Investigating the temperature dependence of the rate constant of the acid-catalysed iodination of propan-2-one for the determination of the activation energy of the reaction

1   Introduction

Propan-2-one, commonly known as acetone (PubChem), is a dimethyl ketone with the chemical formula CH_3COCH_3. It is commonly found in household products such as nail polish remover and furniture lacquer ("Acetone"). More interestingly, propan-2-one react with halogens in *clock reactions*. Clock reactions are chemical reactions wherein an observable change takes place at the end of the reaction ("Rate equations"). These reactions are often used in the study of kinetics to understand how the constituent reactants affect the rate of the reaction, which can then be used to extrapolate properties of the reaction system such as activation energy. Fascinated by studying how something as simple as the colour change of a reaction can be used to investigate properties of the reacting system, I decided to pursue the following **research question**:

> **How does the temperature (5.0, 15.0, 25.0, 35.0, 45.0) °C affect the rate constant of the sulfuric acid catalysed iodination of propan-2-one, as measured by a colorimeter at 470 nm, and how can this relationship be used to measure the activation energy of the reaction?**

2   Theoretical Framework and Hypothesis

2.1   The iodination of propan-2-one

Propan-2-one is iodinated, commonly via an acid-catalyst, to form 1-iodopropan-2-one and hydroiodic acid as shown below ("Acetone Iodine Kinetics"),

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{\text{acid catalyst}} CH_3COCH_2I(aq) + HI(aq) \tag{2.1}$$

A proposed four-step mechanism, termed α-halogenation, for the reaction is given by Farmer as follows:

Step I:

$$CH_3COCH_3(aq) + H^+(aq) \rightleftharpoons CH_3COHCH_3{}^+(aq) \tag{2.2}$$
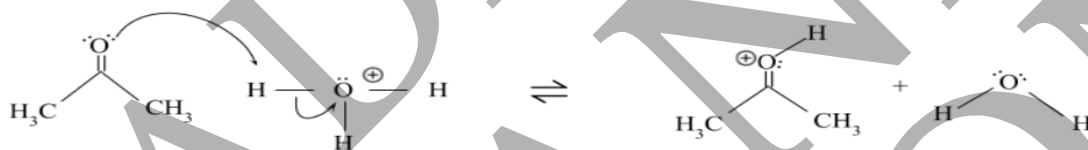

Figure 1: Step 1; drawn on Google Drawings by author

The acid-catalyst protonates propan-2-one as the oxygen atom donates one of its lone pair electrons to the acid via a coordinate bond. This creates a positive charge on the oxygen which is unstable due to oxygen's electronegativity.
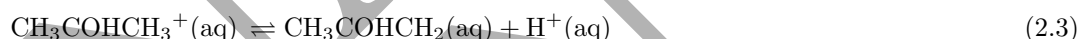
Step II:

$$CH_3COHCH_3{}^+(aq) \rightleftharpoons CH_3COHCH_2(aq) + H^+(aq) \tag{2.3}$$

Figure 2: Step 2; drawn on Google Drawings by author

Due to the unstability of the formal charge on the oxygen atom, a carbocation is formed as the electrons in the π bond shift to the oxygen atom to remove the formal charge. The water molecule then abstracts the α-hydrogen to form an enol.

Step III:

$$CH_3COHCH_2(aq) + I_2(aq) \longrightarrow CH_3COCH_2I^+(aq) + I^-(aq) \tag{2.4}$$
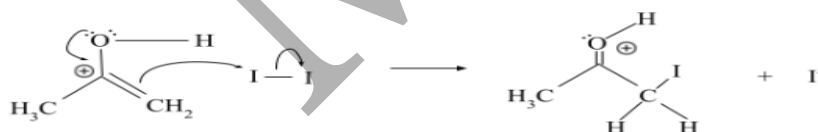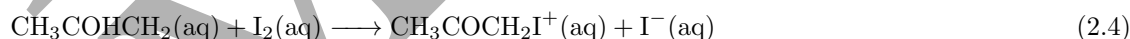

Figure 3: Step 3; drawn on Google Drawings by author

As the lone pair of electrons on the OH form a π cloud, the adjacent π bond on the C=CH$_2$ gets "pushed" towards the I$_2$ molecule via repulsion, this creates a partial positive and negative charge on each iodine atom which forms CH$_3$COHCH$_2$I$^+$ via a nucleophilic attack.
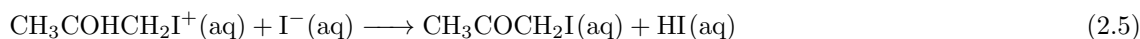
Step IV:

$$CH_3COHCH_2I^+(aq) + I^-(aq) \longrightarrow CH_3COCH_2I(aq) + HI(aq) \tag{2.5}$$

Figure 4: Step 4; drawn on Google Drawings by author

The iodide ion then deprotonates CH$_3$COHCH$_2$I$^+$(aq) to form 1-iodopropan-2-one and hydroiodic acid.

2.2 Rate expressions, rate constants, and the Arrhenius Equation

The instantaneous rate of a reaction is defined as the change in concentration of the reactant over an infinitesimally small point in time. That is, the rate is defined as the time derivative of the concentration of the reactant. The iodination of propan-2-one can be measured via colorimetry due to the presence of iodine. As iodine is used up to form iodopropan-2-one, the orange-coloured solution becomes colourless over time. Thus, the rate of the reaction can be monitored via the change in concentration of iodine over time. The rate can be expressed as,

$$rate = -\frac{d}{dt}\left([I_2]\right) \tag{2.6}$$

A negative sign is introduced as the concentration of iodine decreases over time as it is used up. Thus, there are fewer frequent collisions between particles as the reaction progresses, resulting in a reduced rate. Colorimetry tracks how the absorbance of the solution changes over time. Absorbance is defined by Beer Lambert's law as (Clark):

$$a = \varepsilon c l \tag{2.7}$$

where a is the absorbance which is a dimensionless quantity, ε is a constant known as molar absorptivity in dm^3 mol^{-1} m^{-1}, which measures the probability of electron transitions as the colour changes (Clark), c is the concentration in mol dm^{-3} and l is the distance the light travels through the solution in m. Substituting eq. (2.7) in eq. (2.6) and pulling the constants out of the derivative

$$-\frac{da}{dt} = -\varepsilon l \frac{dc}{dt} \tag{2.8}$$

As the change in colour occurs due to the iodine, $\frac{dc}{dt}$ tracks the change in iodine's concentration. Thus,

$$-\frac{da}{dt} = -\varepsilon l \frac{d}{dt}\left([I_2]\right) \tag{2.9}$$

Thus we see that measuring the rate of change of absorbance is another method of measuring the rate of the reaction.

