5.9   Candidate Individual Investigation Report 0410

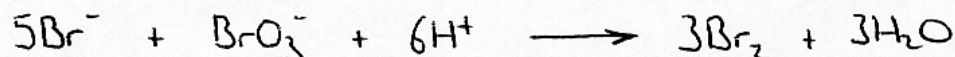**Kinetics of the reaction between bromide and bromate(v) ions**

Investigation into how the concentration of the reactants affect the rate of reaction between bromide, bromate(V) and hydrogen ions.

Planning

Aims

The chemical equation for the reaction I am going to investigate is given below:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

I aim to vary the concentration of potassium bromide, bromate(V) and hydrogen ions. From my results I intend to work out reaction rate and prove that the rate equation is:

$$rate = k\,[Br^-]\,[BrO_3^-]\,[H^+]^2$$

This will allow me to determine the rate constant and the order of the reaction. I will also investigate the effect temperature has on reaction rate. I should be able to use my results and the Arrhenius equation to calculate activation enthalpy.

Background Knowledge

The "rate of reaction" is the speed at which reactants are converted to products. It is not possible to measure reaction rate directly; we have to measure the change in amount of a reactant/product in a certain time.
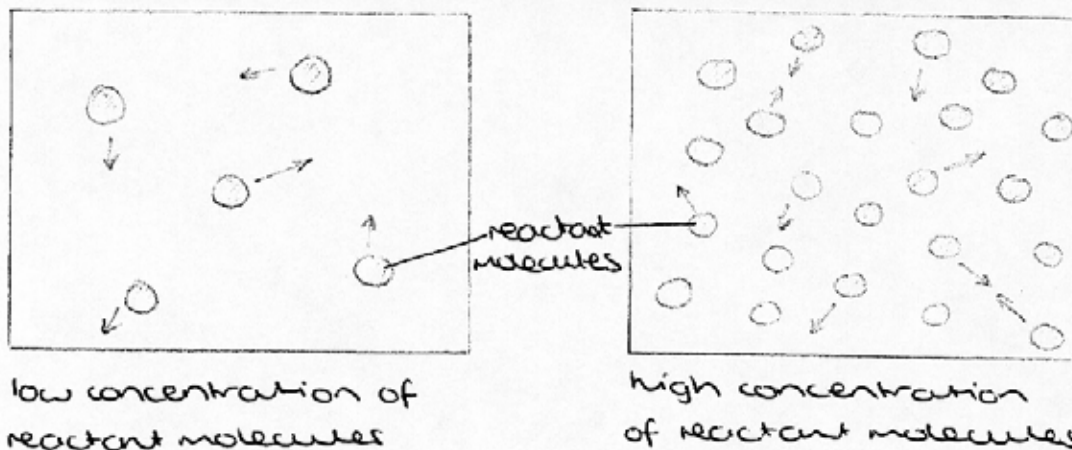
$$rate = \frac{change\ in\ property}{time\ taken}$$

There are several factors that effect reaction rate, they are:
- concentration
- temperature
- surface area
- the presence of a catalyst

CONCENTRATION:
To understand the effects of concentration the collision theory must be referred to. This "assumes that the rate of any step in a reaction depends on the frequency of collisions between the particles involved." (5) Simply the collision theory states that for a reaction to occur the 2 reactant molecules must collide. Increasing the concentration increases the number of reactant molecules in the same volume of solution therefore they collide more often, increasing the rate of reaction. The diagrams below show this affect.

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Diagrams showing the effect of increasing concentration

low concentration of reactant molecules

high concentration of reactant molecules

TEMPERATURE:

As the temperature is increased the average speed of the particles increases because they have more energy. This increase in speed means they collide more frequently resulting in an increase in the reaction rate. Temperature, however, has a large influence on reaction rate as just a 10°C rise can result in the reaction rate being doubled. As the kinetic energy of a particle is proportional to its absolute temperature we can predict the relative increase in the number of collisions when the temperature is raised by 10K. In this case from 300 to 310K.

$$\tfrac{1}{2}mV^2 \propto T$$

T is the absolute temperature. We can rearrange this equation for a particle of constant mass. V_1 is the velocity at temperature T_1 and V_2 is the velocity at temperature T_2.

$$\frac{(V_1)^2}{(V_2)^2} = \frac{T_1}{T_2}$$

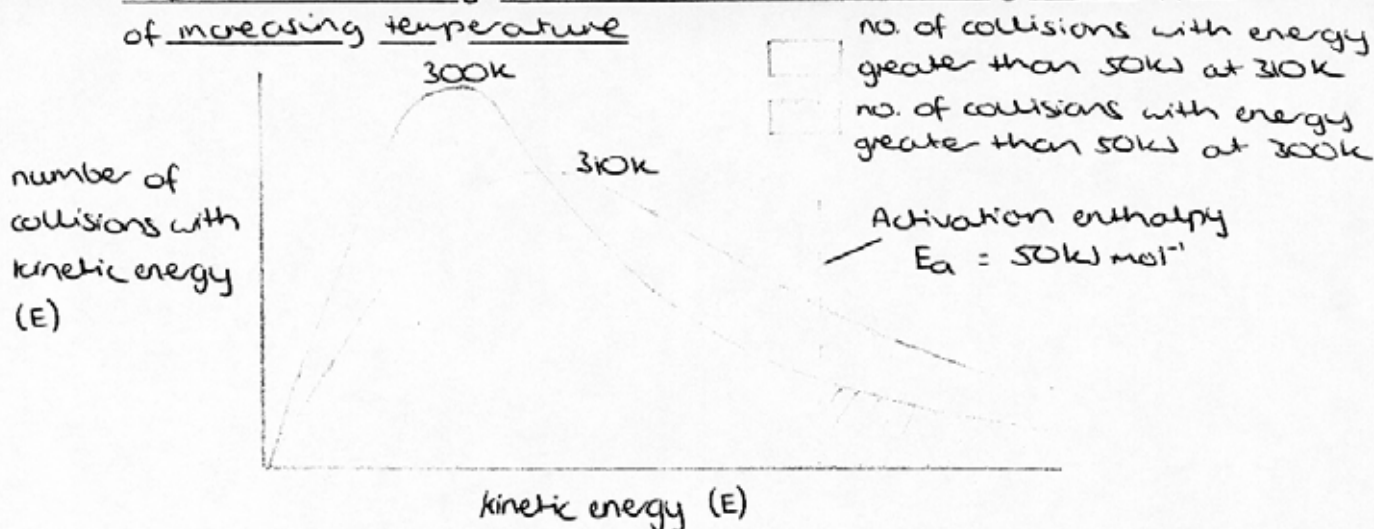sub in values:

$$\frac{(V_1)^2}{(V_2)^2} = \frac{310}{300}$$

$$\therefore V_1 = \left(\sqrt{\frac{310}{300}} \right) V_2$$

$$V_1 = \sqrt{1.03}\; V_2$$

$$V_1 = 1.016\, V_2$$

This shows that the speed of the particles at 300K is only 1.016 times greater, there has only been an increase of 1.6%. But we already know that the reaction actually proceeds about 100% faster. This is because every collision does not result in a reaction. "A reaction will only occur if the colliding particles possess more than a certain minimum amount of energy, known as the activation energy." (3) Increasing temperature raises the amount of molecules that collide with this amount of energy. The distribution of kinetic energies below is known as the maxwell-boltzmann distribution. From this diagram it is apparent why temperature has such an important effect.

The Maxwell-Boltzmann distribution showing the effect of increasing temperature

300K

310K

□ no. of collisions with energy greater than 50kJ at 310K

□ no. of collisions with energy greater than 50kJ at 300K

Activation enthalpy
$E_a = 50 kJ mol^{-1}$

number of collisions with kinetic energy (E)

kinetic energy (E)

The shaded area represents those collisions with the required activation energy. The transition state theory shows what actually happens during a collision. It explains why such a small fraction of collisions result in a reaction. "When 2 molecules approach each other, the electron clouds experience a gradual increase in their mutual repulsions." (4) The kinetic energy is converted to potential energy and the molecules slow down, so molecules that weren't moving fast enough don't react at all. When temperature is increased the molecules have enough energy to overcome these forces and a reaction occurs.

SURFACE AREA:
When using solids a larger surface area means the reaction rate will be increased due to a larger number of reaction sites. Therefore a powdered solid would react more quickly than one in larger pieces. But this is not important to my experiment as I am using solutions.

THE PRESENCE OF A CATALYST:
"A catalyst is a substance that increases the rate of reaction without being used up itself." (1) It works by lowering the activation energy in one of several ways, by:
• Increasing the frequency of collisions between reactants.
• Changing the relative orientation of the reactant molecules.
• Donating electron density to the reactants.
• Reducing the intramolecular bonding between the reactant molecules.
• Providing and alternate pathway or mechanism for the reaction.
Catalysts are used in many industrial processes.

The concentration of potassium bromide solution will be varied first. I will then have a table of results with concentration against time. I need to calculate reaction rate but I cannot measure the amount of products produced directly. To get around this problem methyl orange has been added to the mixture. The reaction will therefore be studied as a clock reaction. The first bromine formed will be destroyed by reaction with phenol, which is also deliberately added to the mixture to allow us to study the reaction.
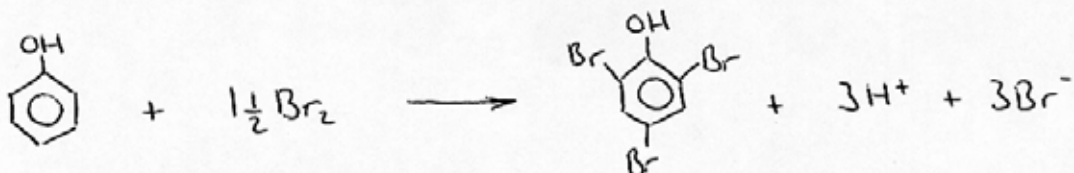
When all the phenol has been used up the next bit of bromine formed will react and bleach the methyl orange indicator. In each trial the same amount of phenol will be added therefore it will be a fair test. The time it takes to go colourless is a measure of how fast the reaction is taking place. The amount of bromine needed to decolourise the mixture is the same for each trial, so the rate of reaction is proportional to the reciprocal of the reaction time.

$$\text{rate} \propto \frac{1}{\text{time}}$$

Using this equation I can work out reaction rate and produce a graph plotting concentration against rate of reaction. This graph will allow me to determine the order of reaction. (see model graph below)
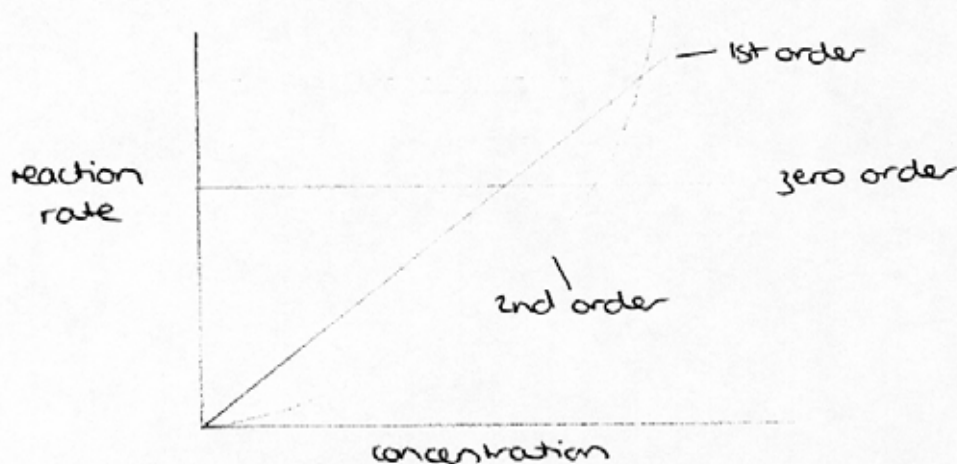
If the graph shows a horizontal line the reaction is zero order with respect to that reactant. When a reaction is zero order:
rate = k[X]°
But as X° always equals 1,
reaction rate = k
So for zero order reactions the rate is independent of the concentration of X. It has no effect on reaction rate. If the graph is a diagonal line the reaction is first order and if it is a curve then its second order.
Once the order of the reaction is known with respect to each of the reactants involved a rate equation can be produced. For a general reaction in which A and B are the reactants the rate equation is:

$$\text{rate} = k[A]^m[B]^n$$

"m and n represent the order of the reaction. If m was 2 we would say the reaction is second order with respect to A." (1) The overall order is given by (m + n). I intend to prove through my experiments that the rate equation for this reaction is:

$$\text{rate} = k[Br^-][BrO_3^-][H^+]^2$$

Rate equations can only be determined experimentally; they cannot be predicted from the stoichiometric equation. k in the rate equation is known as the rate constant. It is not affected by a change in concentration but a change in temperature will alter k. Maxwell and Boltzmann derived equations for the distribution of kinetic energies using the probability theory and the kinetic theory of gases. They calculated ~~that~~ the fraction of molecules with energy greater than the activation energy, Ea ~~is given by~~:

Where,

R is the gas constant (8.3 $J K^{-1} mol^{-1}$)
and T is the absolute temperature.

