Question - 01

This question is about the preparation of an ester.

(a) Ester **F** can be prepared from propan-2-ol and ethanoic acid.

Give an equation for this reaction.

Name ester **F**.

Equation

____

Name ____

(2)

This method is used to prepare a sample of ester **F**.

Step 1
Mix 10 cm^3 of propan-2-ol with 10 cm^3 of ethanoic acid.
Add 5 drops of concentrated sulfuric acid.
Reflux this reaction mixture for 20 minutes.

Step 2
Transfer the cooled reaction mixture to a separating funnel.
Add 20 cm^3 of aqueous sodium carbonate and shake the mixture.

Step 3
Transfer the organic layer to a beaker and add 5 g of anhydrous magnesium sulfate.
Decant off the organic liquid.

Step 4
Collect the ester using simple distillation.

(b) Describe how **Step 1** should be done.

In your description you should

- give details of suitable equipment used to add each reagent to the reflux apparatus
- draw a labelled diagram of the apparatus used for refluxing the reaction mixture
- explain any safety precautions needed other than eye protection.

____

____

____

____

____

(6)

(c) In **Step 2** the reaction mixture from **Step 1** is shaken with aqueous sodium carbonate.

State the purpose of the sodium carbonate.

Suggest a precaution that should be taken while this mixture is shaken in the separating funnel.

Give a reason for your suggested precaution.

Purpose of sodium carbonate

Precaution

Reason

(3)

(d) Give the reason for the use of anhydrous magnesium sulfate in **Step 3**.

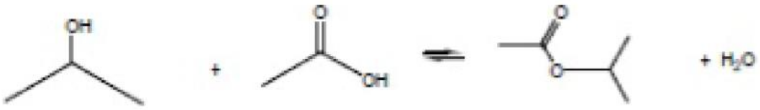
(1)

(e) Suggest how the purity of the ester can be confirmed during the distillation in **Step 4**.

(1)

(a) **M1** $CH_3CH(OH)CH_3 + CH_3COOH \rightleftharpoons CH_3COOCH(CH_3)_2 + H_2O$

M2 Methyl ethyl ethanoate.



Allow ECF from incorrect 5 carbon ester

Allow other valid names
1-methylethyl ethanoate
Isopropyl ethanoate
2-propyl ethanoate
Propan-2-yl ethanoate

2

(b)

This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance.	
Level 3 5-6 marks	All stages are virtually complete (virtually complete means one from stage 1 and two from stages 2 and 3). Answer communicates the whole explanation, including equations, coherently and shows a logical progression through all three stages.
Level 2 3-4 marks	All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies (covered means one from a stage) **OR** two stages virtually complete (virtually complete means one from stage 1 or two from stages 2 and 3). Answer is coherent and shows some progression through all three stages. Some steps in each stage may be incomplete.
Level 1 1-2 marks	Two stages are covered (covered means one from a stage) but the explanation of each stage may be incomplete or may contain inaccuracies **OR** only one stage is virtually complete (virtually complete means one from stage 1 or two from stages 2 and 3). Answer shows some progression between two stages.
0 mark	Insufficient correct chemistry to gain a mark.

Indicative Chemistry Content

Stage 1
1a Measuring cylinder(s) for the propan-2-ol and ethanoic acid (size not required but if specified should be between 10 - 100 cm^3)
Allow 10cm^3 / graduated pipette or burette

1b (Dropping/teat) pipette for sulfuric acid (NOT graduated or other qualification for pipette)

Stage 2 Diagram e.g. below to include
2a Labelled condenser shown vertical and open at top and bottom i.e. in cross section

2b Labelled water in at the bottom and water out at the top of the vertical condenser

2c Labelled reaction flask recognisable as either pear shaped or round bottomed

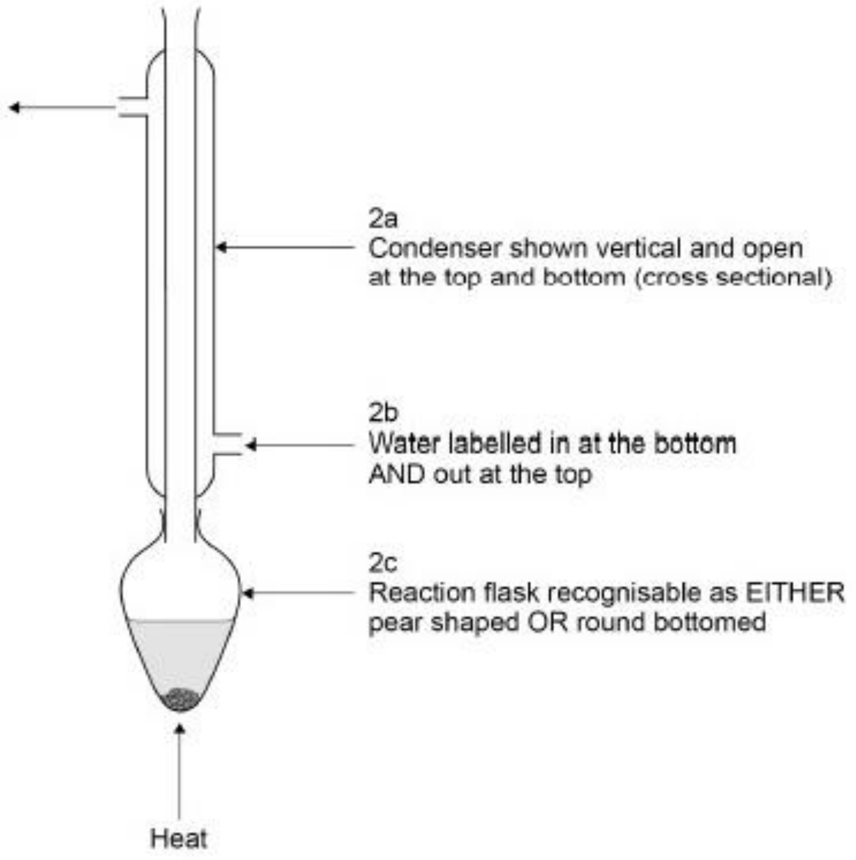
Stage 3 Safety
Needs precaution AND reason for each suggestion

3a Use a fume cupboard/fume hood/well-ventilated lab space
AND to avoid breathing in harmful/toxic/corrosive compounds

3b Wear gloves
AND as compounds are corrosive

3c Add glass beads/chips (to the mixture before heating)/labelled as anti-bumping granules/chips
AND to ensure smooth boiling/reduce size of bubbles