It is well known from collision theory that the rate of the reaction is dependent on the concentration of the reactants. As a result, we can formulate an expression between the rate of the reaction and the concentration of the constituent reactants which we term the rate expression. For a reaction of the form,

$$wM + xN \longrightarrow yP + zQ \tag{2.10}$$

the equation that relates the rate of the reaction r and the concentration of the reactants is given by (Brown and Ford 289),

$$r = k[M]^h[N]^j \tag{2.11}$$

where h and j are defined as the order of each reactant. The order is a measure of how dependent the rate of the reaction is on the concentration of the reactant. An order of 1 implies that doubling the concentration doubles the rate of reaction while an order of 2 implies that doubling the concentration increases the rate of reaction by a factor of 4. A proportionality constant k is added which is termed the rate constant. It has been found that the rate expression for the iodination of propan-2-one is as follows (Farmer),

$$r = k[CH_3COCH_3][H^+] \tag{2.12}$$

Thus, the concentration of iodine does not affect the rate as it is zero-order. This is interesting as it implies that step I is the rate determining step.

It is also known that the rate of the reaction is dependent on temperature. The rate constant is dependent on the temperature of the reaction and is related by Arrhenius' equation (Brown and Ford 301),

$$k = Ae^{\frac{-E_a}{RT}} \tag{2.13}$$

where A is the pre-exponential factor which is a measure of the frequency with which successful collisions occur between reactant particles (Brown and Ford 301), E_a is the activation energy of the reaction—the minimum energy required for the reaction to take place—with units J, R is the universal gas constant 8.31 J K^{-1} and T is the temperature measured in K. The relationship between temperature and the rate constant can be used to determine the activation energy of the reaction.

By taking the natural logarithm of eq. (2.13) we can linearise the Arrhenius equation as follows,

$$\ln(k) = \ln(Ae^{\frac{-E_a}{RT}})$$
$$= \ln(A) + \ln(e^{\frac{-E_a}{RT}})$$
$$\therefore \ln(k) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A) \tag{2.14}$$

According to eq. (2.14), the natural log of the rate constant is proportional to the reciprocal of temperature. **Thus, it is hypothesised that higher temperatures will lead to a higher rate constant.** Furthermore, plotting $\ln(k)$ against $\frac{1}{T}$ will result in a linear curve with gradient $\frac{-E_a}{R}$ and vertical axis intercept $\ln(A)$. As R is a constant, we can easily extrapolate the activation energy of the reaction from the calculated gradient.

2.3 Maxwell-Boltzmann curves

It was stated in the previous subsection that temperature affects the rate of a reaction. This can be easily understood with a tool known as the Maxwell-Boltzmann curve which is a distribution of the kinetic energies of the reactant particles of a system. The area under the curve represents the total number of reactant particles in the system. Only the area under the curve in fig. 5 past E_a
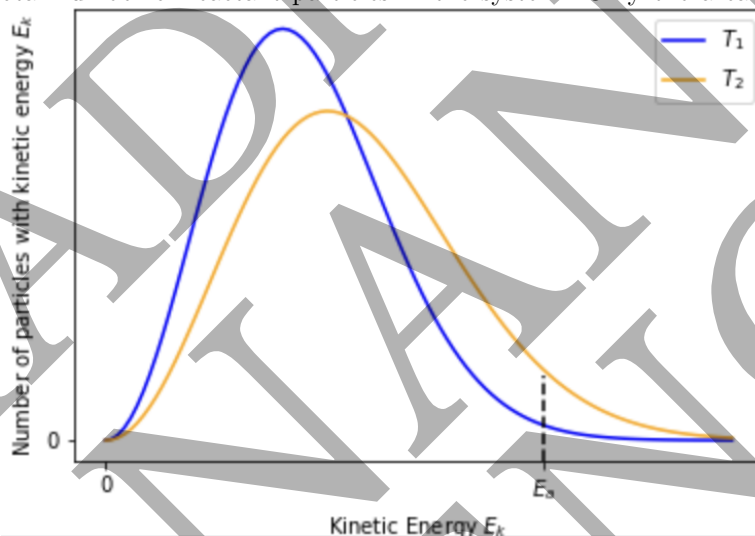

Figure 5: Maxwell-Boltzmann curves at two temperatures where $T_2 > T_1$; plotted by author using Python

contains particles that will take part in the reaction as it is only these particles that have the minimum activation energy. It is clear from fig. 5 that the area under the Maxwell-Boltzmann curve for T_2 is greater than T_1. This implies that at higher temperatures, more reactant particles have an energy greater than or equal to the activation energy, thus leading to more frequent collisions between particles and thus a greater rate of reaction. This fact, combined with the Arrhenius equation, shows that a higher temperature is expected to increase the rate constant.

3 Experimental Design

3.1 Variables

Independent variable: Temperature
The range of temperatures in °C that were investigated were 5.0, 15.0, 25.0, 35.0 and 45.0. Temperatures above 45.0° C could not be investigated as it was found during the trial experiment that the reaction happened too quickly for the cuvette to be placed in the colorimeter; temperatures below 5.0° C could not be investigated as the reaction took too long to progress. An increment of 10.0° C was chosen as this was determined to be the optimal change in temperature that had enough variation in the initial rate to have scope for analysis.

3

Dependent variable: Absorbance

A vernier labquest device was used to create a plot of absorbance against time once the cuvette was placed in the colorimeter. The colorimeter was set to a wavelength filter of 470 nm. This was chosen as the colour of iodine is orange, which implies that the wavelength absorbed is that of orange's complementary colour: blue. The wavelength of blue light is 470 nm ("Wavelength"). Once the reaction was completed, the initial rate of reaction was determined by computing the tangent the moment the absorbance started to decrease. As the solution in the cuvette was coloured, and the colorimeter was calibrated at 0.00 absorbance, the measured absorbance values initially rose to the actual absorbance value of the solution. Thus, the slope of the tangent could not be computed at $t = 0$ but only when the absorbance started to decrease. The rate constant—the focus of this investigation—can be extrapolated from the initial rate of reaction by using the rate equation outlined in eq. (2.12).