At a given temperature rate of reaction is proportional to $e^{-Ea/RT}$
Since the rate constant k is a measure of reaction rate we can write:

$$k \propto e^{-Ea/RT}$$

$$\text{OR} \quad k = Ae^{-Ea/RT}$$

The last equation is known as the Arrhenius equation. "A is the Arrhenius constant and can be regarded as a collision frequency and orientation factor in the reaction rate." (3)
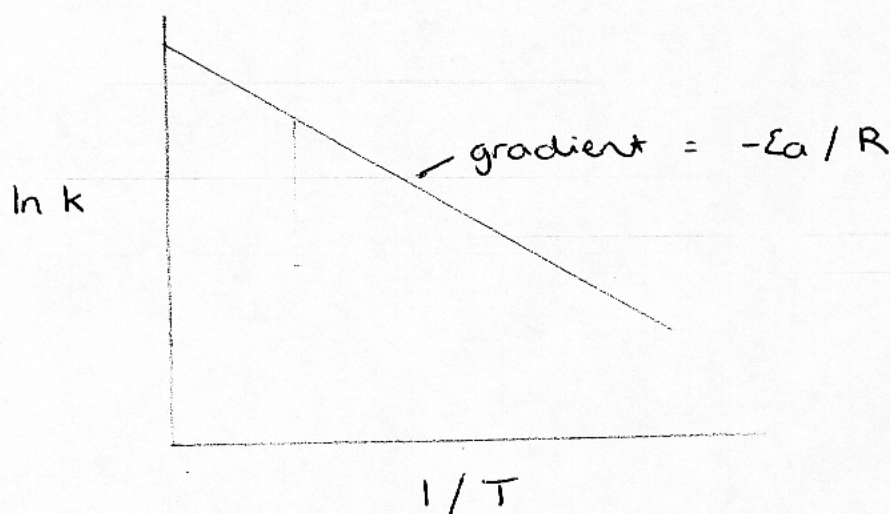
Taking the log (base e) form of the equation,

$$\ln k = \ln A - \frac{Ea}{RT}$$

Rearranging in the form y = mx + c

$$\ln k = -\frac{Ea}{R} \times \frac{1}{T} + \ln A$$

A value for rate can now be substituted for ln k. So a graph of ln k against 1/T should be a straight line with gradient -Ea/R. From this gradient activation energy can be calculated.


gradient = $-Ea/R$

ln k

1/T

In some reactions changing the concentration of a particular reactant has no effect on the rate. When this is the case it means there are two steps involved in the reaction, this is known as the mechanism of the reaction. "The mechanism of a reaction is a proposal about the series of steps involved in going from reactant to products." (6) It is a suggestion based on scientific evidence. Where there are two or more steps it is the slowest step that determines the overall rate. This is called the rate determining step. I will suggest a mechanism for the reaction based on the rate equation.

Apparatus

For this experiment I will need:
- 5 burettes
- 0.005M potassium bromate(V) solution
- 1M sulphuric acid solution
- 0.0001M phenol solution
- methyl orange indicator
- 0.01M potassium bromide
- distilled water
- 2 beakers
- white tile
- magnetic stirrer
- stopwatch

sulphuric acid solution

distilled water

potassium bromide solution

phenol solution

burettes

stand

potassium bromate(v) solution

beakers for mixing solutions
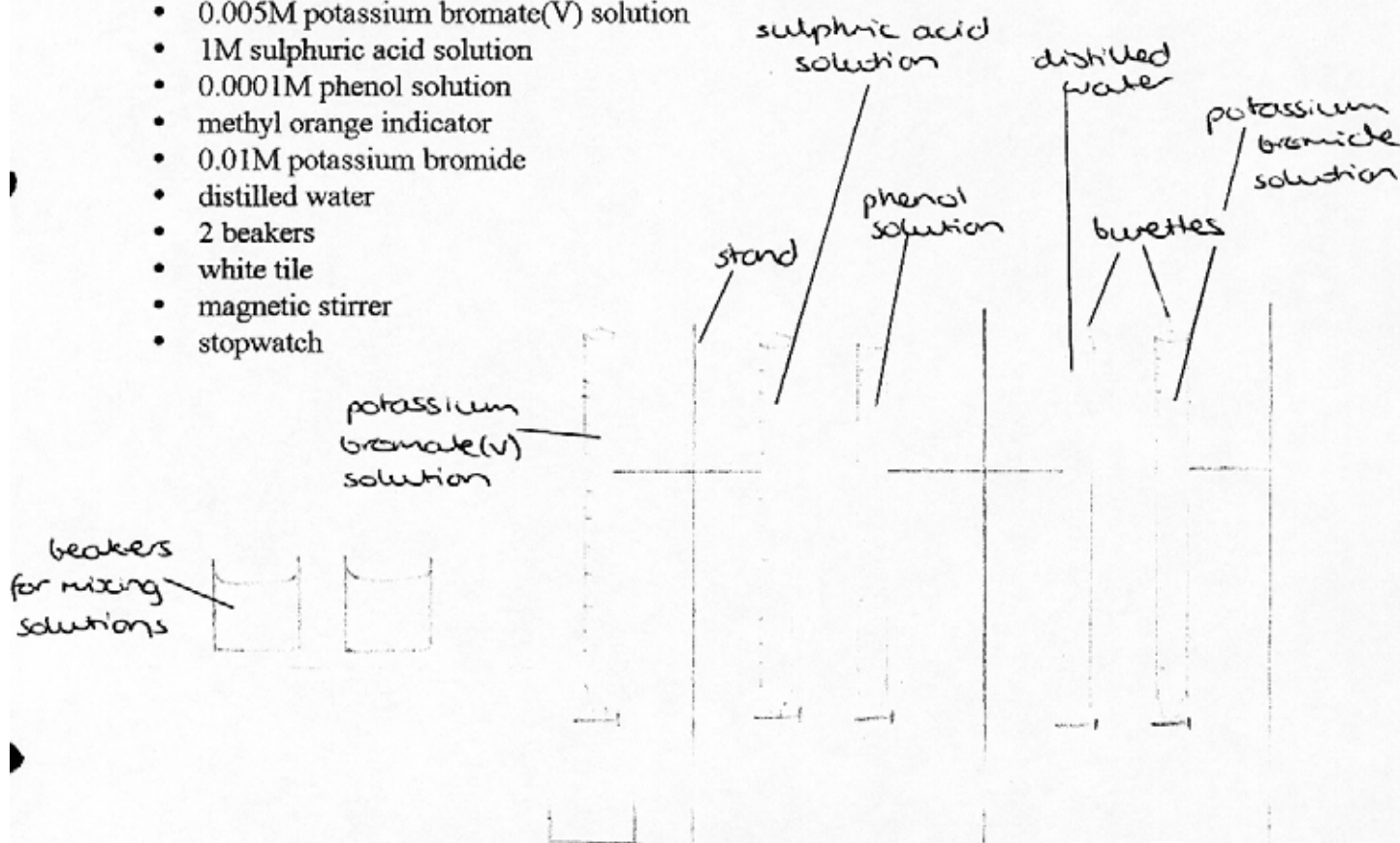
Method for investigating the effect of changing concentration

The first experiment was to vary the concentration of potassium bromide solution. I am changing the concentration because due to the kinetic theory it should have an effect on reaction rate.
1. Take 5 burettes, which should be washed out with water. They are then washed out with the solution going into them and filled with one of the solutions listed above. All the burettes are labelled to avoid any confusion with the solutions. When filling a burette it should always be held below head height to allow it to be controlled better and to avoid spillage.
2. 10cm³ of potassium bromate(V) solution, 15cm³ of sulphuric acid solution and 10cm³ of phenol solution are added to a beaker. Always read the burette at eye

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level. 5 drops of methyl orange indicator is also added to the beaker. The same bottle should be used in each trial.

3. 10cm³ of potassium bromide solution of the required concentration is added to another beaker. For most trials the potassium bromide will need mixing with distilled water to lower the concentration.

4. The potassium bromide solution is poured into the first beaker and the stopwatch is started. The complete mixture is stirred and the time taken for it to go completely colourless is recorded.

5. The beakers are then washed out and the experiment is repeated with varying concentrations of potassium bromide. But the volume of potassium bromide solution is always made up to 10cm³ with distilled water to make it a fair test. Each concentration is repeated 3 times. All other factors such as temperature should be kept constant and the same apparatus should be used each time. Any anomalous results should be investigated.

Precision and Reliability

Burettes have been used rather than measuring cylinders for measuring the volumes of solutions as they are specifically designed to be more accurate. The percentage error associated with a 50cm³ burette of grade B is ±0.1cm³. This is far more accurate than the value for a 25cm³ measuring cylinder, which is ±0.5cm³. When using a burette the measurement should be read from the bottom of the meniscus. It should also be read at eye level to avoid a par lax error.

Each measurement in my actual experiment will be carried out 3 times to confirm my result. Repetitions increase reliability by showing that a result within experimental error can be achieved more than once. An average will then be taken from the 3 repetitions. This average time can be used to work out reaction rate. Volumes of either 10 or 15cm³ have been used to keep the percentage errors to a minimum whilst still having volumes that are manageable.

$$\text{Percentage error} = \frac{\text{error}}{\text{measurement}} \times 100$$

So for measuring 10cm³ from a burette the error would be

$$\% \text{ error} = \frac{0.1 \times 100}{10.0}$$

$$= 1\%$$

If volumes are too small then the percentage errors become too large. I have taken into account precision and reliability in my planning which should give me a reliable set of results. This same method should be followed when the concentrations of sulphuric acid solution and potassium bromate(V) solution are varied. But then the potassium bromide solution should be kept at a constant concentration as only one variable can be altered at once.

There are also sources of error associated with procedures, temperature can be a problem in all kinetic investigations as there is no guarantee that the room temperature

will be the same in the laboratory from one day to the next. It is not possible to find a value for errors associated with procedures but I can discuss in my conclusion how big effect I think this had.

A preliminary experiment was carried out, 8 different concentrations were used to allow the full range of results to be seen. This table shows my results:

Concentration of potassium bromide (mol dm⁻³)	0.01 x (10/45) =0.0022	0.008 x (10/45) =0.0017	0.006x (10/45) =0.0013	0.005 x (10/45) =0.0011	0.004 x(10/45) =0.00088	0.003 x (10/45) =0.00066	0.002 x (10/45) =0.00044	0.001 x (10/45) =0.00022
time taken for the mixture to go colourless (seconds)	35.5	41	53.5	57.5	65	81	128.5	290

If time allowed I would use all of these concentrations in my actual experiment to give me a larger range of results. But time was limited so I chose not to use the two lowest concentrations as they took a long time to decolourise. In this experiment I shook the complete mixture by hand but I was not sure if this was giving me accurate results. I therefore decided to carry out 3 trial experiments using different methods. In the first experiment the magnetic stirrer was used, in the second the mixture was shook by hand and in the third the mixture was not interfered with. The potassium bromide solution was simply poured in and left to react. In all trials the above method was followed and the time taken for the solution to go colourless was recorded. The results are shown below:

concentration of potassium bromide solution (mol dm⁻³)	time taken for mixture to decolourise stirring by hand	time taken for mixture to decolourise using the magnetic stirrer	time taken for the mixture to decolourise without stirring
0.0022	28.5	21	22
0.0017	31	26.5	30.5
0.0013	33	37.5	41.5
	38.5	43.5	36.5
0.00088	48.5	49	50.5
0.00066	73	64.5	57.5

These results have been plotted on a graph. (see graph 1) The graph shows a reliable trend for the results obtained from shaking the mixture by hand and using the magnetic stirrer. It was, however, difficult to determine exactly when the mixture had become clear. Especially for the lower concentrations. To overcome this problem the mixture could be placed on top of a white tile, so that any colour would be obvious against the white background. I therefore decided that shaking the mixture by hand would be the best option. From graph 1 it is apparent that 6 points is enough to identify the trend even if one of these points is inaccurate. The concentrations I have chosen are appropriate, as the reaction is not too fast or too slow, so it will be easy to observe the change. I therefore think my choice of concentrations is justified.

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Once I have determined the effect of the 3 different concentrations the effect of temperature can be investigated. From my background knowledge I also know that this has an effect on reaction rate, and I expect the effect to be greater than that of varying the concentration. For this extra equipment will be needed, including:

- bunsen burner
- tripod
- gauze
- large beaker
- boiling tubes
- ice cubes
- thermometer
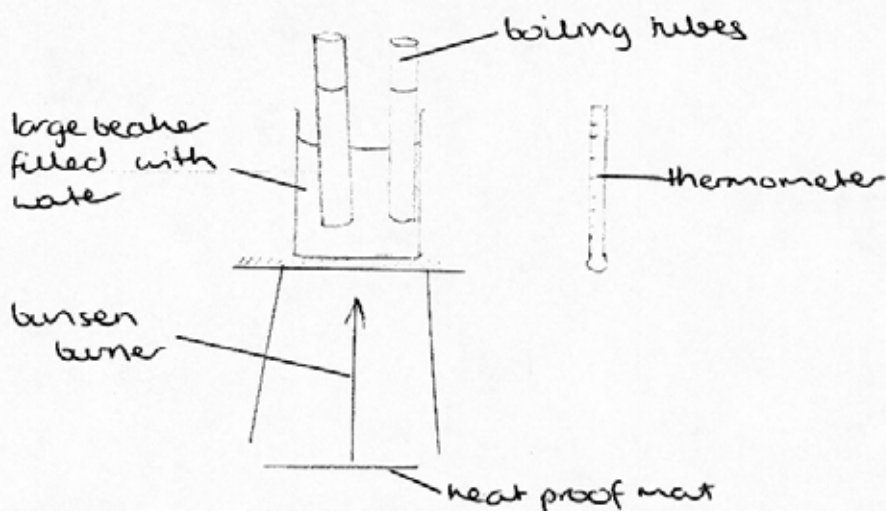
Method for investigating the effect of temperature

1. The apparatus should be set up as before with the extra equipment listed above. Wash out the apparatus as before and follow all the measures listed to ensure accuracy.
2. 10cm³ of potassium bromate(V) solution, 15cm³ of sulphuric acid solution and 10cm³ of phenol solution should be mixed in a boiling tube and 5 drops of methyl orange indicator should be added. Always from the same bottle.
3. 10cm³ of potassium bromide should be added to another boiling tube.
4. The large beaker should be filled with water and placed on the tripod as shown in the diagram. The water should be heated or cooled to the required temperature and the boiling tubes should be placed in the beaker so they are also heated to this temperature.
5. The solutions are then mixed and the stopwatch is started. The time taken for the mixture to go colourless is recorded. A white tile can be held behind the beaker to allow the colour change to be observed more easily. The thermometer should also be placed in the large beaker and should be checked often to ensure the solutions are at the right temperature.

Modifications

When I used the method above to obtain some results I found there were several problems and some modifications are needed. Firstly the volumes of solutions suggested were too large. When the solutions were mixed the volume was too great to fit in the boiling tube. I have therefore decided to half all volumes to 5cm³ of potassium bromate(V) solution, 7.5cm³ of sulphuric acid solution and 5cm³ of phenol solution. Only 3 drops of methyl orange indicator will now be added to the boiling tube. The

volume of potassium bromide solution added to the second boiling tube will also be reduced to 5cm³. This reduction in volumes will increase the percentage error of my results but it is necessary as the original volumes were unmanageable. All concentrations will remain unchanged. There was another problem in the method when it came to measuring the temperature of the solutions and keeping them at a constant temperature. By just taking the temperature of the water I had no guarantee that the solutions in the boiling tubes were at the correct temperature. I therefore took another thermometer and put one in each boiling tube to monitor the temperature of the actual reactants. When they had both stabilised at the right temperature I removed the thermometer and poured the potassium bromide solution into the first boiling tube. I then put the thermometer back into the mixture to ensure that the temperature did not change.

