1. Research Question:

How does the time taken for 20 mL of carbon dioxide gas to evolve in a eudiometer depend on the temperature of the solvent (20°C, 35°C, 50°C, 65°C), in a calcium carbonate and 0.25M hydrochloric acid reaction and hence, what is its activation energy?

1.1 Introduction

A year ago, I was sent to emergency since I had appendicitis, causing me severe stomach pain. One of the first medicines I took to help relieve the pain was antacids tablets containing calcium carbonate which helps relieve heartburn, indigestion and an upset stomach caused by too much stomach acid. (Haskins, 2013) It does this by neutralizing some of the hydrochloric acid present in the stomach acid which is essential in the digestive system for breaking down food into nutrients and killing bacteria. (National Library of Medicine, 2016) These tablets did not relieve my pain, but rather made me feel extremely gassy very quickly and I wondered if my high body temperature was a result of this. Upon learning Topic 6: Kinetics, I learned how reaction rate can be influenced by temperature which could explain my reaction to this medicine and hence decided to investigate the temperature dependence of the neutralization reaction of calcium carbonate and hydrochloric acid in this IA. Additionally, by expanding my IA to determine the activation energy of this reaction, a practice used in pharmaceutical manufacturing to determine drug stability, I can gain insight into the conditions that led to my reaction to the tablets I had taken.

2. Background Information:

2.1 Calcium carbonate and hydrochloric acid reaction

Hydrochloric acid and calcium carbonate neutralize to form calcium chloride, carbon dioxide and water as shown in the balanced equation below

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \quad (1)$$

This reaction is a first-order overall reaction with respect to HCl, meaning that the rate of reaction is dependent solely on the concentration of HCl. (Notari et al., 1965) This can be represented in the rate expression below:

$$Rate = k[HCl]^1$$

Where Rate is the rate of reaction, k is the rate constant and [HCl] is the concentration of HCl. By rearranging the equation to isolate for the rate constant k, I get the following equation.

$$k = \frac{Rate}{[HCl]^1} \quad (2)$$

2.2 Measuring Rate of Reaction

In this investigation, I will determine the rate of reaction, a measure of products produced per unit of time. Since this reaction produces CO_2 gas, using a eudiometer to collect this gas would be appropriate. Specifically, I will measure the time for 20 mL of CO_2 gas to be evolved in the eudiometer. Through beta testing, I determined that 20 mL in the eudiometer was the optimal amount of gas so that the reaction would not be too slow or fast to be recorded. Hence, by dividing 20 mL by the time taken for 20 mL of gas to be evolved, I can determine how much gas is evolved per second. In addition, by using stoichiometry, I can determine the rate of reaction with the units $\frac{M}{s}$ which would be the appropriate units for a first-order overall reaction.

Through initial research of this reaction being a first-order reaction and beta testing, I found that the time for 20 mL of CO_2 gas to be evolved decreases logarithmically as temperature increases. Hence, the range I chose for temperature increments was 20°C to 65°C to fully observe this logarithmic decrease. While it may seem illogical given that calcium carbonate and hydrochloric acid react at room temperature (20°C) and stomach acid is normally 37°C, I wanted to simulate the most extreme cases of this reaction as pharmacies tend to do to increase shelf life and effectiveness of medicines. Many factors could influence the temperature of stomach acid such as having a hot beverage immediately before taking an antacid tablet. However, I capped my extremes at 65°C as through beta-testing, reaching HCl temperatures of 80°C would result in a decrease in volume as water evaporates by around 0.15 g per 10 mL of 0.25M HCl whereas the decrease of volume in 65°C HCl was negligible.