Controlled variables

Table 1: Controlled variables

Quantity controlled	Reason for control	Method of control
Molar concentration of reactants	Concentration affects the rate of the reaction as given by the rate expression. Thus, concentration was kept constant in order to see how only temperature affects the initial rate of the reaction	The same concentration of each reactant was used in all the trials. $[CH_3COCH_3] = 1.0$ mol dm^{-3} $[H_2SO_4] = 1.0$ mol dm^{-3} $[I_2] = 0.00500$ mol dm^{-3}
Type of acid catalyst	Catalysts increase the rate of reaction by providing an alternate pathway for the reaction with a lower activation energy. Different acid catalysts will therefore change the activation energy differently.	The same 1.0 mol dm^{-3} sulfuric acid catalyst was used for all the trials.
Airflow	Significant airflow increases evaporation which causes temperature loss as the most energetic particles evaporate first. As a result, airflow was minimised in order to reduce temperature loss	The experiment was conducted in a room away from any air-conditioning or fan units.
Intensity of mixing	Mixing increases the frequency with which successful collisions occur thereby increasing the rate of reaction. Thus, it is imperative that extent to which mixing occurs remains constant in order to avoid changes in the initial rate of reaction due to mixing	The solution was not mixed together when the reactants were added. They were immediately transferred into a cuvette and placed into the colorimeter
Wavelength of Colorimeter	As the initial starting colour of the solution is always orange, the colorimeter must be set to the same wavelength for each trial to obtain maximum absorbance	The wavelength of the colorimeter was set to 470 nm for every trial.

3.2 Apparatus and Chemical Solutions

1. Burette $\times$ 4

2. Retort stand $\times$ 2

3. Thermometer $\times$ 2

4. Vernier colorimeter

5. Vernier labquest

6. Laptop

7. Test-tube

8. 100 mL Erlenmeyer Flask

9. Kettle

10. Ice cubes

11. Cuvette $(1.0 \times 1.0 \times 4.1)$ cm$\times$ 5

12. Plastic container $(20.0 \times 11.5 \times 11.0)$ cm

13. Standard solution flask $\times$ 2

14. 125.0 cm^3 amber bottle $\times$ 2

15. 25.0 cm^3 CH$_3$COCH$_3$

16. 25.0 cm^3 1.0 mol dm^{-3} H$_2$SO$_4$

17. 250.0 cm^3 distilled H$_2$O

18. 25.0 cm^3 0.050 mol dm^{-3} I$_2$

Preparation of 0.0050 mol dm^{-3} I$_2$ solution

The iodine solution available at the lab was of 0.050 mol dm^{-3}. During the trial experiments, it was found that this concentration was unsuitable for the experiment as the colour was too dark. As a result, the absorbance readings were greater than the maximum possible reading of the colorimeter. Through trial and error, it was found that a $10\times$ dilution worked best. As a result, a 0.0050 mol dm^{-3} solution was prepared by adding 25.0 cm^3 0.050 mol dm^{-3} I$_2$ and 225.0 cm^3 distilled H$_2$O into a standard solution flask

and mixing thoroughly. This produced an iodine solution with a much lighter orange colour that allowed for the colorimeter to track absorbance. The prepared 250.0 cm³ 0.0050 mol dm⁻³ I₂ solution was then immediately transferred into two amber bottles to be stored as I₂ is a photosensitive compound.

Preparation of custom water bath

Unfortunately, a water bath was not available in the lab for use. As a result, a custom water bath had to be prepared. This was done by taking a plastic container of dimensions $(20.0 \times 11.5 \times 11.0)$ cm and filling a quarter of it with water. For temperatures below 25°C, ice cubes and cold water was added until the temperature reached the desired temperature. Once the temperature increased, more ice cubes were added to reduce the temperature. For temperatures above 25°C, water was heated in a kettle and was poured into the container. As the container was made of plastic—a good insulator—heat loss wasn't as significant. If the temperature reduced, some water was taken out using a beaker and was replaced with hot water from the kettle.

3.3   Experimental Considerations

Table 2: Safety, ethical and environmental considerations

| Chemical	Safety, ethical and environmental considerations	Precautions to be taken + waste disposal
Propan-2-one ("Acetone Safety Data")	• Liquid and vapour form is highly flammable • Can cause eye irritation if in contact • Can cause damage to organs through repeated exposure • Can cause drowsiness or dizziness through prolonged inhalation • Poses an environmental concern	• Labcoats, goggles and gloves are to be worn at all times • Hands to be washed immediately if skin comes into contact • Bottle to be kept away from sources of flames such as bunsen burners or heaters • Mask to be worn during trials to avoid inhalation • Chemical to not be disposed down sink; to be disposed according to local waste disposal laws • Workspace to be cleaned thoroughly after use
Iodine ("Iodine Safety Data")	• Can cause severe skin burns and eye damage • Extremely toxic to aquatic life • Can generate thermal decomposition reactions	• Labcoat, goggles and gloves to be worn at all times • Bottle to be kept away from sources of flames such as bunsen burners or heaters • Bottle to be stored in amber bottle to prevent the need to keep remaking stock solution and avoid waste generation • Hands/articles of clothing to be immediately washed with water if iodine comes in contact • Chemical to not be disposed down the sink; to be disposed according to local waste disposal laws • Workspace to be cleaned thoroughly after use
Sulfuric acid ("Sulfuric Acid, ACS")	• Corrosive; can cause burns and eye damage if in contact with skin • Can react in highly exothermic neutralisation reactions with water which can pose a fire-risk • Poses an environmental concern	• Labcoat, goggles and gloves to be worn at all times • If skin comes in contact, area of contact to be rinsed with water immediately • Chemical to not be disposed down the sink; to be disposed according to local waste disposal laws • Workspace to be cleaned thoroughly after use
Iodopropan-2-one ("9 SDS Word")	• Liquid and vapour form is flammable • Can cause eye damage and skin irritation if in contact • Poses aquatic concerns	• Labcoat, goggles, and gloves to be worn at all times • If skin comes in contact, area of contact to be rinsed with water immediately • Chemical to be disposed immediately after the trial is complete according to local waste disposal laws
Hydroiodic acid ("Hydriodic Acid Material")	• Causes severe skin burns and eye damage • Causes respiratory irritation	• Labcoat, goggles, and gloves to be worn at all times • If skin comes in contact, area of contact to be rinsed with water immediately • Chemical to be disposed immediately after the trial is complete according to local waste disposal laws

3.4   Method

1. Connect the colorimeter to the vernier labquest and laptop; calibrate it with a cuvette filled with distilled H₂O at 470 nm

