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CHEMISTRY IA: Kinetics of the hydrolysis of ethyl ethanoate

1. INTRODUCTION

Sodium ethanoate is an inexpensive chemical which has a variety of important uses and applications in real life. For example, it is added to food to preserve it and enhance its flavour, and unlike other food additives, it has no known harmful effects (Wasserman, n.d.). Moreover, it can be used as a reagent in molecular biology, where it is used to extract DNA (Wasserman, n.d.). As such, given its industrial significance, it is worth investigating the chemistry behind it. One common way of producing sodium ethanoate is through the hydrolysis reaction of ethyl ethanoate using aqueous sodium hydroxide, where ethyl ethanoate (an ester) reacts with sodium hydroxide to form sodium ethanoate (a salt) and ethanol (an alcohol), as follows (Babalola, 2019):

$$\mathrm{CH_3COOC_2H_5\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + C_2H_5OH\ (aq)} \tag{1}$$

After reaction completion, the ethanol can easily be distilled, leaving sodium ethanoate. This investigation is based upon the research question: **"How does the rate constant of the hydrolysis reaction of ethyl ethanoate using sodium hydroxide vary with absolute temperature?"** The accuracy of the experimentally determined relationship can be evaluated by calculating the activation energy (E_a) of the reaction from the data gathered and comparing it to a literature value. The activation energy (in $\mathrm{kJmol^{-1}}$) of a reaction is a measure of the minimum energy that must be provided to two reactant particles undergoing collision to result in a successful chemical reaction, i.e. form products (Brown and Ford, 2014, pgs. 280–281). This means that a higher activation energy indicates that there are less frequent successful collisions taking place. The relationship between absolute temperature, T, and rate constant, k, is given by the Arrhenius equation as follows (Brown and Ford, 2014, pgs. 300-302):

$$k = Ae^{\frac{-E_a}{RT}}, \tag{2}$$

where R is the gas constant ($= 8.31\mathrm{JK^{-1}mol^{-1}}$) and A is the frequency factor—indicative of the frequency of collisions with the correct orientation for the reaction to occur. Alternatively, (2) is often better expressed in its logarithmic form:

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{3}$$

As such, we can see that a plot of $\frac{1}{T}$ on the x-axis against $\ln k$ on the y-axis should result in a straight line of negative gradient $\frac{E_a}{R}$, from which the activation energy could be found out. However, a method of determining the rate constants for different temperatures is needed. Reaction (1) is second order (Das et al., 2011), and we know that for a second-order bimolecular reaction, the rate expression is (Brown and Ford, 2014, pgs. 291–292):

$$\mathrm{rate} = kc_Ac_B,$$

where c_A and c_B are the concentrations of two different reactants. Considering the case in which $c = c_A = c_B$, our rate expression becomes:

$$\mathrm{rate} = kc^2 \tag{4}$$

Mathematically, (4) can be expressed as a differential equation as follows:

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = kc^2$$

Separating and integrating both sides, we get:

$$\int_{c_0}^{c} -\frac{1}{c^2}\mathrm{d}c = \int_{0}^{t} k\mathrm{d}t$$

$$\Rightarrow \left[\frac{1}{c}\right]_{c_0}^{c} = [kt]_0^t$$

$$\Rightarrow \frac{1}{c} - \frac{1}{c_0} = kt, \tag{5}$$

where c_0 is the initial concentration and c is the concentration of the reactants at time t. This is known as the integrated rate law, which is a convenient way of determining the rate constant of a reaction at a given temperature (OpenStax, 2014). From (5), we can see that plotting time against $\frac{1}{c}$ will result in a straight line of positive gradient k and y-intercept $\frac{1}{c_0}$.

Finally, in order to determine the concentration of the reactants in (1) at a certain time, titrations using the titrant sodium hydroxide in the presence of excess HCl could be employed. In this case, a titration would indicate the volume of a known concentration of NaOH solution required to neutralise the titrand HCl mixed with a sample of the reaction in (1). The volume and concentration of HCl, alongside the sample volume of the reaction mixture must be known. The purpose of the HCl is to serve as a quenching reagent, i.e. to stop the reaction from proceeding and for the remainder of it to react with the sodium hydroxide until the endpoint of titration is reached. From the measured volume of NaOH, the concentration of the reactants could be calculated as follows:

The concentration of the reactants ethyl ethanoate and sodium hydroxide at time t is simply expressed as:

$$c = \frac{n}{V},$$

where n is the number of moles and V is the volume of the sample. Based on the purpose of HCl, it can be deduced that:

$$n_{\mathrm{HCl}} = n + n_{\mathrm{NaOH}}$$

$$\therefore c = \frac{n_{\mathrm{HCl}} - n_{\mathrm{NaOH}}}{V}$$

$$\therefore c = \frac{V_{\mathrm{HCl}}c_{\mathrm{HCl}} - V_{\mathrm{NaOH}}c_{\mathrm{NaOH}}}{V}$$

$$\therefore \frac{1}{c} = \frac{V}{V_{\mathrm{HCl}}c_{\mathrm{HCl}} - V_{\mathrm{NaOH}}c_{\mathrm{NaOH}}} \tag{6}$$

2. EXPERIMENTAL DESIGN

2.1 Variables

Independent Variable: The absolute temperature at which the reaction was carried out in Kelvin. Five conditions were chosen at intervals of 10: 293K, 303K, 313K, 323K and 333K (20, 30, 40, 50 and 60 °C). These intervals were chosen as to allow for significant variability in the temperatures (a difference of 10K is a lot), and hence noticeable changes in the rate constants, which would potentially allow for the construction of a graph with a clear linear trend between $\frac{1}{T}$ and $\ln k$.

