJ mol}^{-1}$$

[6]

- (b) The uncertainty in each temperature reading is $\pm 0.1 \text{ }^\circ\text{C}$.

The uncertainty in each mass reading is $\pm 0.005 \text{ g}$.

Determine whether the mass of Na₂O or the temperature change has the greater percentage uncertainty.

Show all your working.

$$\% \text{ uncertainty in mass of Na}_2\text{O} = (2 \times 0.005 \div 1.24) \times 100 = 0.81\%$$

$$\% \text{ uncertainty in } \Delta T = (2 \times 0.1 \div 35.0) \times 100 = 0.57\%$$

(two readings for each), so the mass of Na₂O has the greater percentage uncertainty.

[2]

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

Explain your reasoning.

Use a greater mass of Na_2O (e.g. double the mass) with the same volume of water. This gives a larger ΔT , so the percentage uncertainty in both the mass and the temperature change is reduced, as the absolute uncertainties stay the same. [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 nitrate(III) [1]

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

Element oxidised *sodium, Na*

Oxidation number change from *0* to *+1*

Element reduced *nitrogen, N*

Oxidation number change from *+3* to *0*

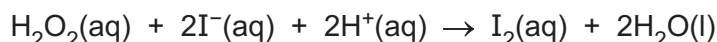
[2]

- (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 / $10^{-6} \text{mol dm}^{-3} \text{s}^{-1}$
	$[\text{H}_2\text{O}_2(\text{aq})]$ / mol dm^{-3}	$[\text{I}^-(\text{aq})]$ / mol dm^{-3}	$[\text{H}^+(\text{aq})]$ / 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

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

Exp 1 $\rightarrow$ 2: $[\text{I}^-]$ doubles and rate doubles, so first order in I^-

Exp 1 $\rightarrow$ 3: $[\text{H}_2\text{O}_2]$ doubles and rate doubles, so first order in H_2O_2

Exp 3 $\rightarrow$ 4: $[\text{H}^+]$ doubles and rate is unchanged, so zero order in H^+

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

$$k = \text{rate} \div ([\text{H}_2\text{O}_2][\text{I}^-]) = 2.00 \times 10^{-6} \div (0.0100 \times 0.0100) = 0.0200$$

$$k = \dots 0.0200 \dots \text{units } \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \dots [3]$$

(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 .

Measure k at several different temperatures, with T in kelvin.

Plot a graph of $\ln k$ (y-axis) against $1/T$ (x-axis); this is a straight

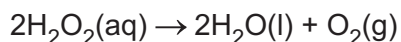
line, as $\ln k = -E_a/RT + \ln A$.

Measure the gradient of the line: gradient = $-E_a/R$.

$E_a = -\text{gradient} \times R = -\text{gradient} \times 8.314 \text{ (J mol}^{-1}\text{)}.$

[3]

(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.

Your answer should include relevant equations.

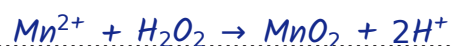
$E^\ominus(\text{MnO}_2/\text{Mn}^{2+}) = +1.51 \text{ V}$ is more positive than $E^\ominus(\text{O}_2/\text{H}_2\text{O}_2) = +0.70 \text{ V}$,

so MnO_2 is reduced and oxidises H_2O_2 to O_2 ($E_{\text{cell}} = +0.81 \text{ V}$):



$E^\ominus(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = +1.78 \text{ V}$ is more positive than $+1.51 \text{ V}$, so H_2O_2 is

reduced and oxidises Mn^{2+} back to MnO_2 ($E_{\text{cell}} = +0.27 \text{ V}$):



MnO_2 is used up in the first step and regenerated in the second, so it is a

catalyst. Overall: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

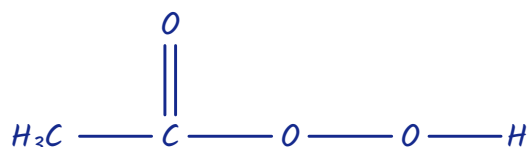
[4]

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

Peroxyethanoic acid, CH_3COOOH , is used as a disinfectant.

(i) Suggest the structure for CH_3COOOH .

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 cm^3 equilibrium mixture contains concentrations of $0.500 \text{ mol dm}^{-3}$ $\text{H}_2\text{O}_2(\text{aq})$ and $0.500 \text{ mol dm}^{-3}$ $\text{CH}_3\text{COOH}(\text{aq})$.