3d Use an electric heater/water bath
AND as compounds are flammable



6

(c) **M1** To neutralise/remove/react with (excess) acid

M2 Remove stopper/bung OR tip the funnel upside down and open the tap

M3 There will be a build up of pressure/gas/carbon dioxide

M3 must be linked to their precaution in M2

OR

M2 Allow add stopper

M3 To prevent spillage

3

(d) Drying agent/To remove water

Not dehydrating agent

1

(e) Compare boiling point to a data book/known value

Boils at sharp boiling point/over a narrow temp range

1

Question - 02

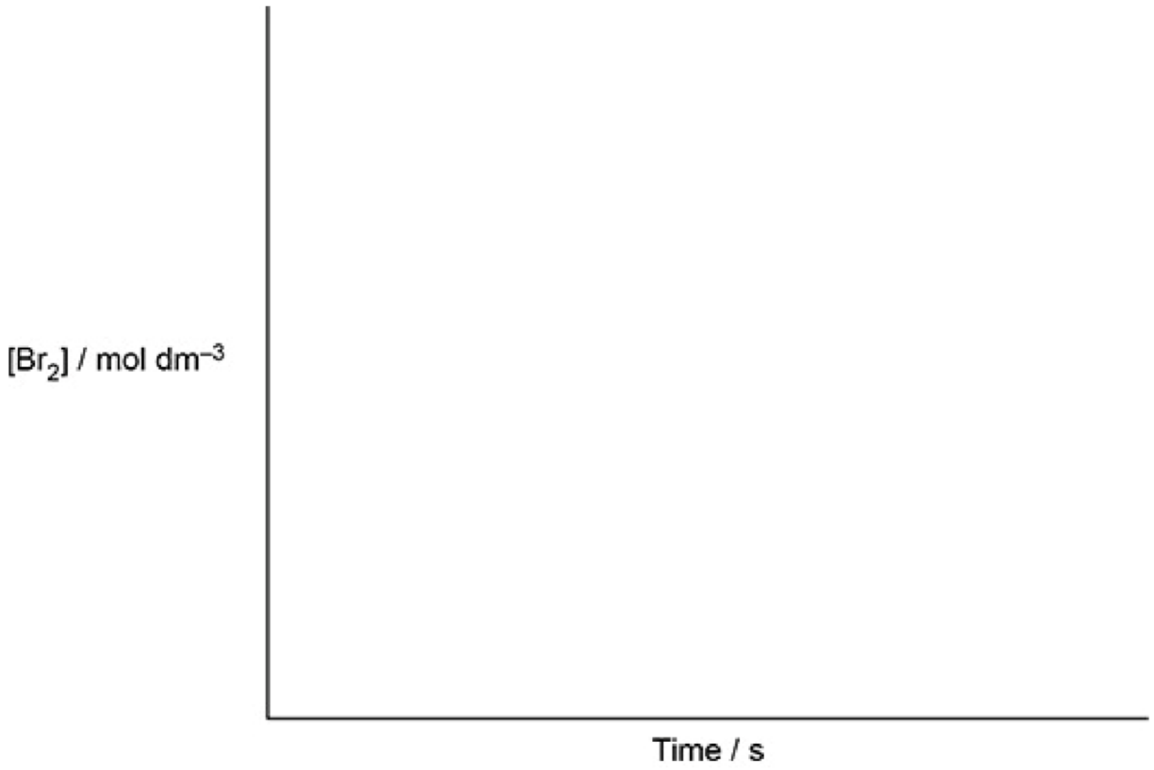
Propanone reacts with bromine in alkaline conditions.

$$CH_3COCH_3 + Br_2 + OH^- \rightarrow CH_3COCH_2Br + Br^- + H_2O$$

The rate equation for this reaction is

$$Rate = k\,[CH_3COCH_3]\,[OH^-]$$

(a) Sketch a graph on the axes provided to show how, at constant temperature, the concentration of bromine changes during this reaction.



(1)

(b) The table shows the initial rate of this reaction for experiments using different mixtures containing propanone, bromine and hydroxide ions.

Experiment	**[CH_3COCH_3] / mol dm^{-3}**	**[Br_2] / mol dm^{-3}**	**[OH^-] / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
1	1.50×10^{-2}	2.50×10^{-2}	2.50×10^{-2}	2.75×10^{-11}
2	1.50×10^{-2}	2.50×10^{-2}		8.25×10^{-11}
3	3.75×10^{-3}	5.00×10^{-2}	1.00×10^{-1}	

Complete the table above.

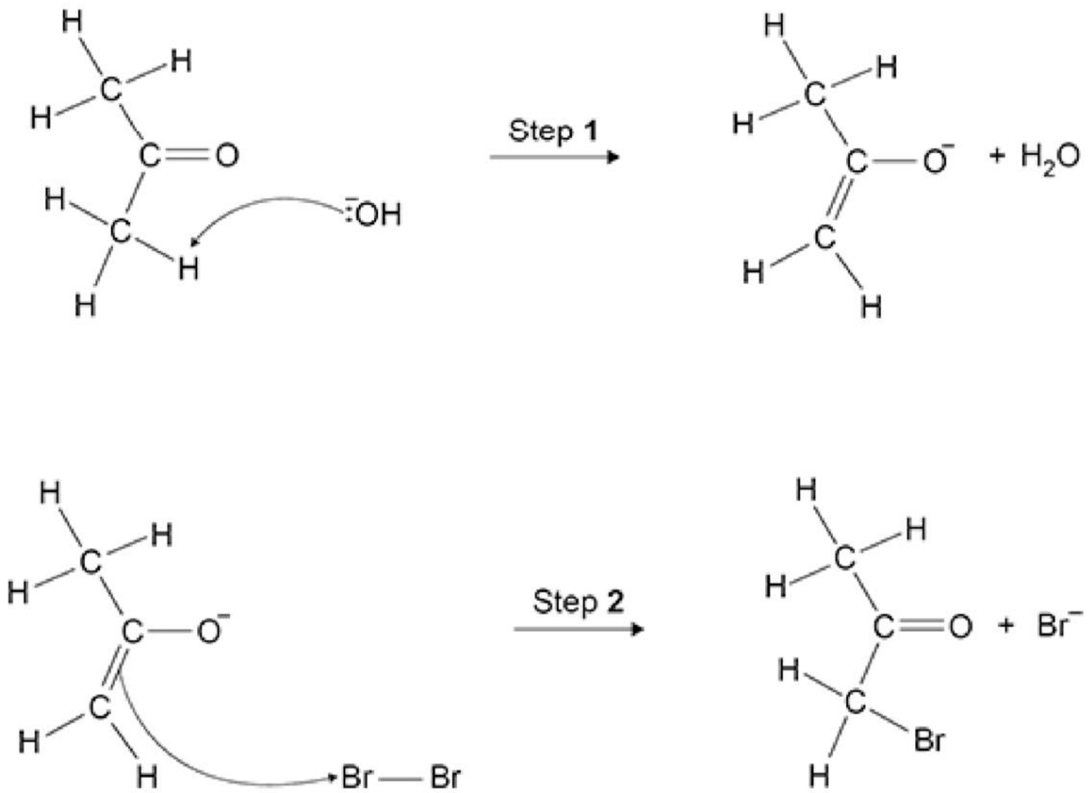
Use the data from experiment **1** to calculate the rate constant *k* for this reaction.

