IB Chemistry
Higher Level

How does the addition of an 0.1 moldm^{-3} iron (III) chloride catalyst affect the activation energy of the decomposition of hydrogen peroxide?

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Introduction

In my study of chemical kinetics, I encountered the properties of hydrogen peroxide (H_2O_2), a chemical is notably used as a bleaching agent in the processing of shark fins - a traditional Chinese dish. As someone who has been hospitalised after eating a contaminated bowl of shark fin soup, I am conscious of the health risks in consuming the product. This led me to question the role of hydrogen peroxide in my food poisoning, as well as how to reduce these impacts. A study by the Hong Kong Centre of Food Safety showed that samples of shark fin were found to have residual hydrogen peroxide with concentrations as high as 1.5%. Fortunately, the health risks to this were minimised as hydrogen peroxide readily decomposes into water and oxygen upon heating.

$$2H_2O_2\ (aq) \rightarrow 2H_2O\ (l) + O_2\ (g)$$

In light of this information, I was interested in finding out how to increase the rate of decomposition of hydrogen peroxide. One way this could be done was by reducing the reaction's activation energy. I thus decided to examine the impact of adding an iron (III) chloride catalyst. This was because iron chloride is a homogenous catalyst, which encourages higher catalytic activity as they are more easily accessible to the reactants.

Background Information

In any given reaction, the activation energy (E_A) is the minimum amount of energy required for bond dissociation in the reactants to occur. Provided that reactants also collide in the sufficient orientation, the ensuing reaction forms a transition state, from which these bonds reform to create the reaction's products. The literature value for the uncatalyzed decomposition of hydrogen peroxide is +75kJ/mol.

Adding a catalyst would lower the E_A by providing an alternative reaction pathway, as illustrated by Figure 2 on page 4. Hence, the frequency of successful particle collisions would increase, as demonstrated by the Maxwell-Boltzmann diagram on page 4. A method of deciphering a reaction's activation energy would be through an equation devised by Svante Arrhenius, which characterises the relationship between temperature and reaction rate. The equation is as follows:

$$k = Ae^{-Ea/RT}$$

In this equation, k is the rate constant, A is frequency of collisions in the correct orientation, T is the temperature in Kelvin, and R is the universal gas constant. A rearranged version of the natural logarithm of this reaction results in the following equation:

$$\ln k = (-E_A \div R) \times (1 \div T) + \ln A$$

This is in the same format as the equation of a straight line. Therefore, one can find the activation energy by plotting a graph of ln *k* against 1÷T. The gradient in this line would therefore equal $-E_A \div R$, from which one can multiply by -R to compute the E_A value.

With an iron (III) chloride catalyst, the rate expression for the decomposition of hydrogen peroxide is $r = k[H_2O_2][Fe^{3+}]$. In this expression, *r* is the rate of reaction: the change in concentration of H_2O_2 per second. The rate of reaction will be experimentally collected via measuring the time taken for a certain volume of oxygen gas to be produced. As oxygen is one of the products of this reaction, another method that could have been used to measure the rate of reaction is by measuring the change in mass as oxygen escapes from the flask. However, this was not used because the low quantity of reactants used would create the risk for a higher rate of uncertainty.

The reaction mechanism for the decomposition of H_2O_2 (Haber and Weiss, 1932) is that of a chain reaction, as shown below:

1. Chain initiation: $Fe^{3+} + H_2O_2 \rightleftharpoons [Fe^{III}OOH]^{2+} + H^+ \rightleftharpoons Fe^{2+} + HOO\bullet + H^+$
2. Chain propagation: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + 2OH\bullet$
   $Fe^{3+} + H_2O_2 + OH\bullet \rightarrow Fe^{3+} + HOO\bullet + H_2O \rightarrow Fe^{2+} + H^+ + O_2 + H_2O$

Another proposed mechanism (Kremer and Stein, 1959) involves the production of an intermediate oxygen complex, which reacts with another H_2O_2 molecule to form water and oxygen while regenerating the ferric ion:

$$Fe^{3+} + H_2O_2 \rightleftharpoons [Fe^{III}OOH]^{2+} + H^+ \rightleftharpoons [Fe^{V}O]^{3+} + H_2O \text{ -> } 2H_2O + O_2 + Fe^{3+}$$

