

# Kinetic studies using UV-VIS spectroscopy Fenton Oxidation

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## **Abstract**

This experiment was performed as part of the NTNU course TKP4105/TKP4110 Felles Lab. The degradation of Naphtol Blue Black (NBB) by oxidation was studied using UV-VIS spectroscopy to monitor the degradation rate.  $\text{H}_2\text{O}_2$  was used as oxidative agent. The activation energy  $E_a$  was found as  $25.89 \text{ kJ mol}^{-1}$ . It was found that the reaction can be approximated as a pseudo-first rate reaction for the parameters in the experiment.

The first attempt to perform this experiment failed, as no reaction was observed for the planned parameters. Because of this no data was collected. This report is written based on measurements and data collected by Ingvild Marie Sørli and Vidar Skjervold, as advised by the supervisor for the experiment.

## Contents

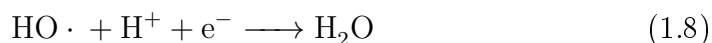
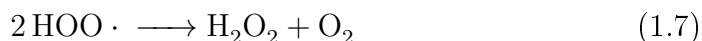
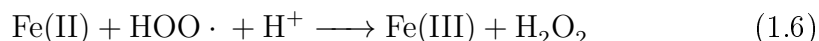
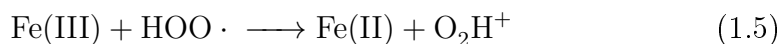
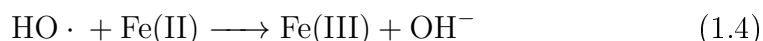
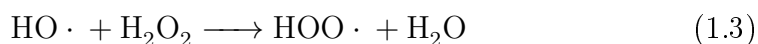
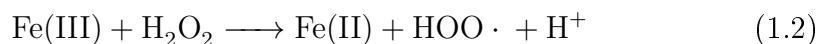
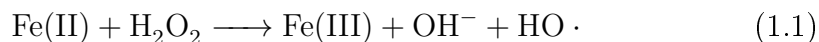
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# 1 Theory

The theoretical background for the experiment is generally found from the lab instruction script.<sup>1</sup>

## 1.1 Fenton Oxidation

Fenton oxidation is a common and effective method for waste-water treatment by oxidation. The active oxidant is hydroxy-radicals, catalyzed by dissolved iron. This happens in a series of reactions, given in equation (1.1) to (1.8).



The different groups of the NBB-molecule absorb different wavelengths of light. For this experiment the absorption of the azo-group and the aromatic rings are monitored. The azo-group absorbs light at 618 nm, while aromatic groups absorb light at 320 nm. By monitoring the decline of absorbance at these wavelengths as the oxidation occurs, the rate of degradation of NBB can be determined.

## 1.2 Kinetics

Kinetic studies of this process are rather complicated, because of the many stages in the reaction. Assuming that hydroxyl radical is the only active oxidant in the reaction, the general rate law can be written as (1.9)

$$r = \frac{-dc_{RH}}{dt} = k_{HO}\cdot c_{HO}\cdot c_{RH} \quad (1.9)$$

To simplify this, it is assumed that the concentration of hydroxyl radical is close to constant during the experiment. The reaction rate law can then be simplified to the expression given in (1.10).

$$r = \frac{-dc_{RH}}{dt} = k_{app} \cdot c_{RH} \quad (1.10)$$

Solving for  $c_{RH}$  and integrating gives (1.11).

$$\ln(c_{RH}) = \ln(c_{RH_0}) - k_{app} \cdot t \quad (1.11)$$

In (1.11)  $c_{RH}$  is concentration of reactant,  $c_{RH_0}$  is the initial reactant concentration,  $k_{app}$  a constant which includes the apparatus and hydroxyl radical concentration, and  $t$  is time in seconds.

