Candidate Code: jtt487

Research Question: How does increasing temperatures of hydrogen peroxide affect the production rate of oxygen involving Manganese Dioxide and Sulfuric Acid? What is its activation energy?

1.1 Introduction

I took a fascinating biology course during the summer. One of the things that I investigated was how oxygen gas plays a role in breaking down organic pollutants in water. When I studied this, I was more interested in how the oxygen gas was produced. In fact, one of the reactions I studied that was used to create oxygen gas was through the redox processes between Manganese (IV) dioxide and hydrogen peroxide (H_2O_2).

With this in mind, I wanted to find a way to investigate this reaction using knowledge I have through topics 7, 17: Chemical Kinetics, as well as learning topics 9, 19: Redox processes. Hence, I planned on designing a lab to measure the activation energy of the reaction and investigate the relationship between temperature and rate of reaction.

2.1 Background information

Oxidation-reduction reactions, also known as redox reactions are reactions involving the transfer of electrons. Furthermore, the involved reaction involves both a reduction and oxidation reaction in an acidic environment.

Table 1: Table displaying the oxidation and reduction half-reactions and the overall equation.

Overall reaction: $MnO_2 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + 2\,H_2O + O_2$	
Oxidation Reaction	Reduction Reaction
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	$Mn^{IV} + 2\,e^- \rightarrow Mn^{II}$

Regarding the Kinetics of chemical reactions, the rate of reaction can be defined as the speed where a chemical change occurs. In order for a reaction to occur, particles need to collide with enough energy at the correct orientation. The rate equation of a reaction is expressed as Rate = k $[A]^m[B]^n$. Where *Rate* is the rate of reaction, expressed in mol $dm^{-3}\,s^{-1}$. k is the rate constant, *[x]* represents the concentration of each reactant and *m+n* represents the total order of the reaction. For this reaction, The rate expression Rate = $k[MnO2]^1[H2SO4]^1[H2O2]^1$ From the Lodz university of technology, Faculty of Process Engineering and Environmental Protection found that the catalytic decomposition hydrogen peroxide can be represented by pseudo first-order rate model (Pędziwiatr et al.)

Next, the minimum energy required for a reaction is known as the activation energy. In kinetics, higher temperatures are related to its kinetic energy, hence higher temperatures mean higher kinetic energy. Therefore, at higher temperatures, more particles in a reaction have enough

kinetic energy required. This can be visualized through a maxwell-boltzmann distribution curve shown in figure one. Altogether, this means that higher temperatures would result in a faster reaction.
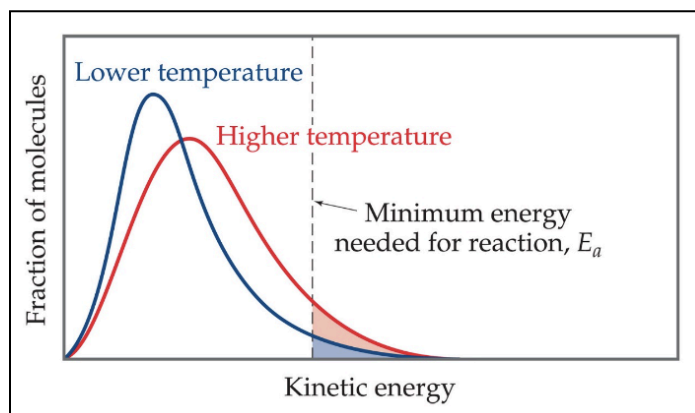

Figure 1: A Maxwell–Boltzmann Distribution curve displaying how more particles have the minimum energy needed for a reaction at a higher temperature.