Methodology

Table 1: Apparatus Used and Margin of Error of Apparatus (if applicable)

Material Used	*Uncertainty Rate*
250cm^3 volumetric flask	±0.15cm^3
Stopwatch	±0.5s (accounting for reaction time)
25cm^3 measuring cylinder	±0.5cm^3
Thermometer	±0.1°K
100cm^3 gas syringe	±0.1cm^3
800cm^3 beaker (to be used as water bath)	N/A
500cm^3 of 1 moldm^{-3} hydrogen peroxide	
200cm^3 of 0.1 moldm^{-3} iron (III) chloride	
450cm^3 of distilled water	
Clamp stand	
Boiling tubes	
Boiling tube rack	

Apparatus Set-Up

Figure 1: A photograph displaying the apparatus setup before the commencement of the experiment, with a boiling tube connected to a gas syringe held by a clamp stand.

Figure 2: An enthalpy diagram showing the change in activation energy for the decomposition of hydrogen peroxide when a catalyst is used. (Burns, 2003)

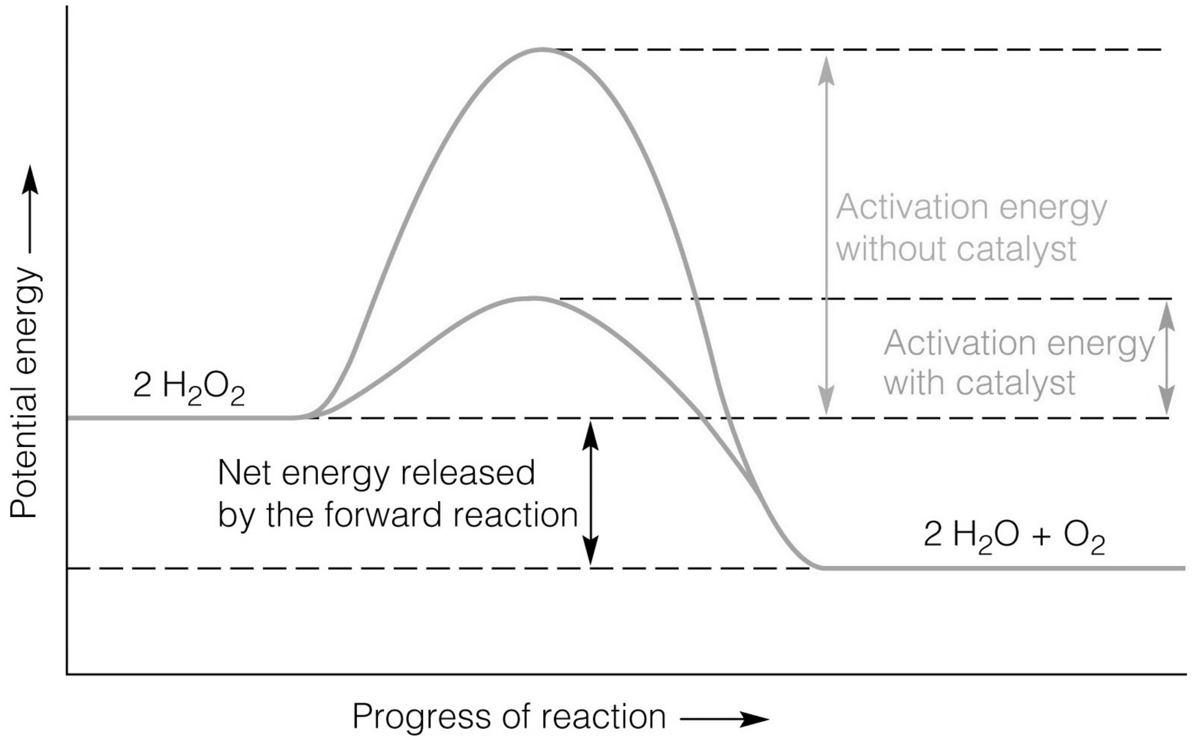
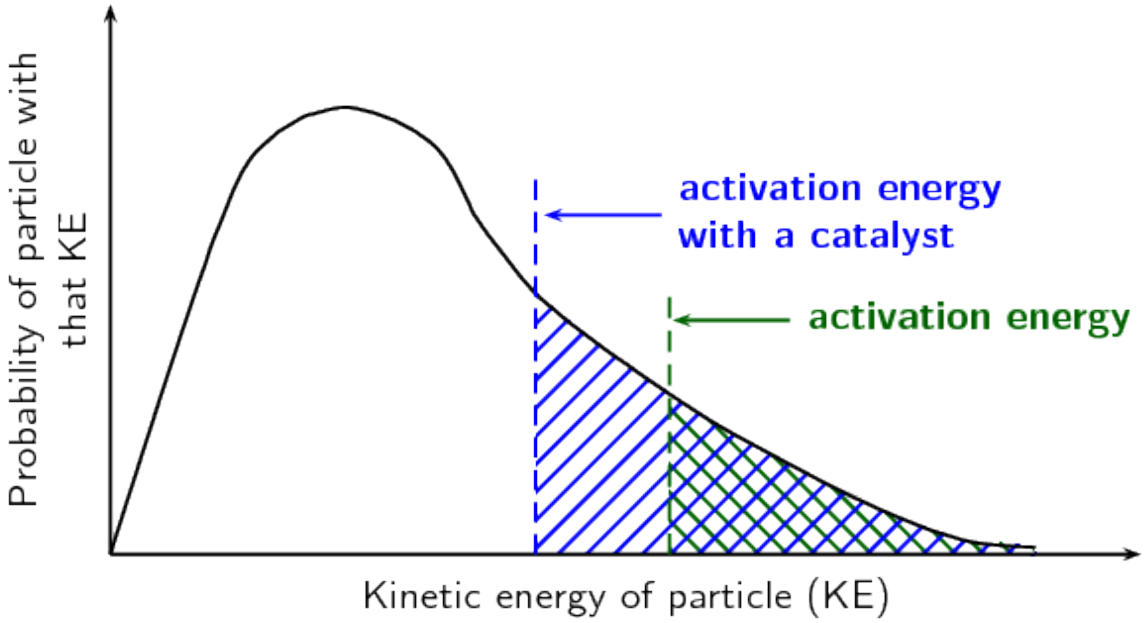


