Lab A – The Arrhenius Equation

Principle of Method

In the titration of an acid, Phenolphthalein is often used as an indicator due to its change in colour after an increase in pH. Such colour change is specifically from colourless to red, and it takes places as a consequence of the formation of the dianion form of Phenolphthalein (Ph_{2-}) from the uncharged, colourless form (Ph) as shown by Figure 1 below.

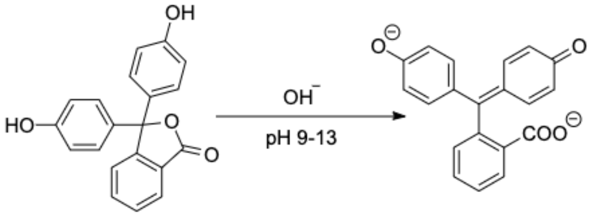

Figure 1. Chemical reaction for ionization of Phenolphthalein from Ph to Ph_{2-} and change in Ph from 9 to 13.

This first initial reaction was performed in the laboratory and preceded the further ionization of Phenolphthalein from Ph_{2-} to Ph_{3-} as shown by Figure 2, whose rate and temperature dependence was measured and plotted. This second reaction causes a further increase in pH, which induces a colour change from red to colourless as the Phenolphthalein Trianon is formed.

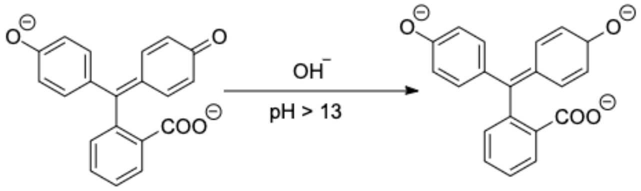

Figure 2. Chemical reaction for the formation of the Phenolphthalein Trianon (from Ph_{2-} and Ph_{3})

The rate constant for the second reaction was observed by monitoring the solution’s absorbance values in the spectrometer as it went from red to colourless, whereas the temperature dependence was measured by performing this same procedure under 0, 10 and 25.1 (room temperature) degrees Celsius.

The obtained data was then processed and analysed based on the derivation of the Arrhenius equation shown below by Equation 1, as described by the Laboratory manual[1]:

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

where Ea represents the activation energy for the reaction, R is the gas constant, T is the temperature in kelvin, and A represents the frequency of encounters between molecules, which can either yield a reaction or not depending on whether such encounter provides enough free energy to overcome the activation barrier energy requirements. The probability for an encounter to be able to overcome the energy of activation and carry on a reaction is represented by the exponential part of the equation.

Given this reaction, the rate constant is then measured as the slope from the straight line formed by a ln(k) vs 1/T plot; as demonstrated by the logarithm form of the Arrhenius equation shown by Equation 2:

$$\ln(k) = \ln(A) - E_a/RT$$

where the slope is given by the last term of the equation $(-\frac{Ea}{R})$.

Given that the nature of the colour is related solely to the anion of Phenolphthalein, the rate constant can be measured through the rearrangement of the rate law shown by Equation 3 below:

$$rate = k'[Ph^{2-}]^a$$

where $k' = k[OH^-]^b$. This law can be derived and integrated in order to give rate as the change in reactant concentration as a function of time. The derivation is dependent on the value of a, and results in Equations 4 and 5 according to the CHEM 201 laboratory manual.

In the case of $a = 1$, a ln(A) vs time plot would be linear and follow Equation 4, at which case, constants k’ and k can be determined from the slope and from the concentration of hydroxide respectively.

$$\ln(A) = -k't + (C + \ln(\varepsilon l))$$

In contrast, in the case of $a = 2$, a 1/A vs time plot would be linear, and follow the Equation 5, at which case, constants k’ and k can be determined from the slope and from the concentration of hydroxide as well as the ε value from Ph^{2-} at 565nm.

$$\frac{1}{A} = \varepsilon l * k't + C$$

where εl represents the molar absorptivity of Ph^{2-}, as well as its pathlength. Whereas the constant b can be determined from the ratio of two runs with different hydroxide concentrations at the same temperature as exemplified in Equation 6:

$$\frac{k_1'}{k_2'} = \frac{[OH^-]_1^b}{[OH^-]_2^b}$$

Procedure

The experiment was carried on as determined by the laboratory manual[1] . During the procedure, 100µL of Phenolphthalein was the volume determined as the correct one for carrying out the procedure, once it resulted in an absorbance value of 1.460 at a spectrometer zeroed at 565nm and 0 transmittance. Having set the correct volume of reactant for the solution, the absorbance was measured in different temperatures and using a different NaOH concentration, as instructed by the laboratory manual[1]. The following information is shown below by Tables 1, 2, 3 and 4.

