

Factors Affecting The Briggs-Rauscher Reaction

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1 Abstract

The aim of this investigation is to examine factors affecting the BriggsRauscher oscillating reaction. In the first experiment, the concentration of Hydrogen Peroxide was varied and an average rate of oscillation calculated. In the second experiment the concentration of Potassium Iodate was varied and the rate of each oscillation measured and an average calculated. In both experiments, the concentration of the reactant was directly proportional to the rate of oscillation.

In addition, experiment 3 explored the effect of varying temperature with oscillation rate. The results showed that varying temperature had an exponential affect on the rate of oscillation. Lastly, the fourth experiment put to the test, the effect of stirring on oscillation rate. However, inconveniently the results appeared to be illegitimate as they showed evidence that stirring decreased the rate of oscillation, which seemed unreasonable.

2 Underlying Chemistry

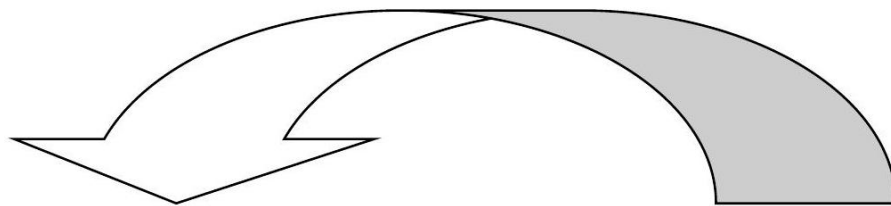
Oscillating Chemical Reactions An oscillating chemical reaction, is one in which the concentrations of one or more components periodically oscillates as the reaction progresses and this determines the behavior of the overall reaction. In an oscillating reaction, the behavior of the system is determined by the decrease in Gibbs free energy of the overall reaction, this occurs far from thermodynamic equilibrium. The energy-releasing reaction will follow at least two different pathways, depending on the concentrations of its components and the system will periodically oscillate between the two, as each state is unstable and kinetically dependent. That is to say that, the oscillations are the results of mutual coupling between the different routes the reaction can take (directly or indirectly depending on the number of steps in each pathway) and hence the reaction will restart itself on the initial pathway after a fixed time, under certain conditions.

Another feature present in oscillating reactions is that one of the pathways will result in the production of a specific intermediate whilst the other pathway will consume it. Furthermore, the concentration of this intermediate will determine which pathway the reaction will take, acting as a kinetic "trigger." More specifically, a low concentration of the intermediate will trigger the producing pathway, resulting in a high concentration of that intermediate. On the other hand, if the concentration of the intermediate is high, the system switches to the consuming pathway diminishing the intermediate's concentration. This process will repeat as the concentration of the intermediate varies, resulting in chemical oscillations. (Nicolis G. and Portnow J., 1973).

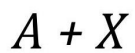
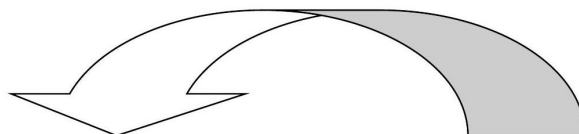
Feedback As previously discussed, oscillating reactions have at least two simultaneous processes. The mutual coupling effect of these processes results in closed feedback loops for the kinetic variable involved - usually concentration. Furthermore, the term feedback refers to the system kinetically acting upon itself, this exists in a closed chain of action resulting in one of two processes.

1. The producing pathway - in which the system self-produces known as, positive feedback.
2. The consuming pathway - where the system self-inhibits, this is called negative feedback

Likewise, there are two types of feedback itself, systematic and non-systematic feedback. However, this investigation will focus solely on non-systematic feedback as this is the feedback present in the Briggs-Rauscher reaction. This type of feedback is when the output (the product in a chemical reaction) acts upon the input of the same system in an auto catalytic loop, where the product acts as a reactant. As this type of feedback only affects the input, the transmission system (the rate constant in a reaction) is unaffected.



System



Rate constant (k)



Transmission

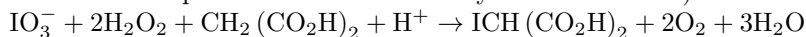
In this reaction, the substrate A is reacting to the intermediate X , causing A to change into X . It is important to consider that this is not necessarily a single step in the system, but multiple steps divided into different pathways. (Shakhashiri B.Z, 1986)

3 The Briggs-Rauscher Reaction

Also called the Oscillating Clock Reaction, because its oscillations follow a pattern similar to the grandfather clock. Just as the clock's pendulum swings from its point of equilibrium, continually changing its position until it runs out of energy, a similar process occurs in the Briggs-Rauscher reaction. The reaction was first discovered by two Chemistry teachers from San Francisco, who published the discovery in the Journal of Chemical Education in May 1972.