Figure 3: A Maxwell-Boltzmann graph displaying the amount of particles that surpass, or are equal to, the activation energy in reactions occurring with and without a catalyst. (Horner, Davies, and Toerien, 2012)



Investigation Variables

The **independent variable** of this investigation is **temperature (K).** This will be altered via changing the temperature of the water bath in which the reaction occurs. A kettle has been kindly lent out for use during this investigation, and I hence will pour hot water into my water bath until the thermometer reading is commensurate with the temperatures I intend to investigate below. This independent variable has been chosen as I am able to, using the Arrhenius equation, find the activation energy of this reaction through the gradient of a graph of ln k against 1/T. The temperature values that were tested were 328.0K, 333.0K, 338.0K, 343.0K and 348.0K. These values were chosen as the high temperatures would decrease the time taken for the reaction to occur. Furthermore, the use of five different values increases the reliability of any trendline that my results infer.

The **dependent variable** of this investigation is **the time taken for 10cm^3 of oxygen gas to be produced**. This will be measured through a gas syringe with a bung connected to the boiling tube that the reaction occurs in. This dependent variable has been chosen as one can find the rate of reaction using the previous equation: $r = k[H_2O_2][Fe^{3+}]$, in which the concentration of both H_2O_2 and Fe^{3+} are of 0.1 moldm^{-3}. Calculating k is integral in plotting the graph of ln k vs 1/T, which can be multiplied by the negative of the gas constant to result in the activation energy value.

