Q1.

This question is about rates of reaction.

Potassium manganate(VII), $KMnO_4$, reacts with sodium ethanedioate, $Na_2C_2O_4$, in the presence of dilute sulfuric acid.

$$2\ MnO_4^-(aq) + 16\ H^+(aq) + 5\ C_2O_4^{2-}(aq) \rightarrow 2\ Mn^{2+}(aq) + 8\ H_2O(l) + 10\ CO_2(g)$$

The reaction mixture is purple at the start and goes colourless when all the $MnO_4^-(aq)$ ions have reacted.

The rate of reaction can be measured as $\frac{1000}{t}$ where t = the time taken for the mixture to go colourless.

A student investigated how long it takes for this reaction mixture to go colourless at different temperatures. The same concentrations and volumes of each reagent were used in an experiment at each temperature. The table below shows the results.

Temperature / °C	32	38	44	54	67
Time *t* / s	155	85	50	22	9
$\frac{1000}{t}$	6.45	11.8	20.0	45.5	

(a) Complete the table above.

(1)

(b) State the independent variable in this investigation.

_____

(1)

(c) The student noticed that the temperature of each reaction mixture decreased during each experiment.

Suggest how the student calculated the temperature values in the table above.

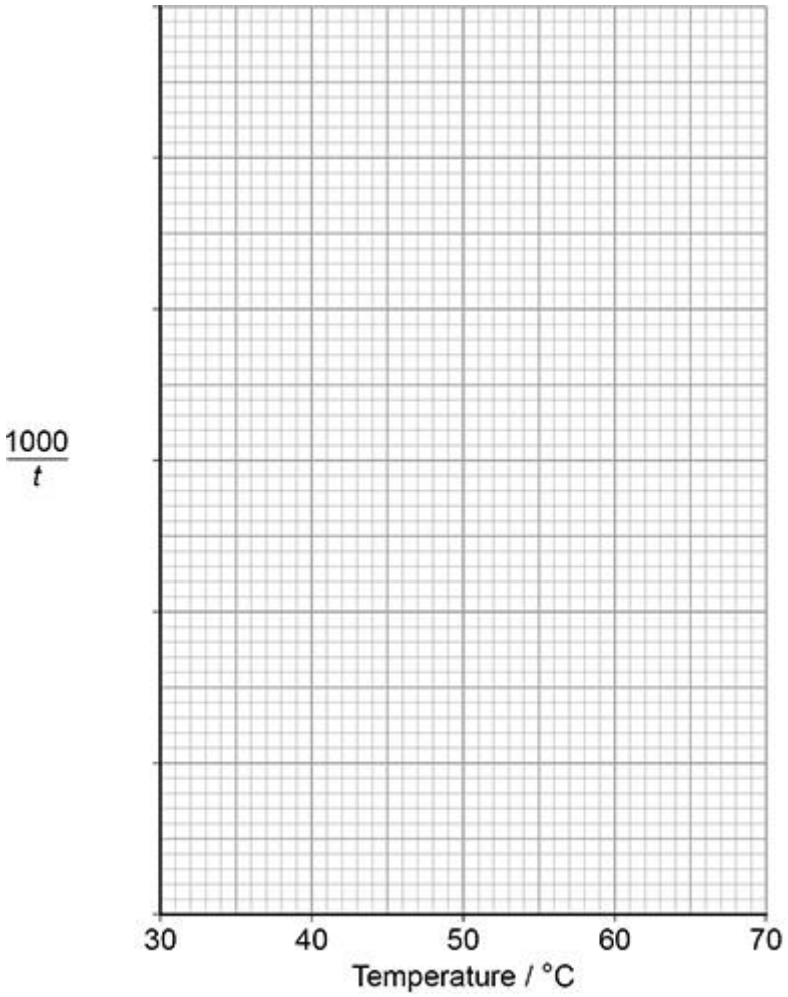
_____

_____

_____

(1)

(d) Use the data in the table to plot a graph of $\frac{1000}{t}$ against temperature.



(3)

(e) Use your graph in part (d) to find the time taken for the mixture to go colourless at 60 °C
Show your working.

Time *t* _____ s

(1)

(f) The investigation shows that increasing the temperature causes the rate of reaction to increase.

Explain why a small increase in temperature causes a large increase in the rate of reaction.

_____

_____

_____

_____

_____

_____

(2)

(Total 9 marks)

Q2.

A student investigates the effect of temperature on the rate of reaction between sodium thiosulfate solution and dilute hydrochloric acid.

$$Na_2S_2O_3(aq) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + SO_2(g) + S(s) + H_2O(l)$$

The student mixes the solutions together in a flask and places the flask on a piece of paper marked with a cross.

The student records the time for the cross to disappear. The cross disappears because the mixture becomes cloudy.

The table shows the student's results.