Dependent Variable: The rate constant of the second-order reaction in $\mathrm{mol^{-1}dm^{3}min^{-1}}$. The units of the rate constant can be worked out by rearranging (4) for k and dividing $\mathrm{moldm^{-3}min^{-1}}$ (units of rate) by $\mathrm{mol^{2}dm^{-6}}$ (units of c^2). The rate constant is not directly measurable and therefore had to be mathematically determined by conducting a series of experiments on how the concentration of the reactants changes with time at equal intervals of 5, 10, 15, 20, 25 and 30 minutes. $\frac{1}{c}$ values were calculated using the measured volume added during titration. The gradients of the $\frac{1}{c}$-time graphs were calculated to find the values of k. A final graph of $\frac{1}{T}$ against $\ln k$ showed the linear relationship and allowed the activation energy to be determined.

There were also a number of other factors which might have affected the accuracy of the experiment in determining the rate constants, and therefore had to be controlled. The table below summarises these variables.

Table 1: Identifying and analysing control variables.

Control	**Explanation**
Volumes and initial concentrations of chemicals	The same initial concentrations were used for the reactants ethyl ethanoate and sodium hydroxide to act as a control and also for (4) to apply, since it is assumed that the initial concentrations are equal. The concentration and volume of hydrochloric acid used in titration were also kept constant throughout the experiments as changing it could have potentially had an effect on the volume of sodium hydroxide used in titration. Finally, the volume of the reaction sample taken at time intervals also remained constant at $10\mathrm{cm^3}$.
Reading volume appropriately from the burette	When taking readings from the burette, the volume was measured at eye level to prevent parallax error—that is, the misreading caused due to the distortion when viewing from different angles. Furthermore, all readings were taken from the bottom of the meniscus—a curve caused as a result of surface tension in the liquid—which is the true volume of a concave meniscus. This minimised random error from the volume readings.
White background under the conical flask	Since the base of the burette is blue, and the indicator phenolphthalein generates a pink/purple colour, there would be subjectivity in deciding when the endpoint of titration was reached. As such, placing a white paper under the conical flask reduced this subjectivity and made it easier to observe colour changes, preventing systematic error.
Volumetric drop rate of burette	During titrations, sodium hydroxide was made to flow at the same constant rate (dropwise) throughout all trials by adjusting the stopcock. This helped minimise random error in the volume recorded. Additionally, allowing the sodium hydroxide to flow slowly drop by drop made it easier to observe indicator change and ensured that any extra volume that was possibly added after the endpoint of titration was minimal.
Swirling conical flask	Swirling the conical flask during the titration allowed the sodium hydroxide to quickly react with the solution so that any parts of the solution which temporarily turned pink/purple from the titrant would turn back to colourless immediately, making it easier to determine when the endpoint of titration was reached; in other words, it was done to ensure that the titrant was evenly combined with the titrand.

Use of distilled water	After each titration trial, the contents in the conical flask were disposed of and then it was cleaned using distilled water and dried to ensure that nothing remained in there that would have had an effect on the subsequent titrations. Similarly, this was also done for the measuring cylinders.
Stirring	The reaction mixture in the water bath was stirred upon mixing the reactants in order to ensure that they were reacting together and that the reaction was proceeding such that products were formed. Furthermore, the solutions were stirred for the same duration (30 seconds) across all temperatures, serving as a control.

2.2 Apparatus and Chemicals

- Burette ($\pm 0.05\text{cm}^3$)
- 100cm^3 measuring cylinders ($\pm 1.0\text{cm}^3$)
- 500cm^3 of 0.04moldm^{-3} ethyl ethanoate
- 2000cm^3 of 0.04moldm^{-3} sodium hydroxide
- 1000cm^3 of 0.04moldm^{-3} hydrochloric acid
- Phenolphthalein
- Clamp
- 200cm^3 test tube
- Two 100cm^3 test tubes
- Test tube holder
- Water bath
- Conical flask
- Thermometer (± 0.1℃)
- Stopwatch ($\pm 0.01\text{s}$)
- 25 ml pipette ($\pm 0.06\text{cm}^3$)
- Stirrer
- Funnel

2.3 Procedure

100cm^3 of ethyl ethanoate and 100cm^3 sodium hydroxide of equal concentration (0.04moldm^{-3}) were measured using 100cm^3 measuring cylinders and then poured into separate test tubes which were placed in a test tube holder in a water bath set at 20℃. The temperature of the water in the water bath was measured using a thermometer. After about 10 minutes, such that the heat from the water was transferred to the content of the test tubes, the ethyl ethanoate and sodium hydroxide were mixed and placed in a 200cm^3 test tube that remained in the water bath. A timer on the stopwatch was started and the solution was stirred using a stirrer for 30 seconds. At equal time intervals of five minutes, three 10cm^3 samples of the reaction mixture were measured using a 25cm^3 pipette. More than one sample was taken in order to increase the reliability of the measurements and minimise random error. Each sample was then added to 10cm^3 of 0.04moldm^{-3} hydrochloric acid—also measured using the pipette—in a conical flask. After adding one drop of phenolphthalein, the sample was titrated using sodium hydroxide. The burette was stopped when the endpoint of titration was reached—that is, when the colour of the entire sample turned pink/purple. The burette was held in place using a clamp and sodium hydroxide was poured in through a funnel. The initial and final volumes of the NaOH in the burette were recorded and the difference found. The mean volume was then calculated from the three samples, which was used to calculate the $\frac{1}{c}$ values according to (6). Titrations were carried out for the other time intervals until 30 minutes into the reaction taking place. Finally, the experiment was repeated for the remaining four temperatures.