Give the units for the rate constant.

k ____________________ Units ____________________

(5)

(c) The figure below shows an incomplete mechanism for this reaction.



Complete the mechanism in the figure by adding four curly arrows and any relevant lone pair(s) of electrons.

(4)

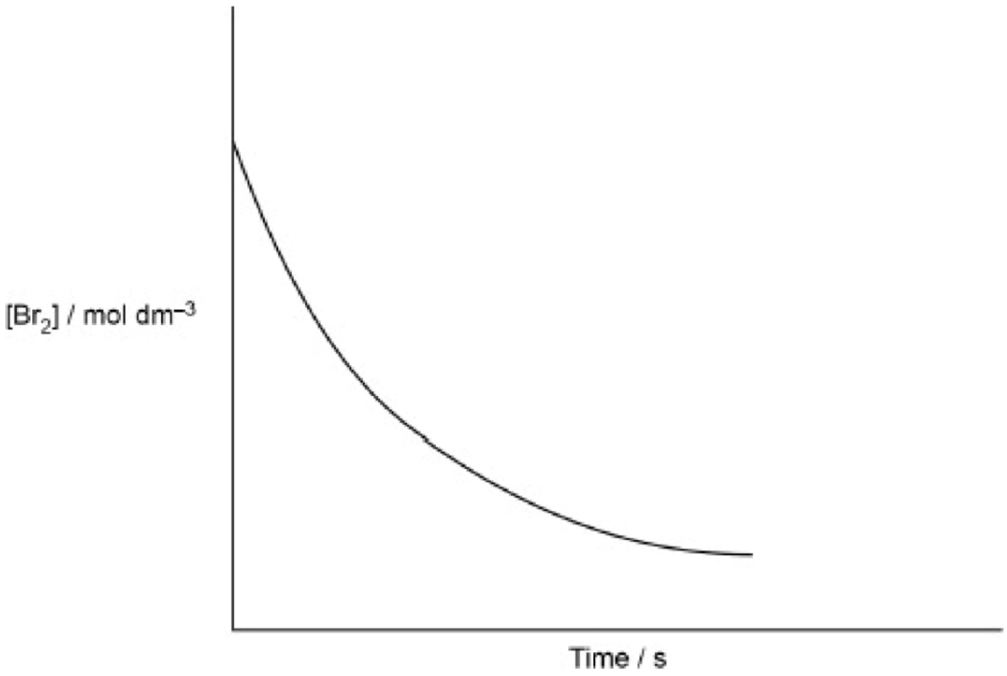
(d) Use evidence from the rate equation to explain why Step **1** is the rate determining step.

____

____

(1)

(a) Curve e.g.



Curve with decreasing gradient

1

(b) **M1** For [OH$^-$] = 7.50 × 10^{-2}

M2 For rate = 2.75 × 10^{-11}

M3 $k = \frac{\text{rate}}{[CH_3COCH_3][OH^-]}$

M3 For rearranging rate equation

OR

$$k = \frac{2.75 \times 10^{-11}}{(1.5 \times 10^{-2}) \times (2.5 \times 10^{-2})}$$

For inserting correct numbers in rearranged equation

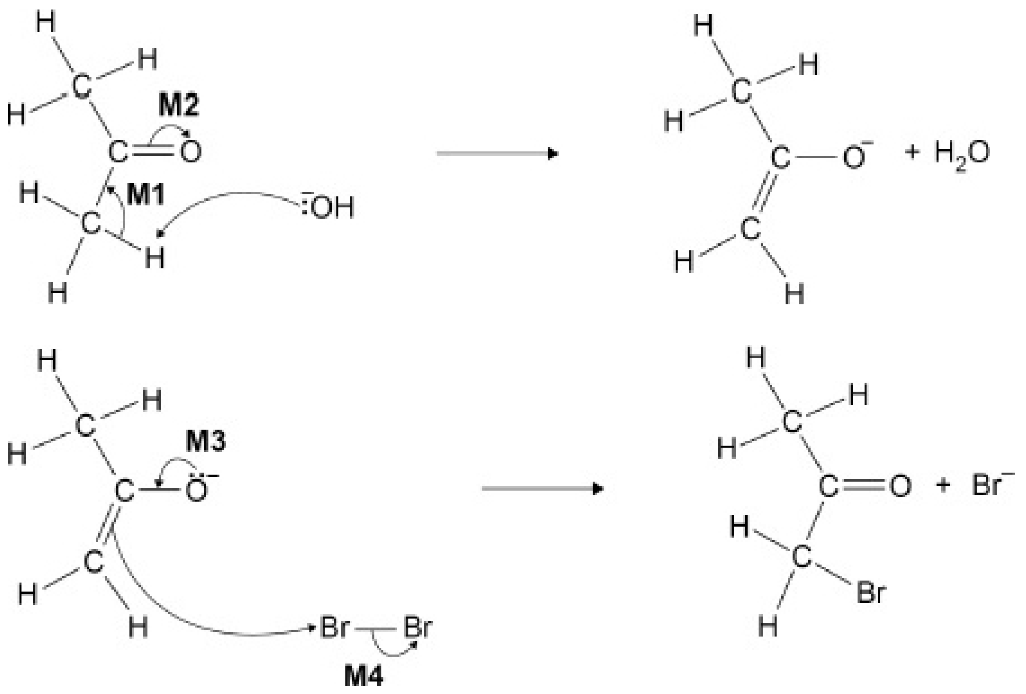
M4 k = 7.3(3) × 10^{-8}

M5 Units = mol^{-1}dm^{3}s^{-1}

If rearrangement upside down lose M3 but can score M4 for 1.36 × 10^7 as ECF
M5 for mol dm^{-3} s as ECF

5

(c)



M1 Arrow from C-H bond to C-C

M2 Arrow from C=O bond to O

M3 Arrow from lone pair on O to C-O bond

M4 Arrow from Br-Br bond to Br

Dipoles must be correct if shown for M4

4

(d) Step 1 includes CH_3COCH_3 and OH^- and these are also in the rate equation
OR
Step 1 contains all the species in the rate equation

Br_2 not in step 1 and not in rate equation so it has to be step 1

1

Question - 03

Which is the correct general formula for non-cyclic compounds in the homologous series?