Arrhenius Equation

$k = Ae^{\frac{-Ea}{RT}}$, which can be rewritten as $ln\ k = -\frac{Ea}{RT} + ln\ A.$

In this equation, k is the rate constant, A is the frequency of successful collisions, R is the natural gas constant (8.31 J K^{-1} mol $^{-1}$), and T is the temperature in K. With the latter equation, this equation is in the form of $y = mx + b$. The independent variable is $\frac{1}{T}$, the dependant variable is $ln\ k$, the slope of the equation is given as $-\frac{Ea}{R}$, and the y-intercept (b) is given as $ln\ A$. The next part of this investigation is to determine its activation energy. Therefore, from this graph, the slope from the line of best fit can be determined to calculate the activation energy of the reaction.
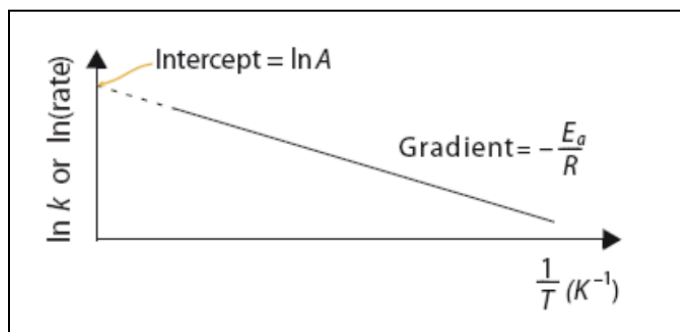

Figure 2: A Graph of a linearized Arrhenius equation. On the x-axis, it is represented by $\frac{1}{T}$ or K^{-1} and the y axis represents ln K.

3.1 Hypothesis

I hypothesize that the rate of reaction between hydrogen peroxide, sulfuric acid and manganese dioxide will increase with temperature. As discussed in the background information, an increase in temperature would result in an increase in the average kinetic energy of the particles. Therefore, it will lead to increased successful collisions leading to a higher rate of reaction.

4.1 Variables:

Table 2: Table displaying the independent and dependent variable with its significance.

Independent Variable:	Temperature (K ±0.1 K) Range of Temperature Used: 303.0 K, 308.0 K, 313.0 K, 318.0K, 323.0 K	Significance: Temperature was selected as the independent variable to determine the rate of reaction, and alternate temperatures provide the data to complete the arrhenius plot. Measured in Kelvin, and a digital temperature probe is used to determine the temperature.
Dependant Variable:	Time taken for 45 mL of Oxygen Gas to be evolved (s)	Significance: Time was selected as the dependent variable to determine the relationship with the independent variable (Temperature) and the rate of reaction. Measured in seconds as it is important to find the rate constant (k)

Table 3: List of Controlled Variables with its significance

Controlled variables:	Significance:
Pressure in the room	The pressure in the room is aimed to be at a constant value of 101.3 kPa. This is important because the Ideal Gas Law (pV = nRT) is used to determine the amount of moles of oxygen gas produced. It is difficult to maintain a constant pressure in this environment, so it is assumed to be constant.
Volume of Hydrogen Peroxide Solution and concentration	For each reaction, 15.00 ± 0.01 mL of 1.8% Hydrogen peroxide solution was used. Keeping this value constant is important because the concentration of the reactant can affect the rate of reaction. This would ensure that the changes in data were only a result of changes in temperature.
Volume of Sulfuric Acid and concentration	For each reaction, 0.10 ± 0.01 mL of 6% Sulfuric acid was used. The sulfuric acid is a strong acid that will provide an acidic environment for the redox reaction to occur.
Amount of MnO_2 used	For each reaction, 0.25 ± 0.01g of Manganese powder was used. Manganese dioxide is also the excess reagent.
Number of swirls	For each reaction, the manganese dioxide power was swirled once with the sulfuric acid. Thus, the reactants become more uniformly mixed.

5.1 Apparatus and Materials

- 15 mL of 6% Hydrogen Peroxide
- 10 mL of 60% Sulfuric Acid
- 0.25 g of Manganese(IV) Oxide
- Eudiometer (± 0.1 mL)
- Digital Temperature probe (± 0.1K)
- Electronic Balance (± 0.01 g)
- Thermometer (± 0.1 K)
- Graduated cylinder (± 0.05 mL)
- Large Beaker
- Two Test Tubules
- Hot plate (±1℃)
- Filter Flask (With Gas opening and stopper)
- Tube (50 cm)
- Retort Stand
- Water Bath Container
- Stopwatch (0.01 s)

5.2 Procedure

5.2.1 Setup of Apparatus
1. Set the hot plate at the desired temperature. (First: 298K.) With a clean temperature probe, ensure the temperature is correct.
2. Put a large beaker filled with 500 mL of water on the hot plate.
3. Beside it, fill the water bath with water until it overflows.
4. Fill up the Eudiometer until it overflows, then place it upside down inside the water bath. Secure this using a retort stand.
5. Using the tubes, connect one end of the tube with the flask, and the other end to the eudiometer.