2.4 Safety Considerations

Ethyl ethanoate is highly flammable therefore it was important to make sure that there was no source of ignition near the experiment site. When disposing of it, small amounts of ethyl ethanoate were flushed down a sink, but with a large quantity of water. Due to its flammability, care was needed to avoid any build-up of vapour in the sink. Sodium hydroxide is corrosive, so care was needed in order to prevent eye or skin contact. As such, safety glasses and gloves had to be worn at all times. Furthermore, some of the temperature intervals were very hot, e.g. 60℃, therefore it was important not to directly touch the test tubes in the water bath. There were no notable ethical or environmental issues All remaining chemicals from the experiment were returned to the technician rather than being disposed of.

3. RESULTS & ANALYSIS

Table 2: Relationship between time, volume of sodium hydroxide used in titration, and inverse concentration for $T = 293\text{K}$ (20℃)

Time **t/ minutes** **$\Delta t = \pm 0.25$**	**Volume required to reach endpoint** **V_{NaOH}/ cm^3** **$\Delta V_{\text{NaOH}} = \pm 0.10\text{cm}^3$**				**Inverse concentration** **$\frac{1}{c}$/ dm^3 mol^{-1}**
	Trial 1	Trial 2	Trial 3	**Mean**	
5.0	2.95	2.95	2.90	2.93 ± 0.03	35 ± 0.78
10.0	3.40	3.30	3.40	3.37 ± 0.05	38 ± 1.0
15.0	3.50	3.60	3.50	3.53 ± 0.05	39 ± 1.0
20.0	3.90	3.90	3.95	3.92 ± 0.03	41 ± 0.81
25.0	4.20	4.20	4.15	4.18 ± 0.03	43 ± 0.72
30.0	4.35	4.25	4.30	4.30 ± 0.05	44 ± 1.0

Table 2 shows data for the first condition ($T = 293\text{K}$). The data in red represents processed data while the rest is raw data[1]. The time uncertainty was recorded as ±0.25 minutes (±15 seconds), since time was needed while transferring the mixture from the test tube to the pipette. This required approximately 30 seconds, therefore the sample was withdrawn 15 seconds before the time of the interval, and finishing 15 seconds after, hence the uncertainty. Although the uncertainty of the burette is ±0.05, the uncertainty in the volume column header is recorded as ±0.10 because the volume was calculated as $V_{\text{NaOH}} = V_{\text{final}} - V_{\text{initial}}$. It therefore follows that:

$$\Delta V_{\text{NaOH}} = \Delta V_{\text{final}} + \Delta V_{\text{initial}} = 0.05 + 0.05 = 0.10$$

Calculation examples are demonstrated below using values from the first row of the table:

Calculation of mean:

$$\bar{V} = \frac{V_1 + V_2 + V_3}{3} = \frac{2.95+2.95+2.90}{3} = 2.933... \approx 2.93\ (3\ s.f.)$$

Uncertainty in mean:

$$\Delta\bar{V} = \pm\frac{V_{\text{max}} - V_{\text{min}}}{2} = \pm\frac{2.95-2.90}{2} = \pm 0.025 \approx \pm 0.03\ (1\ s.f.)$$

Calculation of $\frac{1}{c}$:

$$\frac{1}{c} = \frac{V}{V_{\text{HCl}}c_{\text{HCl}} - V_{\text{NaOH}}c_{\text{NaOH}}} = \frac{10}{10\times0.04 - 2.93\times0.04} = 35.3... \approx 35\ (2\ s.f.)$$

Uncertainty in $\frac{1}{c}$:

$$\frac{\Delta(1/c)}{1/c} = \frac{\Delta V}{V} + \frac{\Delta V_{\text{HCl}}}{V_{\text{HCl}}} + \frac{\Delta V_{\text{NaOH}}}{V_{\text{NaOH}}}$$

$$\Delta\left(\frac{1}{c}\right) = \pm\frac{1}{c}\left(\frac{\Delta V}{V} + \frac{\Delta V_{\text{HCl}}}{V_{\text{HCl}}} + \frac{\Delta\bar{V}_{\text{NaOH}}}{\bar{V}_{\text{NaOH}}}\right) = \pm 35\left(\frac{0.06}{10} + \frac{0.06}{10} + \frac{0.03}{2.93}\right)$$

$$\pm 0.778... \approx \pm 0.78\ (2\ s.f.)$$

Note that in calculating $\Delta\left(\frac{1}{c}\right)$, the uncertainties of c_{NaOH} and c_{HCl} were not accounted for as the solutions were prepared by the technician and as such, it had to be assumed that these uncertainties were negligible. The values of the mean volume were formatted to three significant figures as the precision of the burette allowed for such. While it would have also been appropriate to quote the $\frac{1}{c}$ values to three significant figures, they were formatted to two due to the uncertainty

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[1] Strictly speaking, the NaOH volumes is not raw data, as the difference between final and initial volume was found, making it processed data. However, considering the vast amount of data that had to be collected, this is the closest to raw data and had to be considered as such in order to avoid excessive tables and numbers.

in the volumes of the solution and of the HCl, which limited the precision of $\Delta\left(\frac{1}{c}\right)$ to two significant figures and hence the $\frac{1}{c}$ values too.