I found that the mixture went very fast above 40°C so thought about lowering the concentration to slow down the rate of reaction. When I experimented with lower temperatures, however I found that I could not lower the concentration as the reaction was already very slow and this would have made the reaction time too long. I therefore decided not to increase the temperature above 40°C and to use the temperatures listed below:

10°C
15°C
20°C
25°C
30°C
35°C and 40°C.

This range of temperatures also made it easier to keep the temperature of the solutions stable as they are not too much below or above the room temperature.

This table links the chemical ideas used to the units and modules on the course.

Chemical Topic	Module included	AS or A level
concentrations of solutions	chemical Ideas 1.5	AS - level
collision theory	chemical Ideas 10.1	AS - level
reaction rates	chemical ideas 10.2 and 10.3	A - level
order of reaction / rate equations	chemical ideas 10.3	A - level

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Risk Assessment

There are always risks involved when using chemicals. In general eye protection should be worn at all times, even while setting up and clearing away. Also any spillage should be cleared immediately.

Sulphuric acid - solutions stronger than 1.5M should be labelled corrosive, solutions stronger than 0.5M but weaker than 1.5M should be labelled irritant. Eye protection should be worn and the skin should be washed immediately if it comes into contact with it.

Phenol - toxic if swallowed and when in contact with the skin. Solutions stronger than 0.1M should be labelled harmful. But my solution is weaker than this.

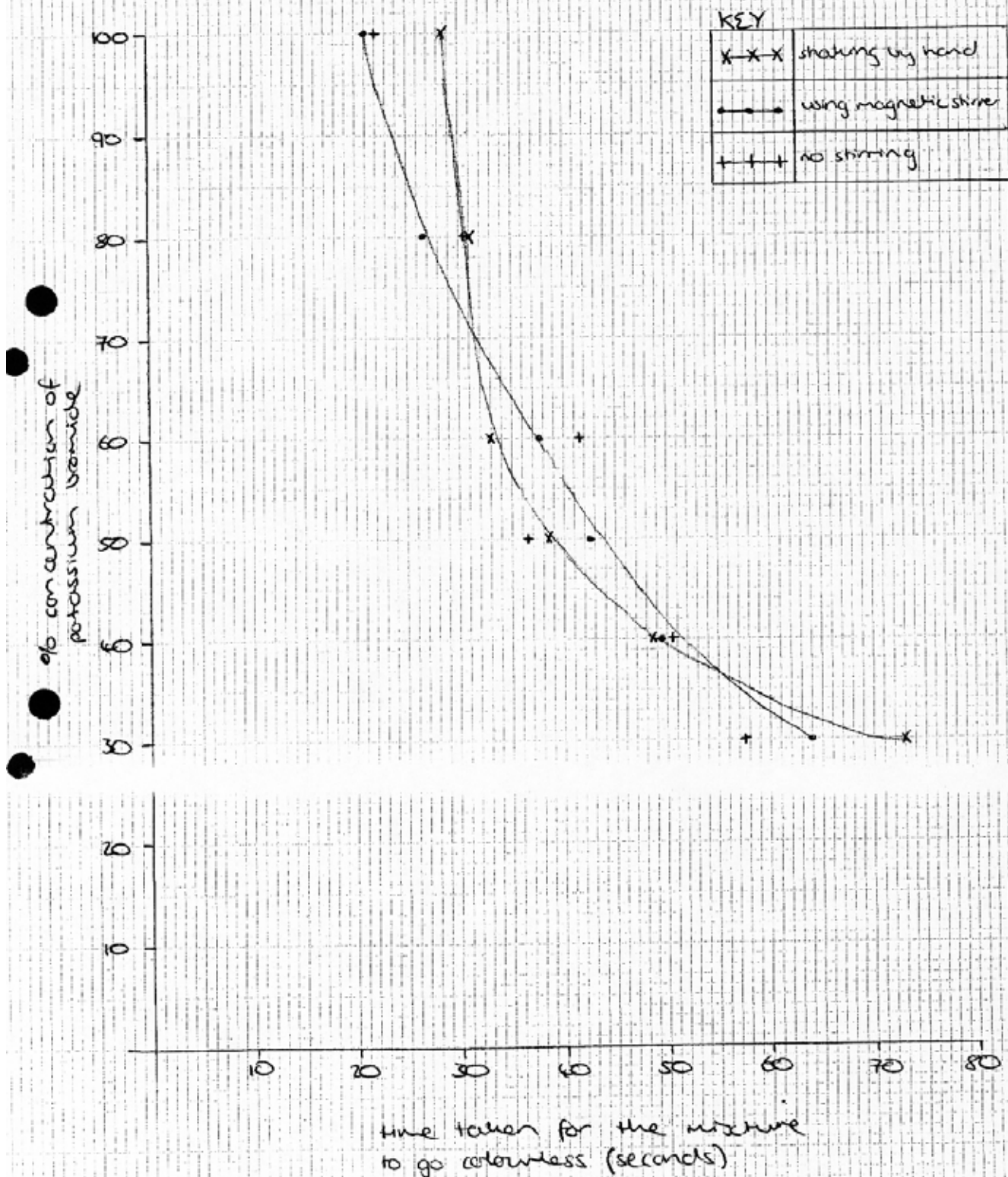Potassium bromate - oxidising and toxic if swallowed.

Potassium bromide - has minimal hazards but would be harmful if ingested.

References

(1) 'Chemical Ideas' - Burton, Holman, Pilling and Waddington
(2) 'Chemistry in Action' - Michael Freemantle
(3) 'Chemistry in Context' - Graham Hill and John Holman
(4) 'A-level Chemistry' - E.N.Ramsden
(5) www.wantwit.com/chem/kinetics
(6) www.avogadro.co.uk/kinetics

Graph 1 - preliminary results, the time taken for the mixture to go colourless using different concentrations of potassium bromide

KEY

X—X—X	shaking by hand
•—•—•	using magnetic stirrer
+—+—+	no stirring

% concentration of potassium bromide

time taken for the mixture to go colourless (seconds)

Implementing and Analysing

First a preliminary experiment was carried out and the results were recorded in my planning. This preliminary experiment allowed me to determine the most appropriate method in order to get the most accurate results. The method was as reliable as possible given the conditions and equipment and the experiment was carried out in a systematic and methodical manner. Some modifications had to be made to improve the method particularly when temperature was varied and safety issues were taken into account at all times.

In all 4 variables were altered, they were:
- concentration of potassium bromide solution.
- concentration of potassium bromate(V) solution.
- concentration of sulphuric acid solution.
- temperature at which the reaction was carried out.

Results when the concentration of potassium bromide solution was varied

The results were recorded correct to one decimal place. This is because it was not possible to determine exactly when the mixture had fully decolourised, it was therefore inappropriate to use more than one decimal place. Human reaction times also have a slight effect on the results so I feel that although the stopwatch could record to 2 decimal places if needed, one was more than satisfactory in this experiment. The concentration of potassium bromide solution has been shown in the table in mol dm-3. The concentration had to be worked out as the concentration within the overall mixture. The calculation used was:

overall concentration = concentration of KBr (mol dm-3) X $\frac{\text{volume of KBr}}{\text{total volume}}$

e.g. 0.01 (mol dm-3) X (10/45) = 0.00222

A table to show the time taken for the mixture to decolourise as the concentration of potassium bromide solution is varied.

concentration of potassium bromide solution (mol dm-3)	time taken for the complete mixture to decolourise (seconds)			average time taken for the mixture to decolourise (seconds)	reaction rate = (1/time) units are seconds-1
	trial 1	trial 2	trial 3		
0.00222	34.9	35.6	34.1	34.9	0.0286
0.00177	45.3	43.2	45.9	44.8	0.0223
0.00133	53.6	52.7	54.0	53.4	0.0187
0.00111	63.5	64.4	64.9	64.2	0.0156
0.000888	86.1	84.8	83.7	84.9	0.0118
0.000666	112.7	109.8	114.2	112.2	0.0089

I did 3 trials for each concentration in order to get a reliable set of results but took the average of all 3 in order to work out reaction rate. Reaction rate is more appropriate to

plot on a graph than the time taken for the solution to decolourise. This is because from the graph of reaction rate against concentration the order of the reaction can easily be determined. There are several improvements that could be made to graph 1 showing my preliminary results. Firstly as concentration is being varied it is the independent variable and should therefore be plotted on the x-axis. Also I have plotted percentage concentration of potassium bromide instead of the actual concentration (in mol dm-3) within the mixture. I will take into account these improvements when I plot a graph of my actual results.

Graph 2 shows that when concentration is plotted against the time taken for the mixture to decolourise we get a smooth curve. There is a negative correlation which shows that as concentration decreases reaction time increases. It is not possible however to work out information about the rate equation from graph 2. For this graph 3 must be referred to. On this graph:
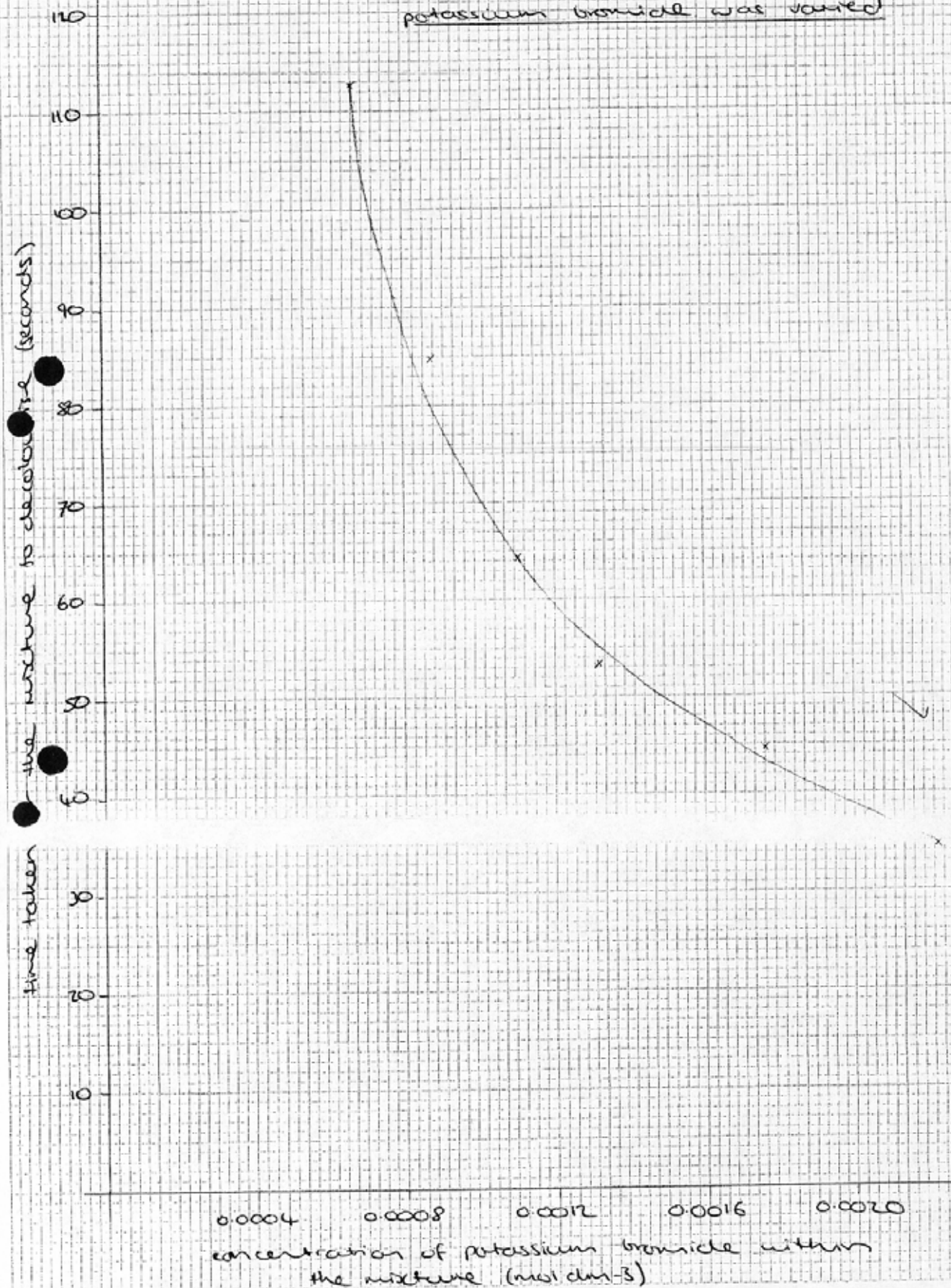
rate $\propto$ [Br⁻]

or

rate = constant $\times$ [Br⁻]

So the reaction is first order with respect to potassium bromide.

The graphs of rate against concentration have a line of best fit going through the origin. I know the line would go through the point (0,0) as if the concentration was nothing then the reaction would not occur and the reaction rate would also be nothing.