A	alcohols	$C_nH_{2n+2}O$	○
B	aldehydes	$C_nH_{2n+1}O$	○
C	esters	$C_nH_{2n+1}O_2$	○
D	primary amines	$C_nH_{2n+2}N$	○

A

alcohols $C_nH_{2n+2}O$

Question - 04

Which compound has *E–Z* isomers?

A	$CH_2=CHBr$	○
B	$CH_2=CBr_2$	○
C	$CHBr=CHBr$	○
D	$CBr_2=CHBr$	○

C

$CHBr=CHBr$

Question - 05

Which compound is an isomer of ethyl ethanoate?

A butyl methanoate ○

B methyl propanoate ○

C methyl butanoate ○

D propanoic acid ○

B

methyl propanoate

Under suitable conditions, 2-bromobutane reacts with sodium hydroxide to produce a mixture of five products, **A**, **B**, **C**, **D** and **E**.

Products **A**, **B** and **C** are alkenes.

A is a structural isomer of **B** and **C**.

A does not exhibit stereoisomerism.

B and **C** are a pair of stereoisomers.

Products **D** and **E** are alcohols.

D and **E** are a pair of enantiomers.

(a) Give the names of the **two** concurrent mechanisms responsible for the formation of the alkenes and the alcohols.

Mechanism to form alkenes ____

Mechanism to form alcohols ____

(2)

(b) Define the term stereoisomers.

____

____

____

(2)

(c) Deduce the name of isomer **A**.

Explain why **A** does **not** exhibit stereoisomerism.

Name ____

Explanation ____

____

____

(2)

(d) Outline the mechanism for the reaction of 2-bromobutane with sodium hydroxide to form alkene **A**.

(3)

(e) Deduce the name of isomer **B** and the name of isomer **C**.

Explain the origin of the stereoisomerism in **B** and **C**.

Name ____

____

Explanation ____

____

____

(2)

(f) Draw 3D representations of enantiomers **D** and **E** to show how their structures are related.

(2)

(g) A student compares the rates of hydrolysis of 1-chlorobutane, 1-bromobutane and 1-iodobutane.

The suggested method is:

- add equal volumes of the three halogenoalkanes to separate test tubes
- add equal volumes of aqueous silver nitrate to each test tube
- record the time taken for a precipitate to appear in each test tube.

State and explain the order in which precipitates appear.

Order in which precipitates appear ______________________________________

____

____

Explanation ____

____

____

(a) (for alkenes) elimination

Allow base elimination

Not nucleophilic elimination

1

(for alcohols) nucleophilic substitution

1

(b) (Different molecules/compounds with the) same (molecular and) structural formula

1

Different spatial arrangement of atoms

Allow different spatial arrangement of bonds/groups

1

(c) **A** = but-1-ene

Not butene

1

two groups/atoms/Hs the same on one of the C=C carbons

Allow two groups/atoms/Hs the same on first C

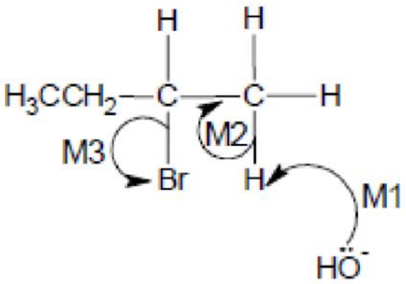
Not two groups the same on one <u>side</u> of C=C

Ignore references to no chiral carbon

Ignore 'priority' i.e. 2 groups with the same priority… gets M2 for '2 groups the same…'

1

(d)



If wrong halogenoalkane used then max 2/3

***M1** lone pair on O, negative charge (anywhere) and curly arrow from lone pair to H on carbon 1*

Not if (covalent) NaOH / additional arrows to or from NaOH / additional arrows to or from Na^+

1

***M2** curly arrow from C(1)−H to C(1)−C(2)*

M2** is standalone from **M1

***Allow** ecf if H on carbon 3 attacked in **M1** for curly arrow from C(3)−H to C(2)−C(3)*

***Not** as ecf if H on carbon 2 attacked in M1 for curly arrow from C(2)−H*

1

M3 *Curly arrow from C−Br to Br (mark is independent)*

Not *if any additional arrows / incorrect polarity or formal charges on C−Br*

1

Allow *ecf for mechanism to form but-2-ene from (c)*

Allow *E1 mechanism*
M1 curly arrow from C−Br bond to the Br
M2 curly arrow from lone pair on O of OH^- *to a correct H on the correct C adjacent to* C^+ *on the carbocation*
M3 curly arrow from a correct C−H bond to a correct C−C bond
penalise M1 for any additional arrow(s) to/from the Br to/from anything else
penalise M2 for any additional arrow(s) on NaOH

(e) Z-but-2-ene **AND** *E*-but-2-ene

Allow *'cis'/'trans' and* ***B*** *and* ***C*** *either way round*

Allow *E/Z but-2-ene, cis/trans but-2-ene*

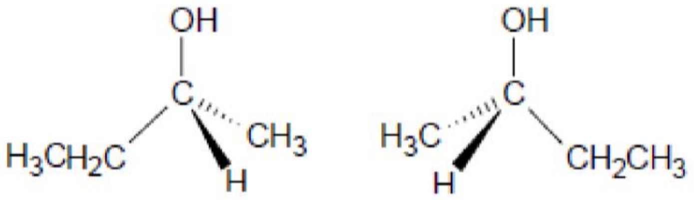
1

lack of/restricted/no (free) rotation around C=C/double bond

Allow *C=C/double bond cannot rotate*

1

(f)