5.2.2 Setup of Solutions
6. Create a 1.8% solution of Hydrogen Peroxide using distilled water and 6% hydrogen peroxide.
7. Measure 15 mL of 1.8 % Hydrogen Peroxide with a graduated cylinder, then transfer it to a tubule where it will be dealt to avoid decomposition with the air.
8. Measure 10 mL of 0.6 M Sulfuric Acid with a graduated cylinder, then transfer it to a tubule.
9. Transfer the hydrogen peroxide tubules into the large beaker.
10. Measure 0.25 g of Manganese(IV) oxide using the electronic balance.

5.2.3 Reaction

11. Remove the hydrogen peroxide tubule and sulfuric acid tubule. And combine all three reactants together into the flask as quickly, but safely possible.
12. Stopwatch started as soon as possible once the experiment flask was sealed off.
13. Once 45 cm^3 of oxygen gas has evolved, which was determined from the eudiometer, the time taken is recorded.
14. Steps (4) to (13) were repeated four times for five trials of data.
15. Steps (4) to (14) were repeated with other temperatures: 298K, 303K, 308K, 313K, 318K

5.3 Safety and Environmental Considerations

Exposure to products and reactants:
Hydrogen peroxide and sulfuric acid can cause irritations to the eyes, throat and cause difficulty breathing if inhaled (*ATSDR*, 2015.) Manganese dioxide was in powdered form which could easily be inhaled or ingested, causing cough or nausea (*ICSC, n.d*.)
As a result, personal protective equipment such as goggles and gloves were used.
Hotplate and Water:
With the hot plate and water bath which was used to heat up the tubules, the temperatures on the hotplate reached up to 200℃ + and the solutions themselves reached up to 50℃. This could cause serious burns with direct contact with the water or the hot plate. As a result, this risk was prevented by using test tube clamps to remove the tubes from the water. When handling the beakers themselves, beaker tongs were used to avoid direct contact with the glass.
Environmental and Ethical Considerations:
Since the solutions contain Manganese (IV) dioxide, which can cause respiratory irritation, the solutions are thrown out at the waste disposal container (*ICSC, n.d*)
There are no ethical concerns related to this investigation.

6.1 Data and Calculations

6.2 Raw Data

Qualitative Observations:
1. Beginning of the reaction was fast and violent, where oxygen gas quickly formed. Shortly after, the reaction began to slow down.
2. Solution was slightly yellow (Due to the hydrogen peroxide), however the reaction caused the flask to become cloudy, and dark, but clear once the reaction finished.
3. The reaction began with small bubbles of air appearing around the Eudiometer. Right after, larger bubbles would evolve from the violent reaction.

Table 4: Raw Data Table of the time taken for 45 mL of Oxygen gas to be evolved from that temperature.

Temperature (K) (±0.1 K)	303.0 K	308.0 K	313.0 K	318.0 K	323.0 K
Trial	Time it takes for 45 mL of gas to be evolved. (s) (±0.01s)	Time it takes for 45 mL of gas to be evolved. (s) (±0.01s)	Time it takes for 45 mL of gas to be evolved. (s) (±0.01s)	Time it takes for 45 mL of gas to be evolved. (s) (±0.01s)	Time it takes for 45 mL of gas to be evolved. (s) (±0.01s)
1	0:53:35	0:33:41	0:20:12	0:17:22	0:13:57
2	0:54:12	0.29:78	0:21:79	0:18:50	0:09:13
3	0:46:08	0:38.41	0:24:27	0:15:13	0:10:18
4	0:44:63	0:32:40	0:26:91	0:15:54	0:15:18
5	0:47:56	0:33:76	0:22:92	0:15:79	0:13:21

6.3 Processed Data

The average time taken for 45 cm³ of gas to be evolved found through this calculation:
Sample Calculation:

Calculation	Uncertainty Propagation
$Average\ time\ =\ \dfrac{\Sigma\ time\ taken\ for\ Gas\ to\ be\ evolved}{Number\ of\ Trials}$ $\dfrac{53.35+54.12+46.08+44.63+47.56}{5}$ $=\ 49.23\ seconds$	$\%\ Uncertainty\ =\ \dfrac{(\Sigma\frac{Uncertainty\ of\ stopwatch}{Time\ for\ each\ Trial})}{5}\times 100\%$ $\%\ Uncertainty=$ $\dfrac{(\frac{0.01}{53.35}+\frac{0.01}{54.12}+\frac{0.01}{46.08}+\frac{0.01}{44.63}+\frac{0.01}{47.56})}{5}\times 100\%$ $\%\ Uncertainty=0.02047\ \%=\pm\ 0.02\%$

The moles of oxygen gas created at the specific temperature was found through these following calculations:
Sample Calculation:

Calculation	Uncertainty Propagation
$PV\ =\ nRT$ $n\ =\ \dfrac{PV}{RT}\ =\ \dfrac{(101300)\,(0.000045)}{(8.31)(303)}$ $=\ 0.001810415\ moles$ $=\ 1.81\ \times\ 10^{-3}\ mo$	$\%\ Uncertainty\ =\ \dfrac{Uncertainty\ of\ Eudiometer}{Volume\ of\ Gas\ Measured}\times 100\%$ $\%\ Uncertainty\ =\ \dfrac{0.1}{45}\times 100\%$ $\%\ Uncertainty\ =\ \pm\ 0.222222\%$ $\%\ Uncertainty\ =\ \pm\ 0.22\%$

To calculate the amount of moles of Hydrogen Peroxide consumed in the reaction, the following mole ratio is used:

Sample Calculation:

$$1 \text{ mol } H_2O_2 = 1 \text{ mol } O_2$$
$$n = 1.81 \times 10^3 \, moles \times 1 = 1.81 \times 10^3 \, moles$$

To calculate the average rate of reaction, the following equation is used:
Sample Calculation:

Calculation
$$Rate = \frac{Concentration}{Time} = \frac{moles}{volume \times time}$$
$$= \left(\frac{1.81 \times 10^{-3}}{0.045 \times 49.23}\right)$$
$$= 8.1721 \times 10^{-4} \, mol \, dm^{-3} s^{-1}$$

These calculations were repeated for all trials, producing table 5.

Table 5: Processed Data Table of the average rate of reaction, with the data used to find this value.

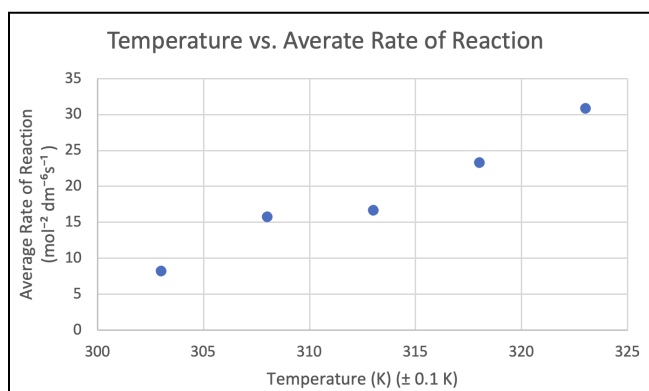| Temperature (K) ($\pm$0.1 K)	Average Time for 45 mL of gas to be created (s)	Moles of Oxygen Gas Created (10^{-3} mol)	Moles of Hydrogen Peroxide used in the reaction (10^{-3} mol)	Average Rate of Reaction (10^{-4} mol dm^3 s^{-1})
303.0	0:49:23	1.81	1.81	8.17
308.0	0:25:19	1.78	1.78	15.71
313.0	0:23:36	1.75	1.75	16.67
318.0	0:16:44	1.73	1.73	23.31
323.0	0:12:25	1.70	1.70	30.81

Figure 3: Graph of the Temperature vs. Average Rate of Reaction

Calculated from table 5, the rate constant k can be calculated using the average rates of reaction. Through the previously mentioned rate expression:

$$Rate = k[MnO2]^1[H2SO4]^1[H2O2]^1$$

As mentioned in 5.2.2, the concentration of Hydrogen peroxide is 1.8% or 0.018 mol dm^{-3}. The concentration of Sulfuric Acid is 6% or 0.06 mol dm^{-3}. Before performing this calculation, the concentration of Manganese dioxide in solution must be calculated.