10 mL of HCl was used for each trial to reduce chemical waste. I decided to alter the concentration of HCl due to 1M HCl reacting too fast and at a non-observable pace during beta testing. Calculations are shown below.

$$M_1V_1 = M_2V_2 \rightarrow M_2 = \frac{M_1V_1}{V_2} = \frac{1M\ HCl \cdot 100\ mL\ HCl}{(100\ mL\ HCl + 300\ mL\ water)} = 0.25M\ HCl$$

To minimize reactant waste, I set the amounts of moles of each reactant equal to each so that there is no excess in any reagent. This was done using Stoichiometry below:

$$0.010\ L\ HCl \cdot \frac{0.25\ mol\ HCl}{1\ L} \cdot \frac{1\ mol\ CaCO_3}{2\ mol\ HCl} \cdot \frac{100.09\ g\ CaCO_3}{1\ mol\ CaCO_3} = 0.125\ g\ CaCO_3$$

Hence for each trial, 10 mL of HCl will react with 0.125 g $CaCO_3$.

2.3 Effect of Temperature

According to collision theory, reactions occur when particles collide with sufficient energy and correct orientation. Temperature is directly proportional to the average kinetic energy of particles in a substance so by increasing the temperature of my solvent, more HCl particles will have sufficient energy to react with the calcium carbonate particles and will move faster, therefore colliding more times with calcium carbonate particles. This is shown in the following Maxwell-Boltzmann distribution curve.

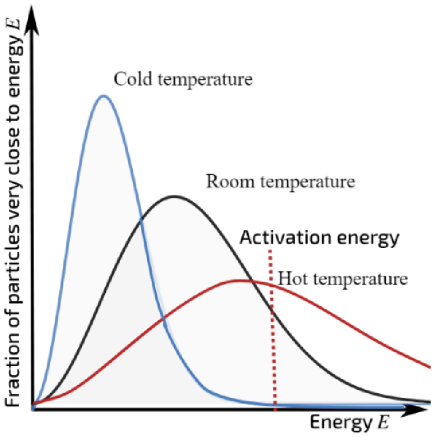

Figure 1: Maxwell Boltzmann distribution curve of different temperatures (shiken)

2.4 Calculating Activation Energy

Using the Arrhenius equation, I can determine the activation energy of this reaction:

$$k = Ae^{\frac{-E_a}{RT}}$$

Where k is the rate constant, A is the Arrhenius Constant, E_a is the activation energy, R is the gas constant (8.31 J/kmol) and T is the Temperature in Kelvin. Rearranging the equation into a linear equation y = mx+b I get:

$$lnk = -\left(\frac{1}{T}\right)\frac{E_a}{R} + lnA \qquad (3)$$

And by plotting lnk and $\frac{1}{T}$ on a graph, I am able to obtain a graph in which the y-intercept is lnA and the gradient is $-\frac{E_a}{R}$. Since R is the gas constant, by multiplying the obtained gradient by -R, I will be able to determine the activation energy of a 0.25M hydrochloric acid and calcium carbonate reaction.

2.5 Hypothesis

If the temperature of hydrochloric acid is increased, then the time for 20 mL carbon dioxide gas to evolve in a eudiometer with decrease since with higher temperature, more HCl particles have

sufficient activation energy to react and more collisions occur resulting in a higher probability of having the correct geometry.

3. Methodology:

3.1 Variables

Independent Variable	Temperature of HCl used in the reaction (20°C, 35°C, 50°C, 65°C). This range was chosen to simulate pharmaceutical practices of testing extremes, 65°C, to gain insight into shelf life and effectiveness. 20°C was chosen as the opposite extreme since room temperature serves as a base value to observe change.
Dependent Variable	Time to evolve 20 mL of CO_2 gas, measured using a eudiometer set-up

Control Variable	**Relevance**	**Method of control**
Concentration of HCl	According to collision theory, increasing concentration affects the rate of reaction since more HCl particles are in a given space.	Create a 400 mL solution of 0.25M HCl, store this solution and use this solution for every trial.
Size of rubber tubing	Larger tubing can cause gas to flow faster, hence lowering time for 20 mL of gas evolved	Use the same rubber tubing for every trial.
Size of Erlenmeyer Flask	During beta-testing, I broke a smaller flask and changed to a larger flask. This changed the rate of reaction since increased volume of flask = decreased pressure which according to collision theory, affects rate	Use a standardized 100 mL Erlenmeyer Flask for every trial so that even if it breaks it can be easily replaced.
Temperature	Temperature tends to decrease when the Erlenmeyer Flask is taken off the water bath which would affect the accuracy of the collected temperature data	Right after adding the $CaCO_3$ and putting on the stopper, put the flask back into the water bath to regulate the temperature to stay at what was recorded.
Swirling of Flask	$CaCO_3$ needs to disperse into the HCl and CO_2 can get stuck while trying to go through the tube which would impact the gas evolved	Maintain a steady swirling of the flask to disperse the $CaCO_3$ and allow CO_2 to escape.