Table 1. Absorbance vs time for Phenolphthalein solution of 0.5 M of NaOH at a temperature of 25.1°C

Absorbance	Time(s)
25.1°C	
1.68	0
1.52	30
1.25	60
0.97	90
0.74	120
0.56	150
0.43	180
0.329	210
0.26	240
0.21	270

Table 2. Absorbance vs time for Phenolphthalein solution of 0.5 M of NaOH at a temperature of 10.0°C

Absorbance	Time(s)
10°C	
0.915	0
0.348	240
0.273	300
0.222	360
0.177	420
0.144	480
0.115	540
0.09	600

Table 3. Absorbance vs time for Phenolphthalein solution of 0.5 M of NaOH at a temperature of 0°C

Absorbance	Time(s)
0°C	
1.22	0
0.81	243
0.662	360
0.542	480
0.44	600
0.356	720
0.295	840
0.238	964
0.195	1080

During the procedure, a room temperature of 25.1°C was recorded in order to perform the data analysis for this experiment. The above raw data was modified and quantitatively analyzed in order to determine ln(A), a, b, k', k and ln(K), as described by the following section.

Results and Calculations

As a measurement of rate of reaction, the absorbance vs time values were directly plotted from the raw data obtained during the lab procedure as shown by Figures 3, 4, 5 and 6

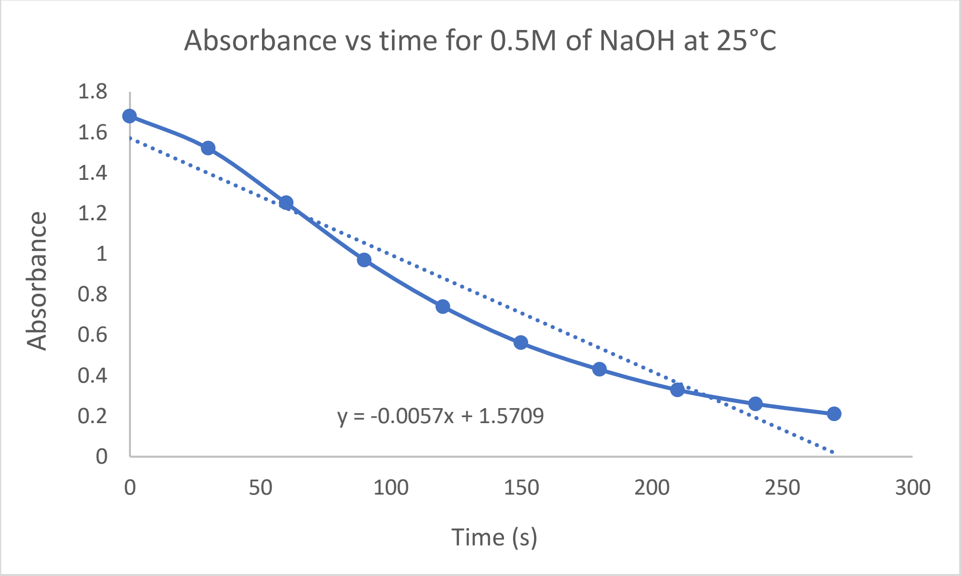

Figure 3. Plot of absorbance vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH at room temperature.