A detailed overview of the control variables, along with the steps taken to minimise their impact on this investigation, can be seen below:

Table 2: Control Variables

Control Variable	*Steps Taken To Minimise Impact*
Surrounding pressure	Data from the Hong Kong Observatory states that there are minimal changes in atmospheric pressure over the course of the two weeks when this experiment was conducted; pressure can therefore be considered as a control variable. Any significant changes could impact the moles of oxygen gas evolved, as per the ideal gas law.
Volume of reactants	The volumes of $FeCl_3$ and H_2O_2 that were kept consistent at 10cm^3 and 25cm^3 respectively. Any changes in volume could affect the calculated rate of reaction. Both of these solutions were measured with a 25cm^3 measuring cylinder.
Concentration of reactants	The concentrations of $FeCl_3$ and H_2O_2 in the experiment were kept at 0.1moldm^{-3} for all trials. This was done by diluting samples of 1 moldm^{-3} to a concentration of 0.1 moldm^{-}3via a volumetric flask. Concentration is another variable that can change an experiment's rate of reaction, which makes discerning the impact of changes in temperature on the rate of reaction unclear.

Risk Assessment

According to its CLEAPSS Hazcard, hydrogen peroxide at high concentrations has the risk of causing irritation to the eyes and skin, and may be harmful if swallowed. As it decomposes to produce water and oxygen, pressure may build up and care needs to be taken when opening a bottle of the chemical.

Furthermore, CLEAPSS states that iron (III) chloride poses the risk of being harmful if swallowed, causing skin irritation and serious eye damage on contact with the skin and eyes. Some suppliers classify solutions more concentrated than 0.2M as corrosive.

To minimise these risks, I will be working with goggles and latex gloves in the entire duration of my experiment. In between sessions, I will store my hydrogen peroxide solution away from heat and light. Both chemicals will be diluted to a concentration of 0.1moldm^{-3} to minimise the impact of any accidents. I will not dispose of these chemicals through the sink, and will instead do so separately through a chemical waste basket.

Experimental Procedure

1. Prepare a standard solution of hydrogen peroxide with a concentration of 0.1 moldm^{-3} by diluting a 1.0 moldm^{-3} sample of the liquid in a volumetric flask.
2. Set up a water bath with a temperature of 348.0K, with a boiling tube attached to a gas syringe within it. This gas syringe will be held up by a clamp.
3. Measure 25 cm^3 of the diluted hydrogen peroxide using a measuring cylinder, and pour it into the boiling tube.
4. Pour 10 cm^3 of 0.1 moldm^{-3} iron (III) chloride into the boiling tube. At the same time, start the timer of a stopwatch.
5. Record any observations as necessary.
6. Stop the timer once 10 cm^3 of oxygen gas has been collected, as per the gas syringe.
7. Repeat steps 3 to 5 thrice, for a total of four experimental attempts.
8. Repeat steps 2 to 7, using a water bath with temperatures of 343.0K, 338.0K, 333.0K and 328.0K.

This experimental procedure was adapted from the Job Foundation of Thermodynamics. The primary differences between the method outlined above and the method shown on their corresponding documents are the stochiometric quantities used, as well as the choice of laboratory glassware in which the reaction is conducted in.

A multitude of methods were attempted in the conduction of this experiment. While several attempts were made using the adapted volumes of 10cm^3 H_2O_2 and 2cm^3 $FeCl_3$ initial observations showed no evidence of a reaction within 10 minutes. The slow rate of reaction could have been due to the small volume of oxygen gas that was expected to be produced (approximately 24.5cm^3), much of which could have escaped before the gas syringe was attached to the boiling tube. I therefore increased the initial volume of H_2O_2 to 25cm^3.

Alternatively, the low temperatures of my initial method could also have hindered the speed at which results were collected. Although had planned on using a range of 278.0, 288.0, 298.0, 308.0, and 318.0K, the slow rate of reaction prompted me to increase the range to 328.0, 333.0, 338.0, 343.0 and 348.0K. As stated by the ideal gas law [$pV = nRT$], increasing temperature would also increase the moles of gas evolved, thus decreasing the time taken to obtain only 10cm^3 of oxygen gas. After implementing these changes, there was a sharp difference in my raw results between the first and second attempts with a water bath at 348K. To sustain the reliability of results, I then completed another trial for all temperatures.

Raw Data

Quantitative Observations

Table 3: A table displaying the time taken in each experiment to produce 10cm^3 of oxygen gas at all investigated temperatures for the catalysed decomposition of hydrogen peroxide.