M1 *any correct 2D or 3D structure of butan-2-ol*

Allow C_2H_5

1

M2 *must show at least one wedge bond and one dash bond in each structure from the chiral C and any bonds* ***in the plane*** *cannot be at 180° to each other*

1

second structure could be drawn as mirror image of first ***or*** *with same orientation of bonds and two groups swapped round*

Allow *ECF for second structure from incorrect first structure, providing molecule is chiral*

(g) Silver iodide then silver bromide then silver chloride

Allow *yellow then cream then white*

Allow *iodide/AgI then bromide/AgBr then chloride/AgCl*

Allow *iodo(butane) then bromo(butane) then chloro(butane)*

Ignore *iodine then bromine then chlorine*

1

bond strength C−I < C−Br < C−Cl

Ignore *incorrect formulae*

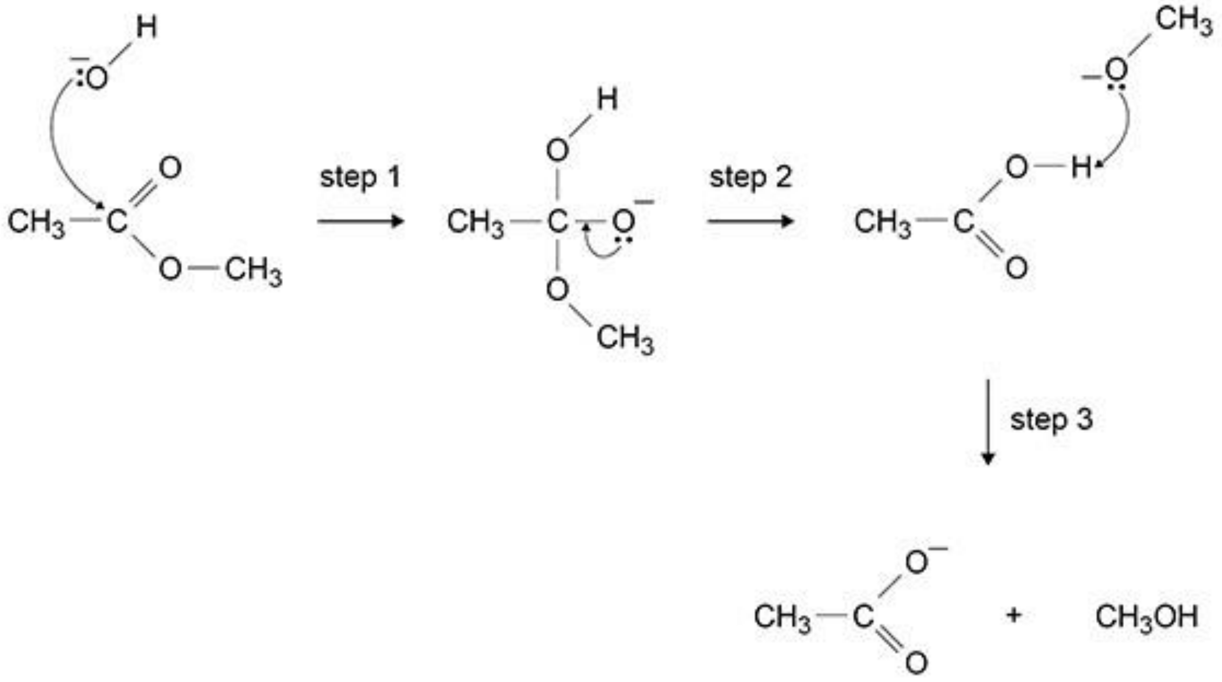
Allow *carbon-halogen bond strength decreases down the group / from Cl to I*

1

Question - 07

This question is about esters.

The diagram below shows an incomplete mechanism for the reaction of an ester with aqueous sodium hydroxide.



(a) Add **three** curly arrows to complete the mechanism in above diagram.

____

(3)

(b) Name the type of reaction shown in the diagram above.

____

(1)

(c) Deduce the role of the CH_3O^- ion in step **3** shown in the diagram above.

____

(1)

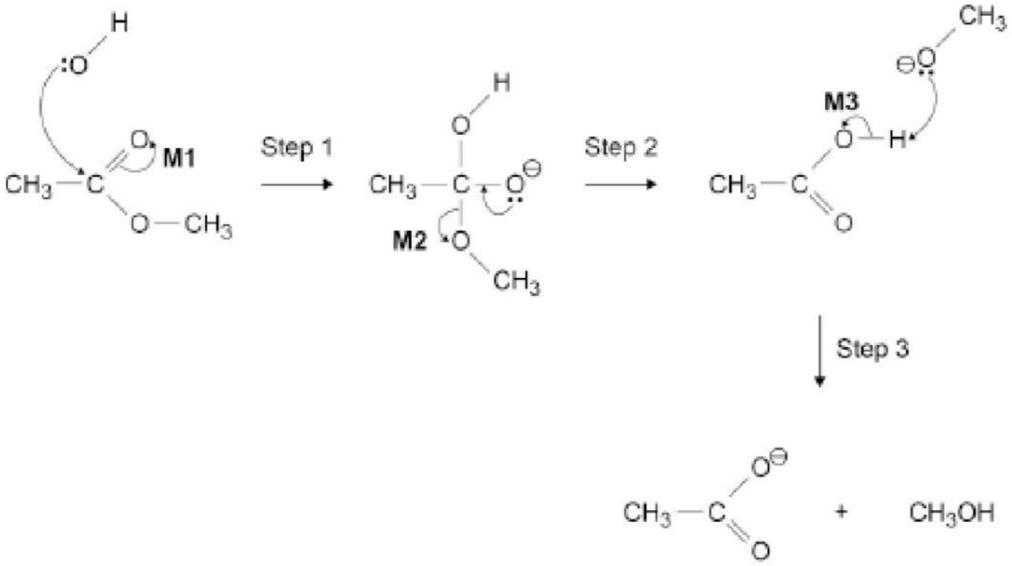
(d) A triester in vegetable oil reacts with sodium hydroxide in a similar way.

Give a use for a product of this reaction.