2. Fill up the four burettes with 0.0050 mol dm^{-3} I$_2$, 1.0 mol dm^{-3} H$_2$SO$_4$, distilled H$_2$O and CH$_3$COCH$_3$

3. Ensure the water bath is at the desired temperature

4. Add 5.0 cm^3 I$_2$, 1.0 cm^3 distilled H$_2$O and 1.0 cm^3 H$_2$SO$_4$ into the erlenmeyer flask

5. Add 1.0 cm^3 CH$_3$COCH$_3$ into the test-tube

6. Set the laptop to start measuring absorbance for 10 minutes

7. Place both into the water-bath and add the two thermometers into each container until the two solutions reach the desired temperature

8. Add the CH$_3$COCH$_3$ into the erlenmeyer flask and immediately fill up a cuvette with the resulting solution

9. Add the cuvette into the colorimeter and wait until the absorbance reading plateaus

10. Using the tangent tool, measure the slope of the tangent the moment the absorbance starts to decrease; this is the initial rate of reaction

11. Wash the cuvette, erlenmeyer flask, and test-tube with distilled water

12. Repeat steps 2-11 four more times for a total of five trials for each temperature

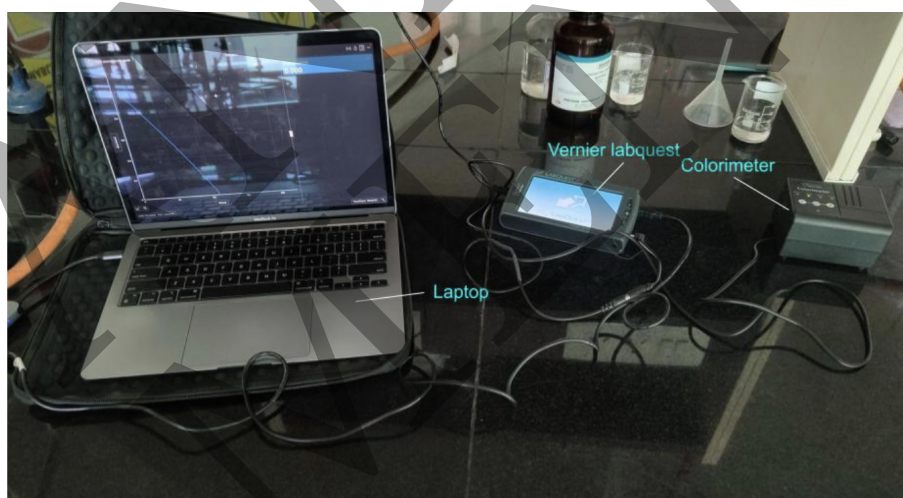13. Repeat steps 2-12 for the remaining sets of temperatures

3.5 Experimental Setup

(a) Burette setup
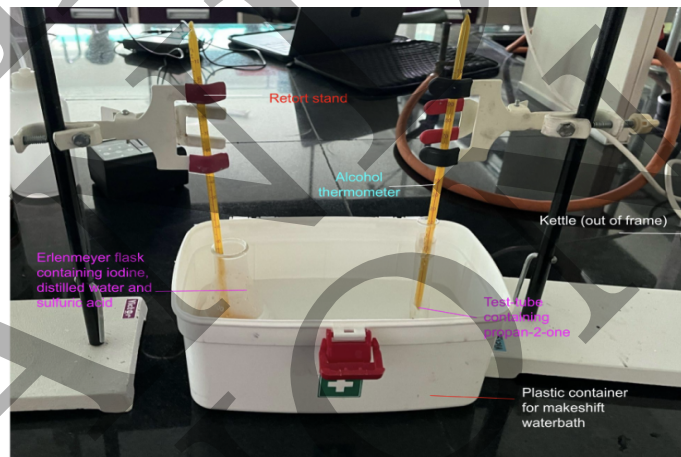
(b) Custom waterbath setup

(c) Colorimeter setup

Figure 6: Experimental setup; annotated on Google Drawings by author

4   Experimental Data

4.1   Qualitative Observations

It was evident that the rate increased significantly at higher temperatures. At 45°C, there was a very small window of time between pouring the propan-2-one into the erlenmeyer flask and the reaction completing. It was also found that at lower temperatures, the reaction did not fully reach completion as the absorbance values plateaued, while at higher temperatures, the absorbance reading hit 0.00. While pouring the contents of the erlenmeyer flask into the cuvette, sometimes the solution overflowed onto the side of the cuvette which would have affected absorbance readings. As a result, at lower temperatures, this was wiped using a tissue. At higher temperatures, the trial was repeated as there was not enough time to wipe the cuvette.

4.2   Raw Data

Table 3: Initial rate of reaction (mol dm^{-3} s^{-1}) for the sulfuric acid catalysed iodination of propan-2-one at each temperature (°C)

Temperature (°C) $\pm$ 0.5°C	Initial rate of reaction (mol dm^{-3} s^{-1})					Standard deviation σ (mol dm^{-3} s^{-1})
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	
5.0	-0.00148	-0.00153	-0.00162	-0.00151	-0.00156	4.77×10^{-5}
15.0	-0.00542	-0.00538	-0.00551	-0.00546	-0.00553	5.55×10^{-5}
25.0	-0.0170	-0.0157	-0.0162	-0.0165	-0.0171	5.18×10^{-4}
35.0	-0.0527	-0.0519	-0.0513	-0.0557	-0.0521	1.54×10^{-3}
45.0	-0.0839	-0.0881	-0.0823	-0.0872	-0.0895	2.68×10^{-3}

The temperature was measured using an analogue alcohol thermometer with divisions of 1°C. Thus, the uncertainty in the measured temperature is half the smallest division: 0.5°C. The digital colorimeter quoted absorbance values to three decimal places which implies that it would have an uncertainty of ± 0.001. However, the Vernier labquest software computed slopes and immediately rounded them off to three significant figures. As a result, the number of decimal places is inconsistent which can be seen in table 3 as the number of decimal places for a reading at 5°C is 5 while at 35.0°C it is 4. Thus, an absolute uncertainty could not be determined for the initial rate of reaction. A manufacturer value was not quoted either. Nevertheless, it is acknowledged and appreciated that there would also be uncertainty at this level.