Temperature / °C	22	31	36	42	49	54
Time, t, for cross to disappear / s	87	48	36	26	44	12
$\frac{1}{t}$ / s^{-1}	0.0115	0.0208	0.0278	0.0385	0.0227	

(a) The student uses a stopwatch to measure the time. The stopwatch shows each time to the nearest 0.01 s

Suggest why the student records the times to the nearest second and not to the nearest 0.01 s

_____

_____

_____

(1)

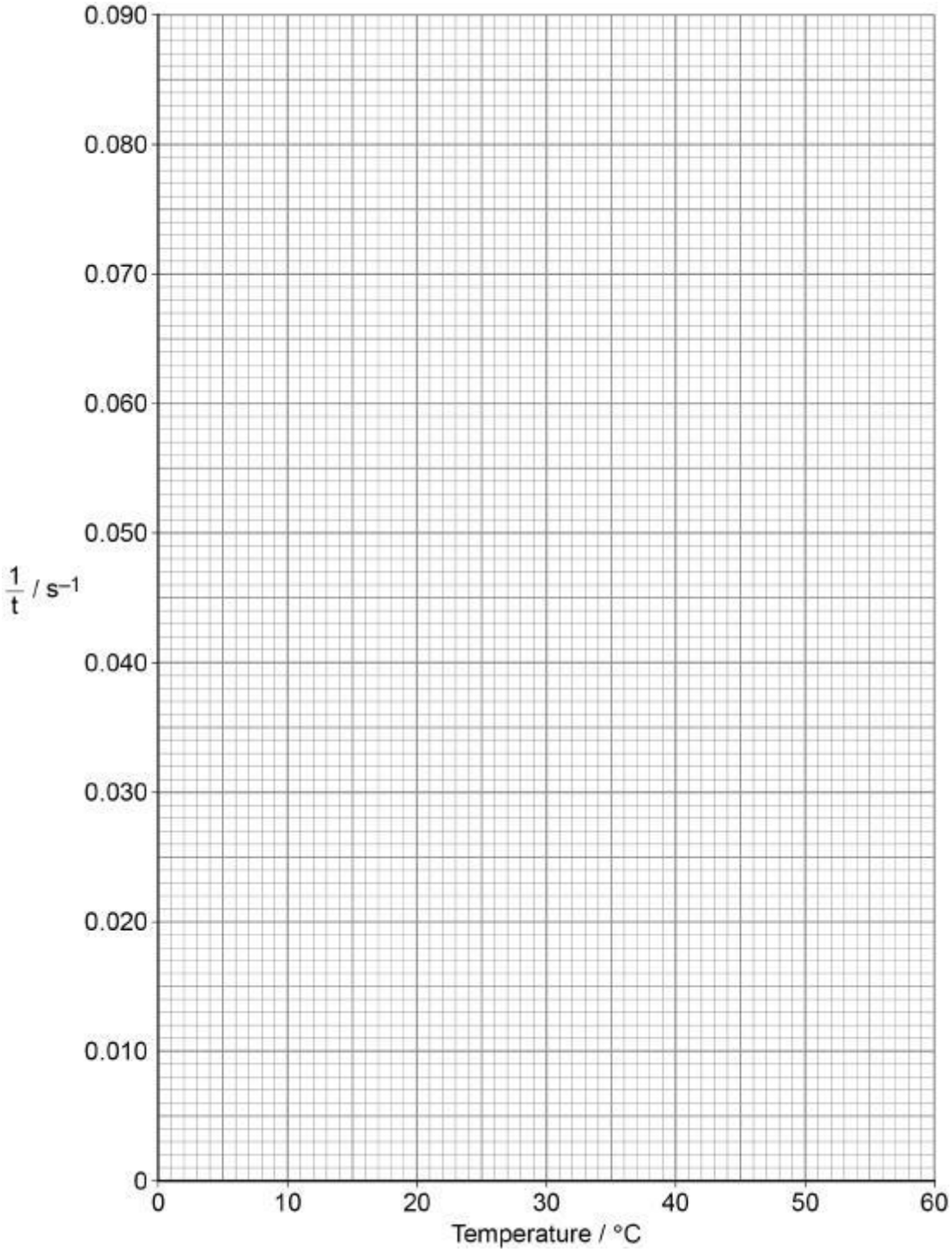
(b) The rate of reaction is proportional to $\frac{1}{t}$

Complete the table above.

(1)

(c) Plot the values of $\frac{1}{t}$ against temperature on the graph below.

Draw a line of best fit.



(2)

(d) Use your line of best fit to estimate the time for the cross to disappear at 40 °C
Show your working.

Time _____ s

(1)

(e) Suggest, by considering the products of this reaction, why small amounts of reactants are used in this experiment.

_____

_____

_____

(1)

(f) The student could do the experiment at lower temperatures using an ice bath.

Suggest why the student chose **not** to carry out experiments at temperatures in the range 1–10 °C

_____

_____

_____

(1)

(Total 7 marks)

Q3.

Methanol (CH_3OH) is an important alcohol with many uses.

(a) Draw a diagram to show how two methanol molecules interact with each other through hydrogen bonding in the liquid phase.

Include all partial charges and all lone pairs of electrons in your diagram.