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

$$K_c = [\text{CH}_3\text{COOOH}] \div ([\text{H}_2\text{O}_2][\text{CH}_3\text{COOH}])$$

$$[\text{CH}_3\text{COOOH}] = 0.37 \times 0.500 \times 0.500 = 0.0925 \text{ mol dm}^{-3}$$

$$n(\text{CH}_3\text{COOOH}) = 0.0925 \times 250/1000 = 0.0231 \text{ mol}$$

amount = ...0.0231..... mol [3]

4 This question is about weak acids.

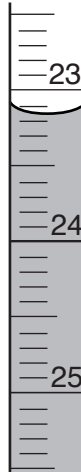
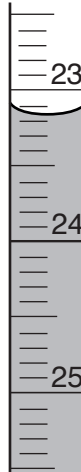
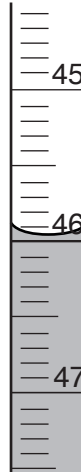
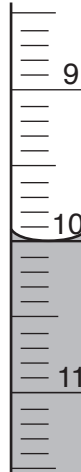
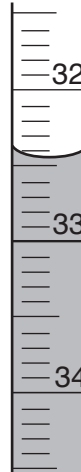
(a) Compound **A** is a weak monobasic acid.

A student is supplied with a 250.0 cm^3 solution prepared from 2.495 g of **A**.

The student titrates 25.0 cm^3 samples of this solution with $0.0840\text{ mol dm}^{-3}$ 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 cm^3 .

Titration 1		Titration 2		Titration 3	
Initial reading	Final reading	Initial reading	Final reading	Initial reading	Final reading
					

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

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

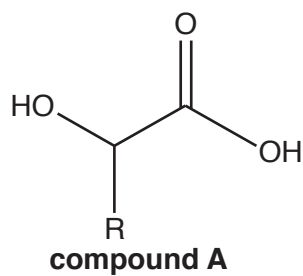
<i>Titration</i>	1	2	3
<i>final reading / cm³</i>	23.15	45.95	32.45
<i>initial reading / cm³</i>	0.60	23.15	10.00
<i>titre / cm³</i>	22.55	22.80	22.45

Titration 1 and 3 are concordant (within 0.10 cm^3):

$$\text{mean titre} = (22.55 + 22.45) \div 2 = 22.50\text{ cm}^3$$

mean titre = ...22.50..... cm^3 [4]

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



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.

$$n(\text{NaOH}) = 0.0840 \times 22.50/1000 = 1.89 \times 10^{-3} \text{ mol}$$

$$A \text{ is monobasic, so } n(A) \text{ in } 25.0 \text{ cm}^3 = 1.89 \times 10^{-3} \text{ mol}$$

$$n(A) \text{ in } 250.0 \text{ cm}^3 = 10 \times 1.89 \times 10^{-3} = 1.89 \times 10^{-2} \text{ mol}$$

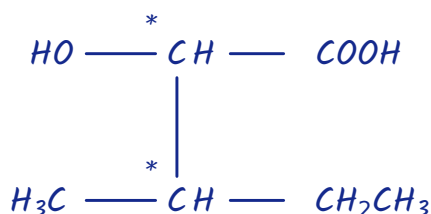
$$M(A) = 2.495 \div (1.89 \times 10^{-2}) = 132 \text{ g mol}^{-1}$$

$$\text{HOCH(COOH)- part, } C_2H_3O_3 = 75, \text{ so } M(R) = 132 - 75 = 57$$

$$R = C_4H_9$$

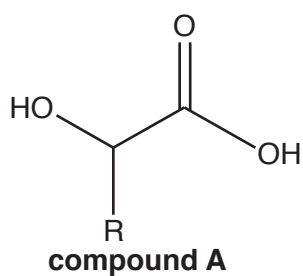
Four optical isomers means two chiral carbon atoms, so R must be

$CH(CH_3)CH_2CH_3$, i.e. A is 2-hydroxy-3-methylpentanoic acid:



* = chiral carbon atom

(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.