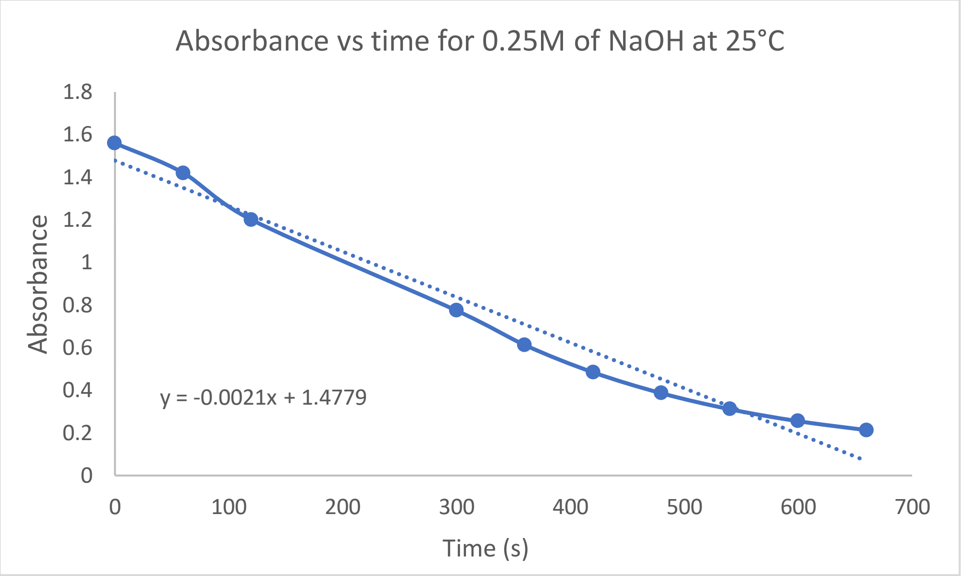

Figure 4. Plot of absorbance vs Time (s) for a Phenolphthalein solution of 0.25M of NaOH at room temperature.

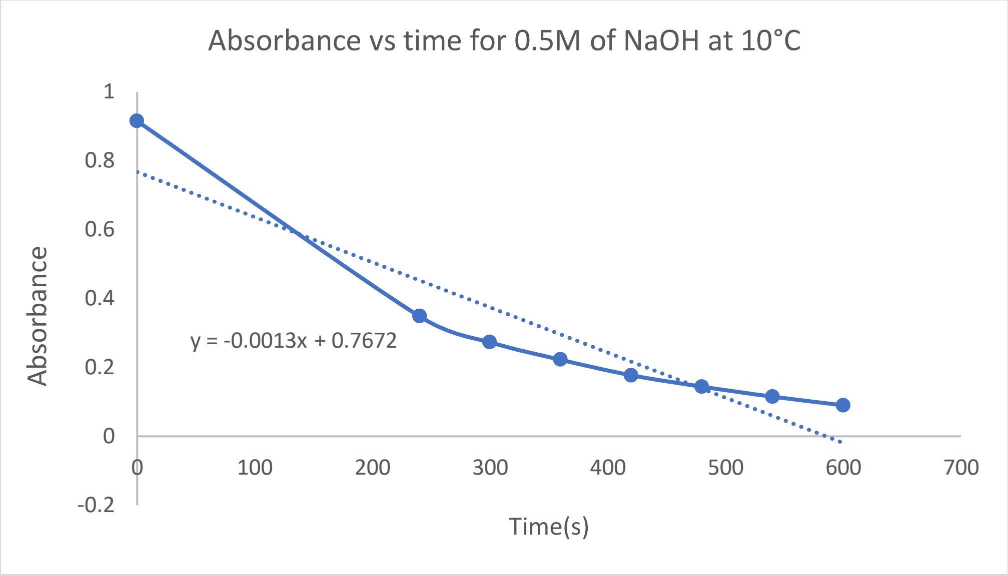

Figure 5. Plot of absorbance vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH at 10 °C