In this experiment the organic compound Naphtol Blue Black (NBB) will be decomposed by the hydroxyl radical. The concentration of naphtol blue black can be monitored by measuring the absorbance of the compound. According to the Lambert-Beer equation (1.12), the absorbance is proportional to the concentration of compound,  $c_{RH}$ , the molar absorbance of the compound,  $\varepsilon$  and the length of lightpath,  $l$ .

$$A = \varepsilon \cdot c_{RH} \cdot l \quad (1.12)$$

By combining (1.11) and (1.12), an expression for change in absorbance over time can be written as (1.13)

$$\ln\left(\frac{A_{RH_0}}{A_{RH}}\right) = k_{app} \cdot t \quad (1.13)$$

### 1.3 Activation Energy

The reaction rate constant can be found from the experimental data and (1.13) by regression. This constant can then be used to calculate the activation energy  $E_a$ , using the Arrhenius equation (1.14), which can be written in linearized form as (1.15).

$$k_{app} = A_r e^{\frac{-E_a}{RT}} \quad (1.14)$$

$$\ln(k_{app}) = \ln(A_r) - \frac{E_a}{RT} \quad (1.15)$$

where  $A_r$  is the Arrhenius pre-exponential factor.

## 2 Experimental

### 2.1 Apparatus

The reaction was performed in an Erlenmeyer flask covered completely with aluminium foil. The aluminium foil protected the experiment from external light pollution. A probe for UV-VIS-spectroscopy (ultraviolet-visible spectroscopy) was placed in the flask together with a pH-meter. A magnetic stirrer ensured continuous and good mixing of the reaction mixture. The Erlenmeyer flask was also placed on a hot plate to achieve isothermal conditions. The pH was controlled with a pH-meter, and was regulated by adding sulfuric acid. All components except hydrogen peroxide were mixed in the reactor before time zero, so that it would reach equilibrium when the temperature was stable.

### 2.2 Procedure

The solutions used in the experiment was prepared according to calculations that can be found in appendix A.

The spectroscope and the pH-meter were calibrated before the experiment started. For each parallell the pH of the NBB-solution was adjusted with sulfuric acid until it reached pH 3. At this point the  $\text{FeSO}_4$  was added. The Erlenmeyer flask was then covered with aluminium foil to prohibit external light sources to interfere with the measurements. Amounts of the different components used for the different parallells can be found in table 2.1.

The temperature was adjusted and the UV-VIS probe was added. Measurements of absorbance was started before  $\text{H}_2\text{O}_2$  was added to initiate the reaction. Adding of  $\text{H}_2\text{O}_2$  to the system was regarded as time zero of each parallell.

The experiment studies the influence of  $\text{H}_2\text{O}_2$  concentration on the decolourization of the NBB by comparing the degradation efficiency, conversion, at a specific reaction time.

**Table 2.1:** Experimental parameters for the different parallells.

Parallell #	T [°C]	V <sub>H<sub>2</sub>O<sub>2</sub></sub> [mL]	pH	V <sub>NBB</sub> [mL]	V <sub>tot</sub> [mL]	V <sub>FeSO<sub>3</sub></sub> [mL]
1	20	5,0	3,0	244,5	250	5,0
2	20	3,0	3,0	244,0	250	5,0
3	20	1,0	3,0	243,0	250	5,0
4	30	1,0	3,0	244,5	250	5,0
5	40	1,0	3,0	244,5	250	5,0

### 3 Results

**Table 3.1:** The table shows the measured experimental conditions for all parallells.

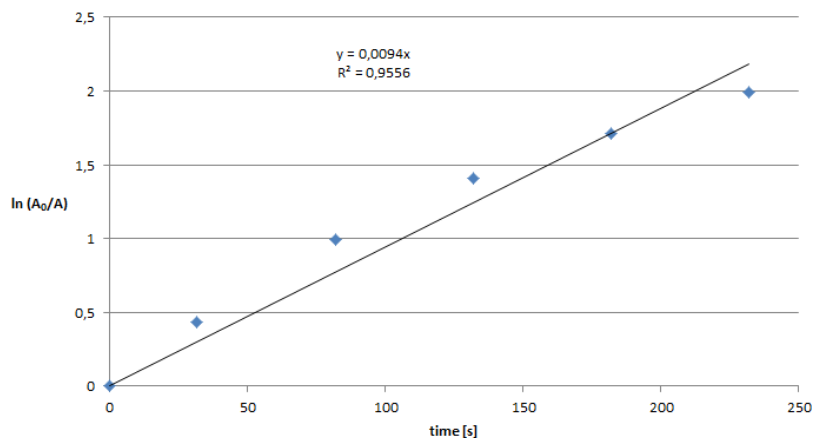
Parallell #	T [°C]	V <sub>H<sub>2</sub>O<sub>2</sub></sub> [mL]	pH
1	21	5,0	3,007
2	21	3,0	3,001
3	21	1,0	3,008
4	31,4	1,0	3,004
5	40,5	1,0	3,007