Calculating the concentration of Manganese Dioxide in Solution:

$$Moles\ of\ MnO_2 = \frac{Mass\ of\ MnO_2}{Molar\ Mass\ of\ MnO_2} = \frac{0.25\ g}{86.9368\ g\ mol^{-1}} = 0.0028765 \approx 0.00288\ mols$$

$$Concentration\ of\ MnO_2 = \frac{moles\ of\ MnO_2}{volume\ of\ solution}\ mol\ dm^{-3}$$

$$Concentration\ of\ MnO_2 = \frac{0.0028765\ mol}{0.025\ dm^3} = 0.115026 \approx 0.115\ mol\ dm^{-3}$$

Now, with all concentrations of the reactants accounted for, the value of k can be determined.

Sample Calculation:

Calculation

$$k = \frac{Rate}{[MnO2]1[H2SO4]1[H2O2]1}\ mol^{-2}dm^{-6}s^{-1}$$

$$k = \frac{8.17 \times 10^{-4}}{0.115 \times 0.06 \times 0.018}\ mol^{-2}dm^{-6}s^{-1}$$

$$k = 6.578099 = 6.58$$

To later determine the activation energy, further calculations can be performed to be substituted into the Arrhenius equation. I.e, through finding $(\frac{1}{T})$ and the Natural Log of the Rate constant (ln K)
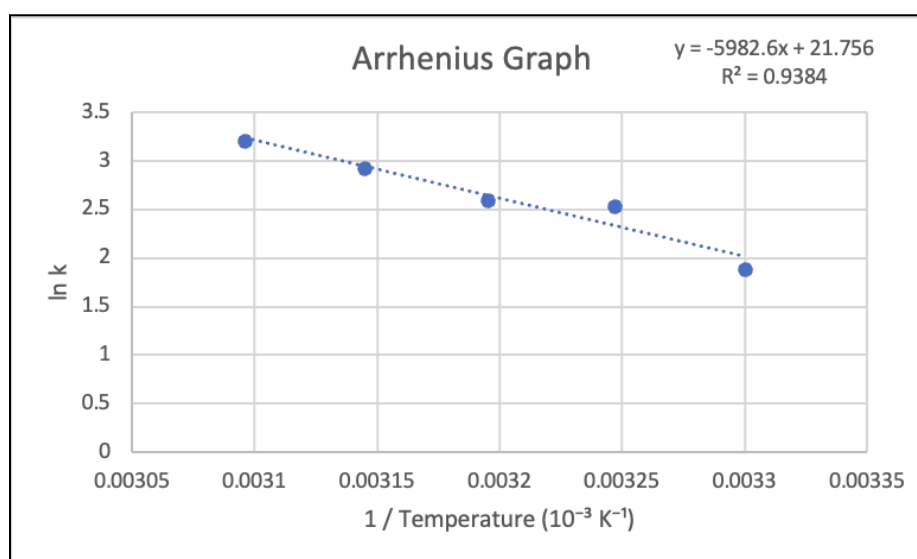
Sample Calculations for $\frac{1}{T}$ at 303.0 K:

Calculation	Uncertainty Propagation
$\frac{1}{T} = \frac{1}{303.0}$	$\%\ Uncertainty = \frac{Uncertainty\ of\ the\ Thermometer}{Temperature} \times 100\%$
$= 0.0033 = 3.3 \times 10^{-3}$	$\%\ Uncertainty = \frac{0.1}{303} \times 100\% = \pm\ 0.033\%$

Sample Calculations for (lnK) at 303.0 K:

$$lnK = ln\ (6.578099839) = 1.883745825 \approx 1.88$$

Table 6: Further Processed Data Table displaying the values required to find the activation energy.