Temperature (±0.1°K)	*Time taken for 10 cm^3 of oxygen to evolve* (±0.5s)			
	trial 1	*trial 2*	*trial 3*	*trial 4*
328.0	31.3	43.2	58.0	42.7
333.0	18.1	21.4	10.5	23.3
338.0	10.6	12.9	16.6	20.8
338.0	13.6	10.6	16.7	11.2
348.0	**29.3**	10.1	8.0	13.12

(Note: The result in bold in Table 3 is anomalous, and will not be included in any further calculations. Furthermore, displayed values are shown to one decimal place to align with the uncertainty of the stopwatch and reaction time. Full values were used in all calculations.)

Qualitative Observations:

Applicable to all runs

1. Reaction started releasing gas immediately after contact, increases magnitude of error as this contact was before the bung was placed or the stopwatch had started.
2. An immediate colour change occurred from colourless (colour of hydrogen peroxide) to orange-brown (initial colour of iron (III) chloride), but there was no colour change during the reaction itself.
3. Boiling tube immediately warm to the touch.

Observations particular to a certain trial

1. For all reactions at 328.0K: gas released for ~20 seconds on average before the reading on the gas syringe began to move.
2. For all reactions at 333.0, 338.0, 338.0 and 348.0K: immediate release of gas for experiments in other temperatures.
3. For trial 3 at 348K: despite adding the same volume of H_2O_2 and catalyst, the final colour of this test tube was significantly darker (brown) than other experiments.

Data Analysis

Calculating the rate of reaction

The mean amount of time taken to produce 10cm^3 of oxygen gas was calculated with the below formula:

(Σ time taken to produce 10cm^3 of oxygen gas for each trial) ÷ (number of trials)

An example calculation is displayed below for reactions at 348K.

$$10.14 + 7.98 + 13.13 \div 3 = 10.4\text{s}$$

This was repeated with trials at all other temperatures to result in the following table:

Table 4: A processed data table displaying the mean amount of time taken (s) to evolve 10cm^3 of oxygen gas for trials at all investigated temperatures

Temperature (K)	*Time taken for 10 cm^3 of oxygen to evolve*
328.0	43.8
333.0	18.3
338.0	15.2
338.0	13.0
348.0	10.4

To calculate the amount of moles of oxygen evolved, a rearranged version of the ideal gas law was used as follows:

$$n = pV \div RT$$

$$n = 101\,000 \times 0.01 \div 1\ 8.314 \times 348$$
$$n = 0.35 \text{ mol [of } O_2 \text{ produced]}$$

This formula was used to find values for *n* at all other temperatures. As the equation for the decomposition for hydrogen peroxide has a molar ratio of 1:2 between O_2 and H_2O_2, the value of *n* was multiplied by 2 to calculate the moles of H_2O_2 that was reacted.

The rate of reaction (r) was calculated by dividing the amount of moles of H_2O_2 reacted by the average time taken for 10cm^3 of oxygen gas to be produced. An example calculation at 348K is displayed below:

$$r = [0.35\times2] \div 10.4$$
$$r = 0.067 \text{moldm}^{-3}\text{s}^{-1}$$

This formula was used to find values for *r* at all other temperatures, which has been summarised in the following table:

Table 5: A processed data table displaying the number of moles of oxygen gas evolved (mol), the number of moles of H_2O_2 *consumed (mol) and the rate of reaction (moldm^{-3}s$^{-1)}$ for each temperature investigated (K) (±0.1K)*

Temperature (K)	Moles of O_2 evolved	Moles of H_2O_2 evolved	Rate of Reaction (moldm^{-3}s^{-1})
328.0	0.37	0.74	0.017
333.0	0.36	0.73	0.040
338.0	0.36	0.72	0.047
338.0	0.35	0.71	0.054
348.0	0.35	0.70	0.067

Calculating the natural logarithm of the rate constant

Using the rate expression of $r = k[H_2O_2][Fe^{3+}]$, the rate constant can be found by dividing the rate of reaction with the product of the initial concentrations of hydrogen peroxide and iron (III) chloride. As the molar ratio of Fe^{3+} and $FeCl_3$ is 1:1, this value need not be changed. An example calculation at 348K is displayed below:

$$k = r \div [H_2O_2][FeCl_3]$$

$$k = 0.067 \div [0.1]\,[0.1]$$
$$k = 6.70$$

The natural logarithm was taken for all values of k to give the y-axis of an Arrhenius graph.