The standard deviation is a measure of the spread of a dataset from its mean and can be calculated using the following equation ("Standard Deviation"),

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(r_i - \overline{r})^2}{N}} \tag{4.1}$$

where r_i is one of the initial rates of the reaction, $\overline{r}$ is the mean of the initial rates for a given temperature and N is the number of rates for a given temperature which is constant at 5. Sample calculation for $T = 5.0$°C:

$$\sigma = \sqrt{\frac{(0.00154 - 0.00148)^2 + (0.00154 - 0.00153)^2 + (0.00154 - 0.00162)^2 + (0.00154 - 0.00151)^2 + (0.00154 - 0.00156)^2}{5}}$$

$$\approx 4.77 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1} \tag{4.2}$$

The calculation to determine the mean initial rate is outlined in the next subsection

4.3   Processed Data

To process the data, the average initial rate of reaction was taken for each temperature reading. Each average was then rounded off to three significant figures as all measured initial rates had three significant figures.
Sample calculation for $T = 5.0$°C:

$$\overline{r} = \frac{(-0.00148 - 0.00153 - 0.00162 - 0.00151 - 0.00156) \text{ mol dm}^{-3} \text{ s}^{-1}}{5} \approx -0.00154 \text{ mol dm}^{-3} \text{ s}^{-1} \tag{4.3}$$

As the standard deviation is different for each temperature, the data is spread differently. Thus, each average rate cannot have the same uncertainty. The uncertainty for each average rate, $\Delta \overline{r}$, was calculated by taking half the difference between the upper bound and lower bound for each rate in table 2. By convention, uncertainties rounded off to one significant figure (Tsokos 11).
Sample calculation for $T = 5.0$°C

$$\Delta \overline{r} = \frac{[-0.00148 - (-0.00162)] \text{ mol dm}^{-3} \text{ s}^{-1}}{2} \approx 0.00007 \text{ mol dm}^{-3} \text{ s}^{-1} \tag{4.4}$$

Thus the percentage uncertainty in the obtained rate is

$$\frac{\Delta \overline{r}}{|\overline{r}|} \times 100 = \frac{0.00007}{|-0.00154|} \times 100 \approx 5\% \tag{4.5}$$

Remembering that a plot of $\ln(k)$ against $\frac{1}{T}$ will give us a straight line. Therefore, we must now calculate k. Remembering that our rate expression is given by,

$$r = k[\text{CH}_3\text{COCH}_3][\text{H}^+] \tag{4.6}$$

We can substitute the average rate found and rearrange to get an equation for k as,

$$k = \frac{\bar{r}}{[\text{CH}_3\text{COCH}_3][\text{H}^+]} \tag{4.7}$$

The total volume of the reaction mixture is given by the sum of the volumes of CH_3COCH_3, I_2, distilled H_2O, and H_2SO_4. All of these were added into their containers using a burette that had divisions of 0.1 cm^3. Thus the uncertainty is half the smallest division: 0.05 cm^3. The total volume is then given by

$$V_{total} = [(1.00 \pm 0.05) + (5.00 \pm 0.05) + (1.00 \pm 0.05) + (1.00 \pm 0.05)] \text{ cm}^3 = (8.0 \pm 0.2) \text{ cm}^3 \text{ uncertainty rounded to 1 s.f} \tag{4.8}$$

We can now use the dilution equation to determine $[\text{CH}_3\text{COCH}_3]$ and $[\text{H}^+]$,

$$c_1 V_1 = c_2 V_2 \tag{4.9}$$

Therefore,

$$c_{initial} V_{initial} = c_{new} V_{total}$$
$$\implies c_{new} = \frac{c_{initial} V_{initial}}{V_{total}} \tag{4.10}$$

As 1.0 mol dm^{-3} CH_3COCH_3 was originally used we have,

$$c_{new \ \text{CH}_3\text{COCH}_3} = \frac{1.0 \text{ mol dm}^{-3} \times (1.00 \pm 0.05) \text{ cm}^3}{(8.0 \pm 0.2) \text{ cm}^3} \approx 0.13 \text{ mol dm}^{-3} \text{ (2 s.f)} \tag{4.11}$$

As the percentage uncertainty of two quantities divided is simply the sum of the percentage uncertainty of the numerator and denominator,

$$\frac{\Delta c_{new \ \text{CH}_3\text{COCH}_3}}{c_{new \ \text{CH}_3\text{COCH}_3}} \times 100 = \frac{0.05}{1.00} \times 100 + \frac{0.2}{8.0} \times 100 = 7.5\%$$
$$\therefore c_{new \ \text{CH}_3\text{COCH}_3} \approx (0.13 \pm 7.5\%) \text{ mol dm}^{-3} \tag{4.12}$$

The concentration for H_2SO_4 was also 1.0 mol dm^{-3}. However, there are two H^+ ions for every molecule of H_2SO_4. Thus, to get $[\text{H}^+]$ we must multiply by 2.

$$\therefore c_{new \ \text{H}^+} = 2 c_{new \ \text{H}_2\text{SO}_4}$$
$$= 2 \times \frac{1.0 \text{ mol dm}^{-3} \times (1.00 \pm 0.05) \text{ cm}^3}{(8.0 \pm 0.2) \text{ cm}^3}$$
$$\therefore c_{new \ \text{H}^+} \approx (0.26 \pm 7.5\%) \text{ mol dm}^{-3} \tag{4.13}$$

It must be noted that the percentage uncertainty for $\bar{r}$ was rounded to one significant figure as the least precise quantity in its calculation had one significant figure while the percentage uncertainty for the obtained concentrations were rounded to two significant figures as the least precise quantity had two significant figures.

Substituting the obtained concentrations in eq. (4.7),

$$k = \frac{(-0.00154 \pm 5\%) \text{ mol dm}^{-3} \text{ s}^{-1}}{(0.13 \pm 7.5\%) \text{ mol dm}^{-3} \times (0.26 \pm 7.5\%) \text{ mol dm}^{-3}}$$
$$\approx (-0.046 \pm 20\%) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \tag{4.14}$$

k was rounded off to two significant figures as its calculation involved both CH_3COCH_3 and $[\text{H}^+]$ which have two significant figures.

Taking the natural log,

$$\ln(|k|) = \ln(|-0.046 \pm 20\%|)$$
$$= (-3.08 \pm 20\%) \tag{4.15}$$

The reason $\ln(k)$ was rounded to three significant figures was because the number of decimal places in the output should equal the number of significant figures in the input to the logarithm (Brown and Ford 357). As -0.046 has two significant figures, the output was rounded to two decimal places. The percentage uncertainty remains constant.