For purposes of conciseness, **Table 7** only shows time and inverse concentration for the other four temperatures. Tables 3 to 6 in the Appendix however show the remaining data (the sodium hydroxide volumes). It can be seen from the table below that the concentrations are increasing at a faster rate as temperature increases, implying higher rate constants, however graphing this data allows us to determine their values, as in **Figure 1**.

Table 7: Processed data showing the relationship between time and inverse concentration from $T = 303\text{K}$ to $T = 333\text{K}$

Time t/ **minutes** $\Delta t = \pm 0.25$	**Inverse concentration** $\frac{1}{c}$ / $\text{dm}^3\ \text{mol}^{-1}$			
	$T = 303\text{K}$	$T = 313\text{K}$	$T = 323\text{K}$	$T = 333\text{K}$
5.0	35 ± 0.78	36 ± 1.4	37 ± 1.6	39 ± 1.3
10.0	37 ± 1.3	38 ± 1.5	43 ± 1.0	45 ± 1.1
15.0	41 ± 1.0	42 ± 1.2	49 ± 1.4	52 ± 1.6
20.0	44 ± 1.5	47 ± 1.1	60 ± 1.8	61 ± 1.6
25.0	48 ± 1.1	53 ± 1.6	67 ± 1.0	69 ± 1.7
30.0	52 ± 1.1	57 ± 1.7	74 ± 1.5	78 ± 1.7

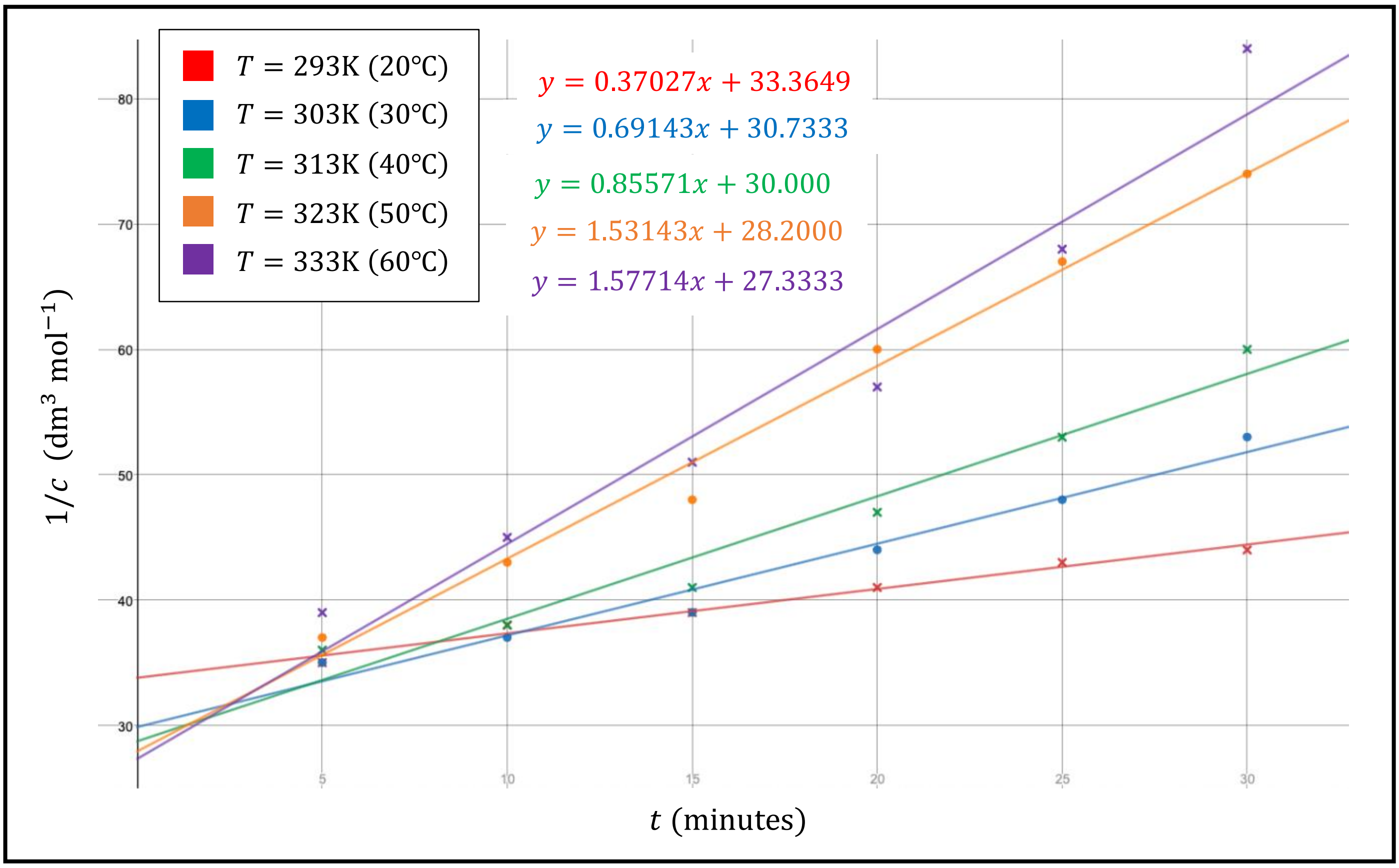

Figure 1: A graph (created using Desmos) showing a linear trend between time and inverse concentration for all temperatures.