Temperature (K) (±0.1 K)	Rate Constant (k) ($mol^{-2}dm^{-6}s^{-1}$)	1 ÷ Temperature (10^{-3} K^{-1})	Natural Log of the Rate constant (Ln k)
303.0	6.58	3.30	1.88
308.0	12.65	3.25	2.54
313.0	13.42	3.19	2.60
318.0	18.77	3.14	2.93
323.0	24.81	3.10	3.21

Figure 4: Arrhenius Plot of the reaction by plotting ln k and the reciprocal of temperature.

With the following data, the Arrhenius equation can then be used to solve for Activation Energy,

$$ln\ k\ =\ ln\ A\ -\ \frac{Ea}{R}\left(\frac{1}{T}\right)$$

$$Gradient\ of\ equation\ =\ -\frac{Ea}{R}\ =\ -5982.6$$

$$Ea\ =\ R\ \times\ Gradient\ of\ equation$$

$$Ea\ =\ 8.31\ \times\ 5982.6$$

$$Ea\ =\ 49715.406\ Jmol^{-1}\ =\ 49.72\ kJ\ mol^{-1}$$

6.4 Error Calculations:

To determine the random uncertainty, the percentage error for the following measurements need to be made. The average uncertainty for time, uncertainty for temperature, uncertainty for volume of gas and uncertainty of the volume of solution. Sample calculations are found previously except for the volume of solution.

Uncertainty of Volume of Solution

$$\% \, Uncertainty \; = \; (\frac{Graduated \, Cylinder \, Uncertainty}{Volume \, of \, Solution \, measured} \times \; 100) + (\frac{Graduated \, Cylinder \, Uncertainty}{Volume \, of \, Solution \, measured} \times \; 100) + (\frac{Digital \, Scale \, Uncertainty}{Mass \, of \, MnO_2} \times \; 100)$$

$$\% \, Uncertainty \; = \; (\frac{0.05}{10} \times \; 100) + (\frac{0.05}{15} \times \; 100) + (\frac{0.01}{0.25} \times \; 100)$$

$$\% \, Uncertainty \; = \; (0.5 + 0.33 + 4) = 4.83\%$$

Finally, the random uncertainty can be determined as the average of the total percentage uncertainty of each temperature.

Table 7: Percentage Errors

Temperature (K) (±0.1 K)	Average % Uncertainty for time measured (%)	Percent Uncertainty for Temperature (%)	Percent Uncertainty for Volume of Gas Evolved (%)	Percent Uncertainty of the Volume of Solution (%)	Total Percentage Error (%)
303.0	±0.02	±0.33	±0.22	±4.83%	±5.4
308.0	±0.03	±0.32	±0.22	±4.83%	±5.4
313.0	±0.04	±0.32	±0.22	±4.83%	±5.41
318.0	±0.06	±0.31	±0.22	±4.83%	±5.42
323.0	±0.08	±0.31	±0.22	±4.83%	±5.44
$Random \, Error \; = \; \frac{\Sigma \, Total \, \% \, Uncertainty}{Number \, of \, different \, Temperature}$			$Random \, Error \; = \; \frac{5.4+5.4+5.41+5.42+5.44}{5}$ $5.414 \approx \; 5.41\%$ (2.dp for consistency)		

7. Evaluation

7.1 Conclusion

The aim of this investigation was to study the relationship between increasing temperatures of Hydrogen Peroxide and the rate of producing oxygen with Manganese (IV) Dioxide and Sulfuric acid. Furthermore, the experiment was to also find the activation energy for this reaction. Nevertheless, the results of this experiment support the hypothesis that proposed that higher

temperatures would have higher rates of reaction. Also, a clear trend is found in the data. Returning to figure four, the graphs further support the hypothesis, where there is a negative relationship between the natural log of the rate constant and the reciprocal of temperature. In terms of the activation energy, the calculated value is **49.72 kJ mol^{-1}** $\pm\ 5.41\%$.

To determine the percentage error, the following equation can be used. The theoretical value for this reaction is taken from an MIT publication that stated the activation energy of the decomposition of hydrogen peroxide is 58 kJ/mole with a Manganese dioxide catalyst.