To convert our temperature into kelvin we add 273 to our temperature in degrees celsius. The absolute uncertainty remains the same as the scale of celsius and kelvin are identical. Thus,

$$T = 5.0 + 273.0 = 278.0 \text{ (K)}$$

$$\therefore \frac{1}{T} = \frac{1}{278.0 \text{ K}} \approx 0.003597 \text{ K}^{-1} \tag{4.16}$$

Calculating the percentage uncertainty of $\frac{1}{T}$ using the equation for the uncertainty of a quantity raised to an exponent as given in (Tsokos 14),

$$\frac{\Delta(\frac{1}{T})}{(\frac{1}{T})} \times 100 = |-1| \times \frac{0.5}{278.0} \times 100 \approx 0.2\% \text{ (1 s.f)} \tag{4.17}$$

The percentage uncertainties were rounded to one significant figure as the absolute uncertainty in temperature was one significant figure. Thus, the percentage uncertainty for all $\frac{1}{T}$ values is 0.2%.

Table 4: $\ln(k)$ and its percentage uncertainty for every $\frac{1}{T}$ K^{-1}

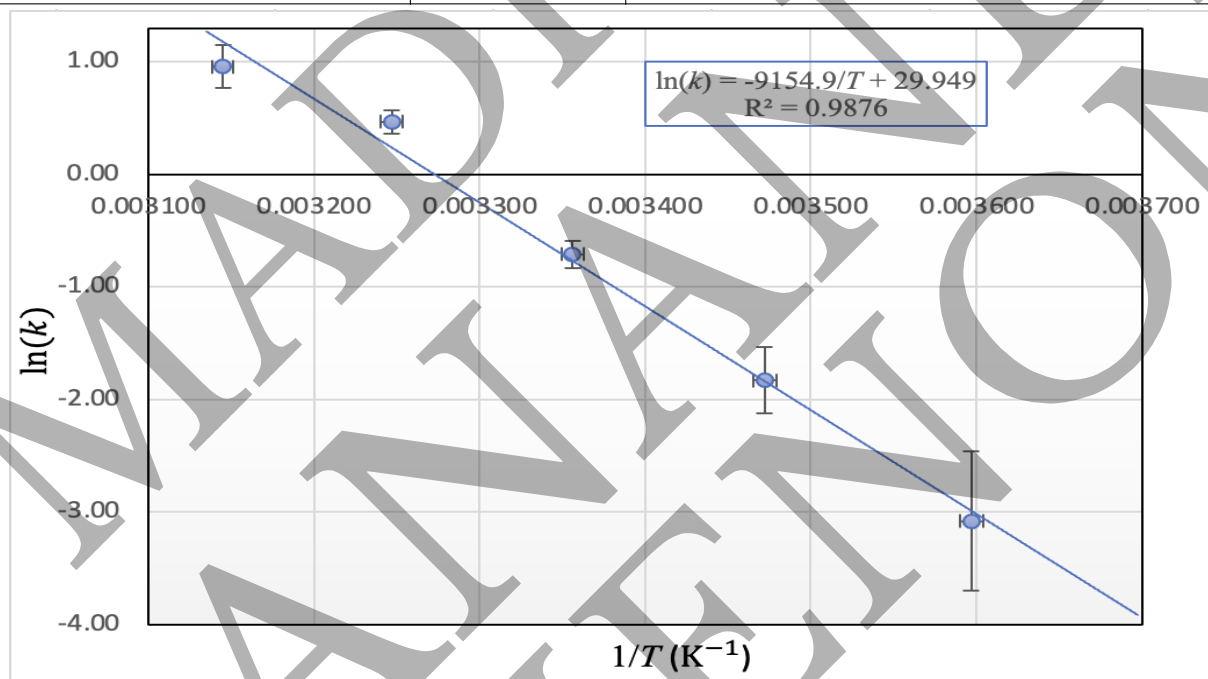| $\frac{1}{T}$ (K^{-1}) $\pm 0.2\%$	$\ln(k)$	$\frac{\Delta \ln(k)}{\ln(k)} \times 100$
0.003597	-3.08	20
0.003472	-1.83	16
0.003356	-0.71	19
0.003247	0.47	19
0.003145	0.96	20

Figure 7: Graph of $\ln(k)$ against $\frac{1}{T}$ (K^{-1}); plotted on Microsoft Excel by author

5   Analysis

It was hypothesised that there would be a negative and linear relationship between the natural log of the rate constant $\ln(k)$ and the reciprocal of temperature $\frac{1}{T}$ with units K^{-1}. The graph above clearly illustrates this linear relationship, thus confirming the hypothesis. It is evident that the size of the error bars increase as $\frac{1}{T}$ increases (T tends to 0). This however does not mean that there is a larger uncertainty associated with smaller values of T as the rate constant is much larger for higher values of T, thus resulting in smaller fractional uncertainties. What is interesting to note however is that the percentage uncertainty in $\ln(k)$ is the same at the largest and smallest temperature: 0.003597 K^{-1} (5.0 °C) and 0.003145K^{-1} (45.0 °C) even though it was noted in section 4.1 that it was easier to maintain the temperature at lower values due to a smaller temperature gradient with the surrounding area. This is further exemplified as standard deviations increased with temperature as shown in table 2, thus showing greater variation, and as a result uncertainty at higher temperatures. The best-fit line either touches the point or goes through the error bars for all values

of $\ln(k)$ except for the value at $0.003247\,\text{K}^{-1}$ ($35.0\,^\circ\text{C}$). This implies that it is an outlier and thus must be rejected. The reason for this could be attributed to change in atmospheric conditions as on the day of carrying out this trial, the lab was colder than usual (the only day where ambient temperature was not constant), resulting in a change in ambient temperature and as a result the temperature gradient. The vertical axis intercept is attributed to both the natural log of the frequency factor $\ln(A)$ and sources of systematic error that shift the curve upwards. As the original relationship was only linear and not proportional, the extent to which systematic error contributes to the axis intercept cannot be determined. Nevertheless, potential sources of systematic error will be addressed in section 6.2. It can however be said that random errors are relatively low due to the fact that no other mathematical model can be used as a line of best fit due to the high R^2 value, implying the line of best fit is a good model for the obtained data.