Table 6: A processed data table showing how k and ln k varies with temperature.

Temperature (K)	*Rate constant (k)*	*ln k*
328.0	1.69	0.53
333.0	3.98	1.38
338.0	4.72	1.55
338.0	5.44	1.69
348.0	6.70	1.90

The x-axis of the Arrhenius graph is of (temperature^{-1}), which was calculated by dividing 1 by the temperature (K) the reaction took place in.

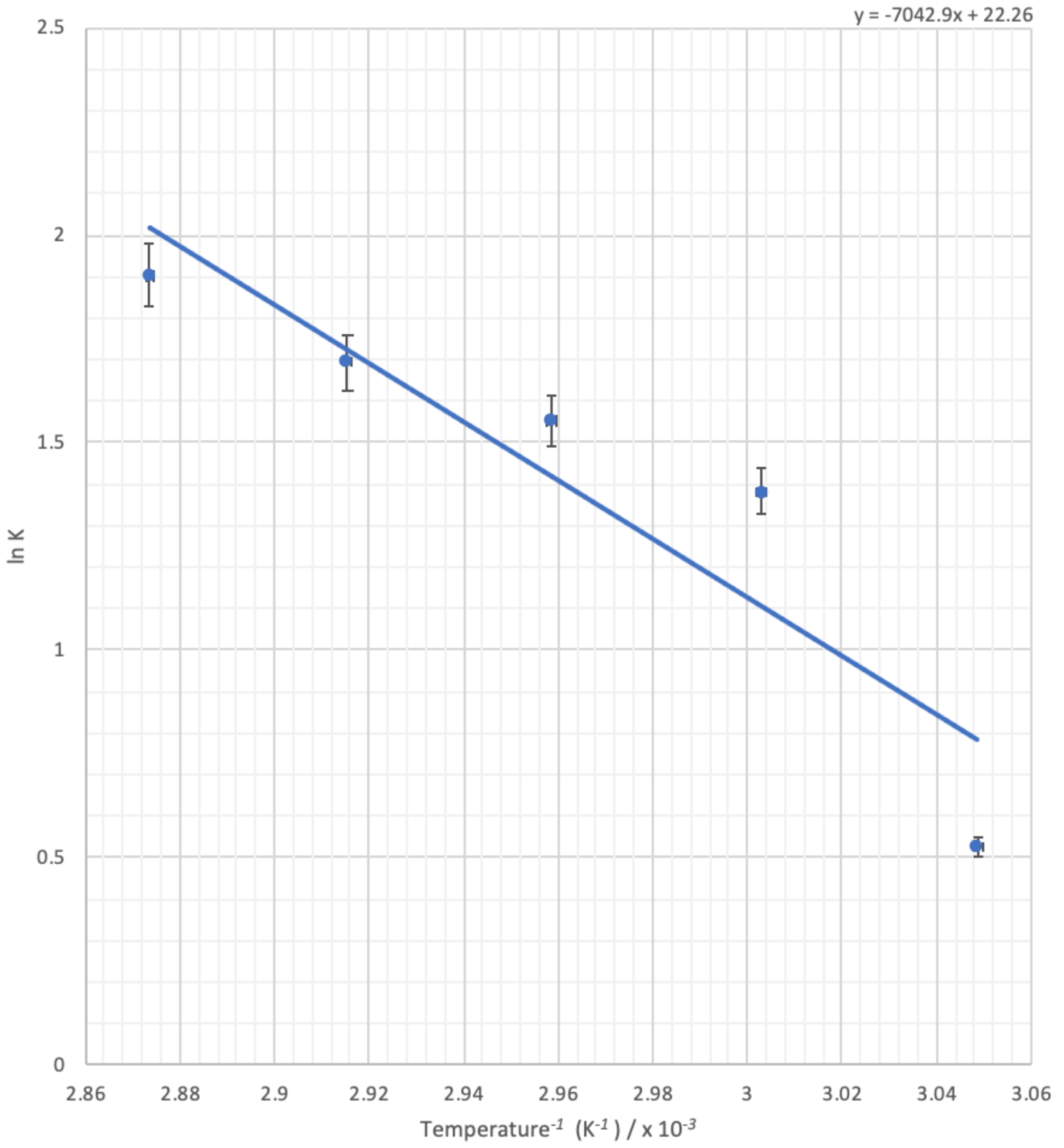
Table 7: A processed data table showing the different temperatures (K^{-1}) of this investigation