**Table 3.2:** The table shows values for  $k_{app}$  found from linear regression in figures 3.1 to 3.5.

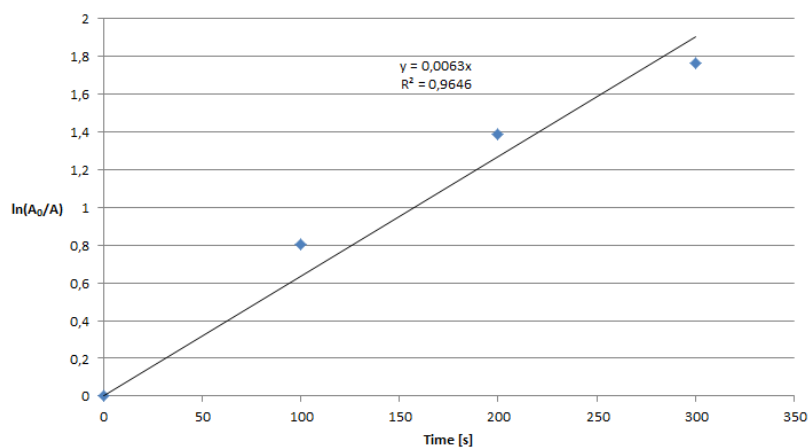
Parallell #	$k_{app}$	T °C	V <sub>H<sub>2</sub>O<sub>2</sub></sub>	pH
1	0,0094	21	5,0	3,007
2	0,0063	21	3,0	3,001
3	0,0014	21	1,0	3,008
4	0,0012	31,4	1,0	3,004
5	0,0028	40,5	1,0	3,007

According to the Arrhenius equation (1.14), the activation energy is found as the slope of the regression line, which gives

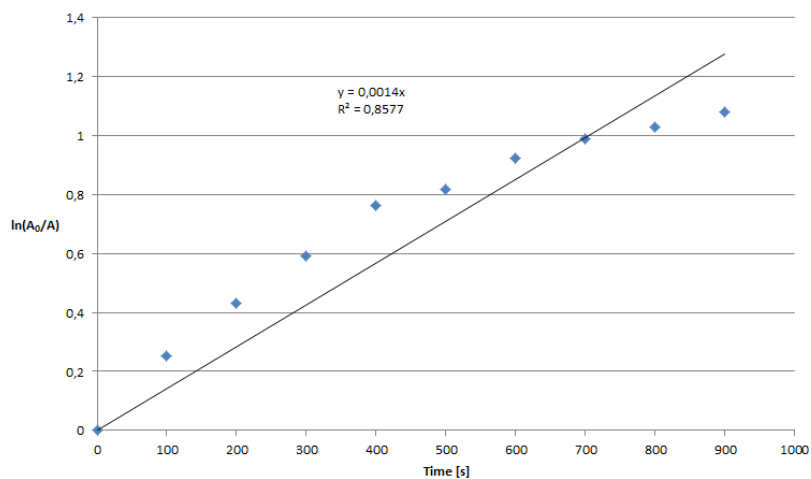
$$E_a = 25.89 \text{ kJ mol}^{-1} \quad (3.1)$$