Determining activation energy

Remembering from the linearised Arrhenius equation that the gradient m is given by,

$$m = \frac{-E_a}{R} \tag{5.1}$$

Substituting in the value of the gradient and universal gas constant,

$$\frac{-E_a}{8.31\ \text{JK}^{-1}} \approx -9150\ \text{K} \tag{5.2}$$

The reason the gradient was rounded to three significant figures was because the computation would have involved the following calculation $m = \frac{\ln(k_2) - \ln(k_1)}{\frac{1}{T_2} - \frac{1}{T_1}}$. As the least precise quantities in the above equation are $\ln(k_2)$ and $\ln(k_1)$ with three significant figures, the gradient was rounded to three significant figures. The uncertainty of the gradient can be determined using maximum and minimum lines. However, since the first point on fig. 7 does not lie on the best-fit line, the minimum line does not pass through the best-fit. As a result, excel was utilised to determine the uncertainty which yielded a value of $\pm543\ \text{k}$ (rounded to 3 s.f). This is equivalent to a percentage uncertainty of approximately 6%

Rearranging for activation energy and converting into kJ,

$$E_a = \frac{-8.31\ \text{JK}^{-1} \times (-9150 \pm 6\%)\text{K}}{1000\ \text{J/kJ}} \approx (76.0 \pm 6\%)\ \text{kJ} \tag{5.3}$$

Thus, the activation energy for the sulfuric-acid catalysed iodination of propan-2-one was determined to be,

$$E_a \approx (76.0 \pm 6\%)\ \text{kJ} \tag{5.4}$$

The literature value for the activation energy of this reaction is given by Delluva et al. to be $(88.5 \pm 1.3)\ \text{kJ}$. Thus, the percentage error between the literature value and the experimentally obtained value is,

$$Percentage\ error = \left| \frac{(76.0 - 88.5)\ \text{kJ}}{88,5\ \text{kJ}} \right| \times 100$$
$$\approx 14.1\%\ (3\ \text{s.f}) \tag{5.5}$$

It is important to note however that the errors involved until here tend to be underestimated as most uncertainties were rounded to one significant figure to maintain convention. Thus, some uncertainties were rounded down, which implies that there should actually be a higher percentage uncertainty with the calculated value of the activation energy. Regardless, the relatively low calculated percentage uncertainty in the activation energy implies that there are fewer random errors. This implies that there are more systematic errors which allows us to infer that the vertical axis intercept in the graph has a significant contribution from systematic errors.

6 Evaluation

Table 5: Strengths

Strength	Impact on Study
A suitable temperature range was chosen with an appropriate number of trials for each temperature.	A total of five temperature values were investigated with a total of five trials at each temperature. This led to a total of twenty-five trials, thus allowing us to first see that the Arrhenius' equation does indeed hold over this temperature range and second helps reduce the impact of random errors due to the repetition of trials. This contributed towards obtaining an activation energy value that is within a 15% limit of the literature value.

Table 5: Strengths (Continued)

An electronic data-logger was used.	The use of an electronic data-logger to plot absorbance over time reduces the possibility of human error such as errors due to reaction time that would otherwise have played a role if absorbance values were manually recorded with the aid of a stop-watch.
Use of plastic cuvettes	Plastic is a better insulator than glass, thus the use of plastic cuvettes minimises heat loss while the absorbance values were being measured in the colorimeter.

Table 6: Limitations and possible improvements

Limitation	**Explanation impact on study**	**Possible improvements**
Heat loss not accounted for (systematic)	There is no doubt that heat loss occurred due to no lid on the water bath and due to the existence of a temperature gradient between the room and the system, thereby leading to heat loss. As temperature affects the rate of reaction, heat loss would result in the measured initial rate corresponding to a different temperature value. To minimise heat loss, the colorimeter was placed as close to the area of mixing as possible and it took approximately the same time for each trial to place the cuvette into the colorimeter.	A water bath, although expensive, is essential for a laboratory and therefore could be purchased. Alternatively, the temperature could be measured after the solution is placed in the cuvette (although this will increase the time taken to place in the cuvette) to identify the instantaneous temperature at which the reaction is taking place. Furthermore, the solution could be heated above the desired temperature and allowed to cool slightly after it is removed from the water bath.
Change in environmental conditions (random)	Due to constraints with lab facility usage, all the trials could not be completed in the same day. As a result, there could be a change in environmental conditions such as ambient temperature, light intensity etc in the lab which could affect readings. The value of $\ln(k)$ at 35.0°C being an outlier is attributed to this cause.	It is recommended all trials are completed in the same day as it is unlikely for environmental conditions to change drastically in the span of a few hours.
Burettes were placed in a well-lit area (systematic)	The burettes containing propan-2-one, iodine, water and sulfuric acid were placed in a well-lit area. As iodine is photosensitive, the light would likely have initiated the conversion into iodine free radicals. This was further exacerbated as iodine was diluted for the experiment.	This error is considered minimal as the iodine was stored in an amber bottle in a dark area. In the event there was more than a day's gap in between data collection, a new stock solution of iodine was prepared. To completely be safe, the experiment could be carried out in a darker room
High temperatures in water bath could have caused boiling (systematic)	As higher temperatures were maintained by using a kettle, the initial temperature of the water when poured from the kettle was over 70.0°C. Propan-2-one has a boiling point of 56.0°C (ECHA), thereby temporarily resulting in boiling of the propan-2-one. Hence, the volume did not stay constant throughout.	This was considered minimal as the water bath immediately cooled to below 56.0°C. This could be avoided by using a water bath that heats up from a smaller temperature to the desired temperature as opposed to using a custom one that cools from a higher temperature to the desired temperature.
The value measured was not the initial rate of reaction for all temperatures (random)	The time taken to place the cuvette in the colorimeter was roughly the same for all temperatures despite the rate increasing exponentially at higher temperatures. Thus, the cuvette was not placed in the colorimeter at the same stage of the reaction for all trials, implying that the measured tangent does not fully correspond to the *initial* rate of reaction	As iodine is zero order with respect to the rate mechanism, this limitation should theoretically be insignificant as the rate of the reaction is expected to be the same throughout the reaction. However, different standard deviation values could imply a contribution to uncertainty. This is inevitable and no practical steps can be taken towards correcting this.

7 Conclusion and Scope for Future Work

This investigation focused on the relationship between **temperature** and **rate constant** for the sulfuric acid catalysed iodination of propan-2-one. It was shown theoretically and then confirmed experimentally that the natural log of the rate constant is linearly related to the reciprocal of temperature. This relationship was then used to extrapolate the activation energy of the reaction to a relatively high degree of accuracy given the equipment available in the lab and the conditions under which the experiment was carried out. Thus the aim of veryifying Arrhenius' equation and extrapolating the activation energy was achieved. Despite there being errors that would have impacted the final measured value of the activation energy, the relatively high R^2 value and low percentage error shows there is a relatively high degree of accuracy and precision for the experiment.