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Graph 2 - A graph showing concentration against
reaction time when the concentration of
potassium bromide was varied

the mixture to decolourise (seconds)

time taken

concentration of potassium bromide within
the mixture (mol dm-3)

0.0004   0.0008   0.0012   0.0016   0.0020

Graph 3 - A graph to show concentration of potassium bromide against reaction rate when the concentration is varied.

reaction rate ($\frac{1}{time}$) seconds^{-1}

concentration of potassium bromide within the mixture (mol dm^{-3})

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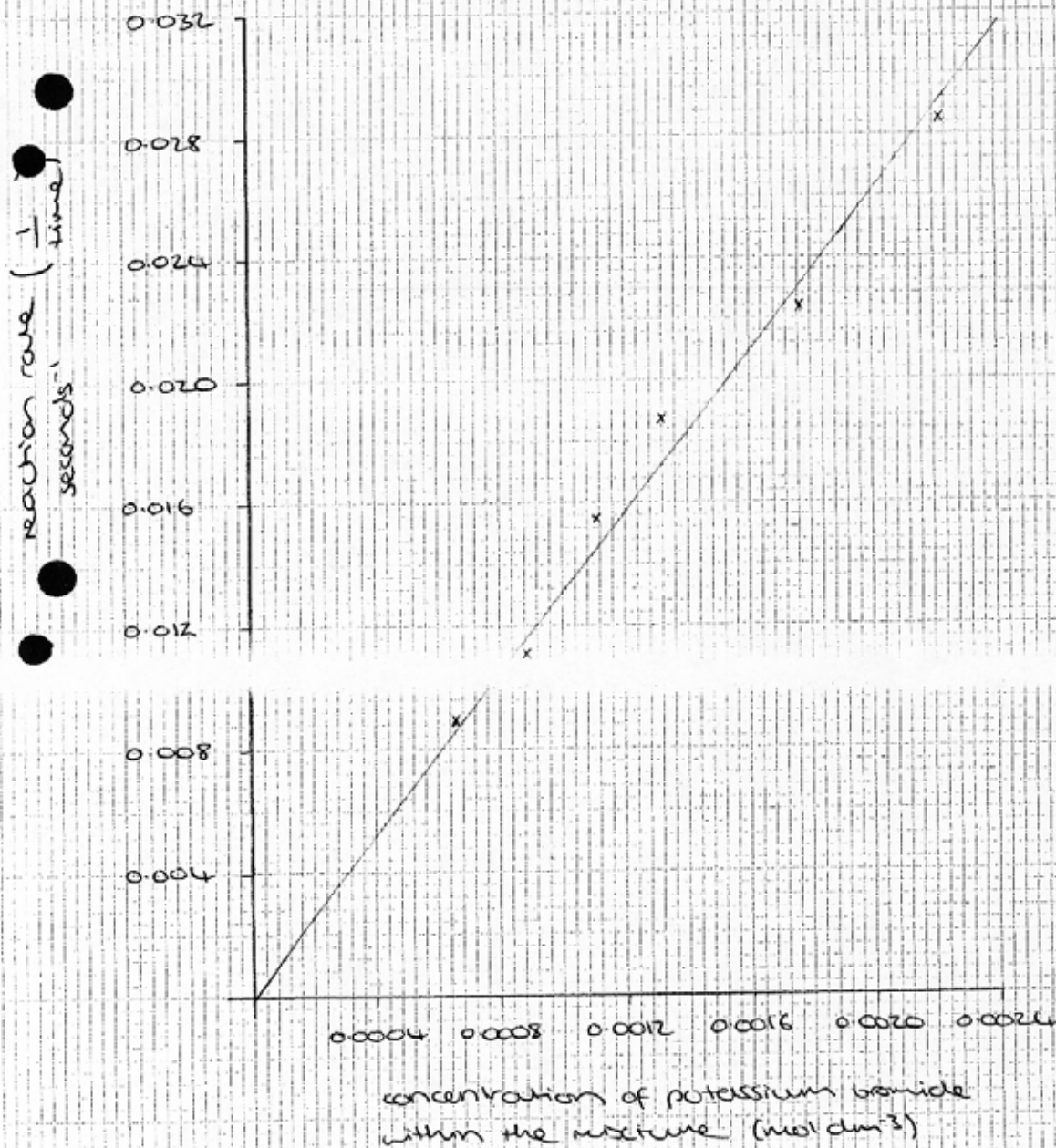
Results when the concentration of potassium bromate(V) was varied

In my planning I stated that I wanted to vary the concentration of all 3 reactants in order to determine the rate equation. Potassium bromate(V) solution was the next to be altered, whilst this was being altered all other variables had to remain constant as only one variable may be changed at once.

A table to show the time taken for the mixture to decolourise when the concentration of potassium bromate(V) solution is varied

concentration of potassium bromate(V) solution (mol dm-3)	time taken for the complete mixture to decolourise (seconds)			average time taken for the mixture to decolourise (seconds)	reaction rate (1/time) units are seconds-1
	trial 1	trial 2	trial 3		
0.00111	38.7	36.9	38.1	37.9	0.0264
0.000888	46.6	47.5	44.9	46.3	0.0216
0.000666	61.3	60.7	58.8	60.2	0.0166
0.000555	82.1	79.4	78.6	80.0	0.0125
0.000444	100.2	97.2	101.4	99.6	0.0100
0.000333	121.1	123.8	116.7	120.5	0.0083

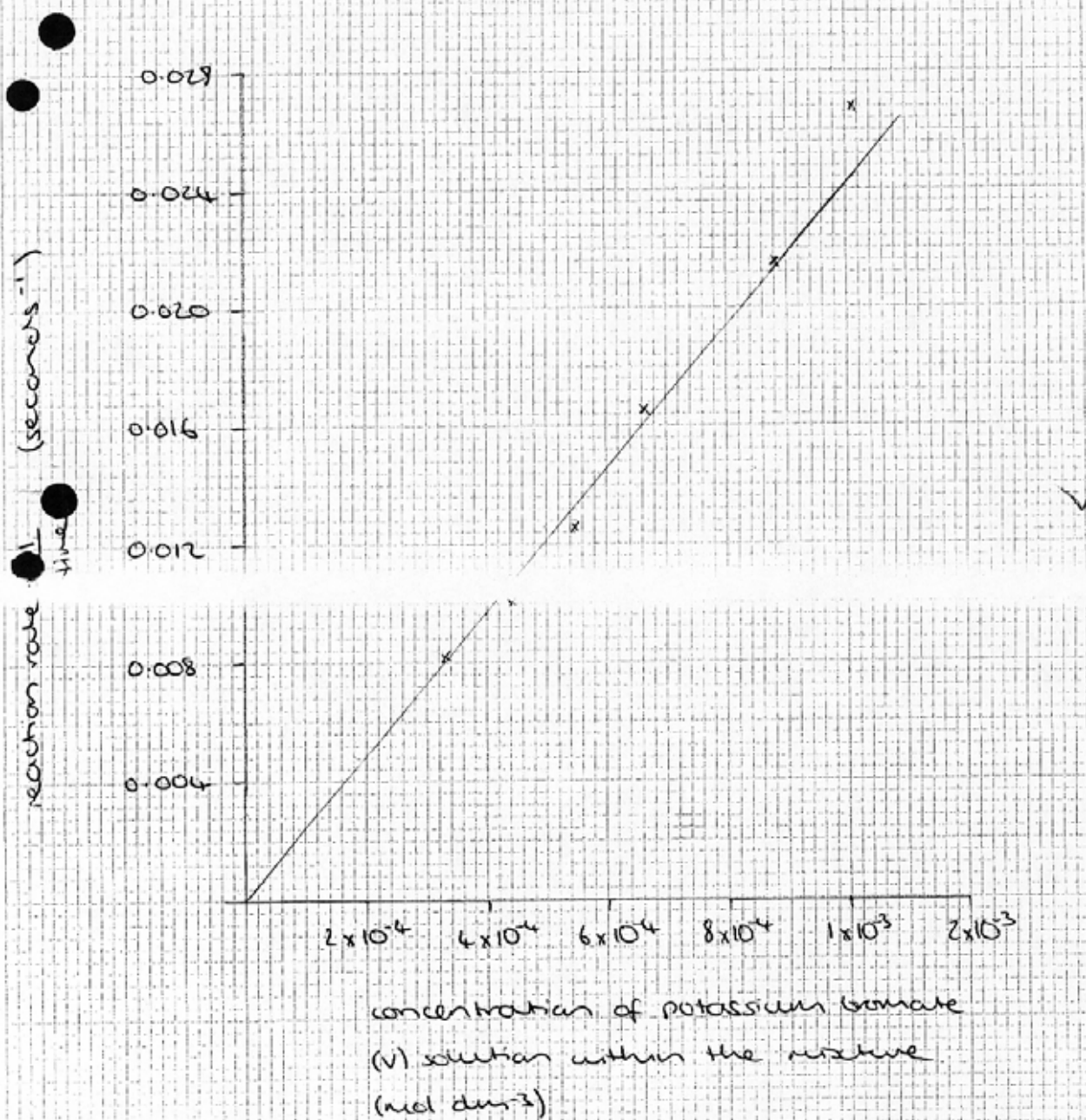These results have been plotted on graph 4. From this graph I can see that:

rate $\propto [BrO_3^-]$
or
rate = constant $\times [BrO_3^-]$
So if the concentration of potassium bromate(V) solution is doubled the reaction rate will also double. This shows that the reaction is first order with respect to potassium bromate(V) solution.

Graph 4 - A graph to show concentration against reaction rate as the concentration of potassium bromate (V) is varied.

concentration of potassium bromate (V) solution within the mixture (mol dm^{-3})

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Results when the concentration of sulphuric acid solution was varied

concentration of sulphuric acid solution (mol dm-3)	time taken for the complete mixture to decolourise (seconds)			average time taken for the mixture to decolourise	reaction rate (1/time) units are seconds-1
	trial 1	trial 2	trial 3		
0.333	33.8	28.9	32.4	31.7	0.0315
0.266	(87.6)	49.9	43.2	46.5	0.0215
0.200	69.6	62.3	64.5	65.4	0.0153
0.166	90.1	93.6	93.9	92.5	0.0108
0.133	-------------	-------------	-------------	-------------	-------------
0.100	-------------	-------------	-------------	-------------	-------------

When the concentration of sulphuric acid was varied the reaction took a lot longer than when the concentrations of the other reactants were varied. I therefore decided not to do below 7.5cm³ of sulphuric acid (0.166 mol dm-3). This left only 4 sets of results so 13.5 and 10.5cm³ of sulphuric acid were used as well. The results are shown below.

A table to show the extra concentrations at which the reaction was carried out

volume of sulphuric acid (cm³)	volume of water (cm³)	concentration of sulphuric acid solution (mol dm-3)	time taken for the complete mixture to decolourise (seconds)			average time taken for the mixture to decolourise (seconds)	reaction rate (seconds -1)
			trial 1	trial 2	trial 3		
13.5	1.5	0.300	36.8	37.2	37.5	37.2	0.0269
10.5	4.5	0.233	44.0	54.1	52.6	50.3	0.0199

The point circled in my table has been left out when working out reaction rate and plotting the graph as it is clearly an anomalous result. Graph 5 shows that the results do not lie on a straight line through the origin when the concentration of sulphuric acid is varied. It is evident that the points would be better if joined with a smooth curve. These results suggest that the reaction could be second order with respect to the concentration of sulphuric acid. So I have plotted reaction rate against concentration squared to see if it is a straight line. (see graph 6)

A table to show the concentration of sulphuric acid squared and reaction rates

concentration of sulphuric acid solution (mol dm-3)	concentration of sulphuric acid solution squared (mol dm-3)	reaction rate (1/time) units are seconds-1
0.333	0.111	0.0315
0.300	0.090	0.0269
0.266	0.711	0.0215
0.233	0.0544	0.0199
0.200	0.0400	0.0153
0.166	0.0277	0.0108

When the concentration squared was plotted against reaction rate the results were not exactly on a straight line. My evidence is therefore not conclusive and I cannot tell from graphs 5 and 6 whether the reaction is first or second order with respect to the concentration of sulphuric acid. I have therefore plotted a graph of log rate against log concentration and the gradient should give me the order of reaction.

A table to show my calculated values for log to the base e of concentration and log to the base e of reaction rate
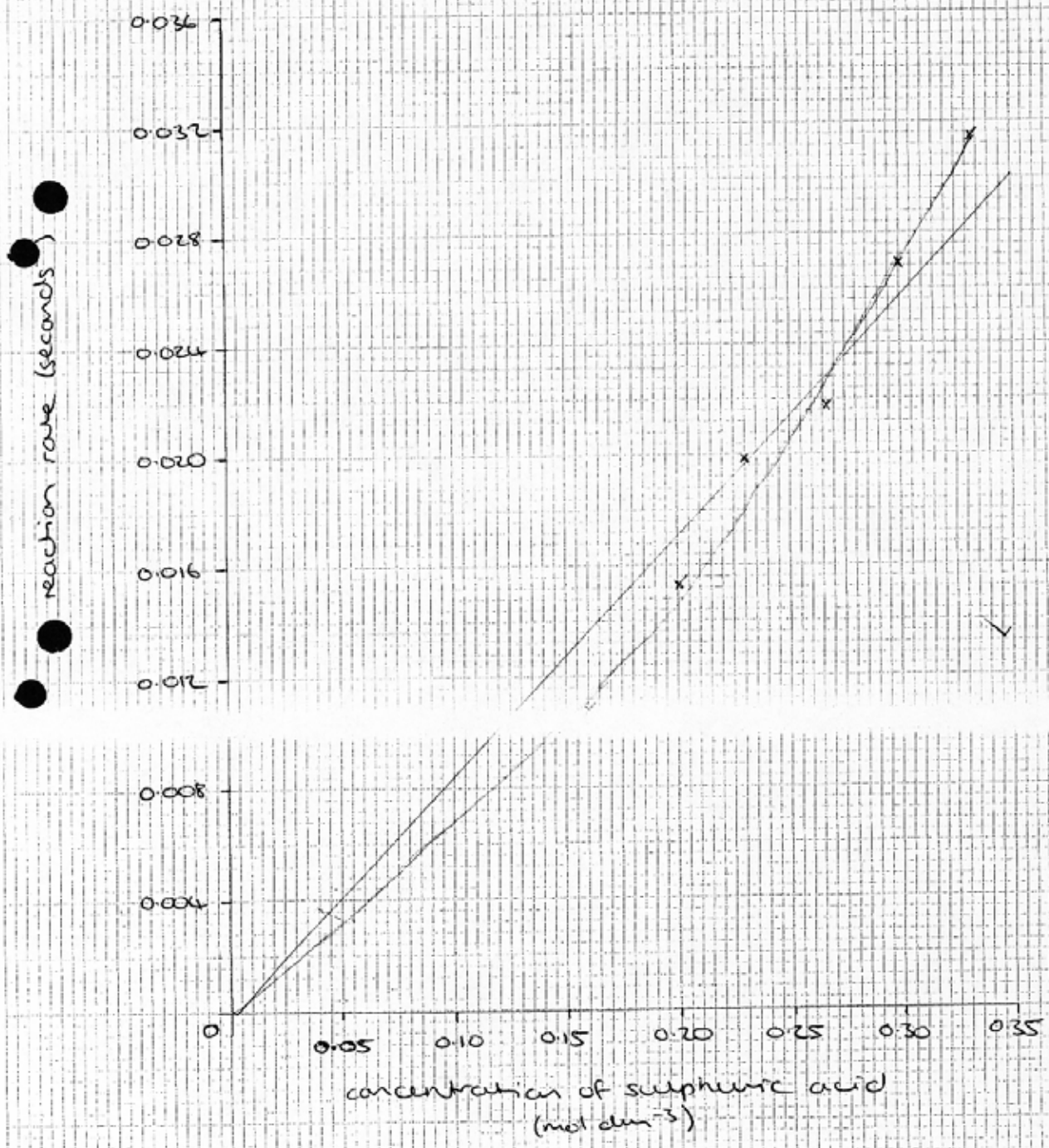
concentration of sulphuric acid solution within the mixture (mol dm-3)	log to the base e of the concentration of sulphuric acid solution	rate of reaction (seconds-1)	log to the base e of rate of reaction
0.333	-1.0996	0.0315	-3.4578
0.300	-1.2039	0.0269	-3.6156
0.266	-1.3243	0.0215	-3.8397
0.233	-1.4567	0.0199	-3.9170
0.200	-1.6094	0.0153	-4.1799
0.166	-1.7958	0.0108	-4.5282