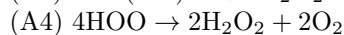
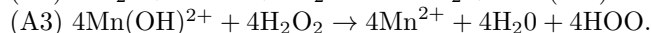
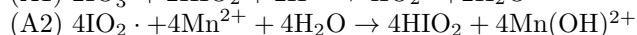
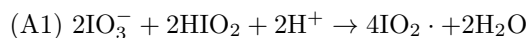
The reaction involves mixing three solutions of Hydrogen Peroxide (H_2O_2), Potassium Iodate (KIO_3^-) and Malonic acid ($\text{CH}_2(\text{CO}_2\text{H})_2$), among other substances which react to display a cyclic array of colourful solutions. The solution cycles between colourless, to amber, to deep blue, finally as the Hydrogen Peroxide decomposes, the finishing mixture is a black-blue solution. [Briggs T.S, Rauscher W.C, 1973]

The overall equation for the Briggs-Rauscher reaction is as follows, (the states of each compound are omitted as they are all solutions).

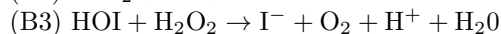
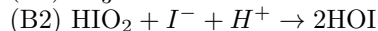


This reaction has two component reactions (1) $\text{IO}_3^-(\text{aq}) + 2\text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{HOI} + 2\text{O}_2 + 2\text{H}_2\text{O}$ (2) $\text{HOI} + \text{CH}_2(\text{CO}_2\text{H})_2 \rightarrow \text{ICH}(\text{CO}_2\text{H})_2 + \text{H}_2\text{O}$

Reaction (1) occurs by two processes, either by a radical process or a non-radical, both of which reduce Iodate (IO_3^-) to Hypoiodous acid (HOI), but the radical process does this much faster than the non-radical. The radical process occurs when the concentration of the intermediate, Iodide is relatively low. As this is a radical process, the $\text{X}\cdot$ represents an unpaired electron attached to compound X.

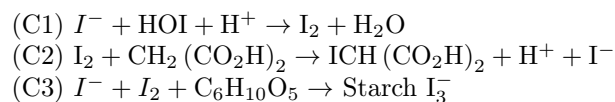


The non-radical process takes over when the concentration of (I^-) is high and is responsible for the colourless solution, in particular, the Iodide production in (B3). And is as follows,



In these reactions, (B1) is the slow consumption of Iodide by Iodate. Additionally, Iodous acid (HIO_2) is reduced to Hypoiodous acid by Iodide and Hydrogen (B2). Similarly, in reaction (B3), the Hypoiodous acid is reduced by H_2O_2 . To continue, the stoichiometric sum of reactions (B1), (B2) and ($2 \times \text{B3}$) results in equation (1).

To continue, as with reaction (1), reaction (2) also takes place in two processes - responsible for the other two colour changes.



In these stages, reaction (C1) produces I_2 which causes the amber colour in the solution. The Iodine formed in (C1) is due to the rapid production of Hypoiodous acid which forms in the radical process (A5), as the radical process is much faster than reaction (C1), the HOI forms faster than it is consumed therefore allowing Iodine to form. Eventually, when the concentration of Iodide is greater than that of HOI, the Iodine will combine with the Iodide formed in (C2), to form the Triiodide ion (I_3^-) which then binds to a Starch molecule, resulting in the Iodine-Starch complex (C3), which is responsible for the blue colour.

Furthermore, any excess HOI will react with Hydrogen Peroxide (B3), which converts Hypoiodous acid to Iodide. Because of this, the Iodide concentration will increase until the concentration threshold is reached and the non-radical process is triggered. Finally, as the non-radical process is much slower than the radical, the production of HOI reaction (B1) and (B2) is less than the consumption of it (B3). Consequently, the result is a decrease in Iodide production (B3) which is necessary for the production of Iodine by reaction (C1). Accordingly, due to the lack of Iodide and Iodine, the Iodine-Starch complex is removed, and the solution becomes colourless.

Eventually, the concentration of Iodide depletes to such an extent to trigger the radical process to restart and so the cycle repeats, resulting in multiple oscillating reactions.

4 Preparation of Reactants

Solution A (Hydrogen Peroxide) Approximately 100 cm^3 distilled water was measured and poured into a 400 cm^3 beaker. Then 75 cm^3 of 100 volume Hydrogen Peroxide (corrosive and powerful oxidising agent) was poured into a 100 cm^3 measuring cylinder.

Whilst stirring continuously, Hydrogen Peroxide was added to the beaker. Then the measuring cylinder was rinsed and the rinses added to the beaker containing the Hydrogen Peroxide. Next, this mixture was transferred to a 250 cm^3 measuring cylinder. Finally, the beaker was rinsed and rinses added to a measuring cylinder and made up to 250 cm^3 with distilled water.

Solution B (Potassium Iodate and Sulphuric Acid) Firstly, 10.75 g of Potassium Iodate was dissolved into a beaker containing 100 cm^3 of distilled water. Secondly, it was placed on a magnetic stirrer/ hotplate. Slowly, 1.08 cm^3 concentrated sulphuric acid (corrosive) was added whilst stirring and the solution transferred to a 250 cm^3 measuring cylinder. The beaker was then rinsed and rinses added to measuring cylinder which was made up to 250 cm^3 with distilled water. Lastly, 1.08 cm^3 of Sulphuric acid was added using 1 cm^3 syringe.