(3)

(b) The bond angle around the oxygen atom in methanol is slightly smaller than the regular tetrahedral angle of 109.5°

Explain why this bond angle is smaller than 109.5°

(1)

(c) Methanol is made by the reaction of carbon monoxide with hydrogen.

$$CO + 2\ H_2 \rightleftharpoons CH_3OH \qquad \Delta H = -91\ kJ\ mol^{-1}$$

The reaction uses a copper-based catalyst, a pressure of 10 MPa and a temperature of 550 K

These conditions are used to provide a balance between equilibrium yield, reaction rate and cost.

Describe how the use of a catalyst, and changes in pressure and temperature, each affect equilibrium yield, reaction rate and cost.

(6)

(Total 10 marks)

Q4.

Sodium thiosulfate reacts with dilute hydrochloric acid as shown.

$$Na_2S_2O_3(aq) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + SO_2\ (g) + S(s) + H_2O(l)$$

(a) Give the simplest ionic equation for this reaction.

_____

(1)

(b) The gas SO_2 is a pollutant.

State the property of SO_2 that causes pollution when it enters rivers.

Give an equation to show the reaction of SO_2 with water.

Property _____

Equation _____

(2)

(c) Draw a diagram to show the shape of a molecule of H_2O
Include any lone pairs of electrons.

State the H-O-H bond angle.

Explain this shape and bond angle.

Diagram

Bond angle _____

Explanation _____

_____

_____

_____

_____

_____

_____

_____

(4)

(d) The initial rate of the reaction between sodium thiosulfate and hydrochloric acid can be monitored by measuring the time taken for a fixed amount of sulfur to be produced.

Describe an experiment to investigate the effect of temperature on the initial rate of this reaction.

Include

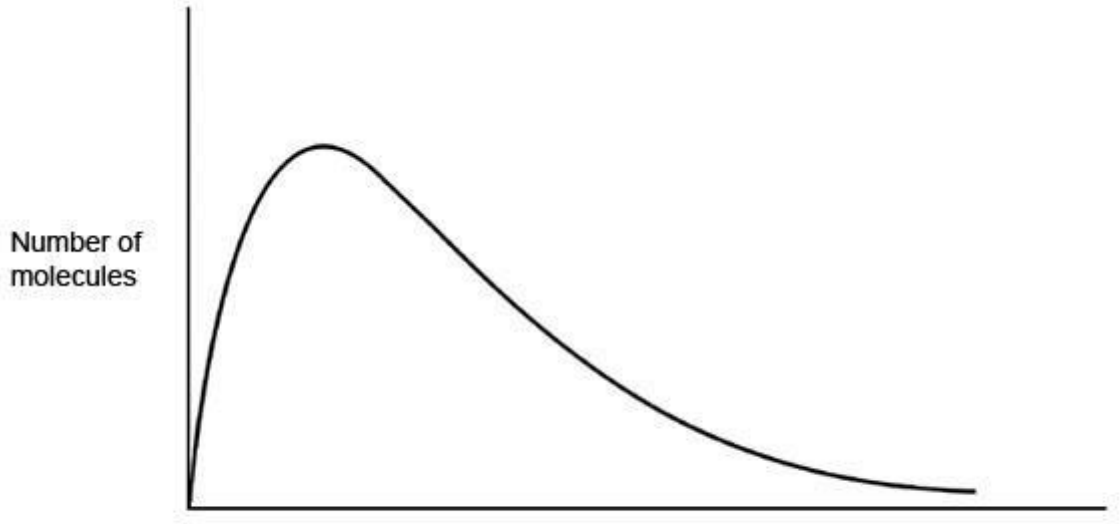
- a brief outline of your method
- how you will measure the time taken for a fixed amount of sulfur to be formed
- how you will present your results in graphical form
- a sketch of the graph that you would expect.

(6)

(Total 13 marks)

Q5.

The graph shows the Maxwell−Boltzmann distribution of molecular energies in a sample of gas at a fixed temperature.



.....

(a) Label the horizontal axis on the graph.

(1)

(b) On the graph, sketch a distribution of molecular energies for this sample of gas at a higher temperature.

(2)

(c) This gas decomposes on heating.

Explain why an increase in temperature increases the rate at which this gas decomposes.

_____

_____

_____

_____

_____

(2)

(Total 5 marks)