____

(1)

(a)



M1: Arrow from C=O bond to O

M2: Arrow from correct C-O bond to O

M3: Arrow from O-H bond to O

3

(b) (Alkaline/base) hydrolysis

1

(c) Base

Allow proton acceptor

Ignore ref to Bronsted Lowry

1

(d) Soap only

1

An acidified solution of butanone reacts with iodine as shown.

$$CH_3CH_2COCH_3 + I_2 \rightarrow CH_3CH_2COCH_2I + HI$$

(a) Draw the displayed formula for $CH_3CH_2COCH_2I$

Give the name of $CH_3CH_2COCH_2I$

Displayed formula

Name ____

(2)

(b) The rate equation for the reaction is

$$rate = k[CH_3CH_2COCH_3][H^+]$$

Table 1 shows the initial concentrations used in an experiment.

Table 1

	$CH_3CH_2COCH_3$	I_2	H^+
Initial concentration / mol dm^{-3}	4.35	0.00500	0.825

The initial rate of reaction in this experiment is 1.45×10^{-4} mol dm^{-3} s^{-1}

Calculate the value of the rate constant, *k*, for the reaction and give its units.

k ______________________

Units ______________________

(3)

(c) Calculate the initial rate of reaction when all of the initial concentrations are halved.

Initial rate of reaction ____________________ mol dm^{-3} s^{-1}

(1)

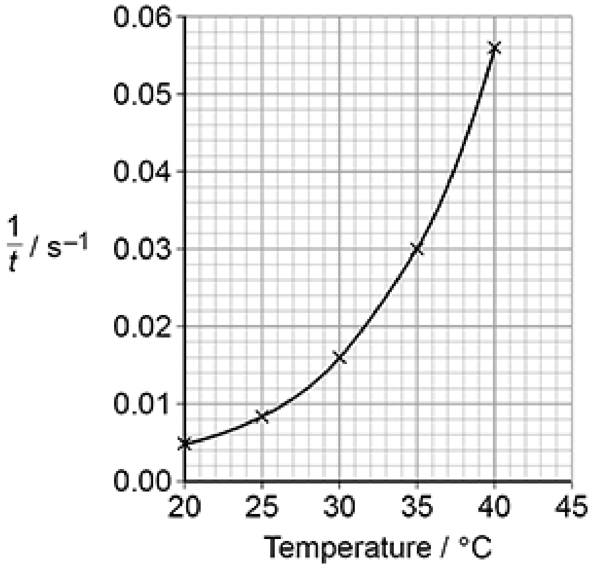
(d) An experiment was done to measure the time, *t*, taken for a solution of iodine to react completely when added to an excess of an acidified solution of butanone.

Suggest an observation used to judge when all the iodine had reacted.

____

____

The experiment was repeated at different temperatures.
The graph below shows how $\frac{1}{t}$ varied with temperature for these experiments.



(1)

(e) Describe and explain the shape of the graph above.

____

____

____

____

____

____

____

(3)

(f) Deduce the time taken for the reaction at 35 °C

Time ______________ s

(1)

(g) For a different reaction, **Table 2** shows the value of the rate constant at different temperatures.

Table 2

Experiment	Temperature / K	Rate constant / s^{-1}
1	$T_1 = 303$	$k_1 = 1.55 \times 10^{-5}$
2	$T_2 = 333$	$k_2 = 1.70 \times 10^{-4}$

This equation can be used to calculate the activation energy, E_a

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Calculate the value, in kJ mol^{-1}, of the activation energy, E_a

The gas constant, $R = 8.31$ J K^{-1} mol^{-1}

E_a ________________ kJ mol^{-1}

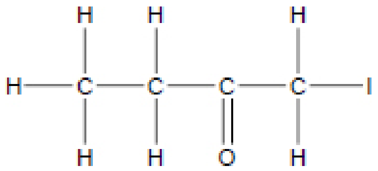
(5)

(h) Name and outline the mechanism for the reaction of butanone with KCN followed by dilute acid.

Name of mechanism ____

Outline of mechanism

(a)



$CH_3CH_2COCH_2I$

Apply list principle for more than one structure given

M1

1-iodobutan-2-one

Allow 1-iodo-2-butanone

M2

(b) $$\frac{\text{Rate}}{[CH_3CH_2COCH_3][H^+]} = k$$

Rearranged expression Or with numbers

M1

$k = 4.(04) \times 10^{-5}$ or 0.00004(04)

If upside down = 24752 mol dm^{-3} s

If multiply = 5.20×10^{-4} mol^3 dm^{-9} s^{-}

M2

mol^{-1} dm^3 s^{-1}

M3

(c) $3.6(25) \times 10^{-5}$ (mol dm^{-3} s^{-1})

Allow 3.59×10^{-5} to 3.63×10^{-5}

1

(d) Brown colour removed

Goes colourless

Allow (orange) brown to colourless

Allow purple to colourless

1

(e) As T increases rate ($1/t$) increases OR time for completion decreases

M1

Exponentially
OR
By a greater/ increasing factor

Or rate increases more and more as temp increases ie description of exponential increase

M2

<u>Many</u> more particles have $E \geq E_a$

NOT just higher collision frequency

NOT just more successful collisions

M3

(f) Time = $\frac{1}{0.03}$ = 33 s

1

(g) $\ln(1.55 \times 10^{-5}/1.70 \times 10^{-4}) = \frac{E_a}{R}\left(\frac{1}{333} - \frac{1}{303}\right)$

Insertion of correct values

M1

$-2.39 = \frac{E_a}{R}(-2.97 \times 10^{-4})$

Evaluate LHS and fraction on RHS

M2

$\frac{2.39 \times 8.31}{2.97 \times 10^{-4}} = E_a$

Re-arrange for E_a

M3

66937

Evaluate

M4

66.9 kJ mol^{-1}

convert to kJ mol^{-1}

M5

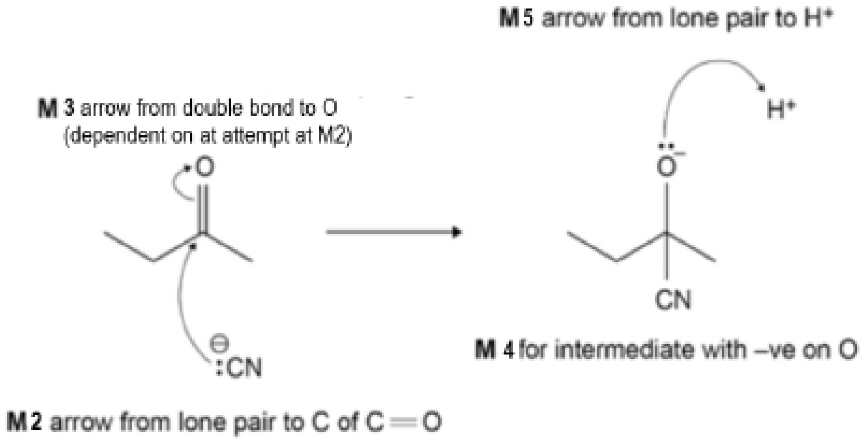
If only k_1 *and* k_2 *reversed this gives a negative answer for* E_a *Lose M1 and M5*

If AE in M2 allow ECF

Allow ECF from M4 to M5 for a correct unit conversion

Allow range 66.3 − 67.1

(h) Nucleophilic Addition



M1M2M3M4M5

ALLOW negative charge anywhere on cyanide
But attacking lone pair must be on C
Do not award M3 without attempt of M2
Allow M2 for attack to a positive carbon following breaking of C=O
Penalise covalent KCN in M2
M3 ignore partial charges unless wrong
Penalise M3 for incorrect connection between CN and C
NB Allow fully displayed or other structural formulae

This question is about isomerism and the dehydration of alcohols.