Solution C (Malonic Acid and Manganese Sulphate) To start with, 0.08 g of starch was added to a small quantity of the distilled water making a slurry. Then, approximately 75 cm^3 distilled water was added to the starch slurry, stirring until completely dissolved. To continue, 4.0 g of Malonic acid (harmful) and 0.85 g of Manganese Sulphate (harmful) were measured out and added to 100 cm^3 of distilled water, stirring until dissolved. Finally the starch solution was added and the mixture was transferred to a 250 cm^3 measuring cylinder. To finish, the beaker was rinsed and rinses added to a measuring cylinder and made up to 250 cm^3 with distilled water. (Epstein I.R, Pojman J.A, (1998).

5 Experiment 1 - Varying the Concentration of Hydrogen Peroxide

Aim The aim of this experiment is to examine the effects of varying the concentration of H_2O_2 on the rate of oscillation.

Apparatus

1. Magnetic stirrer and follower
2. $3 \times 100 \text{ cm}^3$ Conical flasks/ containers
3. $3 \times 50 \text{ cm}^3$ Measuring cylinders
4. Pipette
5. 10 cm^3 measuring cylinder
6. Timer

Procedure The three solutions were made, as explained in the previous page. 10 cm^3 of each was measured into three separate 50 cm^3 measuring cylinders. A 100 cm^3 conical flask was placed onto the magnetic stirred with the follower inside the flask. The three solutions were then poured into the flask and the timer started when the clear liquid mixture turned deep blue.

The times were then noted every time the colour changed back to deep blue, for the first five oscillations, the mixture was then poured down the sink. An average of these times was then calculated and plotted against the concentration of Hydrogen Peroxide. The Hydrogen Peroxide concentration was varied by diluting the liquid with water, a pipette was used for a more accurate dilution.

The concentrations in mol/l of each dilution, is calculated as follows.

$30\% \text{H}_2\text{O}_2$ means that $30 \text{ gH}_2\text{O}_2$ is diluted with 100 g water Hence $300 \text{ gH}_2\text{O}_2$ per litre of water.

To convert to mol/l, divide mass by the gram formula mass of Hydrogen Peroxide.

$$\frac{300}{34} = 8.8 \text{ mol/l}$$

For concentration of 1st dilution: 7.5 cm^3 of H_2O_2 is made up to 10 cm^3 by water.

$$C_1V_1 = C_2V_2$$

$$\therefore (8.8)(7.5) = (10)C_2$$

$$\therefore C_2 = 6.6 \text{ mol/l}$$

Second dilution: 5 cm^3 of H_2O_2 is made up to 10 cm^3 by water.

$$C = 4.4 \text{ mol/l}$$

Third dilution: 2.5 cm^3 of H_2O_2 is made up to the mark with water.

$$C = 2.2 \text{ mol/l}$$

Results Periods of Oscillation (s): 8.8 mol/l : 17, 34, 49, 64, 88

Average Period (\bar{t})