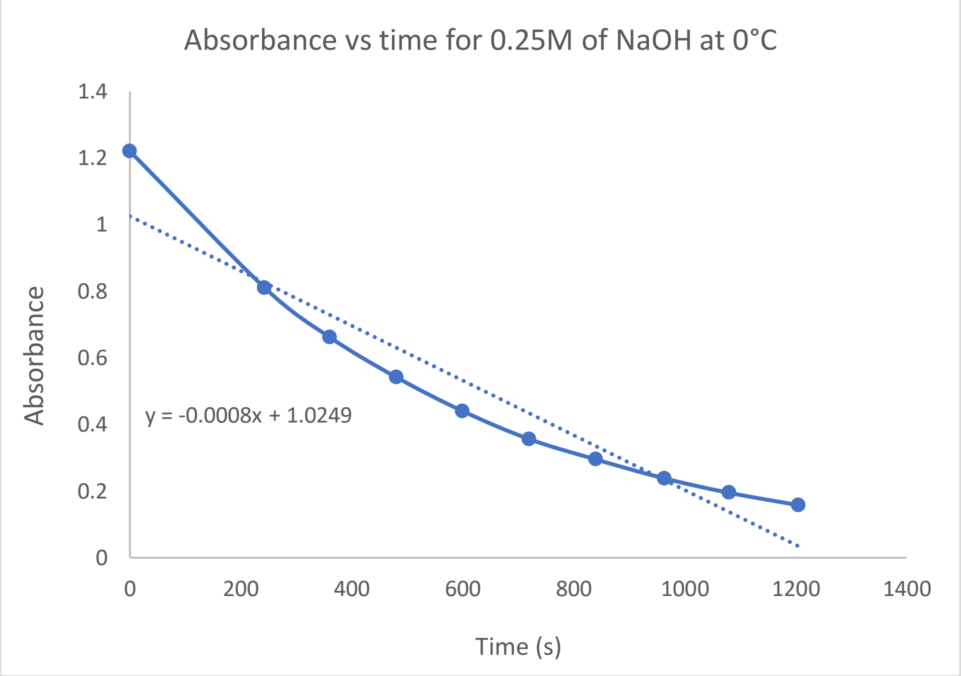

Figure 6. Plot of absorbance vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH at 0 °C

Proceeding that initial procedure, the second section of the data analysis for this experiment was to prepare graphs of ln(A) vs. t and 1/A vs. t, shown in Figures 7, 8, 9 and 10. This was done for both the

Phenolphthalein solution with 0.5M and 0.25M of NaOH at room temperature in order to determine the value for exponent a.

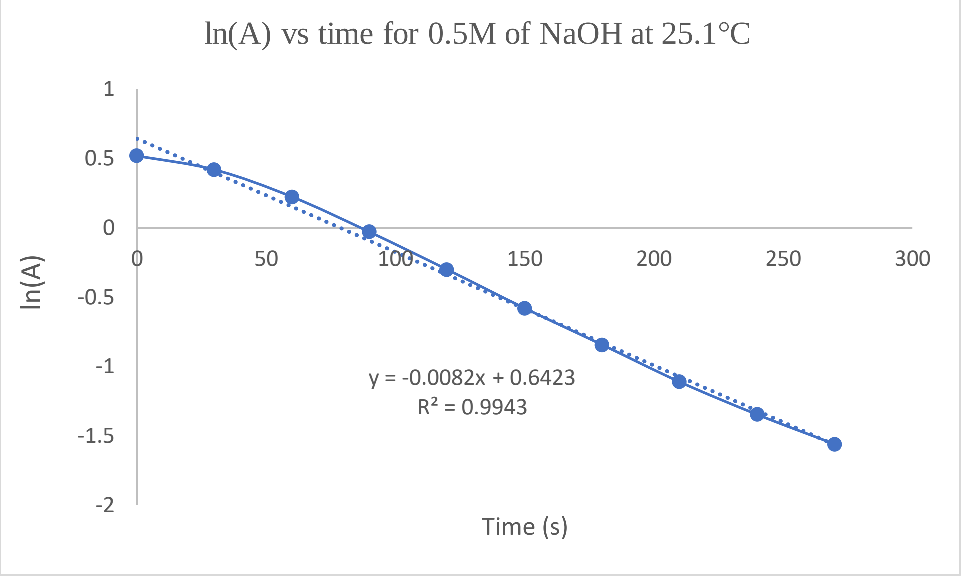

Figure 7. Plot of ln (A) vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH at room temperature.