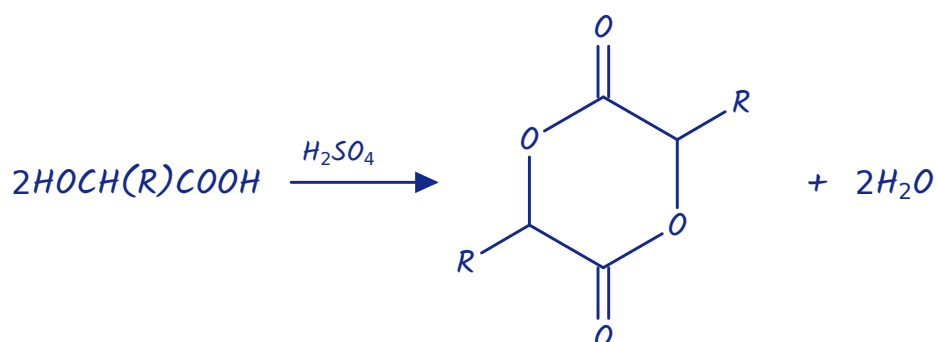
Equation



Type of reaction redox..... [3]

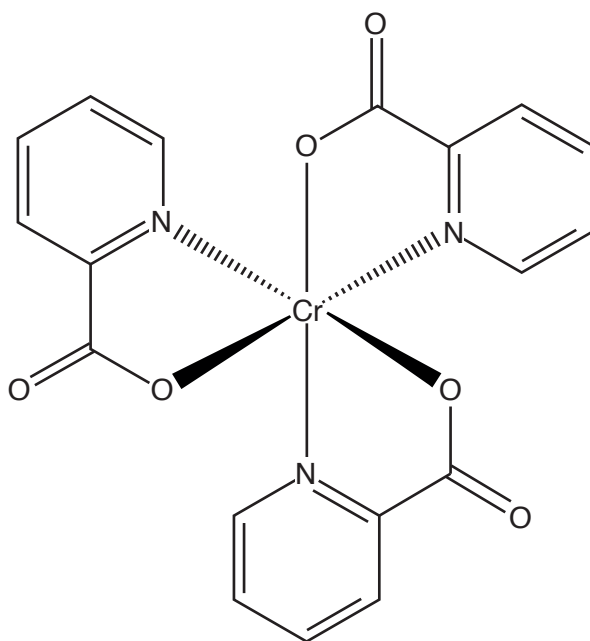
- (ii) Compound **A** is heated with a few drops of concentrated sulfuric acid as a catalyst.
A cyclic 'dimer' of compound **A** forms.

Equation



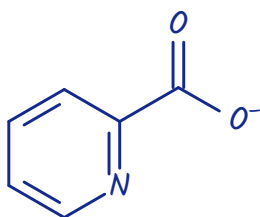
Type of reaction condensation (esterification)..... [3]

- (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.

$$M = 52.0 + 3 \times 122.0 = 418.0 \text{ g mol}^{-1}$$

$$n(\text{Cr}) = 200 \times 10^{-6} \div 52.0 = 3.85 \times 10^{-6} \text{ mol}$$

$$\text{mass} = 3.85 \times 10^{-6} \times 418.0 = 1.61 \times 10^{-3} \text{ g}$$

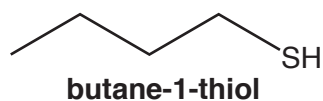
mass = ... 1.61×10^{-3} g [2]

Turn over

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.



(i) Thiols are weak acids.

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

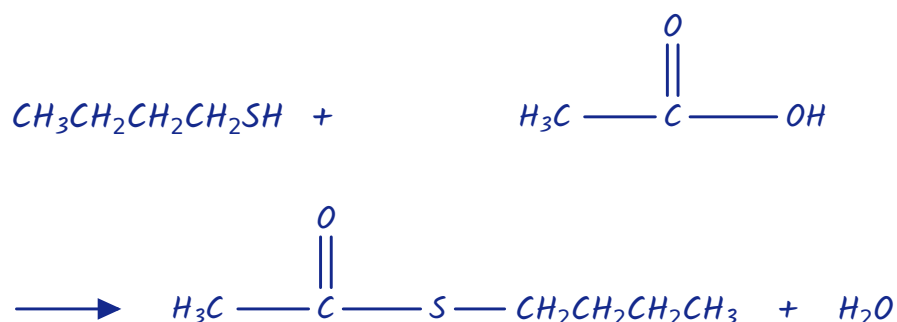
$$K_a = \frac{[H^+][CH_3CH_2CH_2CH_2S^-]}{[CH_3CH_2CH_2CH_2SH]}$$

[1]

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

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

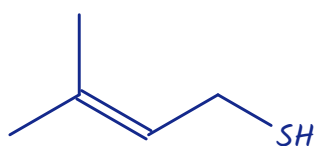
Use structures for all organic compounds with the functional groups clearly displayed.



[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.