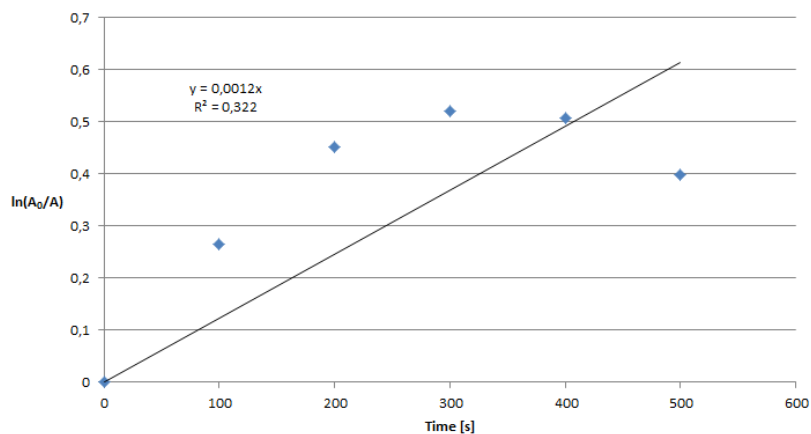
**Figure 3.1:** The figure shows a plot of  $\ln(\frac{A_0}{A})$  at 618.632nm against time in seconds for parallel 1. 5.0 mL  $H_2O_2$  was used to initiate the reaction. The pH and temperature of the system was measured as 3.007 and 21°C respectively. The straight line drawn is a regression line for the datapoints.



**Figure 3.2:** The figure shows a plot of  $\ln(\frac{A_0}{A})$  at 618.632nm against time in seconds for parallel 2. 3.0 mL  $H_2O_2$  was used to initiate the reaction. The pH and temperature of the system was measured as 3.001 and 21°C respectively. The straight line drawn is a regression line for the datapoints.

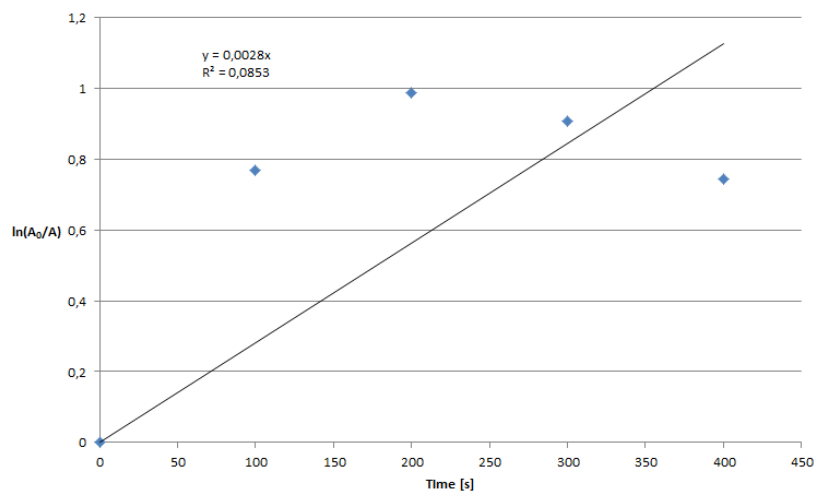


**Figure 3.3:** The figure shows a plot of  $\ln(\frac{A_0}{A})$  at 618.632nm against time in seconds for parallel 2. 1.0 mL  $H_2O_2$  was used to initiate the reaction. The pH and temperature of the system was measured as 3.008 and 21°C respectively. The straight line drawn is a regression line for the datapoints.