Pentan-2-ol has the molecular formula $C_5H_{12}O$

(a) Draw the **displayed** formula of an unbranched position isomer of pentan-2-ol that can be dehydrated to form a single alkene.

(1)

(b) Draw the **skeletal** formula of a chain isomer of pentan-2-ol that can be dehydrated to form a mixture of alkenes.

(1)

(c) Draw the structure of an unbranched functional group isomer of pentan-2-ol.

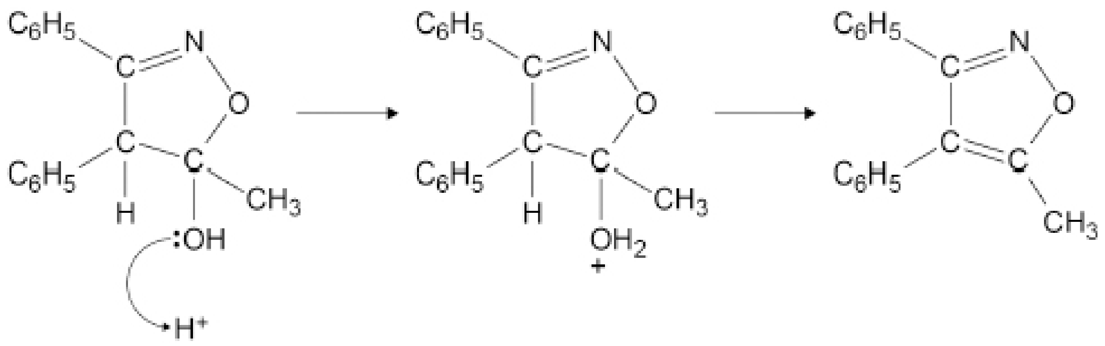
(1)

(d) Another isomer of pentan-2-ol is an alcohol that is **not** dehydrated when heated with concentrated sulfuric acid.

Draw the structure of this isomer.

(1)

(e) An incomplete mechanism for the dehydration of a compound is shown.



Complete the mechanism for this reaction by drawing two curly arrows on the intermediate.

Name the mechanism for this reaction.

____

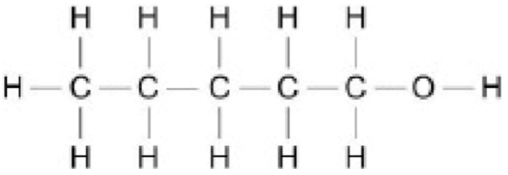
(3)

(f) An isomer of the final product can also form in the reaction in part (e).

Draw the structure of this isomer.

(1)

(a) Displayed formula of pentan-1-ol



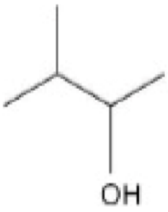
$$\begin{array}{ccccccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \\ & & | & & | & & | & & | & & | & & & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{H} \\ & & | & & | & & | & & | & & | & & & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & & & \end{array}$$

***NOT** pentan-3-ol*

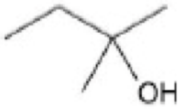
***NOT** -OH*

1

(b) Skeletal formula of 3-methylbutan-2-ol or 2-methylbutan-2-ol



or



***IGNORE** numbers on C atoms*

***IGNORE** 'dots' at junctions*

***IGNORE** other non-skeletal structures*

***IGNORE** skeletal structure of pentan-2-ol*

***NOT** other incorrect skeletal structures*

***NOT** O-H*

***NOT** if bond clearly to H of OH*

1

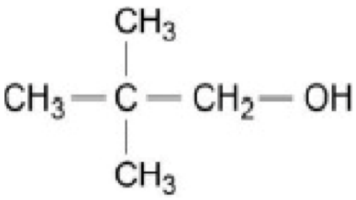
(c) one of these compounds

or

Any structural representation of correct compound

1

(d)

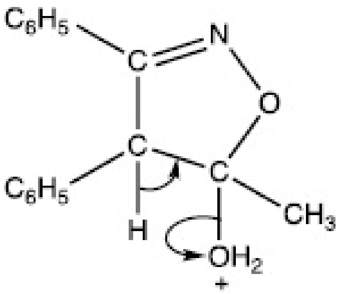


$$\begin{array}{ccccccc} & & \mathrm{CH_3} & & & & \\ & & | & & & & \\ \mathrm{CH_3} & - & \mathrm{C} & - & \mathrm{CH_2} & - & \mathrm{OH} \\ & & | & & & & \\ & & \mathrm{CH_3} & & & & \end{array}$$

Any structural representation of correct compound

1

(e)



M1 loss of H_2O: arrow from C-O bond to O

M2 loss of H^+: arrow from correct C-H bond to correct C-C bond

M3 elimination

M1/M2 *list principle for additional arrows on any structure*

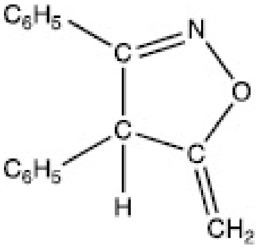
M1 NOT *if arrow to +*

M3 IGNORE *acid-catalysed / dehydration*

NOT *nucleophilic / addition / electrophilic*

3

(f)



Any structural representation of correct compound

If skeletal CH_2 not needed

Allow rings in place of C_6H_5

1

Question - 10

This question is about ethanoic anhydride.

In the gas phase, ethanoic anhydride $(CH_3CO)_2O$ decomposes to form ethenone.