Graph 7 shows the results immediately above. I have drawn a triangle to the line of best fit in order to work out gradient.

$$\text{gradient} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$= \frac{-3.6 - -4.2}{-1.2 - -1.6} \qquad = \frac{0.6}{0.4} \qquad = 1.5$$
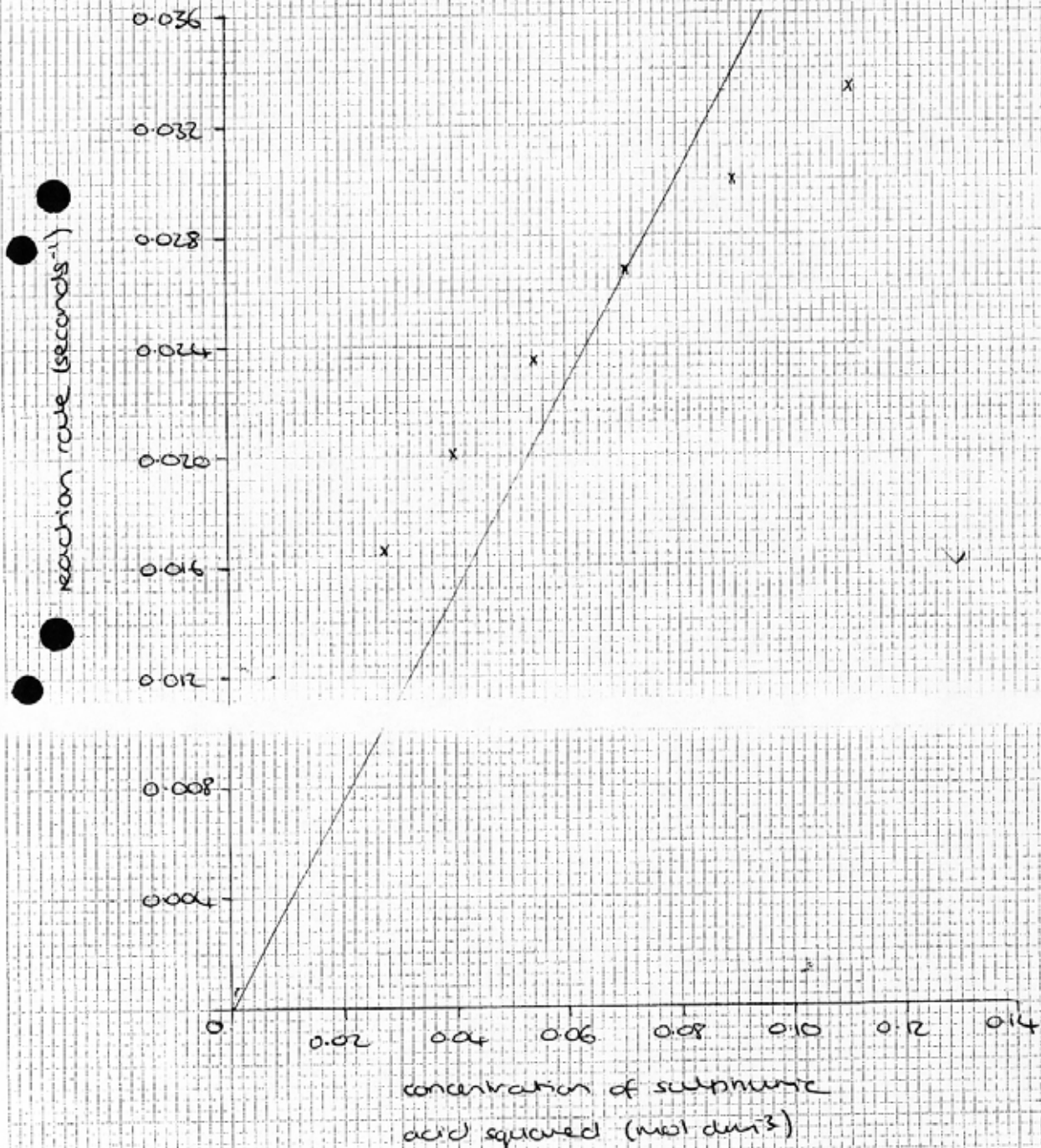
From this I have calculated that the order of reaction with respect to the concentration of sulphuric acid is 1.5, however I know from my research and background knowledge that this value should be 2.

Graph 5 - A graph showing the concentration of sulphuric acid plotted against reaction rate when concentration was varied
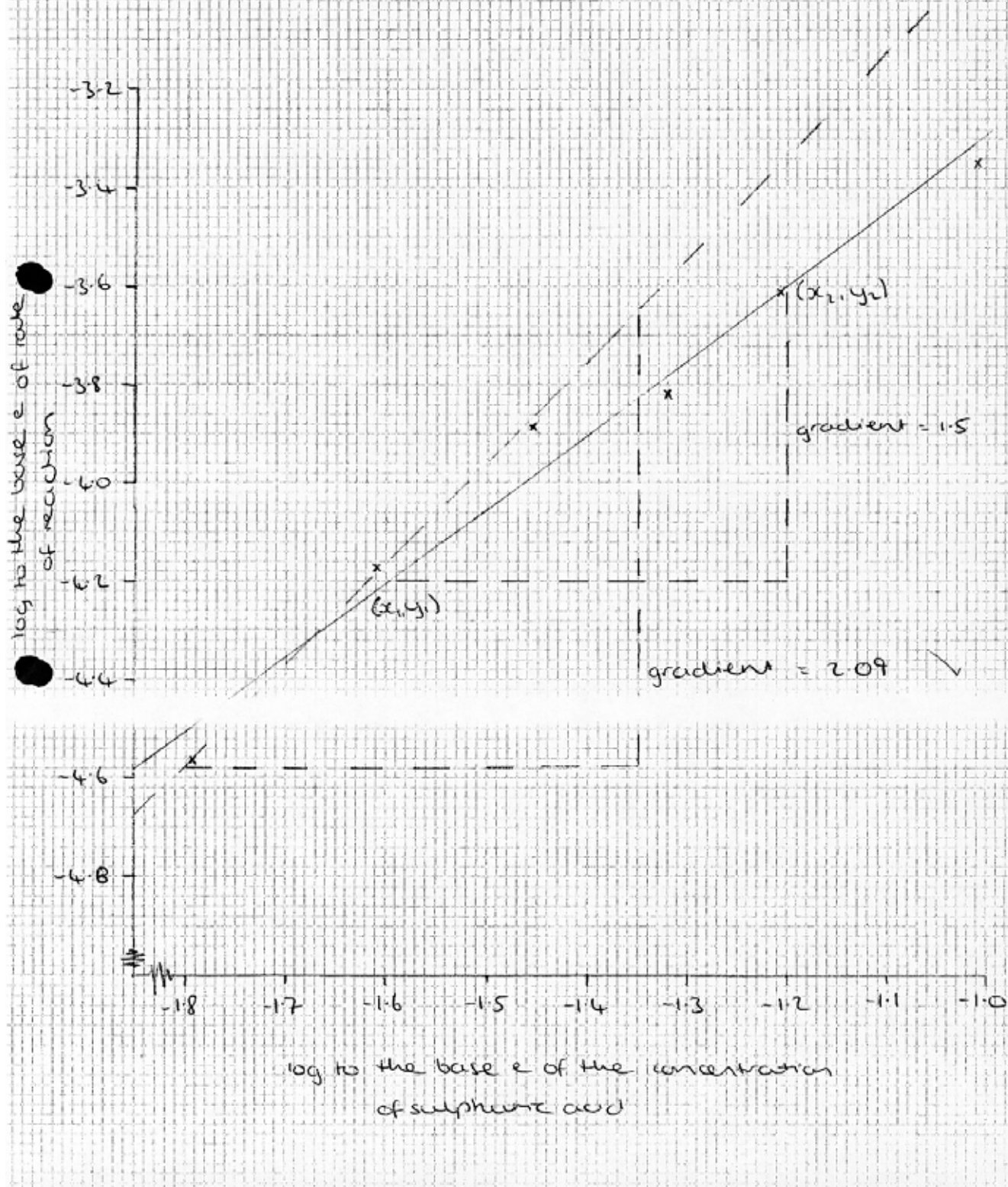
reaction rate (seconds)

concentration of sulphuric acid
(mol dm⁻³)

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Graph 6 - A graph to show concentration of sulphuric acid squared plotted against reaction rate when the concentration was varied.

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Graph 7 - A graph to show the gradient
of the line when log of rate is plotted
against log of temperature.

gradient = 1.5

gradient = 2.09

(x_1, y_1)

(x_2, y_2)

log to the base e of rate of reaction

log to the base e of the concentration
of sulphuric acid

I have now proved the rate equation experimentally. k in the equation, the rate constant is a constant for a given reaction at a particular temperature. Using my values for the concentrations of the reactants at a certain temperature I should be able to calculate k.

$[Br^-]$ $= 0.01$ mol dm^{-3}
$[BrO_3^-]$ $= 0.005$ mol dm^{-3}
$[H^+]^2$ $= 0.1^2$
$= 0.01$ mol dm^{-3}

At 20 C I calculated the reaction rate to be 0.0231 seconds. Using these values I can substitute them into the rate equation and re-arrange to make k the subject.

reaction rate $= k[Br^-][BrO_3^-][H^+]^2$

$k = \dfrac{\text{reaction rate}}{[Br^-][BrO_3^-][H^+]^2}$

$k = \dfrac{0.0231}{(0.01)(0.005)(0.01)}$

$k = \dfrac{0.0231}{5 \times 10^{-7}}$

$k = 46200$

The units of k vary depending on the particular reaction in this case they are:

$k = \dfrac{(\text{mol } dm^{-3})\text{ seconds}^{-1}}{(\text{mol } dm^{-3})(\text{mol } dm^{-3})(\text{mol } dm^{-3})^2}$

$k = 46200 \text{ s}^{-1}\text{mol}^{-3}\text{dm}^{9}$

A change in temperature alters the value of k.

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Results when the temperature at which the reaction occurred was varied

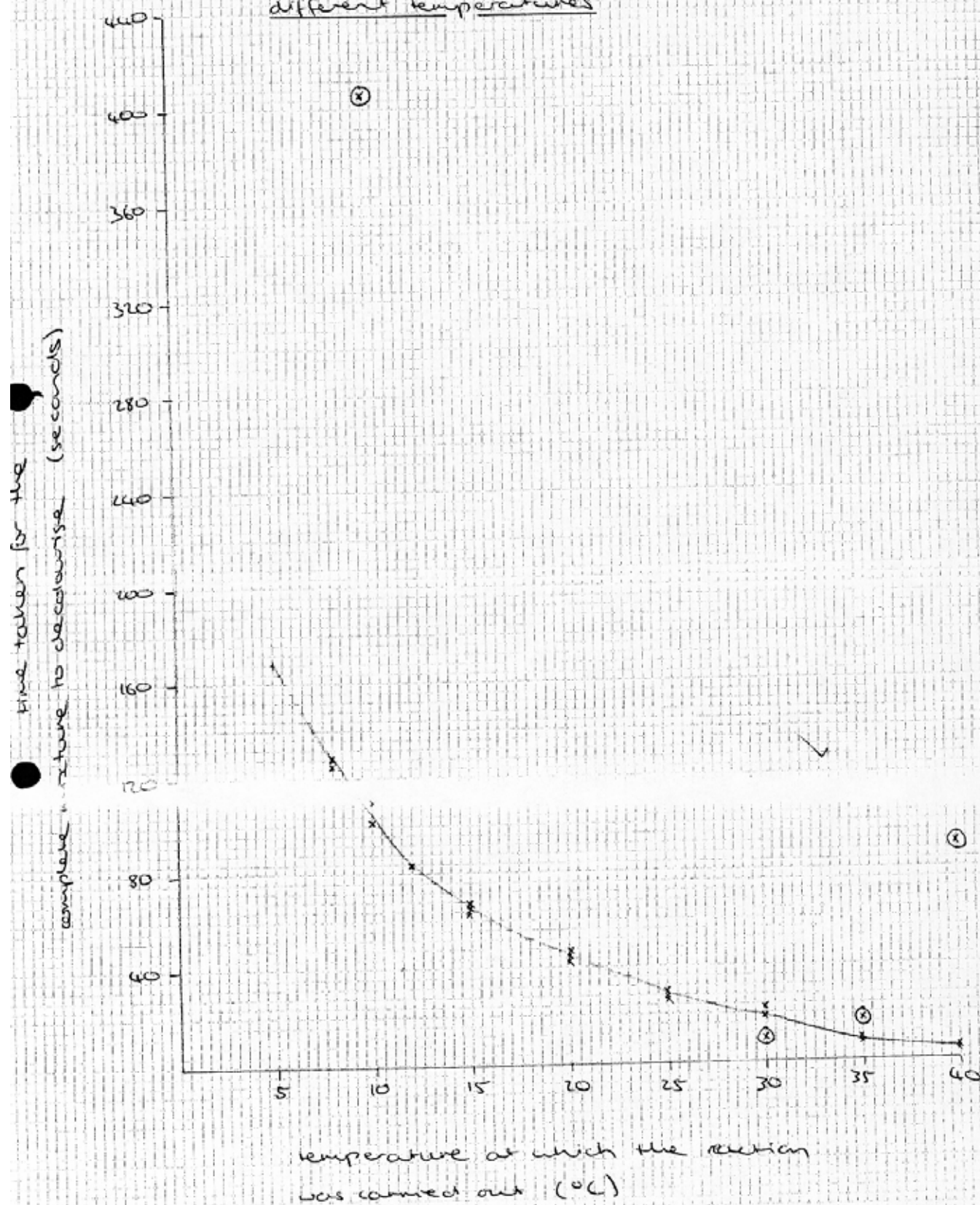| temperature at which the reaction was carried out (°C)	time taken for the complete mixture to decolourise (seconds)			average time taken for the mixture to decolourise (seconds)	reaction rate (1/time) units are seconds-1
	trial 1	trial 2	trial 3		
8	128.9	125.4	------------------	127.1	0.00787
10	103.3	(405.2)	110.9	107.1	0.00934
12	82.6	------------------	------------------	82.6	0.0121
15	62.3	66.7	65.9	64.9	0.0154
20	43.4	42.4	44.2	43.3	0.0231
25	28.4	29.5	29.2	29.0	0.0345
30	23.6	19.4	(10.1)	21.5	0.0465
35	(17.5)	9.6	10.7	10.1	0.0990
40	(90.2)	6.5	5.8	6.1	0.164

In my planning I decided to also vary the temperature at which the experiment was carried out as I know from my background knowledge that a rise in temperature should cause the reaction to proceed more quickly. First I have plotted all of the results against temperature in order to identify any anomalous results. There were several measurements that did not fit into the recognised pattern. These results have been circled in the above table. All the results were converted into seconds in order to work out the average time taken for the mixture to decolourise and that reaction rate. I have re-investigated these anomalous results and ignored them when working out averages. I carried out 2 more trials at each of the temperatures with a result that did not fit the pattern to ensure I had 3 results within experimental error of each other. The results for these re-runs are shown below.