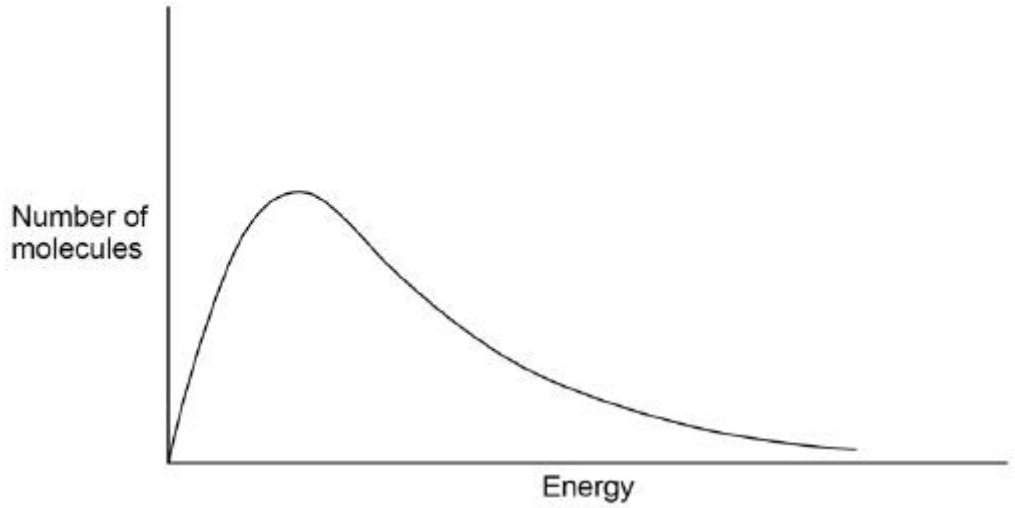
Q6.

Nitryl chloride reacts with nitrogen monoxide according to the equation:

$$ClNO_2(g) + NO\ (g) \longrightarrow NO_2(g) + ClNO(g)$$

The Maxwell–Boltzmann distribution curve in **Figure 1** shows the distribution of molecular energies in 1 mol of this gaseous reaction mixture (sample **1**) at 320 K.

Figure 1



(a) On the same axes, draw a curve for sample **1** at a lower temperature.

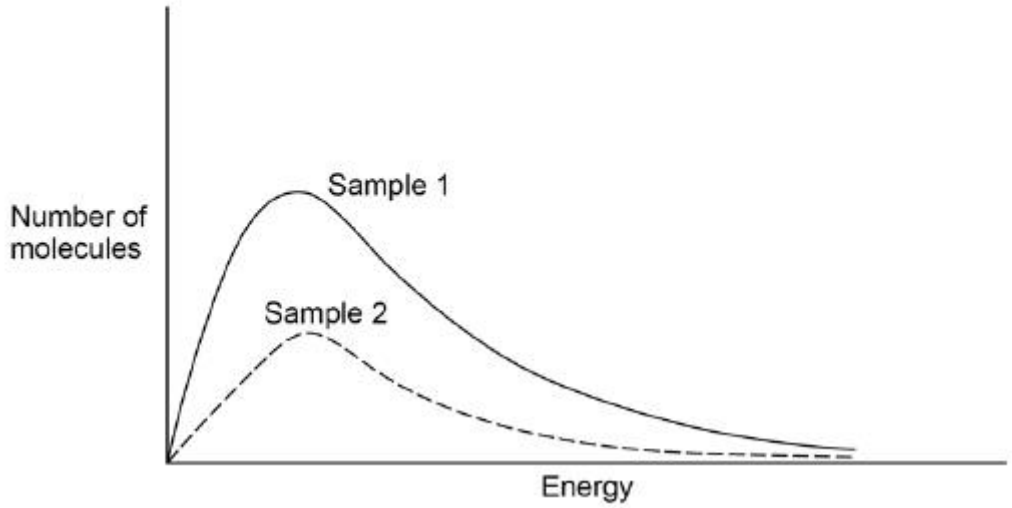
(2)

(b) Explain the effect that lowering the temperature would have on the rate of reaction.

(2)

(c) A Maxwell–Boltzmann distribution curve was drawn for a second sample of the reaction mixture in the same reaction vessel. **Figure 2** shows the results.

Figure 2



Deduce the change that was made to the reaction conditions.

Explain the effect that this change has on the rate of reaction.

Change _____

_____

Explanation _____

_____

_____

_____

_____

_____

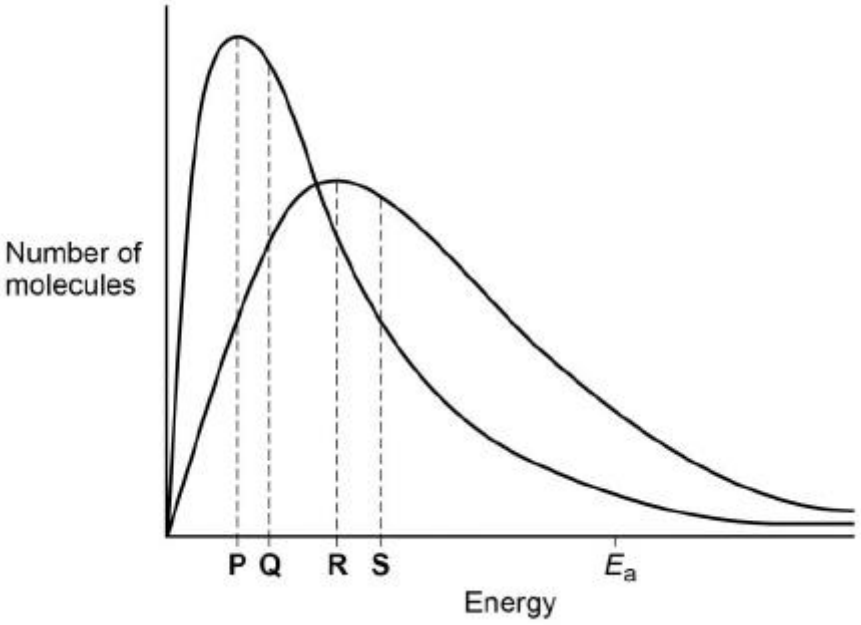
_____

(3)

(Total 7 marks)

Q7.