=

$$\frac{(34 - 17) + (49 - 34) + (64 - 49) + (88 - 64)}{5}$$

$$= 14.2 \text{ s}$$

6.6mol/l: 16, 34, 49, 64, 79

$$\bar{t} = 12.6 \text{ s}$$

4. 4 mol/l : 25, 51, 78, 106, 138

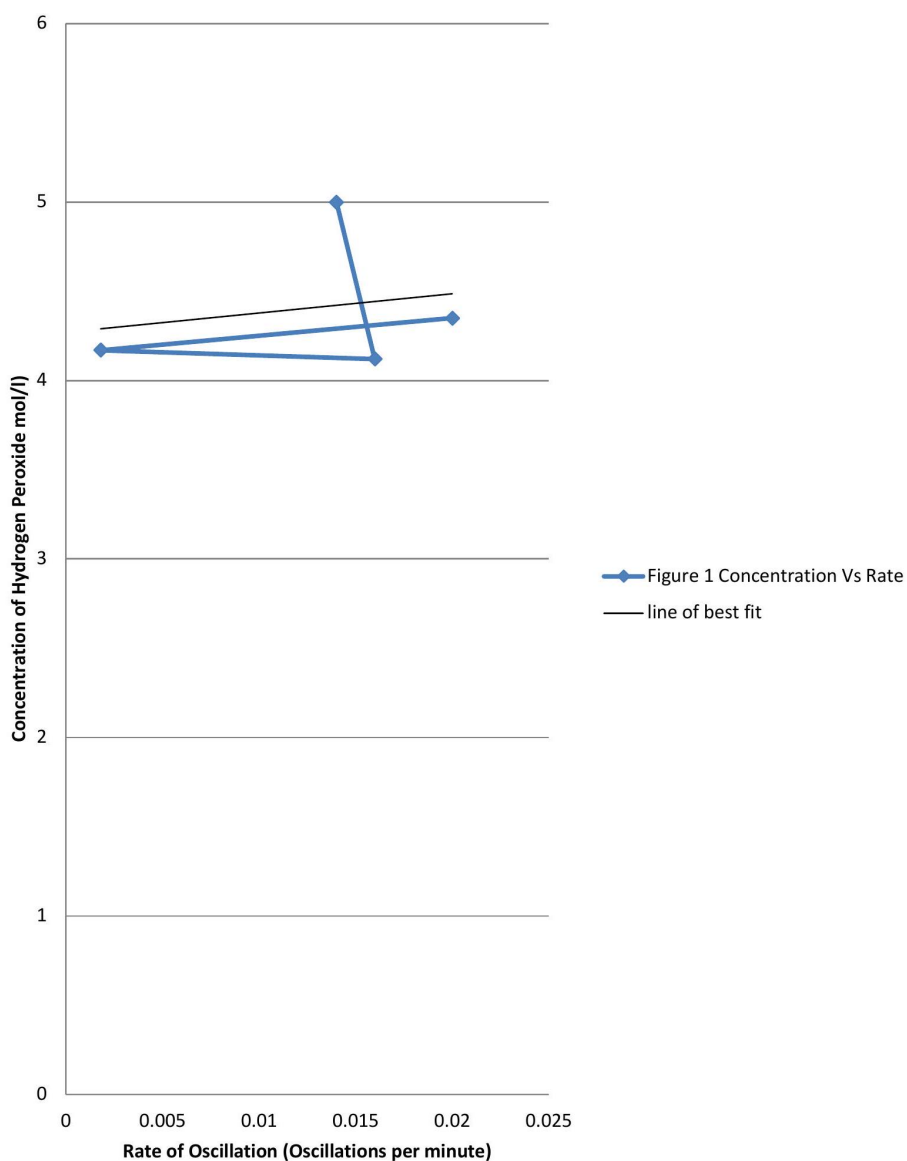
$$\bar{t} = 22.6 \text{ s}$$

2.2mol/l: 27, 63, 106, 157, 187

$$\bar{t} = 32 \text{ s}$$

Concentration of H ₂ O ₂ (mol/l)	Average Period of Oscillation (s)	Rate of Oscillation (Oscillations per minute)
8.8	14.2	4.23
6.6	12.6	4.76
4.4	22.6	2.65
2.2	32	1.88

Table 1
Figure 1. Concentration Vs Rate



Evaluation The results clearly show that the concentration of Hydrogen Peroxide varies directly with the rate of oscillation. This is due to the H_2O_2 being a reactant in reaction (1) which in turn affects reactions (A3) or (B3) depending on the relative concentration of I^- and hence affects the rate of the overall reaction.

In addition to the colour changes that appear, effervescence will also take place as Oxygen, produced in the overall reaction, escapes the container.

Similarly, after the oscillations have stopped, Iodine vapour is produced, and

can be collected if the system is closed.

6 Experiment 2 - Varying the Concentration of Potassium Iodate

Aim The aim of this experiment is to measure the oscillation rate at varying concentrations of Potassium Iodate. From these results, a conclusion can be drawn and a simple relationship between the variables derived.

Procedure The three solutions were again made up and the same procedure as previously explained was carried out. However, in this experiment, the concentration of Potassium Iodate (solution B) was altered, and measurements noted. Different dilutions were made compared to the previous experiment. This is because when the Iodate concentration fell below 5 cm^3 (10^{-4} moles), no visible oscillation appeared. This is because, by decreasing the concentration of KIO_3^- , this decreases the overall production of I^- which is required to react with I_2 to produce the Iodine Starch complex, which produces the deep blue colour and is necessary for the reaction to oscillate. Likewise, the number of moles of Potassium Iodate was calculated in a similar way to the Hydrogen Peroxide in experiment 1.

Results Periods of Oscillation (s):