The gradients (x-coefficients) in the line equations represent the rate constants. We can see that they are increasing with temperature, which is in agreement with (2). Constructing a detailed graph for each individual temperature with error bars will allow us to calculate the uncertainties in the rate constants. **Figure 2** is an example.

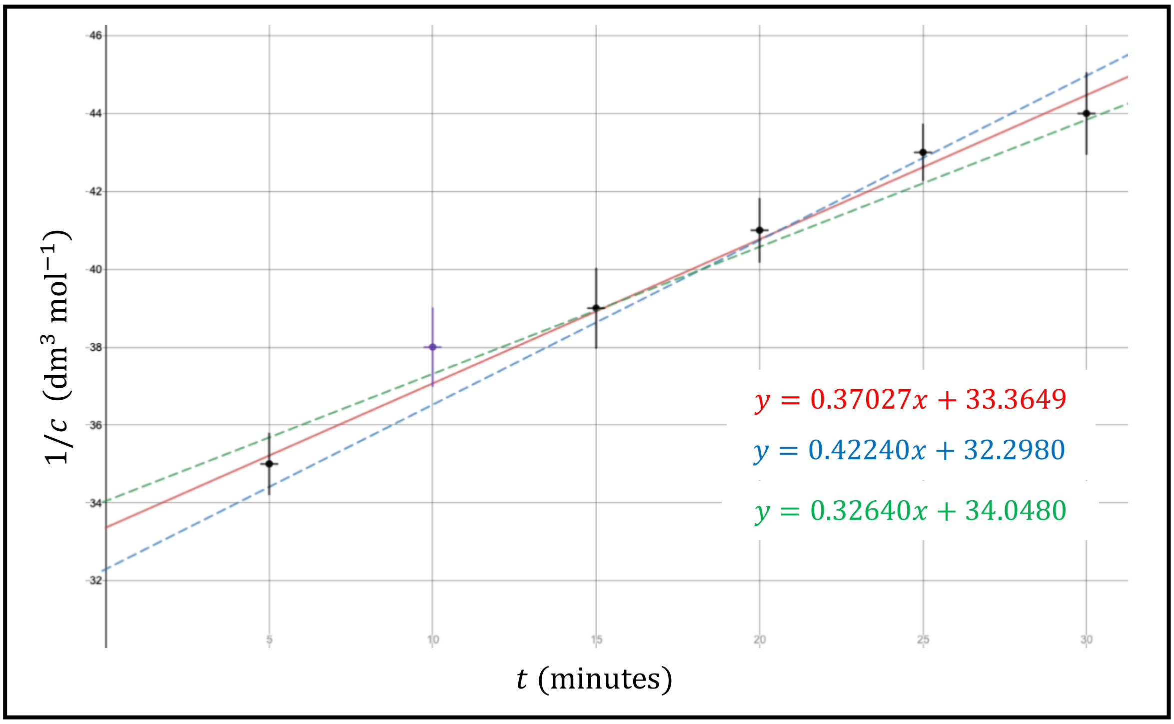

Figure 2: A graph (created using Desmos) showing a linear relationship between time and inverse concentration for $T = 293$K. The line of best fit is indicated with the red line, while the blue and green lines represent the maximum and minimum slopes respectively.

Note that the data point in purple $(10, 38)$ was identified as an anomaly as it did not seem to fit within the general trend, and therefore is not accounted for by the line of best fit. The error bars for the time seem small and negligible in comparison to the error bars for the $\frac{1}{c}$ values, which have percentage uncertainties no greater than 3%, which is not negligible, but sensible and moderate. The uncertainty in the rate constant was calculated using,

$$\frac{m_{\text{max}} - m_{\text{min}}}{2},$$

Where m_{max} is the gradient of the maximum line and m_{min} is the gradient of the minimum line. For example:

$$\Delta k_{293} = \pm\frac{0.42240 - 0.32640}{2} \approx \pm 0.048\ (2\ s.f.)$$

This was done for the other four temperatures by constructing appropriate graphs with error bars in order to determine the gradient uncertainties. **Table 8** summarises the rate constants and their uncertainties at different temperatures, as well as other information needed for an Arrhenius plot.

Table 8: Processed data showing the relationship between inverse temperature and ln$k$.