The question below is about the Maxwell–Boltzmann distribution shown for a sample of a gas, X, at two different temperatures.



Which statement is correct for the higher temperature?

A The area under the curve to the left of E_a decreases. ⬭

B The total area under the curve increases. ⬭

C The activation energy decreases. ⬭

D More molecules have the mean energy. ⬭

(Total 1 mark)

Q8.

This question involves the use of kinetic data to deduce the order of a reaction and calculate a value for a rate constant.

The data in **Table 1** were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Table 1

Experiment	Initial concentration of A / mol dm^{-3}	Initial concentration of B / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.12	0.26	2.10×10^{-4}
2	0.36	0.26	1.89×10^{-3}
3	0.72	0.13	3.78×10^{-3}

(a) Show how these data can be used to deduce the rate expression for the reaction between **A** and **B**.

(3)

The data in **Table 2** were obtained in two experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Table 2

Experiment	**Initial concentration of C / mol dm^{-3}**	**Initial concentration of D / mol dm^{-3}**	**Initial rate / mol dm^{-3} s^{-1}**
4	1.9×10^{-2}	3.5×10^{-2}	7.2×10^{-4}
5	3.6×10^{-2}	5.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$rate = k[\mathbf{C}]^2[\mathbf{D}]$$

(b) Use the data from experiment **4** to calculate a value for the rate constant, *k*, at this temperature. Deduce the units of *k*.

k = _____ Units = _____

(3)

(c) Calculate a value for the initial rate in experiment **5**.

Initial rate = _____ mol dm^{-3} s^{-1}

(1)

(d) The rate equation for a reaction is

$$rate = k[\mathbf{E}]$$

Explain qualitatively why doubling the temperature has a much greater effect on the rate of the reaction than doubling the concentration of **E**.

(3)

(e) A slow reaction has a rate constant $k = 6.51 \times 10^{-3}$ mol^{-1} dm^3 at 300 K.

Use the equation $\ln k = \ln A - E_a / RT$ to calculate a value, in kJ mol^{-1}, for the activation energy of this reaction.

The constant $A = 2.57 \times 10^{10}$ mol^{-1} dm^3.
The gas constant $R = 8.31$ J K^{-1} mol^{-1}.

Activation energy = _____

(2)

(Total 12 marks)

Mark schemes

Q1.

(a) 111(.1)

Allow an answer to a finite number of sig figs (that is correctly rounded)

Allow 110

Do not allow answers with recurring dot above number (ignore dots after the final number)

1

(b) temperature

1

(c) Measure the temperature at the start and end of the reaction and find the mean/average

Measure the temperature at regular intervals during the reaction and find the mean/average

Allow idea of doing the reaction in a water bath

1

(d) **M1** suitable vertical scale

***M1** should use more than half the axis to cover the four points given and the point for 67°C (if plotted)*

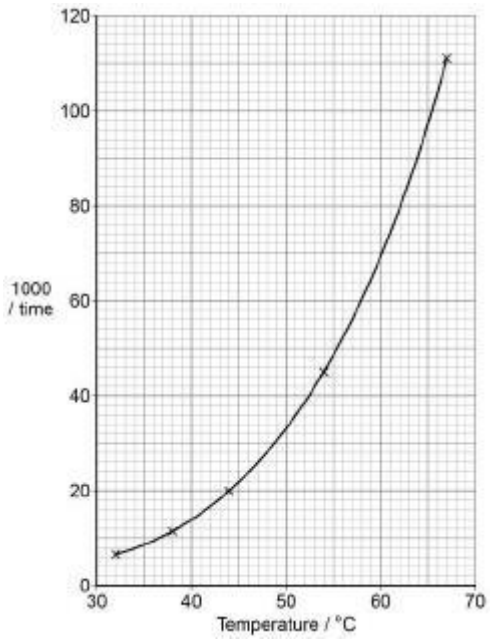
1

M2 points plotted correctly (±½ small square per point)

***M2** allow ECF for plotting of point found in part (a) (if no value found in part (a) allow graph that omits this)*

1

M3 best fit line drawn (within one small square of each point and should be a smooth curve)



M3 *allow ECF for a line based on their plotted points, but only where the line continues to rise throughout the temperature range*

1

(e) $\text{Time} = \frac{1000}{\text{value from graph at 60°C}}$

Answers should be at least 2 sf

Working needs to be shown that includes a value from the graph at 60 °C and/or construction line(s) showing 1000/t at 60 °C on the graph

Use the value their line shows at 60 °C (±½ small square)

1

(f) **M1** many more particles/ions have (energy ≥) activation energy

M1 *need the idea that it is many / much more particles; allow reference to atoms / molecules instead of particles / ions*

1

M2 more successful collisions per unit time / greater frequency of successful collisions

M2 *allow higher proportion of the collisions are successful*

1

[9]

Q2.