Future work could involve using a greater range of temperatures. Although, this experiment cannot be conducted for temperatures greater than $56.0°C$ due to the boiling point of propanone, a smaller temperature increment could be used to add more data points, making the line of best-fit more accurate. This will lead to a better estimation of the activation energy. Alternatively, other acid catalysts could be used to see how changing the properties of the catalyst affects the activation energy. For example, Hu and Baird carried out the iodination of propanone in isobutyric acid and determined the activation energy to be (70.1 ± 4.0) kJ, which is 5.0 kJ smaller than the measured activation energy with a H_2SO_4 catalyst. Finally, different halogens—like bromine—could be explored to see how properties of the halogen changes the activation energy.

As one of the aims of this investigation was to explore kinetics, an investigation into the frequency factor component of Arrhenius' equation could be carried out. A plot of the experimentally obtained values of k against T gives the following curve
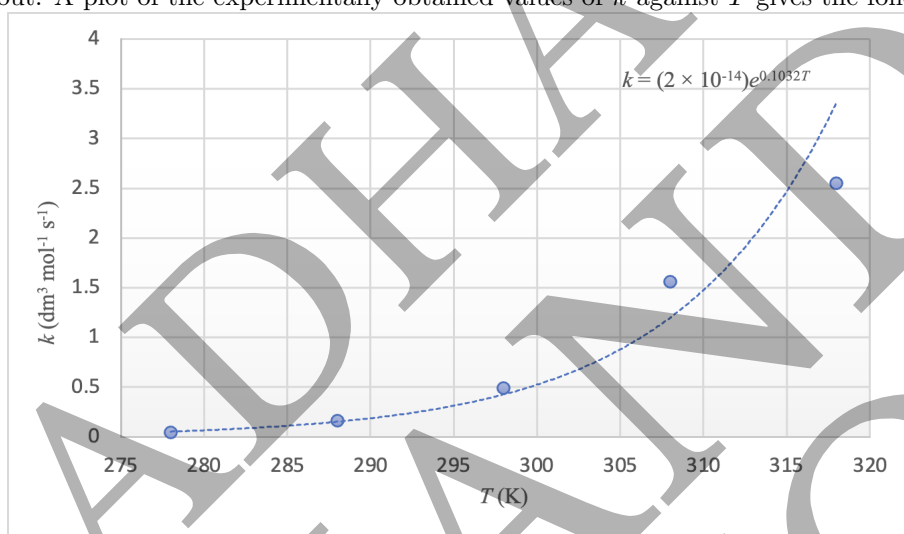

Figure 8: Graph of k against T (error bars omitted for clarity); plotted on Microsoft Excel by author

As T is in the denominator of the exponent in the Arrhenius equation, higher values of T causes $\frac{-E_a}{RT}$ to tend to 0. $e^0 = 1$ which implies that for higher values of T, a plot of k against T should plateau to the value of A, thereby contradicting fig. 8. However, we are once again reminded that at higher temperatures, the frequency of collisions increases. Thus, collisions with the correct orientation should also increase resulting in a higher value of A. More research led to the finding that the Arrhenius equation can be rewritten as (Golshani),

$$k = d^2 \sqrt{\frac{8k_b T}{\mu}} \, e^{\frac{-E_a}{RT}} \tag{7.1}$$

k_b is a constant known as Boltzmann's constant which has a value of 1.38×10^{-23} JK^{-1}. μ is defined as the reduced mass of the reactant particles (Jagannadham) and d is defined as the distance between the centres of the molecule when a collision occurs (Laidler, 81). A further explanation of d and μ is outside the scope of this paper. Thus, it is evident that as T increases, the square root term grows faster than the exponential term which implies that A increases, thus explaining the exponential curve. Although there is a mathematical description, it could be worth exploring this further to perhaps experimentally determine d from eq. (7.1) and compare it to known literature values for atomic and ionic radii of the reactant particles. This would also enable us to quantify the magnitude of the systematic uncertainty in our investigation. As theoretically a vertical axis intercept is expected by $\ln(A)$, it is difficult to estimate the proportion of the experimental axis intercept being contributed from systematic error as A changes with temperature, thereby resulting in different axis intercept values. Thus, being able to investigate this relationship will also help us quantify the systematic error in our experiment.

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Appendix A   Code to plot Maxwell-Boltzmann curves

The Maxwell-Boltzmann curves in fig. 5 were plotted in Python using the Matplotlib package. The code was run on Jupyter Notebook.

```python
#importing mandatory libraries
from matplotlib import pyplot as plt
from matplotlib.lines import Line2D
import numpy as np
import math
%matplotlib inline

x_list = np.linspace(0.1, 0.8, 100) #generating numbers to plot points

def f(x,v):
    return np.sqrt(2/math.pi)*(x**2/v**3)*np.exp(-1*x**2/(2*v**2)) #function to plot curve corresponding to T1
def g(x,v):
    return np.sqrt(2/math.pi)*((x-0.001)**2/v**3)*np.exp(-1*(x-0.001)**2/(2*v**2)) #function to plot curve corresponding
        to T2

#plotting the curves
y_list = f(x, 0.2)
z_list = g(x, 0.25)
fig, ax = plt.subplots()
ax.plot(x_list, y_list, label="$T_1$", color="blue")
ax.plot(x_list, z_list, label="$T_2$", color="orange")


#formatting the axes
plt.xlabel("Kinetic Energy $E_k$")
plt.ylabel("Number of particles with kinetic energy $E_k$")
plt.xticks([0.6], label="$E_a"),plt.yticks([])
plt.axvline(x = 0.59, ymax = 0.19, color = 'black', linestyle="dashed")
labels = [0, "$E_a$"]
xticks = [0.1, 0.59]
plt.xticks(xticks, labels)
yticks = [0]
labels_y = [0]
plt.yticks(yticks, labels_y)
x_fill = np.linspace(0.6, 0.8, 1000)
y_fill = f(x_fill, 0.2)
z_fill = g(x_fill, 0.25)


#creating the legend
handles, labels = plt.gca().get_legend_handles_labels()
line_1 = Line2D([0], [0], label='$T_1$', color='blue')
line_2 = Line2D([0], [0], label='$T_2$', color='orange')
plt.legend(handles=handles)
plt.savefig("maxwellboltzmanncurves")
```