3.2 Materials

Apparatus		Reagents
● Safety Goggles	● Digital Balance (±0.01 g)	● 200 mL HCl (0.25M):

• Ring Stand • Burette Clamp • 50 mL Eudiometer tube (±1 mL) • Pneumatic Trough • Stopper with Rubber Tube • Hot Plate	• 100.0 mL Graduated Cylinder (±0.5 mL) • 100 mL Erlenmeyer Flask (±0.5 mL) • Beaker (500 mL) • Pipette (±0.04 mL) • Stopwatch (±0.2 s) • Weight Boat • 2 Thermometers (±0.1°C)	ACS grade (Is extremely pure) • 2.5 g powdered $CaCO_3$: Laboratory grade (can have some impurities)

3.3 Procedure:

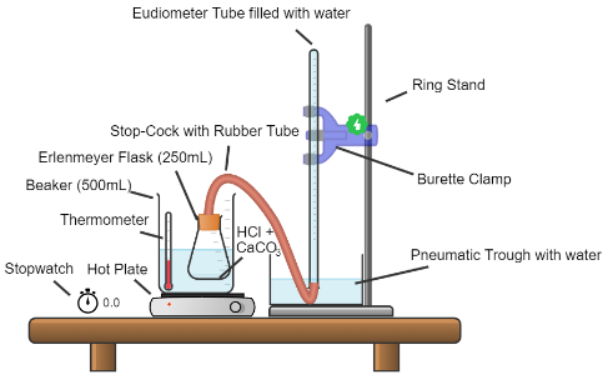

Figure 2: Eudiometer Setup

1. Using a graduated cylinder, measure 100 mL of HCl and 300 mL of water and combine in a beaker to create 400 mL of 0.25M HCl. Use this HCl for all the trials.
2. Fill the Pneumatic Trough about halfway with water. Place it at the bottom of the Ring Stand.
3. Fill the Eudiometer Tube full with water, cover the top with your thumb, flip the tube over into the Pneumatic Trough, attach the tube to the Ring Stand and make sure no air bubbles escape.
4. Attach the end of the tube attached to the stopper into the Eudiometer Tube so that any gas that is siphoned through is collected in the Eudiometer Tube.
5. Fill a beaker with around 100 mL of water and place it on a hot plate set to 100°C with a thermometer and heat the water to 20°C. Add water if the temperature is too hot and remove water if it is too cold until the temperature reaches a stable 20°C.
6. Using a pipette, measure 10 mL of the HCl into a 100 mL Erlenmeyer flask, place this Erlenmeyer flask in the water bath to heat along with a thermometer and wait until the HCl reaches 20°C before proceeding with the reaction.
7. Measure 0.15g of $CaCO_3$ in a weight boat.
8. Take out the Erlenmeyer flask, record the temperature of the HCl, add the $CaCO_3$, put on the stopper, start the timer and put the Erlenmeyer flask back in the water bath while swirling the flask to allow the reaction to proceed.
9. Once the water in the eudiometer displaces 20mL, stop the timer and record the time elapsed.
10. Clean the Erlenmeyer flask and redo steps 3-9 four more times at 20°C.
11. Repeat steps 3-10 but with a controlled temperature of 35°C, 50°C, 65°C.