(a) Idea that it is hard to judge to the nearest 0.01 second *or* Idea that it is hard to judge the exact moment (that it becomes too cloudy / the cross disappears) *or* the idea of reaction time

Ignore ideas relating to accuracy (unless qualified)

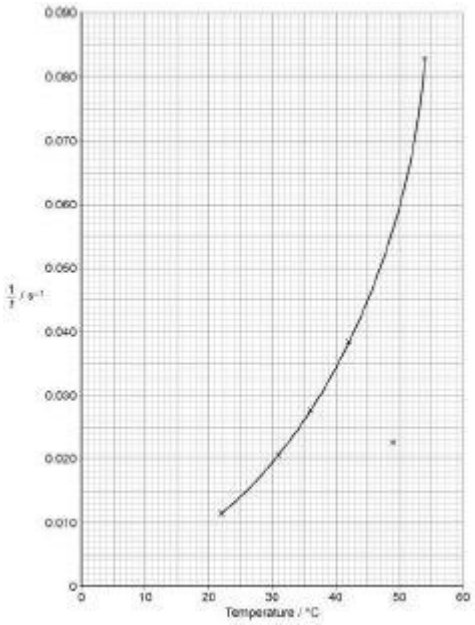
1

(b) 0.083(3….)

1

(c) **M1** points plotted correctly (allow ±1/2 small square for each)

M2 suitable best fit curve that misses point at 49°C and passes within one small square of the other five points



If any points plotted incorrectly: best fit line based on their plotted points which may need to be more than one square away from some points

*If no value calculated in (b), then **M1** and **M2** based on the other points (except the fifth anomalous point). A straight line may be allowed for **M2** for the first four points.*

*If incorrect value calculated in (b): **M1** based on all values being plotted correctly; **M2** based on suitable best fit line for the plotted points (except the fifth anomalous point).*

*Penalise **M2** if best fit line goes to 0,0.*

2

(d)

$$\frac{1}{\text{value from their best fit line at 40°C}}$$

eg $\frac{1}{0.0345}$ *= 29 (s)*

Ignore units

1

(e) as it forms a toxic gas or
SO_2 is toxic/poisonous or
to limit amount of SO_2 formed

Ignore reference to SO_2 being harmful

Ignore reference to acid rain / pollutant

1

(f) reaction would take too long / too slow / take a long time / very slow

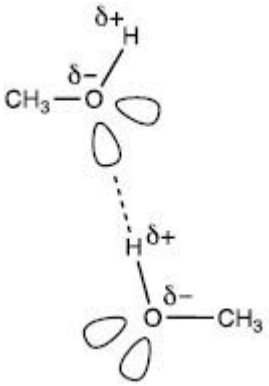
Ignore reaction may not occur
Allow idea that it makes judging the moment when the cross disappears more difficult

1

[7]

Q3.

(a)



M1 on at least one O atom two lone pairs and
on at least one OH δ+ on H and δ- on O

1

M2 dotted line shown between lone pair on one molecule and the correct H on another

1

M3 O····H–O in straight line

1

Accept pair of dots or crosses for lone pair in place of orbital shape (orbital shape may or may not include two electrons)

Ignore any partial charges on C–H or C–O bonds

*For straight line in **M3**, allow a deviation of up to 15°*

If a different molecule containing hydrogen bonding due to O–H bond drawn (e.g. ethanol, water) or an incorrect attempt at the structure of methanol, then maximum of 2 marks (i.e. only penalise if would score all three marks otherwise)

(b) Idea that lone pairs have greater repulsion than bonding pairs

There must be a comparison between the repulsion of a lone pair and bonding pair

Allow covalent bond = bonding pair

1

(c)

This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.	
Level 3 **5-6 marks**	**All stages are covered and the explanation of each stage is generally correct and virtually complete.** (6 v 5) Answer is well structured, with no repetition or irrelevant points, and covers all aspects of the question. Accurate and clear expression of ideas with no errors in use of technical terms.
Level 2	**All stages are covered but stage(s) may be**

3-4 marks	**incomplete or may contain inaccuracies OR two stages are covered and are generally correct and virtually complete** (4 v 3) Answer has some structure and covers most aspects of the question. Ideas are expressed with reasonable clarity with, perhaps, some repetition or some irrelevant points. If any, only minor errors in use of technical terms.
Level 1 **1-2 marks**	**Two stages are covered but stage(s) may be incomplete or may contain inaccuracies OR only one stage is covered but is generally correct and virtually complete** (2 v 1) Answer includes statements which are presented in a logical order and/or linked.
0 marks	Insufficient correct chemistry to gain a mark.