0.02 mol/l : 19, 37, 54, 71, 88

$\bar{t} = 13.8$

0.018 mol/l : 21, 42, 59, 76, 93

$\bar{t} = 14.4$

0.016 mol/l : 18, 38, 57, 74, 91 $\bar{t} = 14.6$

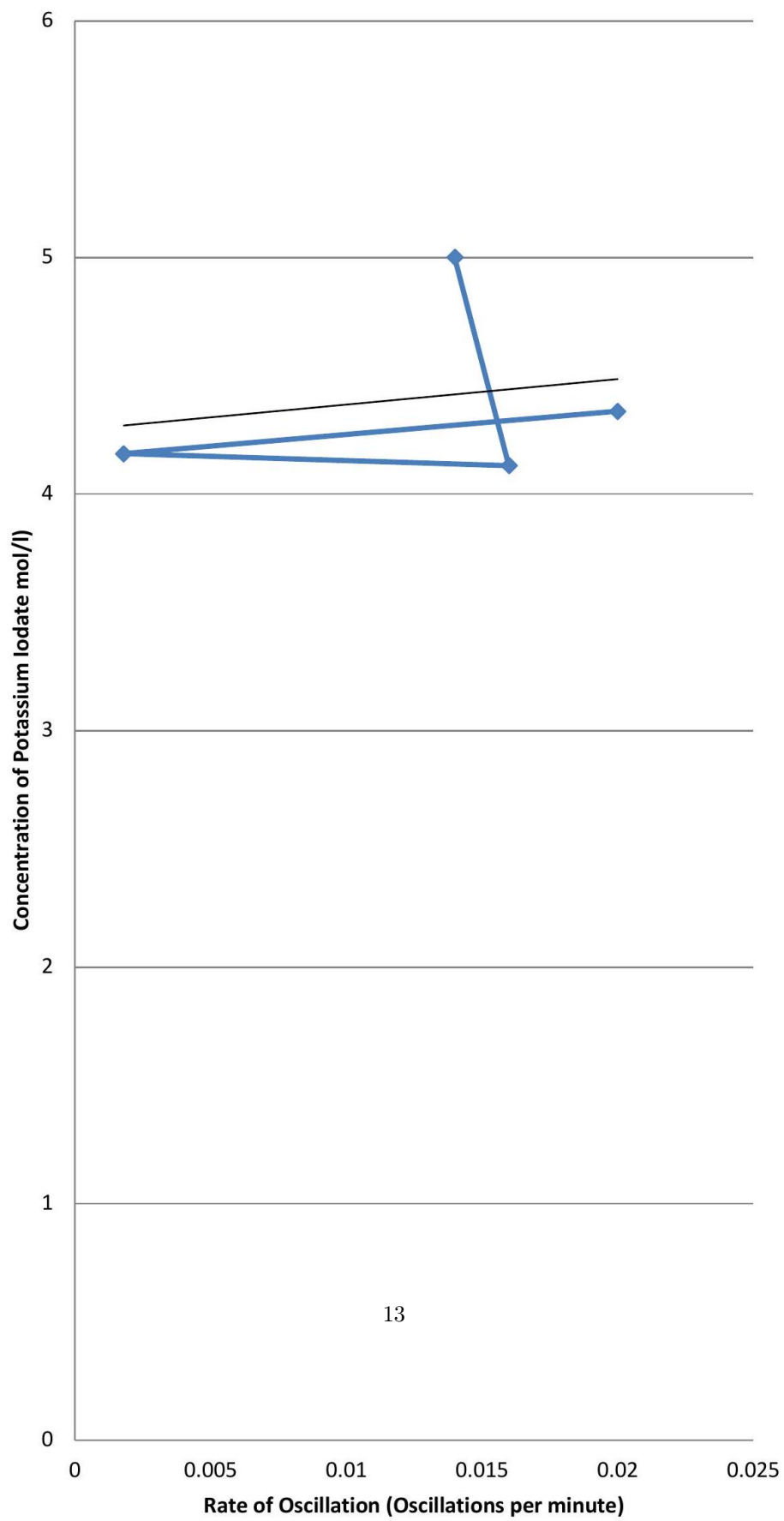
0.014 mol/l : 13, 33, 43, 58, 73

$\bar{t} = 12$

Concentration of KIO_3 (mol/l)	Average Period of Oscillation (s)	Rate of Oscillation (Oscillations per minute)
0.02	13.8	4.35
0.018	14.4	4.17
0.016	14.6	4.12
0.014	12	5.00

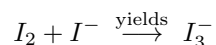
Table 2

Figure 2. Concentration Vs Rate



~ Figure 2 Concentration Vs Rate
line of best fit

Evaluation From the results noted in the table 2 and the graph (figure 2), it is clear that varying the concentration of Potassium Iodate has a similar effect to varying the concentration of Hydrogen Peroxide. This is because decreasing the concentration of KIO_3^- , produces less product in reaction (1) hence less Hypoiodous acid (HOI) is produced. This results in reaction (B3) producing less I^- , which is responsible for the colourless solution and is also necessary for the production of the deep blue colour (I_3^-) by this equation,



Consequently, varying the concentration of solution B decreased the intensity of the blue solution to a much fainter blue, as this was my point of timing reference, it was more difficult and hence less accurate to time this set of oscillations. However, regardless of the intensity of the colour, the reference point was the same (every repetition of blue), therefore the results are still valid.

Hence, from the set of results gained from the 0.014 mol/l solution, it is clear that the general trend was not followed, this is because at this concentration, the blue colour was very faint and so identifying its presence was difficult and less consistent. Furthermore, the graph would have displayed a more obvious trend had the errors been minimized and the number of readings taken increased.

7 Experiment 3 - Varying the Temperature

Aim The aim of experiment 3 is to monitor the change in oscillation rate at different temperatures and make conclusions based on those results.