3.4 Safety Precautions and Risk Assessment:

0.25 M is corrosive to metals and can cause severe skin burns, serious eye damage and respiratory irritation if handled improperly. (MSDS, 2015) Calcium carbonate can cause eye irritation and skin and respiratory tract irritation. (MSDS, 2008) Wear eye protection in a well-ventilated area and thoroughly wash your hands after handling either of these reactants. (MSDS, 2015)

4. Data and Observations:

Table 1: Raw data of reaction rate as a function of temperature

Desired Temperature	Actual Temperature (±0.5°C)	Time for 20mL CO_2 to displace water (±0.2s)
20.0°C	21.5	20.7
	19.7	21.4
	19.5	20.4
	18.8	22.4
	21.9	21.7
35.0°C	35.2	10.2
	34.9	10.6
	33.9	13.1
	36.3	9.8
	34.8	11.1
50.0°C	51.3	8.6
	50.2	8.0
	50.5	8.1
	51.5	7.5
	49.3	8.2
65.0°C	65.2	7.3
	66.1	6.8
	65.9	7.2
	64.9	7.1
	65.4	6.2

The thermometers have a ±0.5°C uncertainty applied to them. The stopwatch has a ±0.05 s uncertainty associated with it, but I decided to increase this uncertainty to ±0.2 s to account for my reaction time.

Table 2: Qualitative observations of the experiment

Before placing $CaCO_3$	During Reaction	After Reaction
● HCl clear, $CaCO_3$ powdered form	● Bubbles take some time to go through tube ● Lot more bubbles at start, slowly reduces as reaction progresses ● Solution fizzes and turns white	● White solution and white precipitate at the bottom ● Solution much thicker than original ● Product didn't vary by temperature

5. Data Analysis

Table 3: Processed Data of the Experiment

Actual Temperature (±0.5K)	$\frac{1}{Temperature}$ $(\pm 1x10^{-5}\frac{1}{K})$	Average Time (±0.2s)	Rate of Reaction $(\pm 1x10^{-4}\frac{M}{s})$	Rate Constant/k $(0.1\frac{1}{s})$	lnk
294.6	$3.39x10^{-3}$	20.7	$7.8x10^{-3}$	$3.1x10^{-2}$	-3.5
292.8	$3.42x10^{-3}$	21.4	$7.5x10^{-3}$	$3.0x10^{-2}$	-3.5
292.6	$3.42x10^{-3}$	20.4	$7.9x10^{-3}$	$3.2x10^{-2}$	-3.5
292.0	$3.42x10^{-3}$	22.4	$7.2x10^{-3}$	$2.9x10^{-2}$	-3.5
295.0	$3.39x10^{-3}$	21.7	$7.4x10^{-3}$	$3.0x10^{-2}$	-3.5
308.4	$3.24x10^{-3}$	10.2	$1.6x10^{-2}$	$6.3x10^{-2}$	-2.8
308.0	$3.25x10^{-3}$	10.6	$1.5x10^{-2}$	$6.1x10^{-2}$	-2.8
307.0	$3.26x10^{-3}$	13.1	$1.2x10^{-2}$	$4.9x10^{-2}$	-3.0
309.4	$3.23x10^{-3}$	9.8	$1.6x10^{-2}$	$6.6x10^{-2}$	-2.7
308.0	$3.25x10^{-3}$	11.1	$1.4x10^{-2}$	$5.8x10^{-2}$	-2.8
324.4	$3.08x10^{-3}$	8.6	$1.9x10^{-2}$	$7.5x10^{-2}$	-2.6
323.4	$3.09x10^{-3}$	8.0	$2.0x10^{-2}$	$8.1x10^{-2}$	-2.5
323.6	$3.09x10^{-3}$	8.1	$2.0x10^{-2}$	$8.0x10^{-2}$	-2.5
324.6	$3.08x10^{-3}$	7.5	$2.2x10^{-2}$	$8.6x10^{-2}$	-2.5
322.4	$3.10x10^{-3}$	8.2	$2.0x10^{-2}$	$7.9x10^{-2}$	-2.5
338.4	$2.96x10^{-3}$	7.3	$2.2x10^{-2}$	$8.8x10^{-2}$	-2.4
339.2	$2.95x10^{-3}$	6.8	$2.4x10^{-2}$	$9.5x10^{-2}$	-2.4
339.0	$2.95x10^{-3}$	7.2	$2.2x10^{-2}$	$9.0x10^{-2}$	-2.4
338.0	$2.96x10^{-3}$	7.1	$2.3x10^{-2}$	$9.1x10^{-2}$	-2.4
338.6	$2.95x10^{-3}$	6.2	$2.6x10^{-2}$	$1.0x10^{-1}$	-2.3