Stage 1
Describes the effect of catalyst use
1a use of a catalyst has no impact on equilibrium yield
1b use of a catalyst gives faster rate
1c use of catalyst lowers costs

Stage 2
Describes the effect of pressure
2a higher pressure gives a higher equilibrium yield
2b higher pressure gives a faster rate
2c the higher the pressure, the greater the cost

Stage 3
Describes the effect of temperature
3a lower temperature gives a higher equilibrium yield
3b higher temperature gives a faster rate
3c the higher the temperature, the greater the cost
Note that converse statements are fine (e.g. 1a higher temperature gives a lower equilibrium yield)

6

[10]

Q4.

(a) $S_2O_3^{2-} + 2\ H^+ \rightarrow SO_2 + S + H_2O$

Allow $S_2O_3^{2-} + 2H_3O+ \rightarrow SO_2 + S + 3H_2O$
Allow $½S_2O_3^{2-} + H^+ \rightarrow ½SO_2 + ½S + ½H_2O$
Allow $½S_2O_3^{2-} + H_3O + \rightarrow ½SO_2 + ½S + 1½H_2O$
Ignore state symbols
NOT multiples
NOT if any spectator ions included (unless crossed out)

1

(b) **M1** acid(ic) / acidity / produces H^+

M1 *Allow low(ers) pH*

Ignore toxic / soluble
Ignore sulfurous / sulfuric / H_2SO_4
Ignore rain
Ignore proton donor (unless qualified, e.g. reacts with water to form a proton donor)
NOT any other named acid

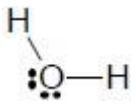
1

M2 $SO_2 + H_2O \rightarrow H_2SO_3$ / $H^+ + HSO_3^-$

M2 *Allow* $SO_2 + H_2O \rightarrow 2\ H^+ + SO_3^{2-}$
Allow $SO_2 + 2\ H_2O \rightarrow H_3O^+ + HSO_3^-$
Allow $SO_2 + 3\ H_2O \rightarrow 2\ H_3O^+ + SO_3^{2-}$
Allow multiples
Ignore state symbols

1

(c) **M1**



M1 *bent shape and 2 lone pairs on O*
Allow any suitable representation of lone pairs (e.g. dots, crosses, lobes with/without dots/crosses)

1

M2 104½°

M2 *Allow 104-105°*

1

M3 lone pairs repel more (strongly) than bond(ing) pairs

M3 *Allow non-bonding pair for lone pair*
Allow covalent bond for bond(ing) pair
Allow shared pair for bond(ing) pair
Allow OH bond for bond(ing) pair
Allow bond for bond(ing) pair
NOT OH or O-H without the word bond for bond(ing) pair

1

M4 so bond angle reduced from/less than 109½° / tetrahedral

M4 *Allow bond angle reduced from 120° if bent with one lone pair in* ***M1***
Allow reduced from 109°
Allow reduced by 2.5° per lone pair or 5° if ***M2*** *correct*

1

(d)

This question is marked using levels of response. Refer to the Mark Scheme Instructions for examiners for guidance on how to mark this question	
Level 3	**All stages are covered and the explanation of each**

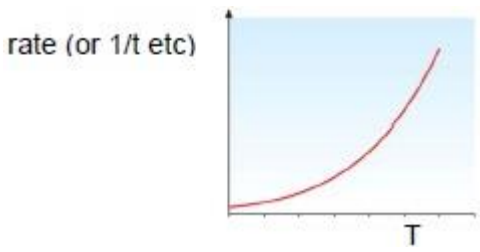
5-6 marks	**stage is correct and virtually complete.** (6 v 5) Answer is well structured, with no repetition or irrelevant points. Accurate and clear expression of ideas with no errors in use of technical terms.
Level 2 **3-4 marks**	**All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages covered and the explanations are generally correct and virtually complete** (4 v 3) Answer has some structure. Ideas are expressed with reasonable clarity with, perhaps, some repetition or some irrelevant points. If any, only minor errors in use of technical terms.
Level 1 **1-2 marks**	**Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR only one stage is covered but the explanation is generally correct and virtually complete** (2 v 1) Answer includes statements which are presented in a logical order and/or linked.
0 marks	Insufficient correct Chemistry to warrant a mark

Indicative Chemistry content

Stage 1 Method
(1a) Idea of using disappearing cross or colorimetry
(1b) Puts acid or thiosulfate into container on/with cross or in colorimeter
(1c) Add second reactant and start timing

Stage 2 Measurements
(2a) Repeat at different temperatures (if number of temperatures stated, must be more than two)
(2b) Record time, t, for cross to disappear / defined reading on colorimeter
(2c) Idea of ensuring other variables (cross, volumes, concentrations) kept constant (apart from T)

Stage 3 Use of Results
(3a) 1/t (or 1000/time, etc) is a measure of rate
(3b) plot of rate (or 1/t etc) (y-axis) against T (x-axis) (can come from labelled axes on sketch) (IGNORE T against rate)
(3c) sketch of plot as shown (Allow 3c if axes not labelled but NOT if incorrectly labelled)



6

[13]

Q5.