Additional Apparatus 3× Thermometers

Waterbath

3 × 50 cm³ beakers

Stirring rod

Procedure In this experiment, 10 cm³ of the three solutions was measured into 3 separate 50 cm³ beakers and placed inside the waterbath along with an empty 100 cm³ conical flask. The temperature of the waterbath was set to 35°C and I ensured that the water level in the waterbath was kept below the level of the liquid in the beakers to ensure they would not tip. Additionally, as the reactants and all of the containers were placed in the water bath and kept there for the duration of the experiment, the magnetic stirrer could not be used so stirring rods were used in its place.

Similarly, as the beakers were small, thermometers could not be left in them, as they would tip over. To overcome this issue, a thermometer was placed in the water bath and another in the empty conical flask (which was much larger than the beakers). When both thermometers displayed the desired temperature, another thermometer was placed separately in each beaker, measuring the temperature of those liquids. Finally, all of the solutions were poured into the conical flask and the timing began.

Results Periods of Oscillation (s): 35°C : 16, 24, 31, 37, 43

$\bar{t} = 5.4$

40°C : 3, 5, 8, 11, 15

$\bar{t} = 2.4$

45°C : 3, 5, 7, 12, 15

$\bar{t} = 2.4$

50°C : 3, 6, 8, 12, 14

$\bar{t} = 2.2$

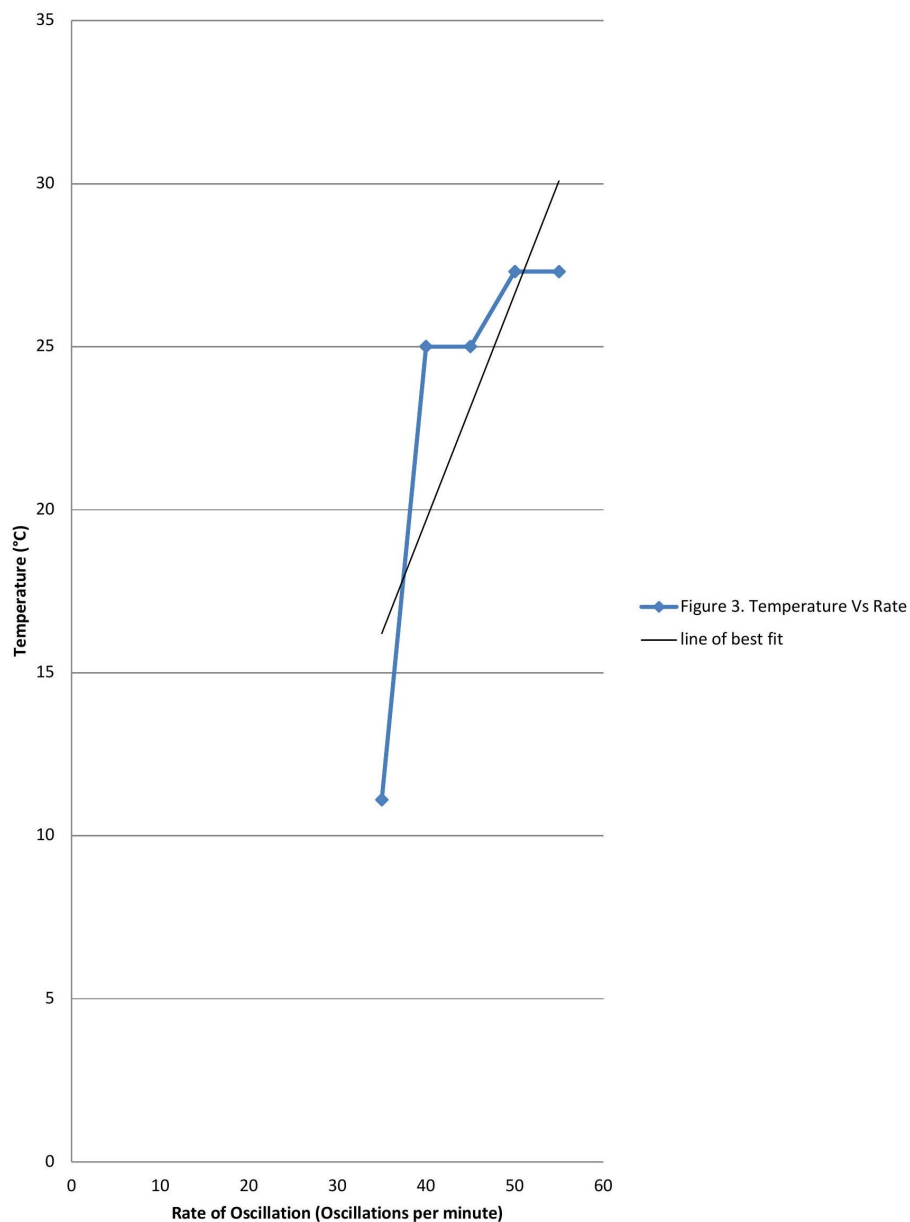
55°C : 3, 6, 8, 12, 14

$\bar{t} = 2.2$

Temperature (°C)	Average Period of Oscillation (s)	Rate of Oscillation (Oscillations per minute)
35	5.4	11.1
40	2.4	25
45	2.4	25
50	2.2	27.3
55	2.2	27.3

Table 3

Figure 3. Temperature Vs Rate



Evaluation This experiment showed the exponential relationship between Temperature and Rate of Oscillation. This is because increasing temperature increases the rate of reaction as the particles will have more kinetic energy and hence will collide more productively. Hence, all of the constituents, which give rise to different colours, will be produced and used up more quickly, resulting in rapid oscillations.