Temperature T/ K $\Delta T = \pm 0.1$K	**Inverse temperature** $\frac{1}{T}$ / $10^{-3}\mathrm{K}^{-1}$	**Rate constant** k/ $\mathrm{mol^{-1}dm^3min^{-1}}$	**ln$k$**
293.0	3.41	0.37 ± 0.048	-0.99 ± 0.13
303.0	3.30	0.69 ± 0.064	-0.37 ± 0.09
313.0	3.19	0.89 ± 0.11	-0.12 ± 0.12
323.0	3.10	1.5 ± 0.11	0.41 ± 0.07
333.0	3.00	1.6 ± 0.12	0.47 ± 0.08

The uncertainty in temperature was simply recorded as the uncertainty of the thermometer ($\pm 0.1℃ = \pm 0.1\text{K}$). The values of the rate constants and their uncertainties were calculated using the graphs, as established previously. From that, the $\ln k$ values were calculated, as well as their uncertainties. The uncertainty of a function can be expressed as its partial derivative multiplied by the absolute uncertainty of its input, i.e. the variable (Farrance and Frenkel, 2012). Since the partial derivative of $\ln k$ is $\frac{1}{k}$, it follows that:

$$\Delta(\ln k) = \frac{\Delta k}{k}$$

For example, using the first row of the table:

$$\Delta(\ln k) = \frac{0.048}{0.37} \approx \pm 0.13\ (2\ s.f.)$$

While some of these uncertainties seem very high in comparison to the $\ln k$ values themselves, it does not matter since $\ln k$ is not a measured variable, and as such, its uncertainty is not necessarily suggesting a lack of accuracy in the calculated values, but they were calculated in order to help in determining the uncertainty of the activation energy. On the other hand, the $\frac{1}{T}$ values were simply calculated by taking the reciprocal of T. For example:

$$\frac{1}{T} = \frac{1}{293} \approx 0.00341 = 3.41 \times 10^{-3}\text{K}^{-1}$$

The uncertainties in the $\frac{1}{T}$ values were regarded as negligible and not recorded due to the following reasoning:

$$\frac{\Delta(1/T)}{1/T} = \frac{\Delta T}{T} \Longrightarrow \Delta\left(\frac{1}{T}\right) = \frac{\Delta T}{T^2}$$

Due to the T^2 in the denominator, the uncertainty becomes miniscule. For example:

$$\Delta\left(\frac{1}{T}\right) = \frac{0.1}{293^2} \approx 0.0000012$$

This results in a percentage uncertainty of about 0.034%, which, again, is negligible.

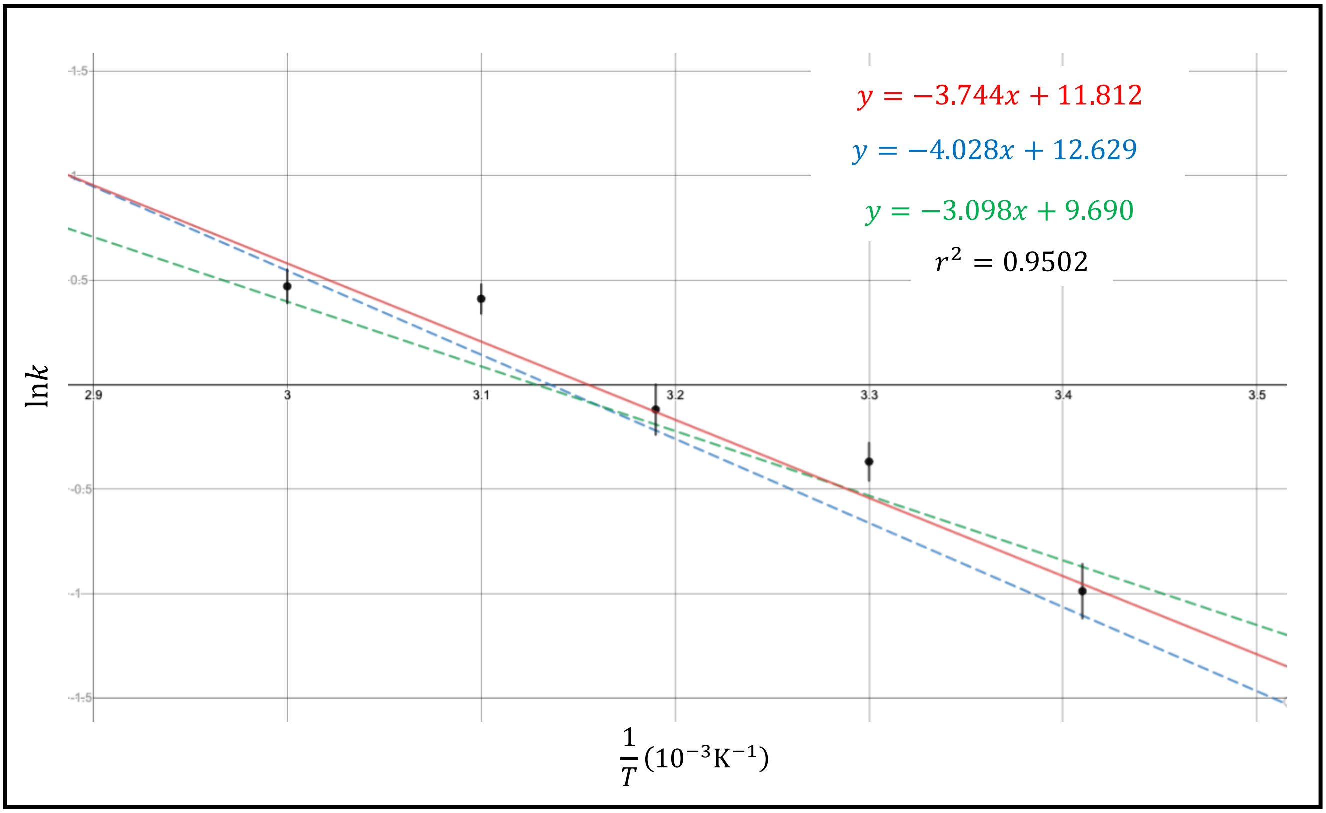

Figure 7: A graph (created using Desmos) showing a linear relationship between $\frac{1}{T}$ and $\ln k$. The line of best fit is indicated with the red line, while the blue and green lines represent the maximum and minimum slopes respectively.