Temperature (K)	*(Temperature)* $^{-1}$ *(K^{-1})*
328.0	0.00305
333.0	0.00300
338.0	0.00296
338.0	0.00292
348.0	0.00287

Table 8: A processed data table showing the change in ln K with (Temperature) $^{-1}$

(Temperature) $^{-1}$ *(K^{-1})*	*ln k*
0.00305	0.53
0.00300	1.38
0.00296	1.55
0.00292	1.69
0.00287	1.90

Figure 3: An Arrhenius graph displaying the change in ln k with (Temperature)$^{-1}$, alongside the equation of the line of regression



Calculation of Activation Energy

As shown in Figure 3, the gradient of the graph's line of regression is -7042.9. Using a rearranged form of the Arrhenius equation, the activation energy can be found by multiplying the negative gradient of the line of regression by the gas constant:

$$E_A = -7042.9 \times -8.314$$
$$E_A = +58.55\text{kJ/mol}$$
$$E_A = +59\text{kJ/mol}$$

For comparison, the literature value for the uncatalyzed decomposition of hydrogen peroxide is +75kJ/mol. Therefore, one can surmise that the addition of an iron (III) chloride catalyst decreases the activation energy of this reaction by approximately 16kJ/mol, or 21%.

Calculation of Random Error

The percentage uncertainty in the calculated value of activation energy lies within the error of the gradient of the Arrhenius' graph. Separate percentage uncertainties were computed in calculating ln k and temperature, and they were used to calculate the uncertainty of the slope.

Percentage Uncertainty in Calculating ln k

The percentage uncertainty in collecting the moles of oxygen gas evolved factors in both the uncertainty of the thermometer and the gas syringe, as both volume and temperature were taken into account in the ideal gas law. Uncertainties in both of these pieces of apparatus were calculated using the following general formula:

Percentage uncertainty = uncertainty of the apparatus itself (see table 1) / the value measured, multiplied by 100.

Example calculations at 348K are displayed below:
Uncertainty of gas syringe: $(\pm 0.1\text{cm}^3 \div 10\text{cm}^3) \times 100 = 1\%$
Uncertainty of thermometer: $(\pm 0.1\text{K} \div 348\text{K})\ 100 = 0.03\%$

The percentage uncertainty in the time taken for 10cm^3 of oxygen to evolve was calculated using the above general formula for all trials. The rate of uncertainty for a particular temperature was the mean value of the percentage uncertainties of its constituent trials.

$$[(\pm 0.5 \div 13.13) + (\pm 0.5 \div 7.98) + (\pm 0.5 \div 10.14)] \div 3 = 0.05\%$$

The percentage uncertainty in the volume of the solution was the sum of the uncertainties in the volumetric flask used to create the standard solution and the measuring cylinder used to extract both the iron (III) chloride and dilute hydrogen peroxide.

Uncertainty of volumetric flask: $\pm 0.15\text{ cm}^3 \div 250\text{ cm}^3 \times 100 = 0.06\%$
Uncertainty of measuring cylinder: $\pm 1.0\text{ cm}^3 \div 35\text{ cm}^3 \times 100 = 3\%$

These uncertainties were summed to create a range of error for all data points on the y-axis. The uncertainty in temperature was restated to give the range of error for points on the x-axis.

Temperature (K)	Uncertainty in time taken for gas to evolve (%)	Uncertainty in moles O_2 collected (%)	Uncertainty in volume (%)	Total y-axis uncertainty (%, 1 significant figure)	Total x-axis uncertainty (%, 1 significant figure)
328	0.01	1.00	2.92	4	0.03
333	0.03	1.00	2.92	4	0.03
338	0.04	1.00	2.92	4	0.03
343	0.04	1.00	2.92	4	0.03
348	0.05	1.00	2.92	4	0.03

Taking these uncertainties into account resulted in the error bars shown on Figure 3 in page 10. Due to the low level of uncertainty, it was infeasible to draw alternate lines of best fit by hand. I thus used Excel's LINEST function to calculate the uncertainty of the graph's slope.