A table to show my results when the reaction was repeated at certain temperatures

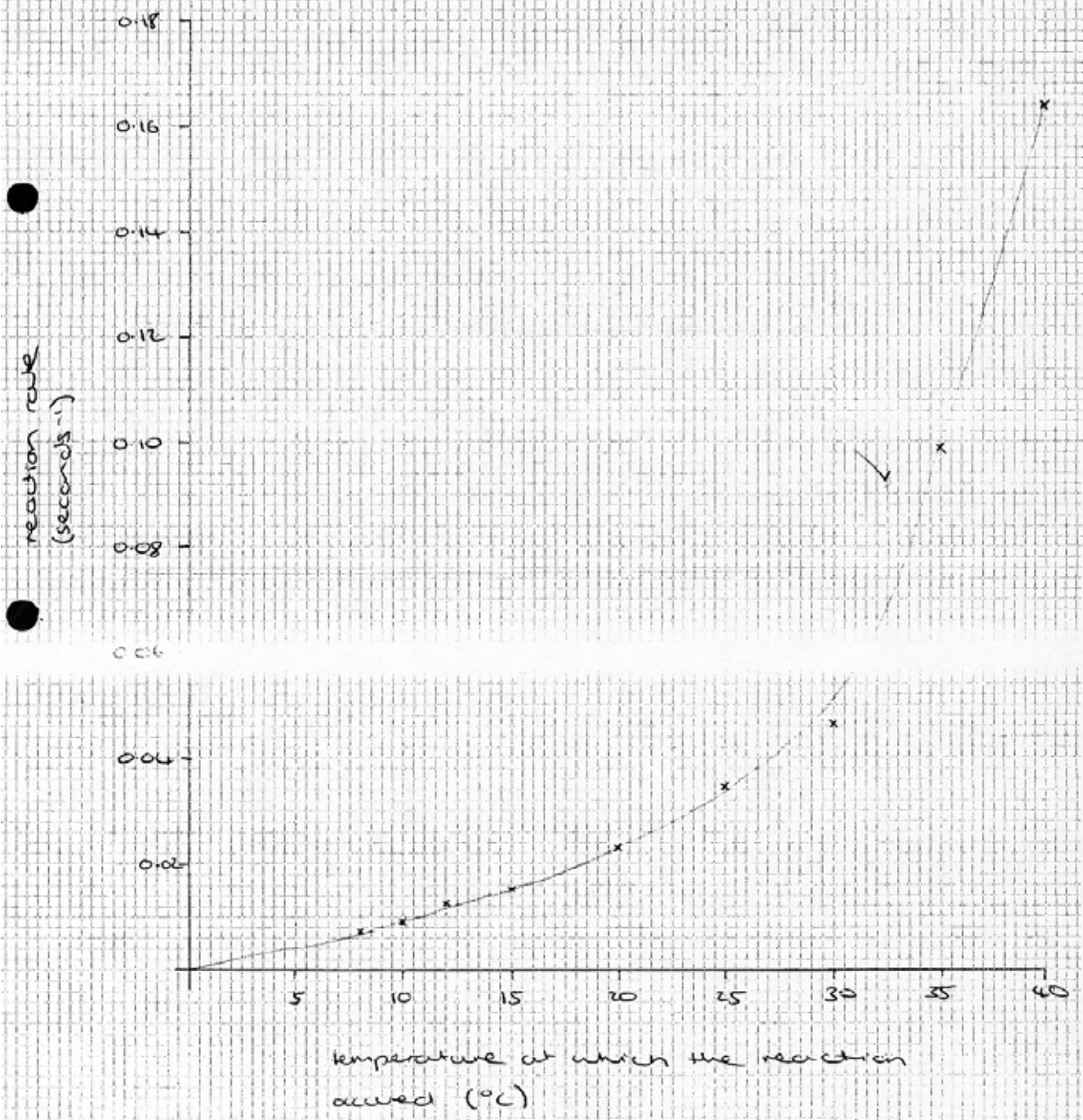| temperature at which the experiment was carried out (°C)	time taken for the mixture to decolourise (seconds) trial 1	time taken for the mixture to decolourise (seconds) trial 2
10	106.4	111.2
30	22.6	21.0
35	11.7	9.9
40	4.9	6.1

It is evident from these extra trials that the results circled are not accurate due to various reasons such as the solutions becoming contaminated for example. The reasons for these anomalous results will be discussed in detail in my evaluation.

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Graph 8 – A graph to show the time it took the mixture to decolourise at different temperatures

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Graph 9 - A graph show the affects of
temperature on rate of reaction

reaction rate
(seconds⁻¹)

0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02

5   10   15   20   25   30   35   40

temperature at which the reaction
occured (°C)

Now I have a set of results for when temperature was varied I can use my results and the Arrhenius equation to calculate activation enthalpy.

At a given temperature rate of reaction is proportional to $e^{-Ea/RT}$
where,
R is the universal gas constant $8.3jk^{-1} \, moles^{-1}$
Ea is activation energy
T is absolute temperature (helium)

as the rate of reaction can be represented by k.
$$k \propto e^{-Ea/RT}$$
or
$$k = Ae^{-Ea/RT}$$

This last equation is known as the Arrhenius equation and A is the Arrhenius constant. This can be regarded as a collision frequency and orientation factor in the reaction rate.
Taking the log (base e) form of the equation. log to the base e is known as the natural log and is denoted by ln.

$$\ln k = \ln A - \frac{Ea}{RT}$$

Rearranging in th form $y = mx + c$

$$\ln k = -\frac{Ea}{R} \times \frac{1}{T} + \ln A$$

I can now substitute my value for reaction rate (1/time) for ln k. A graph of ln k against 1/T should be a straight line with gradient $-\frac{Ea}{R}$

This gradient can be measured and from this activation energy can be calculated.

This table shows the values for log to the base e of reaction rate and 1/absolute temperature

temp. at which the reaction occurred (^{o}C)	absolute temperature equivalent (k)	1/absolute temperature (k^{-1})	Rate of reaction (s^{-1})	log to base e of rate of reaction
10	283	0.00353	0.00934	-4.673
15	288	0.00347	0.0154	-4.173
20	293	0.00341	0.0231	-3.768
25	298	0.00336	0.0345	-3.367
30	303	0.0033	0.0465	-3.068
35	308	0.00325	0.099	-2.313
40	313	0.00319	0.164	-1.808

These results have been plotted on graph 9. From this graph I can see that there is a strong negative correlation. The line of best fit therefore has a negative gradient. A triangle has been drawn to this line in order to calculate the gradient.

$$\text{gradient} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$= \frac{-4 - -1.95}{0.00345 - 0.0032}$$

$$= \frac{-2.05}{0.00025}$$

$$= -8200$$

$$\text{gradient} = -\frac{E_a}{R} = -8200$$

$$R = 8.3 \text{ J k}^{-1}\text{moles}^{-1}$$

$$-E_a = \text{gradient} \times R$$

$$= -8200 \times 8.3$$

$$= -68060$$

$$= 68060 \text{ J moles}^{-1}$$

to convert to kJ moles^{-1}

$$\frac{68060}{1000} = 68.06 \text{ kJ moles}^{-1}$$

Graph 10 - A graph to show the gradient when 1/absolute temperature is plotted against the log of reaction rate

gradient = -8200

(y_1, x_1)

(x_2, y_2)

ln k

log to the base e of reaction rate

-1
-2
-3
-4
-5

0·0030 0·0031 0·0032 0·0033 0·0034 0·0035 0·0036

1 / absolute temperature (Kelvin)

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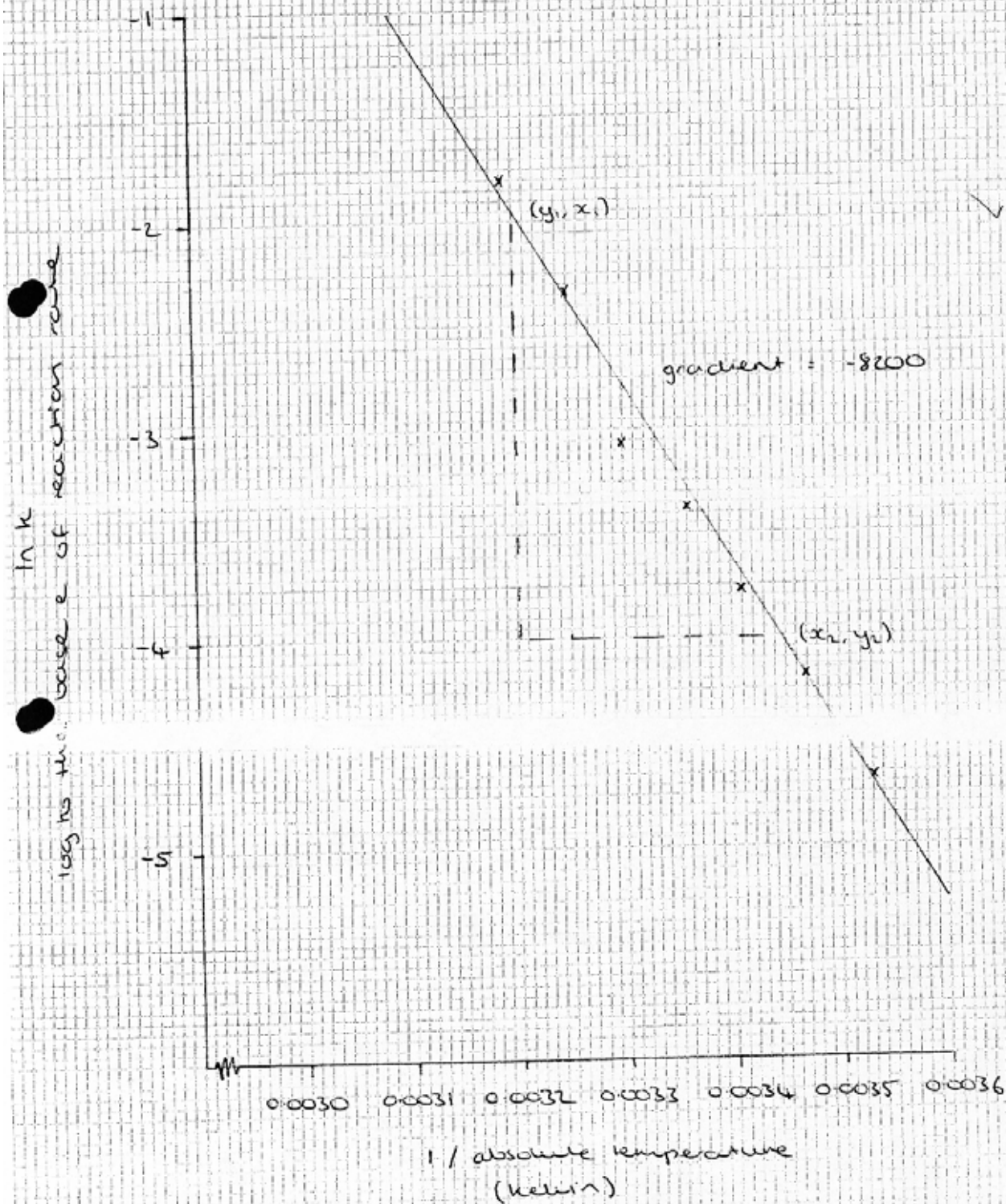
Conclusions

All my results have now been tabulated. Appropriate graphs have been drawn and my results have been processed to work out information such as the rate equation, rate constant and the activation enthalpy.

Four different sets of results were obtained in all. The first 3 of these involved varying the concentration. In general I found that at lower concentrations the reaction took longer to complete as the mixture was slower to decolourise. This can be explained by referring to the collision theory. As I explained in my planning when the concentration is lower there are less reactant molecules they are therefore less likely to collide. If the molecules do not collide as often then they will react less often and the reaction will proceed more slowly. On graph 2 the concentration of potassium bromide has been plotted against the reaction time and it is clear that there is a negative correlation, as concentration decreases reaction time increases.
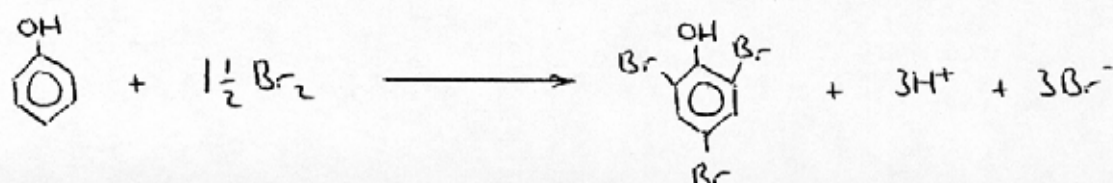
The reaction rate can be worked out by doing the calculation 1/reaction time. The reaction rate was calculated for all sets of results and graphs of concentration against reaction rate were plotted. From these graphs it is possible to determine the order of the reaction. I know through my research that my reaction should be first order with respect to both potassium bromide and potassium bromate(V) solution and second order with respect to sulphuric acid. I proved the first order reactions through my graphs, it was however more difficult proving that the reaction was second order with respect to the concentration of sulphuric acid. This was because all my results suggested that the order was 1.5 When rate was plotted against concentration I got a curve sloping upwards. But I also got a curve when concentration squared was plotted but it was sloping the other way. This suggested to me that the order of reaction was between 1 and 2. To verify this I plotted log of concentration against log rate and measured the gradient. This gradient is equal to the order of reaction and the gradient I calculated was 1.5. I checked this to ensure my calculations were correct but I know that this value should be equal to 2. This inconsistency may be something to do with the mechanism of the reaction or the fact that only ions appear in the rate equation. Reasons for this have been discussed in more detail in my evaluation. For the rest of the experiment I have taken the text book value of 2 to be correct and used this when calculating other information. To work out the overall order the orders with respect to each reactant are added together so it is fourth order overall.