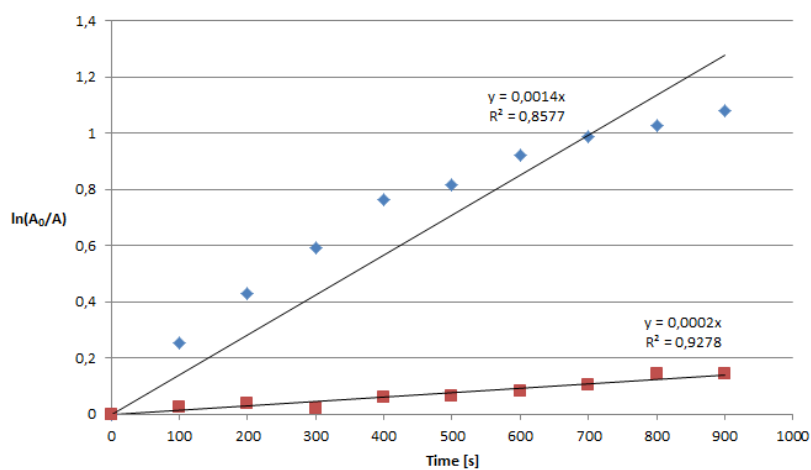


**Figure 3.4:** The figure shows a plot of  $\ln(\frac{A_0}{A})$  at 618.632nm against time in seconds for parallel 2. 1.0 mL  $H_2O_2$  was used to initiate the reaction. The pH and temperature of the system was measured as 3.004 and 31.4°C respectively. The straight line drawn is a regression line for the datapoints.

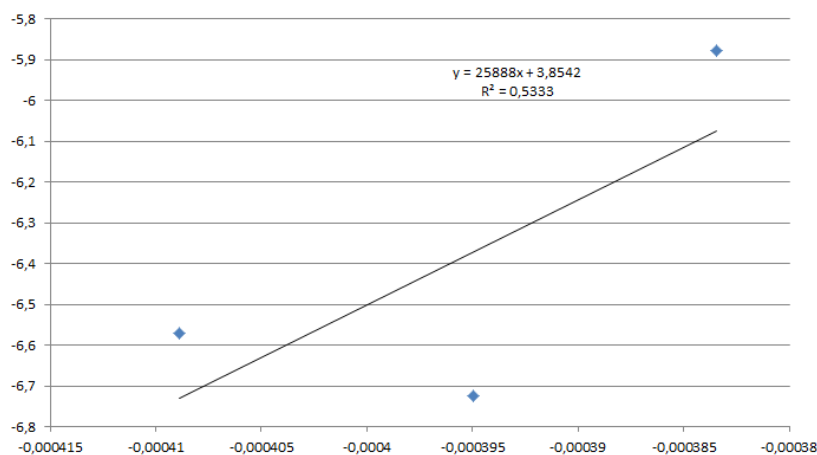




**Figure 3.5:** The figure shows a plot of  $\ln\left(\frac{A_0}{A}\right)$  against time in seconds for parallel 2. 1.0 mL  $\text{H}_2\text{O}_2$  was used to initiate the reaction. The pH and temperature of the system was measured as 3.007 and  $40.5^\circ\text{C}$  respectively. The straight line drawn is a regression line for the datapoints.



**Figure 3.6:** The figure shows a comparison between plots of  $\ln\left(\frac{A_0}{A}\right)$  against time for absorbance at 618.632nm and 320.461nm. 1.0 mL  $\text{H}_2\text{O}_2$  was used at  $21^\circ\text{C}$ . The slope of the lower regression line corresponds to the absorbances at 320.461nm, while the upper corresponds to the absorbances at 618.632nm.



**Figure 3.7:** The figure shows a plot of  $\ln(k_{app})$  against  $\frac{1}{RT}$  for parallel 3 to 5. A linear trendline is drawn in the plot. The data for the plot can be found in table B.7.

## 4 Discussion

In the figures 3.1, to 3.3, the  $R^2$  values for the regression lines are close to 1, which indicate a close to linear correlation between  $\ln(\frac{A_0}{A})$  and time. This might suggest that the assumption of a first-order reaction holds for these experimental conditions. The trendline in figure 3.3 has the lowest  $R^2$  value of the three, which may indicate that the reaction is not first-order for lower concentrations of  $H_2O_2$ .

In figure 3.6 the absorbance over time is compared for the wavelengths of azo-groups (618 nm and aromatic rings (320 nm). It is seen that the slope of the line drawn for the azo-groups is steeper than the one for aromatic groups. This may indicate that azo-groups are more easily oxidized by  $H_2O_2$ .

Figures 3.3 to 3.5 shows plots of absorbance over time for 1.0 mL for three different temperatures. The plots in figure 3.4 and 3.5 do not have the same linear trend as the other parallels. The cause of this may be a hole that was found in the aluminium foil after the last parallel was done. This hole may have caused light pollution to interfere with the measurements, which makes it impossible to determine a relation between absorbance and temperature from these data.