This produced an uncertainty of ±1740 out of a gradient of -7043, which amounted to a rate of random error of 24%, or ±15kJ/mol. Such a degree of uncertainty definitively compromises the reliability of the 59kJ/mol value of activation energy stated earlier.

Evaluation

Conclusion

Despite the uncertainties propagated with the computed value of this experiment, comparisons with the literature E_A value of H_2O_2 decomposition (+75kJ/mol) shows that the addition of an iron (III) chloride catalyst reduces the activation energy by approximately 21%. Similar research using a goethite catalyst - a mineral also containing the Fe^{3+} ion, the reactant catalysing the decomposition of H_2O_2 - has resulted in an activation energy of 32kJ/mol, which can be used as a literature value. Hence, the percentage error of this experiment is as follows:

$$59-32 \div 59 = 46\% \text{ error}$$

Even when accounting for the high random error shown above, it is evident that this experiment still had sources of systematic error. Nonetheless, this investigation has shown the decreasing effects of a Fe^{3+} catalyst on the activation energy of decomposition, which is in line with scientific orthodoxy. The high degree of random error, however, puts into consideration the extent to which the activation energy has decreased.

Strengths

The temperature of the reaction was tightly controlled and recorded, resulting in low random errors in that regard. One of the factors contributing to this low random error is the use of a water bath made of glass, which is a thermal insulator. This prevented the excess loss of heat after boiling water was poured in. Furthermore, the thermometer was added directly into the boiling tube in which the reaction occurred, which resulted in an accurate measurement of temperature. These values were used twice - both in calculations for the moles of gas evolved and in computing 1/T - and thus their low margin of error increased the validity of results.

Limitations	*Impact on Results*	*Improvements*
Random: Use of imprecise apparatus - a measuring cylinder was used to collect both my solutions of ferric chloride and hydrogen peroxide.	This decreases the reliability of my results through the propagation of random error, which amounted to half of the percentage error between my results and the literature value.	This error can be mitigated by using more precise apparatus, especially in measuring reactants. Using a graduated pipette would be of use.
Systematic: A significant volume of gas may have escaped before I connected the gas syringe to each boiling tube. My qualitative observations show that gas started being released immediately, while there was sometimes a 2-3 second gap between the start of the stopwatch timer and movement of the gas syringe.	As the first few seconds of a reaction has the highest rate of reaction, I may have been overestimating the time taken to produce 10cm^3 of gas. This would compromise my value of the rate constant (k). I view this to be the most important source of systematic error, because the small quantities of product involved could have largely escaped in a 2-3 second period of time.	This error can be reduced if this experiment had been collaborative; having another person start the stopwatch would have me connect each boiling tube to the gas syringe in a shorter period of time.
Systematic: As I used the same volumetric flask of H_2O_2 between lessons, a small amount of the solution could have decomposed.	This could have changed the concentration of the hydrogen peroxide, which is integral in calculating the rate constant. This therefore propagates a systematic error.	Provided the time, I could have made a standardised solution immediately before each reaction.
Systematic: As only 10cm^3 of oxygen gas was collected, this rate measured is only an average of the first 10cm^3 - qualitative observations showed that this evolved at a faster rate than the remaining ~50cm^3 of oxygen gas.	This compromises the accuracy of my rate of reaction, which is used in calculating values of the rate constant (k). This hence reduces the accuracy of the gradient of my Arrhenius plot as a systematic error.	In future runs, this experiment could measure higher volumes of gas. However, this would not be sufficient unless a method was deciphered for a minimal amount of gas to escape before the reaction was connected to the boiling tube.

Extensions for Investigation

To further expand on the scope of this experiment, one could examine the impact of other variables on the activation energy of H_2O_2 decomposition - notably, the effects of pH and reactant concentration. Furthermore, the literature value that was cited is not without error; to more closely control the effects of confounding variables (particularly temperature), this experiment could, given the resources, first measure the activation energy of uncatalyzed decomposition of hydrogen peroxide.

This experiment could also serve as a point of comparison with other catalysts for the same reaction, particularly in d-block elements; a further investigation could aim to decipher, and explain, the most effective catalyst of this particular reaction.

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