From the rate equation it is possible to see how many of each ion is involved in the rate determining step. This is done by looking at the power to which each concentration is raised. For example the reaction is second order with respect to H+ so there are 2 H+ ions in the rate determining step. The rate determining step is the slowest step in the mechanism. Most chemical reactions that proceed at a measurable rate are believed to take place in a series of steps. "This series of simple reactions is known as the reaction mechanism." (3) The series of steps must satisfy both the rate and stoichiometric equation. The equations for this reaction are:

$$5Br^- \; + \; BrO_3^- \; + \; 6H^+ \longrightarrow 3Br_2 \; + \; 3H_2O$$
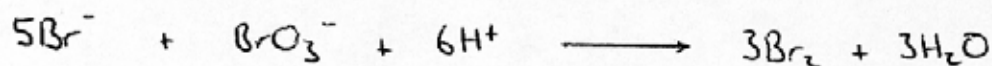
the bromine formed then reacts with phenol:
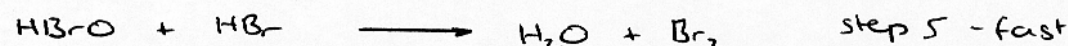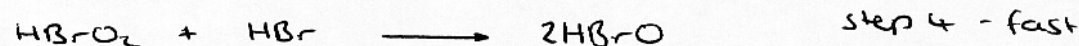

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the rate equation is :

$$\text{rate} = k[Br^-][BrO_3^-][H^+]^2$$
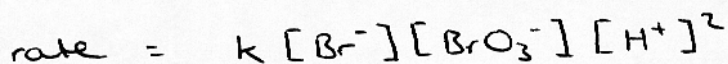
From this rate equation I can see that the rate determining step involves one Br^- ion, one BrO_3^- ion and 2 H+ ions. As the reaction is fourth order overall this suggests that these ions all collide simultaneously. This is, however very unlikely. It is more likely that the slow rate determining step is preceded by faster reactions. Based on this a suggested mechanism is:

$$H^+ + Br^- \longrightarrow HBr \qquad \text{step 1 - fast}$$
$$H^+ + BrO_3^- \longrightarrow HBrO_3 \qquad \text{step 2 - fast}$$
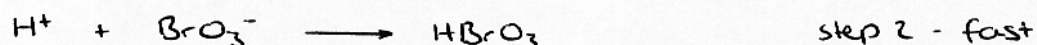
The 2 substances formed then react in the slow rate-determining step.

$$HBr + HBrO_3 \longrightarrow HBrO + HBrO_2 \qquad \text{Step 3 - slow}$$
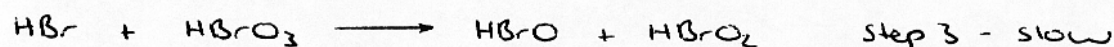
The HBrO and $HBrO_2$ produced in the slow rate-determining step can then react with more HBr forming bromine and water.

$$HBrO_2 + HBr \longrightarrow 2HBrO \qquad \text{step 4 - fast}$$
$$HBrO + HBr \longrightarrow H_2O + Br_2 \qquad \text{step 5 - fast}$$

Mechanisms cannot be proved they are simply suggestions based on chemical knowledge and understanding.
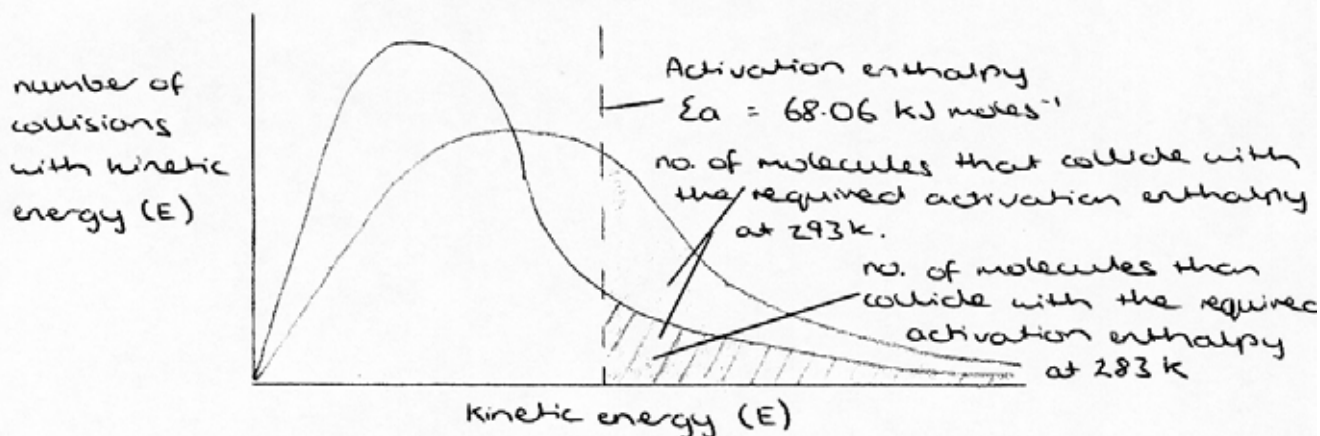
The temperature at which the experiment was carried out was also varied. From my background knowledge I know that temperature has a significant effect on reaction rate. From my results it is clear that as temperature is increased the reaction proceeds faster. The effects of a small rise in temperature are important in terms of reaction rate. A rise in temperature from just 10 to 20°C caused the average reaction time to fall from 107.1 to 43.3 seconds. A drop of 63.8 seconds. The reasons for this can also be explained by the kinetic theory. When the temperature is increased the molecules move faster, this means they collide more often causing an increase in reaction rate. But the effect of temperature is not just due to this. The molecules collide more often but they also collide with more energy. The increase in temperature means that more molecules will collide with the activation energy required to result in a reaction.
By plotting the reciprocal of the absolute temperature against log to the base e of reaction rate I have obtained a graph with the gradient $\frac{-Ea}{R}$

From this graph the gradient was measured and activation energy was calculated. I expected this value to be somewhere between 40 and 100 and it worked out to be 68.06 KJ moles⁻¹. Raising the temperature means that more pairs of molecules will collide with at least this amount of energy and the reaction will proceed faster. The Maxwell-Boltzmann distribution illustrates this effect.

The Maxwell-Boltzmann distribution showing the number of molecules that collide with Ea

number of collisions with kinetic energy (E)

Activation enthalpy
Ea = 68.06 kJ moles⁻¹

no. of molecules that collide with the required activation enthalpy at 293k.

no. of molecules than collide with the required activation enthalpy at 283 k

kinetic energy (E)

If the temperature at which the reaction occurs falls by just 10°C from 20 to 10°C the reaction time is more than doubled. As proved by my calculations below.

At 10°C reaction time is 107.1 seconds
At 20°C reaction time is 43.3 seconds

43.3 x x = 107.1

$$x = \frac{107.1}{43.3}$$

x = 2.473

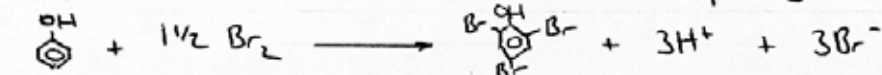So the percentage increase is 247%

The reaction time increases by 247% for just a 10°C fall in temperature so the effects of temperature are obviously very important.

When the temperature was 20°C I used my calculated reaction rate to work out the value of k, the rate constant. The value I got was 46200 s⁻¹mol⁻¹dm¹². This value only applies for this reaction at this temperature as the value of k alters with temperature. A change in concentration however will not affect the value of the rate constant. The units of k also change according to the particular reaction and must always be calculated.

I found that I could not carry out my reaction at temperatures above 40°C. This is because the reaction was going too fast making the reaction time too short. It was too difficult and inaccurate to measure so I chose not to use temperatures above 40°C. I also found that when I attempted to do the experiment at 50°C the mixture would start to decolourise before the potassium bromide was added. The chemical equation for the reaction is:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

the bromine formed then reacts with phenol

$$\text{(phenol)} + 1\frac{1}{2} Br_2 \longrightarrow \text{(tribromophenol)} + 3H^+ + 3Br^-$$

The bromine formed reacts with the phenol until it has all been used they then react with and decolourises the methyl orange indicator. I did not know what caused the mixture to decolourise at this high temperature as the potassium bromide solution was supposed to be the source of bromine. It is possible that the apparatus or solutions could have become contaminated or the potassium bromate(V) solution could have in some

way decomposed to produce the bromine. This could then react with and decolourise the methyl orange indicator but this, however only happened at higher temperatures. When temperature was varied I obtained several anomalous results. These results do not fit in with the overall trend and have been circled in both my table and on my graph. I have ignored these results when calculating average reaction time and reaction rate. This is because they would have altered the general trend and it would have been difficult to identify any kind of pattern with these results included. I will attempt to explain these and any other problems with the experiment in my evaluation.

Evaluation

In general my experiment produced both reliable and accurate results. There were however some anomalous results as a result of certain limitations and problems with procedures. I will attempt to identify the major sources of error and suggest reasons for these results in this evaluation.

My initial method is recorded in my planning. This method was used in my preliminary experiment. Improvements were made to this method before the actual experiment was carried out. For example, it was hard to determine exactly when the mixture had fully decolourised. A white tile was therefore placed under the beaker so that any colour would be obvious against the white background. The method was the same for changing the concentrations of all reactants but the volumes were always made up to the same amount with distilled water in order to make it a fair test. When temperature was varied several alterations also had to be made.

Precision and reliability were taken into account at all times during the experiment. This is why burettes were used rather than measuring cylinders. The percentage error associated with a 50cm³ burette of grade B is ±0.1cm³. This is far more accurate than a measuring cylinder. When the volume used is larger the percentage error will be less. Volumes of 10 and 15cm³ were used when concentration was varied so the percentage errors were kept to a minimum whilst having volumes that were manageable. The volumes used were:

10cm³ potassium bromide solution
10cm³ potassium bromate(V) solution
10cm³ phenol solution
and 15cm³ sulphuric acid solution.

$$\text{percentage error} = \frac{\text{error}}{\text{measurement}} \times 100$$

So the errors were all 1% or less. This is a very small error and will have no significant effect on the results. When temperature was varied these volumes could not be used as they were unmanageable and could not be contained in the apparatus.

beaker

tripod

The total volume of 45cm³ could not be contained in the test-tube.
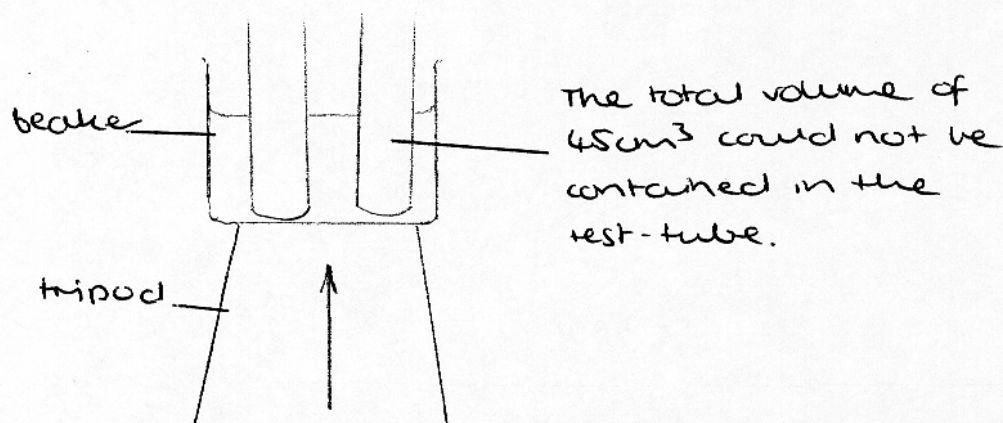
So all volumes were halved in order to keep the ratio the same. This meant the smallest volume measured was 5cm³ so the percentage error associated with measuring this

would be:

$$\% \text{ error} = \frac{0.1}{5.0} \times 100$$

$$= 2\%$$

This is still a small error and should not be a problem in the experiment. The errors associated with apparatus are often very small compared with those associated with procedures. It is difficult to find a value for errors incurred through procedures but the relative importance of them can be discussed.
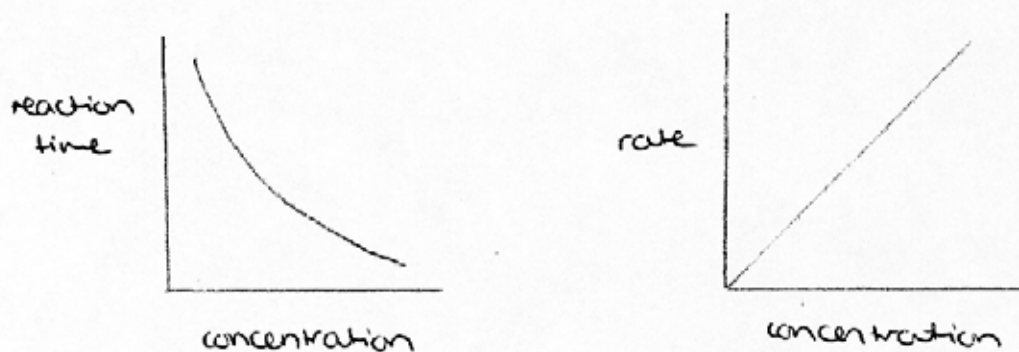
There are several ways of measuring rate, in this experiment the reaction has been studied as a clock reaction. This means the rate is measured by timing how long it takes to produce a small fixed amount of one of the products, in this case bromine. If the rate is high the reaction time is small as rate is the inverse of reaction time.

$$\text{rate} = \frac{1}{\text{reaction time}}$$

This method is effective as in this experiment the first bromine formed is destroyed by reaction with phenol which is deliberately added to the mixture. The next little bit of bromine formed triggers the clock by reacting with and decolourising methyl orange indicator. The amount of bromine required is the same in each trial so it is a fair test. This method gives more accurate results than the progress curve method as it is simple and a graph of rate against concentration will give the order of reaction. It does not rely on taking a series of measurements over the course of the reaction and I do not need to draw tangents to the curve to calculate the rate.