The graph in **Figure 7** shows a strong correlation between $\frac{1}{T}$ and $\ln k$ *as* the line of best fit is within close proximity to all the points. This is reinforced and justified by the high mathematically determined r^2 value of 0.9502. A value of 1 shows a perfect fit between the trendline and the data, i.e. a very strong linear relationship, whereas a value of 0 shows no statistical relationship between the line and the data. This strong linear relationship suggests that there is an exponential relationship between temperature and the rate constant, in accordance with (2) and (3). From (3), the gradient (m) is given as $-\frac{E_a}{R}$, therefore the activation energy is:

$$E_a = -mR = 3.744 \times 10^3 \times 8.31$$
$$= 31113 \text{ Jmol}^{-1} \approx 31 \text{ kJmol}^{-1}$$

Its uncertainty can be calculated as follows:

$$\frac{\Delta E_a}{E_a} = \frac{\Delta m}{|m|} + \frac{\Delta R}{R}$$

But since R is a universal constant, its uncertainty can be assumed to be negligible, therefore:

$$\Delta E_a = E_a \times \frac{\Delta m}{|m|}$$
$$= \pm\left(31 \times \frac{0.465}{3.744}\right)$$
$$= \pm 3.85 \approx 4$$

The activation energy for reaction (1) can therefore be quoted as (31 ± 4) kJmol^{-1}. This translates to a percentage uncertainty of about 13%, indicative of the random error in the experiment and the data.

4. CONCLUSION

In conclusion, the results of this experiment supported the idea that there is an exponential relationship between the absolute temperature (T) at which the hydrolysis reaction of ethyl ethanoate is carried out and the rate constant (k) of the reaction, as evident through the strong linear relationship between $\frac{1}{T}$ and $\ln k$ in **Figure 7**. These results could be explained qualitatively as follows: as the temperature increases, the average kinetic energy of the reactant molecules increases, and hence their average velocity increases, causing them not only to collide more frequently with each other, but also collide with greater force. This, on average, increases the frequency of successful collisions, i.e. collisions which possess sufficient energy (activation energy or higher) to form products, and therefore this results in a greater rate of reaction.

The strength and validity of our experimentally determined relationship however needs to be considered. The activation energy of the reaction was found to be 31 kJmol^{-1}, which allows for comparisons to be made with a literature value. Das et al. (2011) determined the activation energy of the reaction to be 41.4 kJmol^{-1}. This value is likely to be valid and a true representation of the actual value because the researchers used a different procedure in which they employed a pulsating sensor-based conductivity monitoring instrument to track the progress of the reaction. The use of such precise advanced equipment minimised uncertainties and ensured that the data is accurate. The experimental percentage error could therefore be calculated to determine the reliability of our experimental data relative to a more accurate secondary source:

$$\text{Percentage error} = \frac{41.4 - 31}{41.4} \times 100\% \approx 25\%$$

This shows that our value is 25% less than the ‘true’ value. This percentage seems high, however considering the limitations and weaknesses of the experiment (see Evaluation), this is somewhat sensible. The systematic error may be calculated as the difference between total experimental error and random error, i.e. $25\% - 13\% = 12\%$. This possibly shows that both random and systematic errors in the experiment were great (both higher than 10%), which leads us to identifying and evaluating potential sources which may have caused such large errors.

5. EVALUATION

While the large errors were caused by limitations and weaknesses of the experiment, it is still important to acknowledge the strengths which it had. Firstly, the control variables were controlled successfully. The same initial volumes and concentrations were used throughout all trials, and good experimental technique was employed while doing the titrations, from reading off the burette appropriately, to swirling the conical flask. These control variables and procedural elements ensured consistency and potentially helped prevent random error from being even larger than it currently is. The range of temperatures (IV) was also appropriate and could be considered a strength due to the wide range and the spacious increments which allowed for noticeable effects on the rate constants to be detected. The use of the water bath was also a strength as it allowed for the desired temperatures to be reached with almost negligible uncertainties, and for the thermal energy to be spread evenly throughout the water bath. Furthermore, the use of the integrated-rate law, (5), allowed for a viable method of determining the rate constants. This was arguably more effective than using other methods—such as investigating the relationship between time and concentration to find the initial rate of reaction and then using the rate expression to calculate the rate constants—because the integrated-rate law is not susceptible to the subjectivity of determining when the ‘initial’ rate is, and is therefore less biased. While this method involved more mathematics and analysis, it probably led to greater accuracy and objectivity.