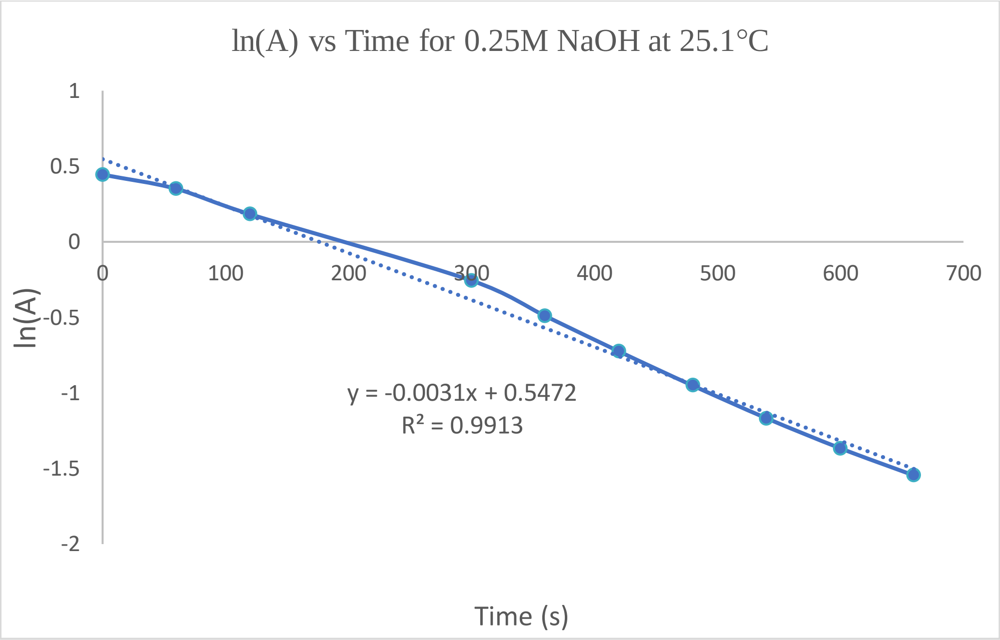

Figure 8. Plot of ln (A) vs Time (s) for a Phenolphthalein solution of 0.25M of NaOH at room temperature.

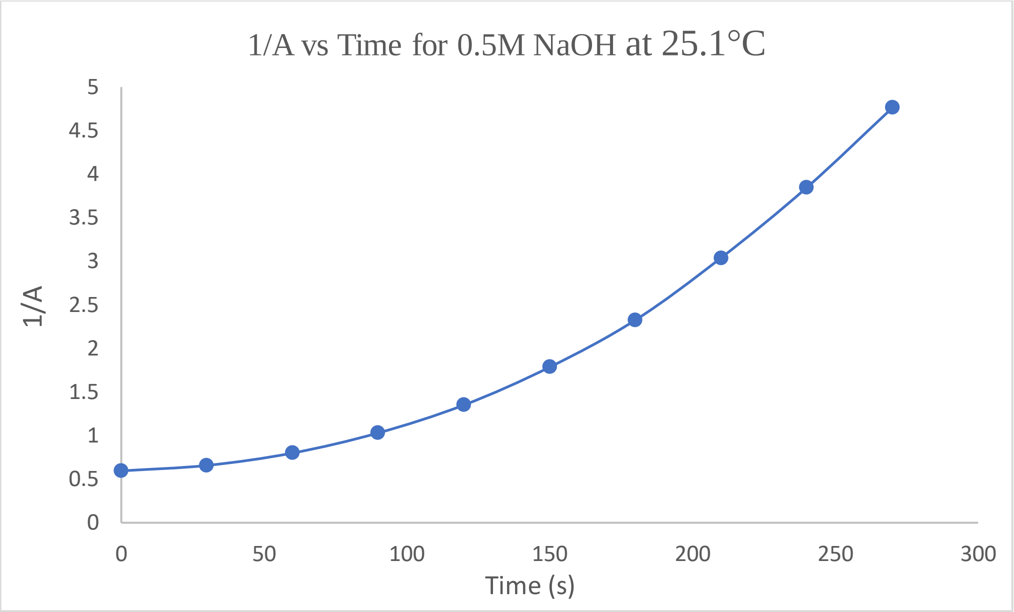

Figure 9. Plot of 1/A vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH at room temperature.