Furthermore, when temperatures surpass approximately 40°C, the rate of oscillation becomes so rapid that it is difficult to distinguish specific rates from different temperatures as the results converge to a rate of approximately 27.3 oscillations per minute. Hence, due to this inconsistency, the validity of this value and the readings taken for temperatures above 40°C should not be taken as accurate or legitimate values as human error played too significant a role in the uncertainty of this experiment.

To continue, since the magnetic stirrer could not be used, the stirring was done by hand, which adds further human error and will have an effect on the results. Furthermore, the dial on the water bath was highly inaccurate and inconsistent, for this reason, the temperature was read from a thermometer, using only the waterbath scale to get as close to the desired temperature as possible.

Abstract

Aim

The aim of the final experiment is to investigate the effect of stirring on the rate of oscillation under certain conditions.

Procedure This experiment follows the same procedure as, Experiment 3 - Varying Temperature - as this allowed me to investigate the effect of stirring, whilst minimizing the time spent on this experiment. Hence, the results gathered for stirring were taken from the previous experiment. To elaborate, the three solutions were made up to 10 cm³ and poured into the beaker, which was heated to 35°C using the water bath. However, unlike the previous experiment, where the mixture was stirred by hand, in this experiment, the solution was left alone. The results of this experiment are compared with the results in the previous experiment, conducted at the same temperature but with stirring involved.

Results Both experiments are conducted at 35°C.

Periods of Oscillation (s):