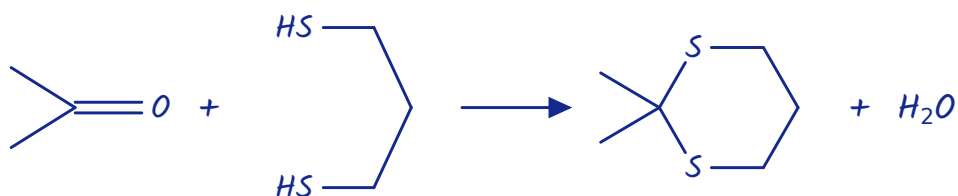


[1]

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

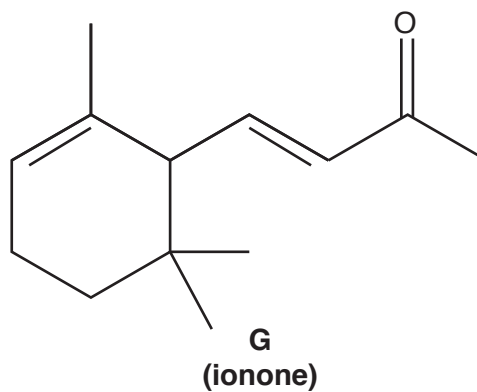
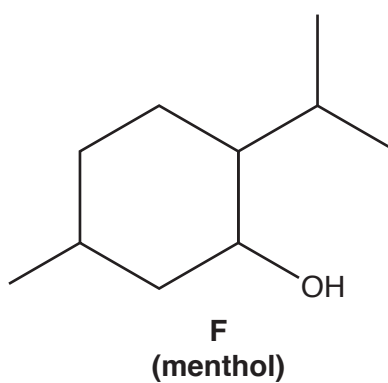
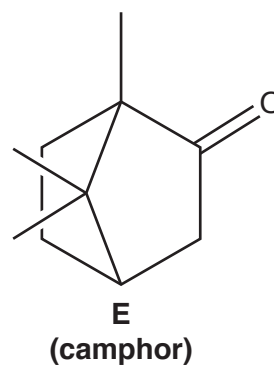
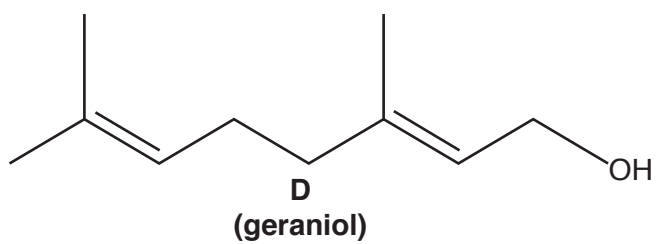
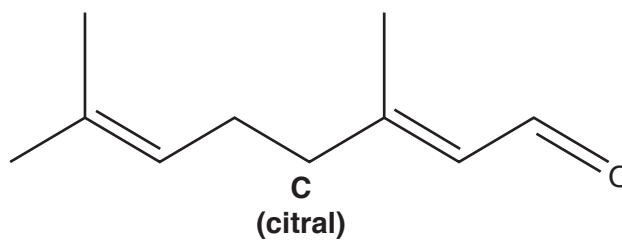
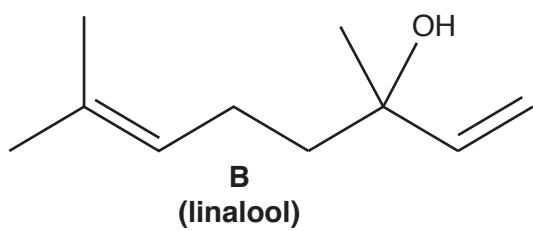
Write an equation for the reaction of propane-1,3-dithiol with propanone.

Use structures for organic compounds.



[2]

(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.

Groups: B alkene + tertiary alcohol; C alkene + aldehyde; D alkene + primary alcohol; E ketone; F secondary alcohol; G alkene + ketone.

1. Add 2,4-DNP (Brady's reagent) to each: C, E and G (carbonyl group) give an orange precipitate; B, D and F show no change.

2. Warm C, E and G with Tollens' reagent: only C (aldehyde) gives a silver mirror, so C is identified.

3. Add bromine water to E and G: G (C=C) decolourises the orange bromine water; E stays orange. E and G identified.

4. Warm B, D and F with acidified potassium dichromate(VI), $H^+/Cr_2O_7^{2-}$: D and F (primary and secondary alcohols) turn from orange to green; B (tertiary alcohol) stays orange, so B is identified.

5. Add bromine water to D and F: D (C=C) decolourises it; F (no C=C) stays orange, so D and F are identified.

[6]

END OF QUESTION PAPER

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