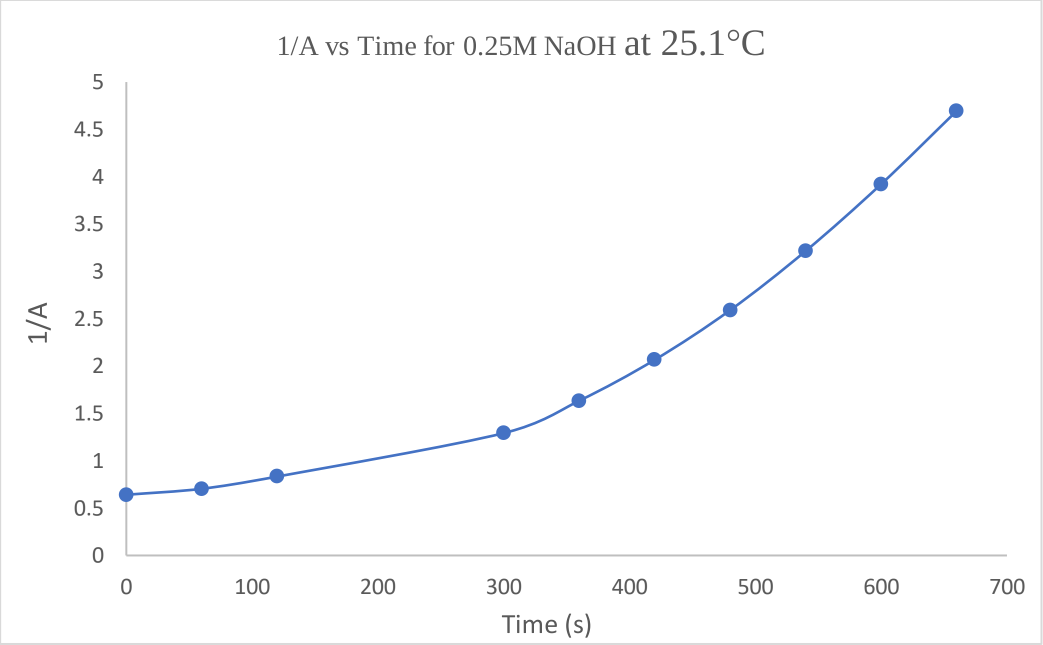

Figure 10. Plot of 1/A vs Time (s) for a Phenolphthalein solution of 0.25M of NaOH at room temperature.

Since linearity was observed in the ln(A) vs. Time plots, it was determined that $a = 1$. In addition to that, the linear regression analysis ran on both of the plots determined k' values of 0.0082 and 0.0031 for the 0.5M NaOH and the 0.25M NaOH solutions respectively. Proceeding those calculations, the value for the b exponent was calculated based in Equation 6 and the result was rounded to the nearest integer, which ultimately defined as the exponent as b = 1. In order to obtain a completely straight line in the plots, one data point was removed from the one with 0.25M of NaOH.

Having the value of exponent a equal to 1, ln (A) vs time plots were prepared for the remaining temperatures as shown by Figures 11 and 12.

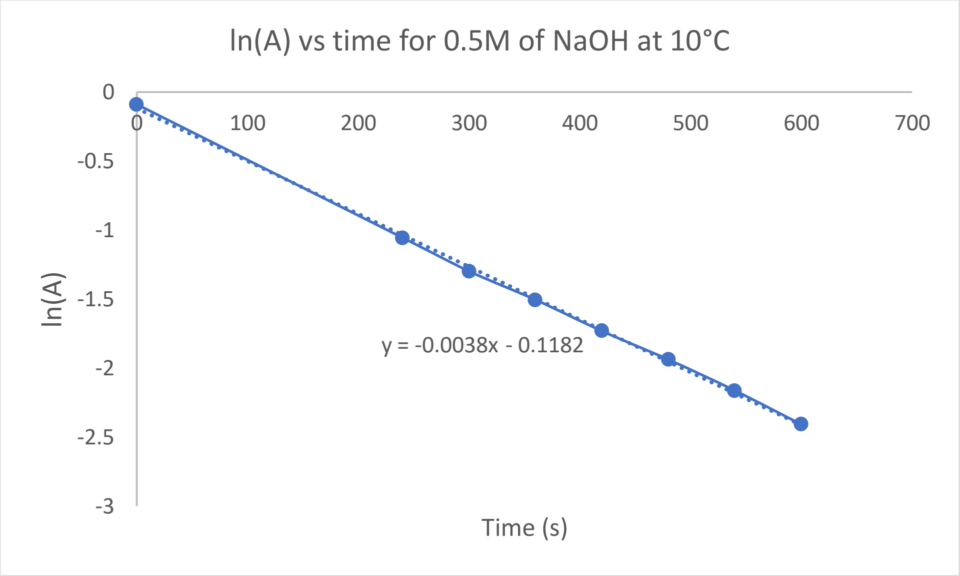

Figure 11. Plot of ln (A) vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH at 10°C.