5.1 Sample calculations

Sample Calculation for $\frac{1}{Temperature}$ uncertainty

The $\frac{1}{Temperature}$ uncertainty can be calculated by converting the absolute uncertainty of the temperature to percent uncertainty then multiplying by the calculated $\frac{1}{Temperature}$ then converting back to absolute uncertainty. Multiplying by 100% is unnecessary in the scenario as it would be immediately converted back so it is not shown in the sample calculation.

Ex. $\frac{0.5}{294.6} \times \frac{1}{294.6} = \pm 0.00000576$ rounded to ±0.00001 to match decimal places with $\frac{1}{Temperature}$

Sample Calculation for Rate of Reaction

The rate of reaction can be determined by using stoichiometry to convert volume of CO_2 gas to moles assuming standard ambient temperature and pressure (SATP) then to molarity of HCl per unit time.

Ex.

$$\frac{0.0200\ L\ CO_2}{20.7\ s} \cdot \frac{1\ mol\ CO_2}{24.8\ L} \cdot \frac{2\ mol\ HCl}{1\ mol\ CO_2} \cdot \frac{1}{0.0100\ L\ HCl}$$

$=7.8\text{x}10^{-3}\frac{M}{s}$

The final answer was rounded to 2 significant figures to match decimal places with the uncertainty although subsequent calculations will use precise values to increase accuracy

Sample Calculation for Rate of Reaction Uncertainty

The uncertainty of the rate of reaction can be calculated by adding the percent uncertainties of the eudiometer uncertainty of ±0.1 mL, the time uncertainty of ±0.2 s and the pipette uncertainty of ±0.04 mL. Then multiplying by the answer will yield the absolute uncertainty. Multiplying by 100% is unnecessary as it would be immediately converted back.

Ex. $(\frac{\pm 0.1\ mL}{20.0\ mL} + \frac{\pm 0.2\ s}{20.7\ s} + \frac{\pm 0.04}{10mL}) \cdot 0.0078$

$= \pm\ 0.0001\frac{M}{s}$

Sample Calculation for Rate Constant/k

Going back to equation 2, I can attain the rate constant using the following equation:

$$k = \frac{Rate}{[HCl]^1}$$

Ex. $\frac{0.78\frac{M}{s}}{0.25M} = 3.1\frac{1}{s}$

Sample Calculation for Rate Constant/k uncertainty

A 100.0±0.5 mL graduated cylinder was used four times to create a 400±2 mL solution. Then propagating the uncertainties to 0.25M I get:

$\frac{\pm 2\ mL}{400mL} \cdot 100\% = \pm 0.5\%$ uncertainty

Then I will convert to the rate uncertainty:

Ex. $(\frac{\pm 0.5\%}{100\%} + \frac{0.0001}{0.0078}) \cdot 3.1 = \pm 0.1\frac{1}{s}$

5.2: Effect of Temperature

As seen in Figure 3, by graphing rate of reaction as a function of temperature, I determined that my experiment increased rate linearly with a temperature increase due to the HCl particles having more energy to react. Error bars have been plotted