However, despite the effectiveness of this method, the way in which the reaction was tracked could be a limitation. To determine the rate constants, repeated titrations were carried out at time intervals. Not only was this method of monitoring the reaction easily susceptible to systematic errors, but could have also led to large cumulative random errors, due to uncertainties resulting from titration equipment, as well as (potential) subjectivity in determining the endpoint of titration and errors due to reaction time. A better alternative could have been to monitor the reaction using different methods, for example, by measuring the conductivity of the reaction as a function of time, as that could also indicative of the reaction rate. However, due to school lacking such equipment (e.g. conductivity probes), this was not possible, and the lengthy method of titrations had to be resorted to.

A weakness of the experiment lies within the values of the NaOH volumes used during the titrations. As can be seen from Tables 2 to 6, the volumes were relatively low (usually ranging from 3 to 7cm^3) for the purposes of a titration. This is considered a weakness as it made it difficult to have a certain level of confidence in the validity of volume differences across time intervals or between different temperatures, since, as aforementioned, titrations are vulnerable to random error. This means that although the graphical analysis suggested strong linear relationships between the variables, it is—to some extent—likely that these results may have occurred by chance, due to the tiny differences in the volumes; differences which are possibly comparable to the potentially erroneous titrant volumes as a result of random error, subjectivity, and reaction time. In order to mitigate these effects, it would have been beneficial to decrease the concentration of the sodium hydroxide (by diluting it), which would have consequently led to needing more volume in the titration (since volume and concentration are inversely proportional). Although, this would have had a knock-on effect on needing to adjust the concentration of the ethyl ethanoate, since the concentrations need to be equal for the mathematics to work, as aforementioned.

Another weakness of the experiment, although minor and unnecessary, was the setup of the thermometer. Instead of being placed inside the test tube where the reaction was held, it was placed in the water bath. This means that the temperature of the water bath may not have necessarily reflected the temperature of the contents of the test tube. That being said, enough time was given (around 10 minutes) for the heat to reach the contents of the test tube, however this may still have not guaranteed equal temperatures and as such, it is important to have the thermometer inside to ensure the temperature the water bath is set to is in effect.

Finally, for future investigations, a possible extension would be to investigate the role of catalysts in the reaction and how they decrease the activation energy, possibly comparing different catalysts and identifying the most useful one. It would also be intriguing to look into the factors which have an effect on the yield of the reaction, considering the industrial significance of ethyl ethanoate.

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APPENDIX

Table 3: Relationship between time and volume of NaOH used in titration for $T = 303\text{K}$

Time $t/$ **minutes** $\Delta t = \pm 0.25$	**Volume required to reach endpoint** $V_{\text{NaOH}}/\ cm^3$ $\Delta V_{\text{NaOH}} = \pm 0.10cm^3$			
	Trial 1	Trial 2	Trial 3	**Mean**
5.00	2.95	2.95	2.90	2.93 ± 0.03
10.0	3.30	3.15	3.15	3.20 ± 0.08
15.0	3.80	3.80	3.90	3.83 ± 0.05
20.0	4.30	4.45	4.25	4.33 ± 0.10
25.0	4.80	4.80	4.90	4.83 ± 0.05
30.0	5.25	5.15	5.20	5.20 ± 0.05

Table 4: Relationship between time and volume of NaOH used in titration for $T = 313\text{K}$

Time $t/$ **minutes** $\Delta t = \pm 0.25$	**Volume required to reach endpoint** $V_{\text{NaOH}}/\ cm^3$ $\Delta V_{\text{NaOH}} = \pm 0.10cm^3$			
	Trial 1	Trial 2	Trial 3	**Mean**
5.00	3.05	3.10	3.20	3.12 ± 0.08
10.0	3.40	3.60	3.50	3.50 ± 0.10
15.0	4.10	4.05	3.95	4.03 ± 0.08
20.0	4.75	4.70	4.65	4.70 ± 0.05
25.0	5.30	5.15	5.35	5.27 ± 0.10
30.0	5.70	5.50	5.55	5.58 ± 0.10

Table 5: Relationship between time and volume of NaOH used in titration for $T = 323\text{K}$

Time $t/$ **minutes** $\Delta t = \pm 0.25$	**Volume required to reach endpoint** $V_{\text{NaOH}}/\ cm^3$ $\Delta V_{\text{NaOH}} = \pm 0.10cm^3$			
	Trial 1	Trial 2	Trial 3	**Mean**
5.00	3.40	3.20	3.35	3.32 ± 0.10
10.0	4.15	4.20	4.25	4.20 ± 0.05
15.0	4.85	5.00	4.90	4.92 ± 0.08
20.0	5.75	5.95	5.85	5.85 ± 0.10
25.0	6.30	6.25	6.30	6.28 ± 0.03
30.0	6.60	6.55	6.65	6.60 ± 0.05

Table 6: Relationship between time and volume of NaOH used in titration for $T = 333\text{K}$

Time $t/$ **minutes** $\Delta t = \pm 0.25$	**Volume required to reach endpoint** $V_{\text{NaOH}}/\ cm^3$ $\Delta V_{\text{NaOH}} = \pm 0.10cm^3$			
	Trial 1	Trial 2	Trial 3	**Mean**
5.00	3.65	3.70	3.55	3.63 ± 0.08
10.0	4.50	4.40	4.45	4.45 ± 0.05
15.0	5.05	5.20	5.25	5.17 ± 0.10
20.0	5.80	5.90	5.95	5.88 ± 0.08
25.0	6.35	6.30	6.45	6.37 ± 0.08
30.0	6.70	6.85	6.80	6.78 ± 0.08