In figure 3.7,  $\ln(k_{app})$  is plotted against  $\frac{1}{RT}$ . Two of the data points in the plot are based on the measurements that may have been corrupted by light pollution. This might be the cause for the lack of any trends between the data points. By linear regression and the Arrhenius equation, the activation energy was determined to be  $E_a = 25.89 \text{ kJ mol}^{-1}$ . A reference value for activa-

tion energy of Fenton oxidation was found<sup>2</sup> as  $E_{a-ref} = 53.96 \text{ kJ mol}^{-1}$ . The reference value was determined for oxidation of an other organic molecule, p-nitroaniline. It will probably deviate some from the actual activation energy for the fenton oxidation of NBB. The biggest cause of error in  $E_a$  is most likely the disturbance of the measurements from light pollution.

## 5 Conclusion

A linear trend between absorbance over time is observed for varied concentrations of  $\text{H}_2\text{O}_2$  in figures 3.1 to 3.3. This supports the assumption that the reaction can be approximated as a pseudo-first order reaction.

For the plots where temperature was varied (figures 3.4 and 3.5), there is no clear linear trend, likely because of an experimental error. This makes it difficult to determine any correlation between temperature and absorbance.

The activation energy found in the experiment was  $E_a = 25.89 \text{ kJ mol}^{-1}$ . This value deviates very much from the reference value. Probable causes for the deviation is light pollution in the measurements for different temperatures, and that the reference value was found for an oxidation of a different compound than NBB.

Absorption over time was compared for two different wavelengths (618 nm and 320 nm). It was observed that the absorbance for 618 nm was generally higher than for 320 nm. This may indicate that the azo-groups (618 nm in NBB are more easily oxidized than the aromatic rings (320 nm).

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Ole Håvik Bjørkedal

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Therese Bache  
Trondheim, November 1, 2013

## References

- [1] *Kinetic studies using UV VIS-spectroscopy. Fenton reaction*, last read 31st Oct. 2013. Available at [http://www.nt.ntnu.no/users/preisig/Repository/TKP\\_4110\\_Felles\\_Lab/experiment%20descriptions/4\\_kinetic\\_studies\\_by\\_the\\_UV-VIS\\_spectroscopy\\_2010-08-18.pdf](http://www.nt.ntnu.no/users/preisig/Repository/TKP_4110_Felles_Lab/experiment%20descriptions/4_kinetic_studies_by_the_UV-VIS_spectroscopy_2010-08-18.pdf)
- [2] Sun, J.H. Sun, S.P. Fan, M.H. Gou, H.Q. Qiao, L.P. Sun, R.X. *A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process* (2007), *Journal of hazardous materials*, issue 1-2, p. 172-177. Abstract available at <http://www.ncbi.nlm.nih.gov/pubmed/17379403>

## List of symbols

Symbol	Dimension	Description
$A_r$	$s^{-1}$	Pre exponential constant in the Arrhenius reaction
$A_{RH_0}$	Dimensionless	Absorption of hydroxyl radical at time zero
$A_{RH}$	Dimensionless	Absorption of hydroxyl
$c_{RH}$	$\text{mol L}^{-1}$	Concentration of hydroxyl radical
$c_i$	$\text{mol L}^{-1}$	Concentration of solution i
$E_a$	$\text{J mol}^{-1}$	Activation energy
$k$	$s^{-1}$	Reaction constant
$k_{app}$	$s^{-1}$	Reaction constant of the absorption
$l$	m	Length of light path through the sample
$R$	$\text{J mol}^{-1} \text{K}$	Universal gas constant
$r$	$\text{mol L}^{-1} \text{s}$	Reaction rate
$T$	K	Temperatur
$t$	s	Time
$\varepsilon$	$\text{m}^2 \text{mol}^{-1}$	Density of component i

## A Preparation of solutions

### NBB

2 L NBB-solution with a concentration of  $10 \text{ mg L}^{-1}$  was made by dissolving 20 mg NBB in 2 L deionized water.