The equation is

$$(CH_3CO)_2O \rightarrow \underset{\text{Ethenone}}{H_2C{=}C{=}O} + CH_3COOH$$

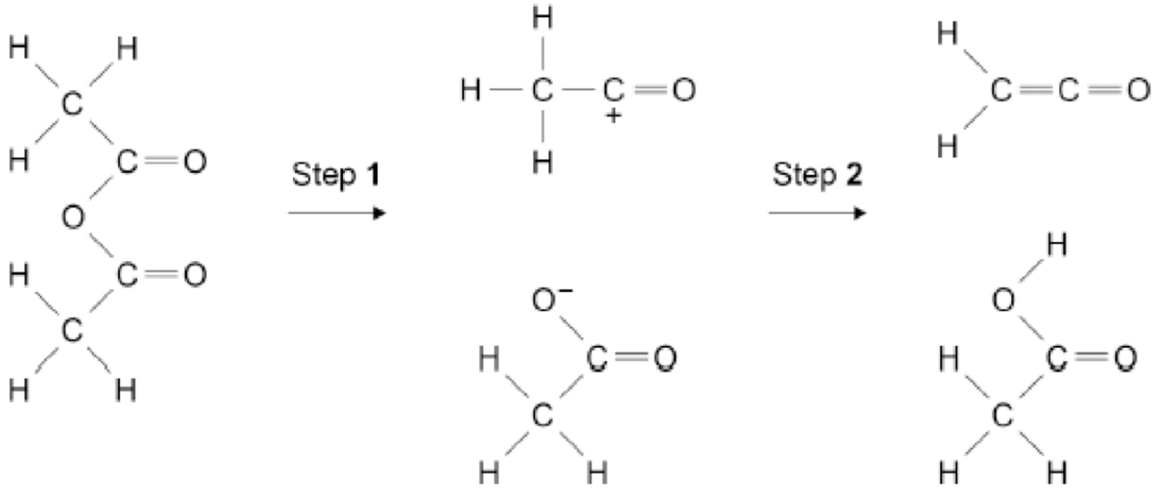
(a) Ethenone is the simplest member of the ketene homologous series.
Ketenes all contain one C=C double bond and one C=O double bond.

Deduce the general formula for the ketene homologous series.

____

(1)

(b) The figure below shows an incomplete suggested mechanism for the decomposition of ethanoic anhydride.



Complete the mechanism in the figure above by adding three curly arrows and any relevant lone pairs of electrons.

(3)

(c) For a chemical reaction the relationship between the rate constant, *k*, and the temperature, *T*, is shown by the Arrhenius equation.

$$k = Ae^{\frac{-E_a}{RT}}$$

For the decomposition of gaseous ethanoic anhydride

the activation energy, $E_a = 34.5$ kJ mol^{-1}

the Arrhenius constant, $A = 1.00 \times 10^{12}$ s^{-1}

At temperature T_1 the rate constant, $k = 2.48 \times 10^8$ s^{-1}

Calculate T_1

The gas constant, $R = 8.31$ J K^{-1} mol^{-1}

T_1 ____________________ K

(3)

(d) Sketch the Maxwell–Boltzmann distribution of molecular energies for gaseous ethanoic anhydride at temperature T_1 and at a higher temperature T_2

Include a label for each axis, and mark on the appropriate axis a typical position for the activation energy.

Explain why the rate of reaction is faster at T_2

Explanation

____

____

____

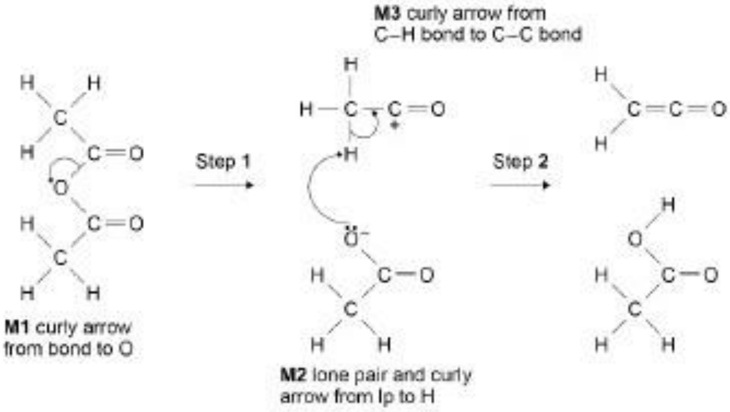
(5)

(a) $C_nH_{2n-2}O$

Allow $C_nH_{2n}CO$ or $(CH_2)_nCO$ or $C_nH_{2(n-1)}O$

1

(b)



Allow other C-O bond breaking for M1

3

(c) M1 $\frac{k}{A} = e^{-Ea/RT}$

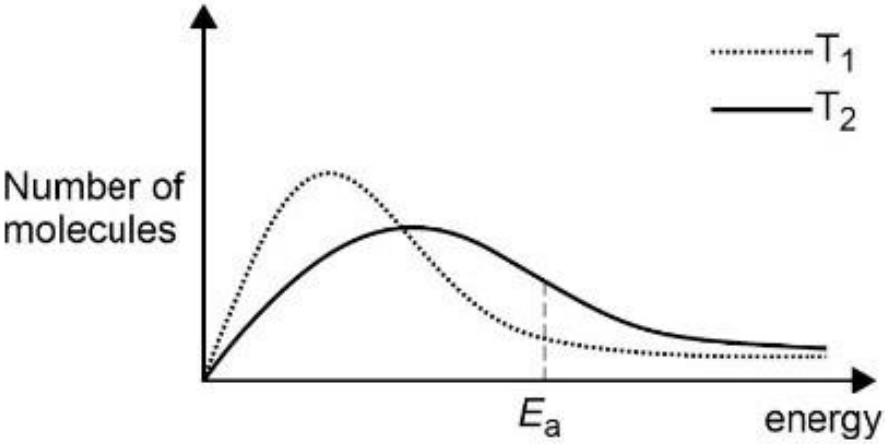
M2 $8.302 = \frac{34500}{8.31 \times T}$

M3 T = 500 K

OR via $\ln k = \ln A - \frac{Ea}{RT}$ or shown with numbers

3

(d)



M5 At T_2 (many) more particles have $E \geq E_a$

M1 x axis labelled correctly (kinetic not required)

AND y axis labelled correctly allow particles

M2 Ea labelled on x axis

M3 Distribution correct shape for T_1

M4 Peak at T_2 lower with max shifted right and only crosses once

5