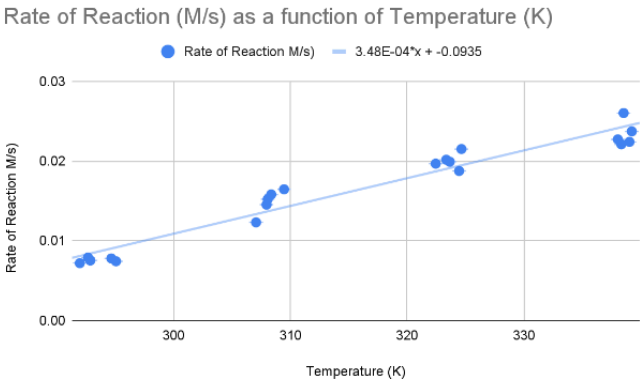

Figure 3: Graph of Rate of Reaction vs Temperature

on the graph, but are not visible due to small uncertainties, hence demonstrating the low impact of random errors. However, random errors are still evident in this graph as shown through some outliers such as (307.0, 0.012) and (338.6, 0.026). Removing these outliers reveals that the rate increases logarithmically to a temperature increase. Nonetheless, both cases demonstrate the essential idea of collision theory, where the rate of reaction increases due to temperature.

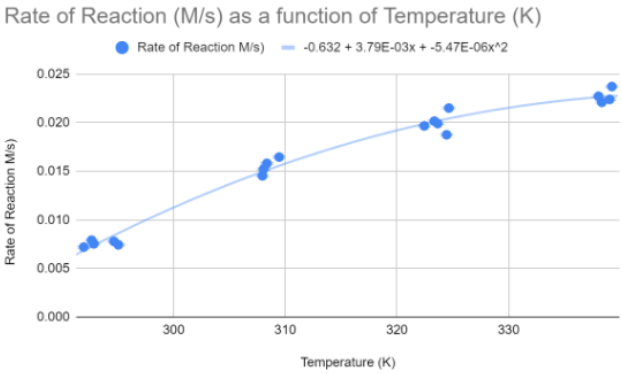

Figure 4: Logarithmic representation of graph without outliers

5.3 Determining Activation Energy

Fulfilling the purpose of investigation, by plotting ln k vs $\frac{1}{Temperature}$, I can determine the activation energy of this reaction. However, systematic errors are visible in this graph, especially on the third data point that is shifted up. According to the Arrhenius equation, this graph should be linear and the third data point does not follow this trend. Nonetheless, the graph is still relatively linear. Random errors are noticeable through the disparity in data points and become extremely evident when determining the uncertainty of the gradient, which was determined to be ±500. The y-intercept of this graph is ln A which is the pre-exponential factor specific to this reaction, detailing the frequency of successfully oriented collisions, this case being 4.95. Going back to background theory, it was determined that the slope of this line multiplied by -R, which is the gas constant 8.31$\frac{J}{Kmol}$ would be the activation energy of this system.

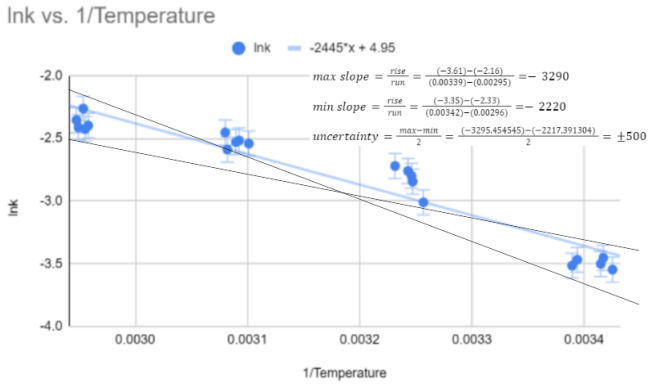

Figure 5: Graph of ln k vs 1/Temperature

$$E_a = -2400 \pm 500 \cdot -8.31 = 20000 \pm 4000 \ \frac{J}{mol}$$

My precise value for activation energy is 20317.95 $\frac{J}{mol}$ which is a relatively small activation energy. Thus, it does not take much energy for HCl particles and $CaCO_3$ to react and this explains why this reaction can occur at room temperature.

6. Conclusion:

Ultimately, the time for 20 mL of carbon dioxide gas to evolve in a eudiometer for a calcium carbonate and 0.25M hydrochloric acid reaction depends on the temperature as with greater temperature, the time the reaction takes decreases and the reaction rate increases. This can be attributed to collision theory: with a higher temperature, more HCl particles have sufficient energy to react and also collide more with $CaCO_3$ particles.