(a) energy

Ignore reference to

- *any units (e.g. J, kJ, J mol^{-1}, kJ mol^{-1})*
- *particles*
- *molecules*
- *kinetic*

***NOT** mean energy or average energy*

***NOT** E*

1

(b) **M1** maximum peak height is lower and displaced to the right of the original

1

M2 all of the following

- starts at the origin but does not follow the original line
- shows separation as soon as possible from the original line
- crosses the original curve once only
- similar area to original curve
- an attempt has been made to draw the new curve correctly towards the energy axis above the original curve but not to touch the original curve (or axis)

1

(c) **M1** an increase in the number/amount/proportion/fraction of molecules with $E \geq E_a$ / with activation energy

or more molecules have $E \geq E_a$ / with activation energy

or more molecules have enough / sufficient energy (to react)

M1

Ignore

- *Molecules have more energy*
- *More energetic collisions*
- *More collisions*

Allow $E > E_a$ in place of $E \geq E_a$

Credit particles for molecules (but not atoms)

*Penalise for **M1** reference to increased activation energy*

1

M2 more successful / effective / productive collisions in a given time / period

or higher rate of successful / effective / productive collisions

or higher frequency of successful / effective / productive collisions

M2

Must refer to <u>both</u> idea of successful / effective / productive collisions and the rate / frequency of collisions

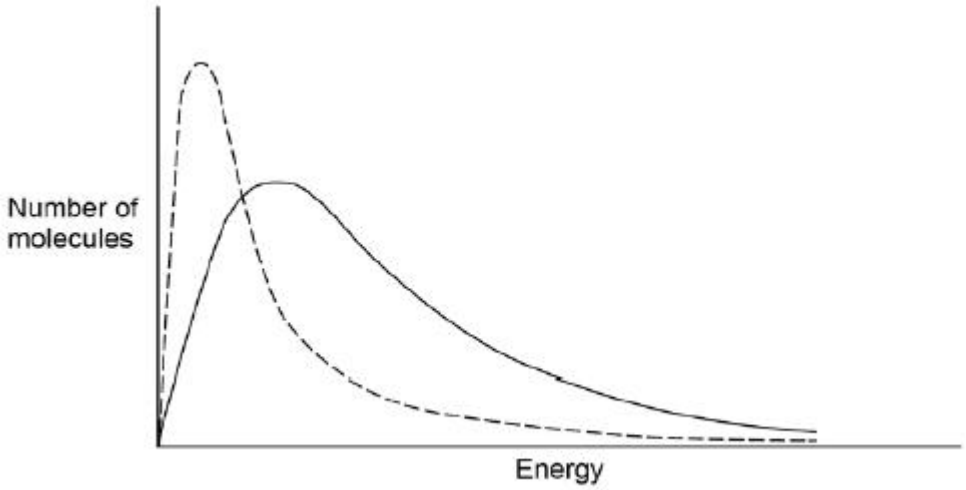
Ignore 'chance of collision'

1

[5]

Q6.

(a)



M1 Curve is higher and displaced to the left
M2 Only crosses the original curve <u>once</u>

2

(b) Rate of reaction decreases (no mark)

Fewer particles will have energy greater than or equal to the activation energy

1

Fewer <u>successful</u> collisions in a given time
Less frequent <u>successful</u> collisions

1

(c) The amount of gas present (or number of molecules) has been reduced / or the pressure has been reduced

1

Rate of reaction decreases (no mark)

Particles are spread further apart

1

Fewer collisions between gas particles so fewer <u>successful</u> collisions

1

[7]

Q7.

A

[1]

Q8.

(a) Consider experiments 1 and 2: [B constant]

[A] increases × 3: rate increases by 3^2 therefore 2nd order with respect to A

1

Consider experiments 2 and 3:

[A] increases × 2: rate should increase × 2^2 but only increases × 2

Therefore, halving [B] halves rate and so 1st order with respect to B

1

Rate equation: rate = $k[A]^2[B]$

1

(b) rate = k $[C]^2[D]$ therefore k = rate / $[C]^2[D]$

1

$$k = \frac{7.2\times10^{-4}}{(1.9\times10^{-2})^2 \times (3.5\times10^{-2})} = 57.0$$

Allow consequential marking on incorrect transcription

1

$mol^{-2}\ dm^{+6}\ s^{-1}$

Any order

1

(c) rate = $57.0 \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3}$ (mol dm^{-3} s^{-1})

OR

Their $k \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2}$

1

(d) Reaction occurs when molecules have $E \geq E_a$

1

Doubling T by 10 °C causes <u>many</u> more molecules to have this E

1

Whereas doubling [**E**] only doubles the number with this E

1

(e) $E_a = RT(\ln A - \ln k) / 1000$

Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ

1

$E_a = 8.31 \times 300\ (23.97 - (-5.03)) / 1000 = 72.3$ (kJ mol^{-1})

1

[12]