Calculating the Percentage Error and Systematic error:

$$Percentage\ Error\ =\ \left| \frac{(Experimental\ value - Theoretical\ value)}{Theoretical\ Value} \right| \times\ 100$$

$$Percentage\ Error\ =\ \left| \frac{(49.72 - 58)}{(58)} \right| \times\ 100\ =\ 14.27\%\ (2\ d.p\ for\ consistency)$$

$$Systematic\ Error\ =\ Total\ Error\ -\ Random\ Error$$

$$Systematic\ Error\ =\ 14.27\ -\ 5.41\ =\ 8.86\ \%$$

This experiment has a slightly high value of systematic error and random error. Regarding the former, the 8.86% systematic error resulted in a lower experimental value for the activation energy than the literature value. One possible explanation for this is the time lag between the stopper and the stopwatch, where time measurements are shorter than their true value. Thus, it suggests a higher rate which means lower activation energy. Regarding the random error, the high random error can be suspected due to certain limitations from the nature of the experiment. Due to limitations such as the loss of gas from the stopper, it is difficult to contain all of the gas that evolved from this experiment. Random error due to uncertainty can be adjusted by more trials.

Table 8: Table of Strengths of the Investigation

Strengths	Significance
High R^2 value	Using Excel, when graphing the Arrhenius plot, the returned R^2 value is 0.9384. This value demonstrates that there is a strong positive correlation between $\frac{1}{T}$ and $ln\ k$ and high accuracy in the data.
Use of Technology	With the apparatus, using electronic measuring devices such as an electronic temperature probe or a digital scale provides more accurate data and reduces errors such as parallax error. The use of Excel and other software reduced the chance of error when performing mathematical calculations.
Effective Setup of Apparatus	Using a water bath (Compared to methods such as direct contact to a hotplate or bunsen burner) as a way of heating the reactant solutions is effective because it allows heat/thermal energy to evenly distribute throughout the solutions when heating the hydrogen peroxide solution.

Table 9: Table of the Limitations of the Investigation

Limitations	Significance	Solution
Uneven pouring of solutions (Random)	Due to the small diameter of the Schlenk flask and the urgency to quickly pour all reactants because gas could be lost, solutions were sometimes unevenly poured. This would make the results be longer or shorter than the true value.	Potential solutions are using different apparatus with this investigation. For example, using a reaction vessel or a burette could result in more even pouring of hydrogen peroxide and acid into solution.
Elimination of Data Points (Systematic)	When collecting data, numerous data points were removed from consideration and the trials had to be repeated because some reactions reacted too quickly or slowly. The removal of these points could affect data due to subjective-bias.	Collecting more trials and data points would more clearly identify what are valid trials and what are outliers.
Loss of Gas when putting stopper on the Schlenk Flask (Human)	To initiate the reaction, all the reactants need to be poured into the Schlenk flask then closed by a stopper. The reaction is very fast, and naturally, some gas escapes. This causes an inaccuracy with the data.	A way to reduce this error is to have multiple researchers assist with the experiment so that trials can be done as quickly as possible. Another method could be using apparatus such as a gas valve.
Time Lag between Stoppers and Stopwatch (Systematic)	After placing all the reactants in the Schlenk flask, the timer would begin to determine the amount of time it takes for the amount of gas to fill up. However, each trial would be slightly affected by this time delay, which affects the average rate of reaction.	One way to avoid this error is to record the reaction and determine the time digitally. Another way to reduce this error is to have multiple researchers assist with the experiment to reduce the time delay.
Issues with mixing the solutions (Systematic)	With every trial, the solution was swirled once to create a more uniform solution. Issues arise where each swirl is produced by a different amount of force.	Using an apparatus such as a stir bar and magnetic hotplate-stirrer could more effectively create a uniform solution and reduce this error.

7.2 Extensions

This investigation can be extended in different ways. The mechanism of the oxidation from MnO_2 is strongly dependent on the pH environment (Pędziwiatr et al.) Nonetheless, one method of exploration is to use different acids and varying concentrations to determine its effect with this reaction. Depending on the strength of the acid and its concentration, it is important to discover new methods to prevent gas production from producing too quickly. From this reaction, 0.6 M Sulfuric acid resulted in very fast production of oxygen, hence either weaker acids or even lower concentrations of acid should be studied to produce observable and sensible results.

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