Stirred: 16, 24, 31, 37, 43

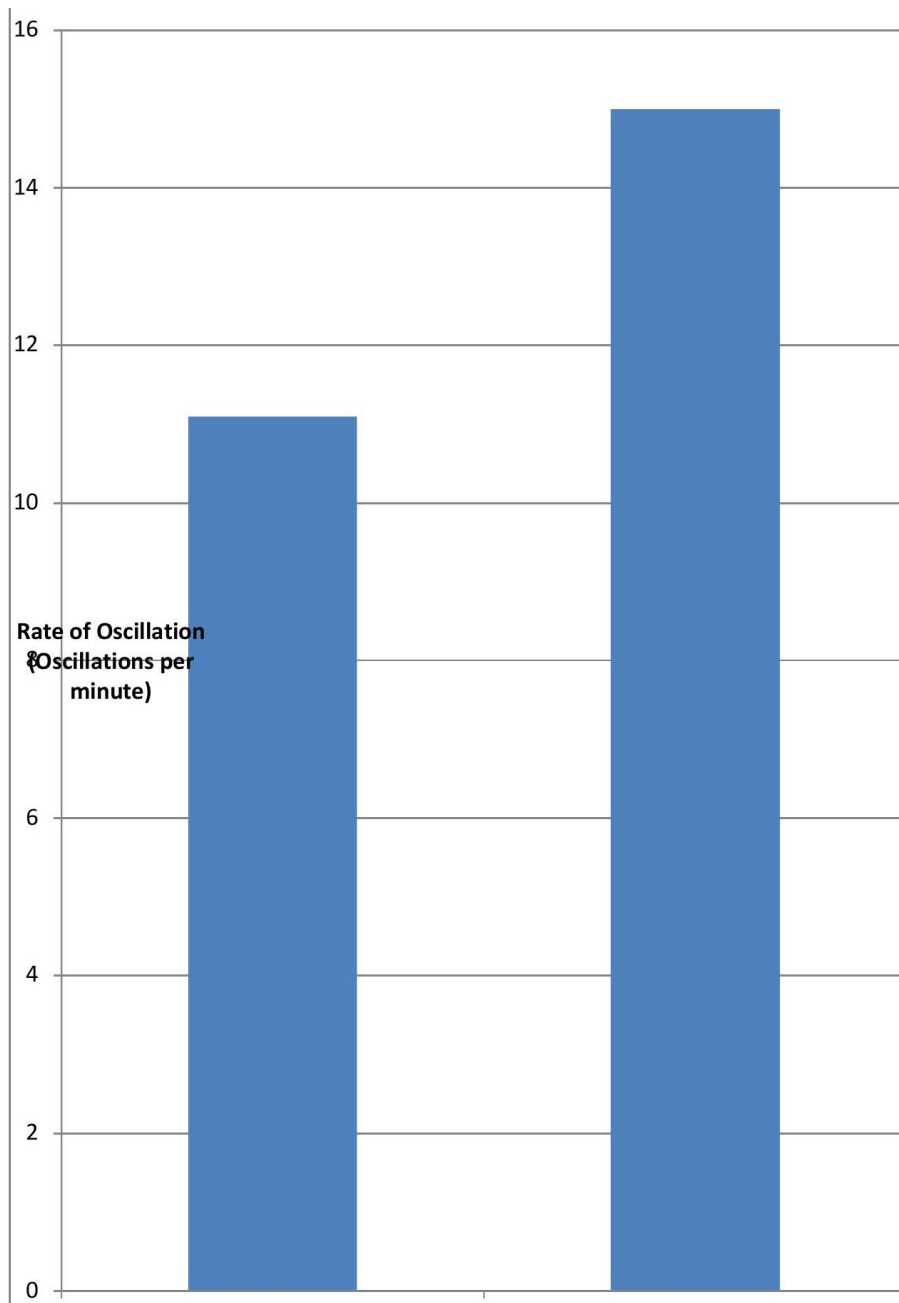
$\bar{t} = 5.4$

Not Stirred: 20, 25, 28, 34, 40

$\bar{t} = 4$

	Average Period of Oscillation (s)	Rate of Oscillation (Oscillations per minute)
Stirred	5.4	11.1
Not Stirred	4	15

Figure 4. Effect of Stirring on Rate



Stirred
Not Stirred
Method

Evaluation The evidence gathered from these experiments suggests that stir-

ring decreases the rate of oscillation. This suggests that the information gathered is inconsistent and invalid, and should not be taken as accurate evidence of the effect of stirring. The reason for this outcome, that stirring decreases the rate of oscillation, could be due to inconsistent stirring, which would cause major fluctuations in oscillations hence affecting the oscillation rate. This error could be minimised by comparing the effect of stirring at multiple temperatures and by taking more readings. Similarly, using a magnetic stirrer instead of a stirring rod would minimise the human error, making the results more reliable.

Conclusion In conclusion, my investigation on the Briggs-Rauscher oscillating chemical reaction has proven to be successful at investigating factors that affect the rate of its oscillations. From my experiments, it was discovered that factors such as Hydrogen Peroxide concentration, Potassium Iodate concentration, temperature and stirring all have an effect on the rate of oscillation of this reaction. To elaborate, it was observed that varying the concentrations of reactants H_2O_2 and KIO_3 has a direct relationship with oscillation rate.

Similarly, in experiment 3, the results showed that varying the temperature has an exponential proportionality on the rate of oscillation. Finally, experiment 4 showed that stirring the mixture, at constant temperature, decreases the rate of oscillation, however, I believe that certain errors have impacted the results too significantly for this to be true.

Evaluation For the first experiment, the results suggested that varying the concentration of Hydrogen Peroxide had a direct correlation with oscillation rate. Similarly, the results obtained from experiment 2 gave evidence to suggest that the concentration of KIO_3 is also proportional to the rate of oscillation.

Although these two experiments were successful in gathering some reliable results, the accuracy and consistency of these could have been improved, had the errors and uncertainties been minimized. These errors include: the human error of using a stopwatch to make timings, instead a high-speed camera should have been used to capture the colour changes and obtain more accurate results. Also, the reference point being sometimes unclear and not well defined for every experiment, especially in experiment 2 as no oscillations occur when the Iodate concentration is less than $5 \text{ cm}^3 (10^{-4} \text{ moles})$

Another error is that the reference point varied for different experiments due to different intensities of blue solution, hence I had to derive a new reference point before every experiment, adding to the human errors. Additionally, for some of the exercises, the magnetic follower did not spin, hence the lack of effective stirring added to the overall uncertainty.

Similarly, experiment 3 produced a plethora of unreliable results due to the oscillations occurring too rapidly at temperatures above 40°C , which resulted in the timings being inconsistent and hence illegitimate. Regardless of these errors, the experiment still showed a direct correlation between temperature and oscillation rate. Finally, the fourth experiment involved investigating the effect of stirring on the rate of oscillation. The results showed that stirring the mixture reduced the rate of oscillation. I believe these results to be inaccurate because of uncertainties such as, the stirring being manual and the experiment being conducted at a temperature just below the threshold for rapid oscillations

to occur (40°C).

To improve the results, the magnetic stirrer should have been used instead of a stirring rod, this would have created a more consistent stir rate and hence decreased the uncertainty. Additionally, the reaction should have been conducted at multiple temperatures to improve the accuracy of the average period of oscillation.

Additionally, I would have liked to have investigated the effect of varying Malonic acid concentration on oscillation rate. Similarly, I would have liked to experiment with other oscillating reactions, such as the Belousov Zhabotinsky reaction or the Bray - Liebhafsky reaction.

8 References

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9 Acknowledgements

I would like to thank the technicians for making up the solutions used in the investigation, as well as offering advice on the individual experiments.