By graphing ln k and 1/T, I determined a negative linear relation between these two variables, which aligns with the Arrhenius equation. By multiplying the gradient of this graph by -8.31, I discovered the activation energy of the reaction is 20317.95 $\frac{J}{mol}$. Comparing to a literature value, I can determine my percent deviation

Muszynskl obtained a literature value of 4.5$\frac{kcal}{mol}$ for this reaction (Muszynskl, 1973) which can be converted using unit conversion to match the units I determined in this investigation:

$$4.5\frac{kcal}{mol} \cdot \frac{4184\,J}{1kcal} = 18828\frac{J}{mol}$$

Next, to compare values, I can use the percent deviation formula as follows:

$$Percent\ Deviation = \frac{experimental\ value - theoretical\ value}{theoretical\ value} \cdot 100\% = \frac{20317.95-18828}{18828} \cdot 100\%$$

$$= 7.91\%\ deviation$$

A 7.91% deviation demonstrates validity in my investigation since my value was not far off from the literature value. This deviation can be attributed to random errors, evident in the ±4000 uncertainty caused by the variance in the graph, but mostly as a result of systematic errors, which affect the entire dataset.

7. Evaluation:

This investigation had strengths in methodology. Most notably, was controlling the temperature during the reaction in a water bath and being efficient with the reactants by controlling the amount of HCl used rigorously with a pipette. However, there were multiple errors which hindered the precision and accuracy of this investigation

Random Errors	**Significance**	**How to minimize**
Inconsistent time to put on stopper	The time it took for me to screw on the stopper had many variations as I needed to put in the $CaCO_3$ and then screw on the stopper which had to do	A different methodology can be considered such as having an open flask on a scale and measuring the time it takes for a certain amount of mass to be

	completely with my reaction time. According to the half-life of this reaction, the fastest point in the reaction is right at the start so this was where it was most impactful.	decreased which can be used to determine how much CO_2 is released in a given period. Then the same stoichiometry can be used but with grams of CO_2 instead of volume
Reaction time	The starting and stopping of the stopwatch were completely based on my reaction time which adds a large layer of uncertainty to the time especially since the reaction occurred so fast.	Dilute the HCl even further and use a camera-based system with video analysis to be more precise as to when the time should start and stop for each reaction.
Limitations in temperature	Temperature is a variable extremely difficult to control as the Erlenmeyer flask was taken out of the water bath to put in the $CaCO_3$. As soon as the flask is taken out, it begins to cool, adding a layer of uncertainty.	A thermal camera would be most optimal to reduce this error, allowing me to see precisely the temperature at every stage of the reaction. Then I can find an average temperature for a given reaction. However, this technology was unavailable to me.

Systematic Errors	**Significance**	**How to minimize**
CO_2 stuck in rubber tubing	The rubber tubing had water, condensation and other unwanted particles stuck inside which would hinder the CO_2 gas travelling through.	Use a larger rubber tubing and wash the tubing after every trial to remove any residue that is built up inside.
CO_2 travelling through the eudiometer	CO_2 takes time to travel through the eudiometer which would add to the time elapsed since the time started right when the calcium carbonated was inserted.	Start the timer as soon as the first bubble reaches the top to remove the time taken for the bubbles to travel through the eudiometer.

7.1 Extension

If given the opportunity to complete this investigation again, I would choose a different methodology to reduce errors. The greatest production of errors in my investigation was as a result of the eudiometer, whether it was due to my reaction time in putting on the stopper or CO_2 gas bubbles getting stuck. These errors can be avoided by using a mass-based system to measure CO_2 released instead of a volume-based system. Specifically, by recording the initial mass of the system and observing the time it takes for the system to reach a certain mass, I can use the same principles in a more controlled way to reduce errors.

Additionally, even though I diluted the HCl, I found that 0.25M reacted too fast due to the reaction's low activation energy, especially at higher temperatures. By diluting HCl even further, more time would elapse for the reaction and would be easier to collect data.

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