When the temperature at which the reaction occurred was varied some modifications had to be made to the method. As already mentioned the volumes had to be halved. Also I found that just measuring the temperature of the water in the beaker was not accurate enough as this did not necessarily mean that my solutions were also at this temperature. So I then put a thermometer in each test tube to make sure both solutions were at the correct temperature. My procedures were limited to the apparatus available at college and also to the time limit as the longest practical session available was about 80 minutes allowing for setting up and packing away.

In all four variables were altered. The first variable was the concentration of potassium bromide solution. My results have been tabulated and drawn on graphs of both reaction time against concentration and rate against concentration. The graphs looked like this:

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These results were exactly as I expected, they show that as concentration decreases reaction time increases. There were no anomalous results and my rate against concentration graph proved clearly that the reaction is first order with respect to the concentration of potassium bromide solution.

The concentration of potassium bromate(V) solution was also varied and the results recorded. As in all variables 3 trials were carried out at each concentration. This proved that the results were reliable as a result within experimental error could be obtained again. The average of these three trials was taken and from this reaction rate was calculated. There were no anomalous results and graph four shows that the reaction is first order with respect to potassium bromate(V) solution which is what I expected.

The last concentration to be varied was that of sulphuric acid. When this concentration was varied the reaction took a lot longer than when the concentrations of the other reactants were varied. I therefore decided not to use the same range of concentrations as with the other two variables and did not go below 0.166 mol dm-3 of sulphuric acid. Three trials were carried out as always and the average taken. In my results table one value has been circled, this is because it does not fit into the expected trend. When the concentration was 0.266 the times taken for the mixture to decolourise were recorded as 87.6, 49.9 and 43.2 seconds. 87.6 is clearly an anomalous result. I am not certain what caused this but can suggest some likely reasons. It is possible than the solution could have been made up wrongly and was actually at a lower concentration than it should have been, this would make the reaction proceed more slowly than expected. I think this is the most likely explanation. Other possibilities are that the solution had become contaminated making it react more slowly. This could have been due to not correctly washing out the apparatus, spillages or to inaccurate timing but I do not think these reasons would not cause such a large error. Because the error is so large this result has been ignored when calculating reaction rate.

Graphs 5, 6 and 7 show my results when the concentration of sulphuric acid was varied. From graphs 5 and 6 it is apparent that the reaction is neither first or second order. To verify this result the natural log of concentration was plotted against the natural log of rate and the gradient of the graph was measured. The value of this gradient should be the order of reaction and my calculated value was 1.5. This result was unexpected as I know from my background knowledge that the order with respect to sulphuric acid should be two and the reaction should be fourth order overall.

When I studied graph 7 carefully it became obvious that the first 3 points seem to be on a line with a steeper gradient than the final 3. This steeper gradient has been added to graph 7 as a dotted line. I have calculated the gradient of this line.
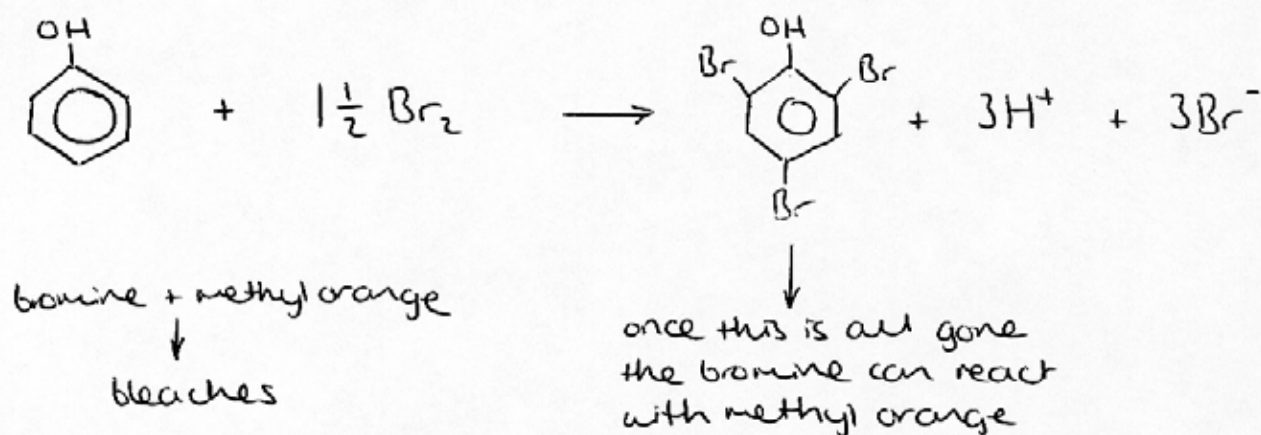
$$\text{gradient} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$= \frac{-3.64 - -4.58}{-1.35 - -1.8}$$

$$= \frac{0.94}{0.45}$$

$$= 2.09$$

The value calculated was just over 2 suggesting that within experimental error the reaction is second order with respect to the concentration of sulphuric acid. The last 3 results seem to show a systematic error as the results are consistently too small and the line has been shifted down. I think this is due to time constraints as we were not able to carry out all the trials in one lesson. The last three concentrations were investigated on a different day and the temperature in the laboratory could have been lower. This would make the reaction rate lower and explain the regular error in these results. It is also possible that on this day the concentration of the sulphuric acid may not have been what it should be again leading to results that were consistently too low.

I know that my results are reliable when concentration was varied as I could repeat a trial and get basically the same results allowing for experimental error. The results corresponded to the pattern I expected and there were few anomalies.

Temperature was the last variable to be altered. Due to the more complicated procedure there were more opportunities for experimental error and I think this explains the increased number of anomalous results. Graph 8 clearly shows these anomalous results and they have also been circled in my table. When the reaction was carried out at 10°C the results for the 3 trials were 103.3, 405.2 and 110.9 seconds. 405.2 seconds evidently does not fit the pattern. I am fairly sure that the concentration of one or more of the solutions was wrong or that too much or too little of one of the reactants was added as my other results are within experimental error. To verify this I repeated the experiment twice more at this temperature and the results were similar.

If too much phenol was present it is possible that the reaction could have taken longer or if a large amount of phenol was added the mixture may not have decolourised at all, particularly at lower temperatures. This is because the first bromine formed reacts with the phenol until it has all been used, the next bit of bromine formed then reacts with and decolourises the indicator. This reaction is shown below:

bromine + methyl orange
↓
bleaches

once this is all gone
the bromine can react
with methyl orange

The reaction would slow down as the reactants are used up and their concentration gets lower and lower. So an increase in the amount of phenol present could have a large effect on reaction time. The other possibility is that any of the concentrations could be wrong. If for example the concentration of sulphuric acid was significantly lower than it should be this could have a large effect on reaction rate. However I think this is unlikely as the solutions were measured from burettes and solution from the same burette was used in each trial. It is possible however that too little of one of the reactant was added so the reaction took a lot longer than expected.

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The result circled when the experiment was carried out at 40°C was also vastly different from the other two trials. In this case I know the anomalous result was due to a mistake in the procedure. The test tube that the mixture was held in had cracked slightly at the bottom. This was due either to the heat or it could have been smashed against the glass beaker whilst stirring. This crack in the test tube was discovered after the trial. It had allowed the water from the beaker to mix with the reacting solution, this diluted the solution. Diluting the solution has the same effect as decreasing the concentration as the molecules are less likely to collide so the reaction occurred much more slowly.

The final two anomalous results occurred at 30 and 35°C. These were however closer to the other results and can be explained through inaccuracies in the procedure. For example the timing could have been inaccurate or too much or too little of one of the solutions could have been added. Spillages or lack of rinsing between runs could also cause these errors. I think a more likely explanation is that the solution was not quite at the correct temperature. It is possible that although the water in the beaker was at the temperature required that the solution in the test tube may not have been. The method was modified to prevent this but the new method was not followed throughout the experiment. It was also very difficult to keep the solution at the exact temperature required.

The most obvious and probably the largest source of error in my reaction and in all kinetic investigations is temperature. This is because a small change in temperature has a significant affect on rate of reaction. The activation enthalpy for this reaction was calculated to be 68.08 KJ moles-1, which is what I expected. If the temperature is increased the number of molecules that collide with this activation energy is also increased. This means the reaction will proceed faster. The practical work was started in June and completed over the Autumn term. The temperature in the laboratory was not recorded at the start of each practical session therefore allowances for temperature could not be made. The experiment was susceptible to temperature and due to time limitations it was not possible to obtain a full set of results in one lesson. The conditions were therefore not constant as the temperature was certainly higher in June. This could be a reason for some inaccuracies. In my preliminary experiment the times taken for the mixture to decolourise at 0.0022M of potassium bromide solution were 28.5, 21 and 22 seconds. In my actual experiment however the same concentration took an average time of 34.9 seconds. This shows an inconsistency and I think this is due to the temperature in the laboratory being lower. Kinetic investigations are appropriate as they produce lots of results however they are susceptible to temperature and wherever possible this should be regulated.

The experiment was also reliant on my reaction times particularly when temperature was varied, as the solution had to be added and the stopwatch started at the same time. This could have caused a slight delay. It was also up to me to decide when the mixture was totally colourless. This could have caused some errors but these were kept to a minimum by it being the same person carrying out the experiment each time, so the error should have been constant.

There were other problems in my experiment which I managed to avoid by altered the procedure. Originally I planned to have temperature variables of 10, 20, 30, 40, 50 and 60°C. But this was not possible as the reaction occurred too fast above 40°C. I also found that the mixture in the test tube decolourised at the highest temperatures before the potassium bromide was added. This should not have happened as the Br⁻ ions are

required to produce the bromine. It is possible that the solution could have become contaminated and contain a small quantity of potassium bromide. This should not have happened as firstly all the burettes were washed out with water and then with the solution that was going into them, so they did not become either diluted or contaminated. The test tubes were also washed thoroughly between trials. Another suggestion for this decolourisation is that the potassium bromate(V) solution in some way decomposed to leave bromine which in turn started to decolourise the mixture. It is not possible to identify the cause of this without further investigation. I would do this if time allowed by heating each of the variables in isolation with the phenol and methyl orange to see if the mixture decolourised. To avoid the problem the reaction was not carried out at this high temperature.

At the start of one practical session when the potassium bromide was added the complete mixture went orange rather than colourless. I repeated this and got the same result. This lead me to believe that the burette which supposedly contained potassium bromide solution actually contained something else. To be sure I emptied and washed out all the burettes and re-filled them this time labelling each one with the chemical it contained.

My procedures were suitable as I was able to achieve a set of results that show a clear trend. Due to the limitations and to certain problems a few anomalous results were recorded, but these have been ignored when looking for a pattern and drawing conclusions. I am therefore confident about the conclusions I have come to, as they are also supported by scientific knowledge. The errors associated with the apparatus were small and the procedural error were kept to a minimum at all times. The method was designed and modified with reducing errors in mind. The unavoidable errors such as room temperature and human reaction time could not be excluded and do account for some anomalous results.

There are improvements that could be made to the experiment. More trials could be carried out at each concentration and temperature to get a more accurate average result. The best way to improve the experiment would be to carry out all the trials on the same day under the same conditions, but this was impossible due to time constraints. The method used when temperature was varied was not very sophisticated and could have been improved by better apparatus. But we only had the equipment available in college. Working with a partner would have made the process more accurate because one person could add the solution while the other stated the stopwatch. It was also difficult to determine exactly when the mixture had decolourised even when the white tile was used. This meant the results could only be recorded to one decimal place. The experiment could also be carried out in a water bath to ensure that temperature did not affect the results.

5.10   Commentary on Individual Investigation Report 0410

Kinetics of the reaction between bromide and bromate(v) ions

Introduction

This is another example of a very popular type of individual investigation in which reaction kinetic are explored. It contains a particularly good analysing section in which a variety of graphs are used to find out how reaction rate is affected by concentration of reactants and temperature. This investigation also demonstrates how an original plan can be modified when initial results are not of sufficient quality to enable meaningful conclusions to be drawn.

Planning

It is unfortunate that his report begins with an aim to prove some text book information, rather than an aim to explore the relationships between reaction rate and concentration and temperature. The expected background theory on order of reaction and the Arrhenius equation is covered. However, additional material on the effect on reaction rate of surface area and of a catalyst are included, even though they are not followed up in the actual investigation. This illustrates the candidates lack of selectivity. The risk assessment is rather brief and makes no mention of the bromine produced in the reaction. A list of references is included which are linked to specific sections of text, but they lack page number detail. This part of this section can just be regarded as a good match with the descriptors at level P8a but does not satisfy the descriptors at P11a.

The plan includes a general account of experimental procedure including preliminary work and modifications made in the light of experience to try to ensure that the results obtained are accurate and reliable. More detail about procedures are found later in the report together with explanation about the choices made. This part of this section satisfies all of the requirements at level P8a and most of the descriptors at P11a.

Overall, the plan satisfies the descriptors at level P8 but does not quite meet the requirements at level P11. A mark of 9 or 10 is therefore appropriate, with a mark of 9 being most suitable in this case.

Implementing

All data is recorded to an expected precision and in an appropriate format. Tables of data are clearly labelled and there is a coherent and clear sense of purpose in the way that the experimental evidence is presented. Additional data is collected when initial results are not felt to be satisfactory. It is a pity that temperatures are not recorded to one decimal place, nevertheless, the requirements of all of the descriptors for the recording strand of implementing are satisfied, up to, and including, level I11b.

Analysing

The raw data is used to calculate initial reaction rates which are then used to draw graphs in order to explore the relationship between reaction rate and concentration and temperature.

The graphs are suitably annotated and are clearly drawn. The evidence collected about the effect of hydrogen ion concentration on reaction rate is explored in particularly rigorous detail.

Values for both the rate constant and activation enthalpy are carefully calculated. The implications of the derived experimental results on a possible reaction mechanism are thoughtfully discussed and causes of unexpected measurements are suggested.

Overall. This is a strong analysis section that uses underlying chemical knowledge and understanding to make sense of the evidence collected. It satisfies all of the descriptors up to, and including, level A11 and a mark of 11 is therefore appropriate.

Evaluating

This section contains a comprehensive and thorough discussion of some of the factors that could have contributed to inaccurate evidence. Limitations in the experimental procedures are identified and problems with particular sets of data are noted. The uncertainty associated with some measurements is evaluated but this is not extended to timing and temperature measurements. The relative significance of errors and uncertainties are assessed. Improvements to procedures are suggested but this feature is rather limited.

Overall, the evaluation satisfies the requirements of the descriptors at level E8 but does not fully meet the requirements at level E11. A mark of 9 or 10 is therefore appropriate, with a mark of 9 being most suitable in this case.

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