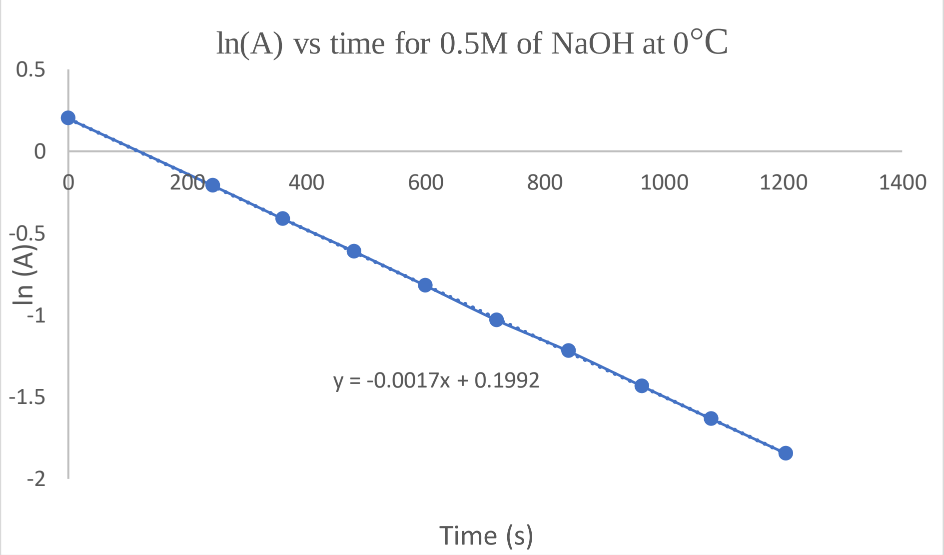

Figure 12. Plot of ln (A) vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH at 0°C.

Where in Figure 7, two data points were removed and in Figure 8, one data point was removed in order to obtain a completely straight line. As indicated by the laboratory manual[1], a linear regression analysis was performed for both plots in order to determine k and k' for each temperature, which were ultimately determined as 130.64, and 261.28 respectively for 10°C; and 294.57, and 589.14 for 0°C.

Having obtained the k and k' values for each temperature, a plot of ln(k) vs 1/T was prepared as shown by Figure 13, and the values for Ea and the pre-exponential factor A were determined as 42174.46 J/mol and 101185.243 respectively. These values were calculated based on the slope value for the linear regression analysis of the plot.