### FeSO<sub>4</sub>

500 mL FeSO<sub>4</sub>-solution with a concentration of  $1 \text{ mg L}^{-1}$  was made by dissolving 0.5 mg FeSO<sub>4</sub> in 500 mL deionized water.

### H<sub>2</sub>SO<sub>4</sub>

250 mL H<sub>2</sub>SO<sub>4</sub>-solution with a concentration of  $1 \text{ mol L}^{-1}$  was made by diluting 13.4 mL 95% H<sub>2</sub>O<sub>2</sub> =  $18.7 \text{ mol L}^{-1}$  with deionized water. Calculation is shown in (A.1)

$$\begin{aligned} V_1 &= \frac{c_2 V_2}{c_1} \\ &= \frac{1 \text{ mol L}^{-1} 250 \text{ mL}}{18.7 \text{ mole/L}} \\ &= 13.4 \text{ mL} \end{aligned} \tag{A.1}$$

### H<sub>2</sub>O<sub>2</sub>

0.1 mL H<sub>2</sub>O<sub>2</sub> was diluted with 60 mL deionized water.

## B Tables of plot data

**Table B.1:** The table shows the data used to produce the plot in figure 3.1. The absorbance is measured for 618.632 nm

time [s]	Absorbance	$\ln(\frac{A_0}{A})$
0	1,293099791	0
32	0,837693223	0,434145603
82	0,480487753	0,989995813
132	0,31558233	1,410377956
182	0,233905857	1,709878841
232	0,17634511	1,992354625

**Table B.2:** The table shows the data used to produce the plot in figure 3.2. The absorbance is measured for 618.632 nm

time [s]	Absorbance	$\ln(\frac{A_0}{A})$
0	1,348051157	0
100	0,601344565	0,807247151
200	0,336884111	1,386676254
300	0,23071819	1,765218234

**Table B.3:** The table shows the data used to produce the plot in figure 3.3. The data was also used in figure 3.6. The absorbance is measured for 618.632 nm

time [s]	Absorbance	$\ln(\frac{A_0}{A})$
0	1,109246767	0
100	0,860616796	0,253787139
200	0,720113987	0,432026961
300	0,614051872	0,591357069
400	0,517537089	0,762355283
500	0,489849821	0,817337619
600	0,440789822	0,922868307
700	0,412145705	0,990059536
800	0,396149138	1,029645725
900	0,377185542	1,078699256

**Table B.4:** The table shows the data used to produce the plot in figure 3.4. The absorbance is measured for 618.632 nm

time [s]	Absorbance	$\ln(\frac{A_0}{A})$
0	1,394482495	0
100	1,069723023	0,265123617
200	0,888027887	0,451275508
300	0,827765707	0,521548502
400	0,839756383	0,507166824
500	0,936666396	0,397951469

**Table B.5:** The table shows the data used to produce the plot in figure 3.5. The absorbance is measured for 618.632 nm

time [s]	Absorbance	$\ln(\frac{A_0}{A})$
0	1,46274254	0
100	0,67776215	0,769272
200	0,54405445	0,98901908
300	0,5900552	0,90785231
400	0,69465913	0,74464714



**Table B.6:** The table shows the data for absorbance at 320, 461nm used to produce the plot 3.6

time [s]	Absorbance	$\ln(\frac{A_0}{A})$
0	0,721991501	0
100	0,702270691	0,027694438
200	0,694486159	0,038841135
300	0,706864923	0,021173776
400	0,678917394	0,061513906
500	0,677566134	0,063506204
600	0,665459117	0,081536163
700	0,651007106	0,10349281
800	0,625380486	0,143653125
900	0,624066432	0,145756543

**Table B.7:** Data used for the plot in figure 3.7

Parallell #	T [°C]	$\frac{-1}{RT}$	$\ln(k_{app})$
1	21	-0,00041	-4,66705
2	21	-0,00041	-5,06721
3	21	-0,00041	-6,57128
4	31,4	-0,00039	-6,72543
5	40,5	-0,00038	-5,87814