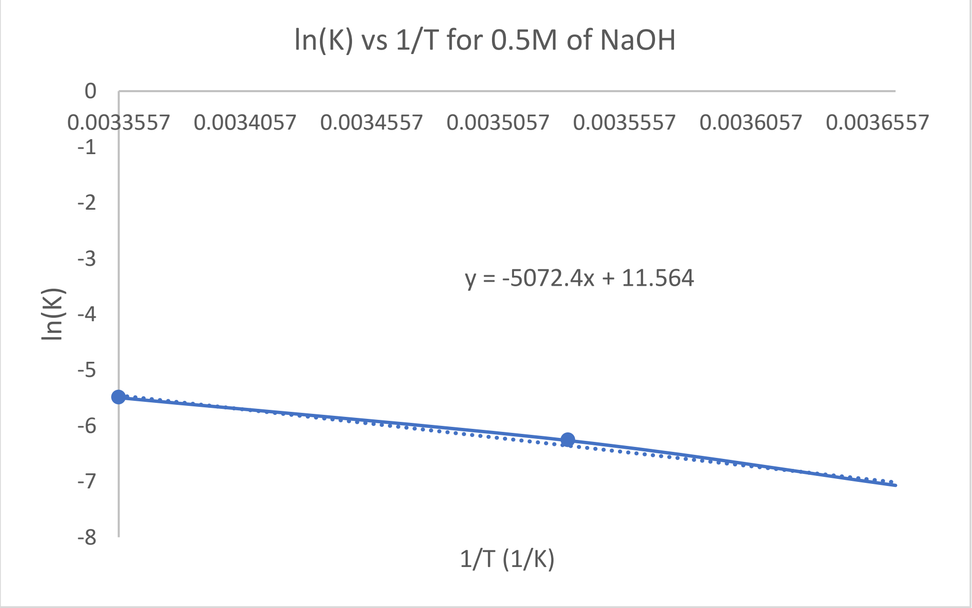

Figure 13. Plot of ln(k) vs Time (s) for a Phenolphthalein solution of 0.5M of NaOH. The k values were obtained experimentally from monitoring the absorbance of the same compound at temperatures of 0°C, 10°C and 25°C.

Discussion

In order to derive the necessary formulas for this experiment and to accept all the results obtained as accurate values, it was assumed that the influence of temperature on the pre-exponential factor A was irrelevant and could be ignored. Also, the a exponent value was determined through measuring the linearity of the ln(A) vs time plots through its' R_2 values; once their closeness to 1 is directly proportional to their linearity level.

According to the references values used for this report[3] the exponents a and b, determined through the rate law for the reaction of Phenolphthalein with sodium hydroxide, experimentally measured as 1 L/mol-min and 1.42 L/mol-min at 25°C respectively, were determined as 1 L/mol-min C and 1.1 L/mol-min at 23°C respectively. This comparison is indicative that the values obtained by this experiment were measured accurately enough in order to ultimately obtain a value that is very close to the truth. The sources of error for the small deviation in the exponent b value could have been caused by mistakes made while making the Phenolphthalein solution, or simply by an statistical error inherent to the pipette used while making the solution.

Regarding the value for the energy of activation of the reaction Ea of 42.167 KJ/mole is indicative of a very endothermic reaction, and it is consistent with the literature values of 43.094 KJ/mole[2].

The difference in slope for the plots of absorbance vs time for each temperature and NaOH concentration lead to the conclusion that the rate for the reaction is more heavily dependent on temperature than it is for the NaOH concentration. This can be concluded because if the rate was to be more heavily dependent on NaOH concentration, then the slopes for the 0.5M of reagent would have more similar value than the slope for 0.25M, thus indicating a correlation between similar concentrations. In fact, the slope for 0.25M of NaOH at 25°C is more similar to the slope value for 0.5M of NaOH at 10°C than this latter value is similar to 0.5M of NaOH at 25°C, which indicates very little rate dependence to concentration of NaOH.

Conclusion

The kinetics of a Phenolphthalein reaction with sodium hydroxide were monitored through absorbance measurements from the laboratory’s spectrometer and plotting the data obtained in order to find exponent’s a and b, the pre-exponential factor A, and the Exponential factor Ea. Overall, the results were extremely accurate, being almost exactly the same as the literature values, except for the b exponent value.

Answers to questions

The way to show this is to calculate the ratio of square root dependence between A2 and A1, as shown below, where T1 = 273K and T2 = 283K

$$\frac{A1}{A2} = \frac{\sqrt{T1}}{\sqrt{T2}}$$

$$\frac{A1}{A2} = \frac{\sqrt{273}}{\sqrt{283}} = 0.98$$

Where the proximity of the ratio value to 1 indicates negligible change between A1 and A2, and thus, negligible temperature influence on A. On the other hand, the ratio between the exponential term of the rate equation is not so similar, in fact, it almost reaches 2. This ratio value indicates an approximate doubling of the value, which proves the higher effect of T in the exponential term of the rate law, and its contraposing little effect for the pre-exponential factor, A.

$$\frac{e^{-\frac{Ea}{RT}}}{e^{-\frac{Ea}{RT}}} = 1.93$$

References

[1]Exp. C, Chem 201 Manual 2020

[2]Mukhtar A, Shafiq U, Khan AF, Qadir HA, Qizilbash M, 2015. Estimation of parameters of arrhenius equation for ethyl acetate saponification reaction. Research Journal of Chemical Sciences, 5: 46-50.

[3]Nicholson, L. (1989). Kinetics of the fading of phenolphthalein in alkaline solution. Journal of Chemical Education, 66(9), 725-726. doi:10.1021/ed066p725