Oda Bentzen and Jane Bastiansen
Group B20
Felleslab TKP4105 and TKP4110

30. september 2021

ST9: Leaching kinetics of Oxides from Battery waste

1 Introduction

The purpose of this experiment is to obtain an understanding of the kinetics of leaching. In this experiment, the leaching kinetics of mixed metal oxides, in this case copper(II) oxide and iron (III) oxide, and graphite, in the presence of sulphuric acid, are going to be studied. The kinetics will be tracked by removing a small volume from the reaction mixture, before analyzing it using UV-Vis spectrophotometer. The temperature, the concentration of H_2SO_4, and the solid/liquid ratio will be held at a constant, whilst the percentage of metal oxides and graphite will differ. The leaching process will be studied as a function of these parameters, and modelled accordingly.

2 Theory

2.1 Leaching and filtration

Leaching is a heterogeneous reaction, which takes place at the interface between a solid and liquid phase.[1] The leaching process works by immersing a solid matrix with a soluble part into a leachant. After some time has passed, the soluble part will be somewhat or completely dissolved in the leachant, depending on the reaction rate.[2]

In this experiment, the leaching kinetics of mixed metal oxides and graphite in the presence of sulphuric acid, will be studied. The mixed metal oxides consists of copper(II) oxide (CuO) and iron(III) oxide (Fe_2O_3). The set reaction to be studied will be the reaction between sulphuric acid (H_2SO_4) and copper(II) oxide:

$$\mathrm{H_2SO_4 + CuO \rightarrow CuSO_4 + H_2O} \tag{2.1}$$

This is because iron(III) oxide and graphite are non-leachable components, and therefore they will not undergo a detectable reaction, whilst copper(II) oxide forms copper sulfate, as seen in reaction (2.1), which has a blue colour.[2]

The efficiency of the leaching process can be calculated by the following equation:

$$\text{Efficency} = \frac{\mathrm{m_{solidmixture} - m_{driedcake}}}{\mathrm{m_{solidmixture}}} \cdot 100 \tag{2.2}$$

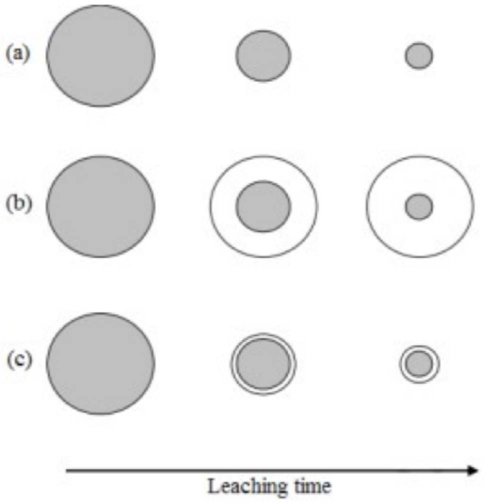
This shows how much the inorganic acid, H_2SO_4, is able to dissolve the metal oxide, CuO, at different reaction conditions.

2.2 Shrinking core model (SCM)

There are several methods that can be used to understand the pathway through which the reactions proceed. One of these methods is the shrinking core model (SCM). This model is used to describe situations that occur in heterogeneous liquid-solid reactions, in which spherical solid particles are being consumed, either by dissolution or by reaction in a liquid. As a result, the amount of the material being consumed is “shrinking.”[3]

The different ways the particles react at the surface are:

- The soluble part of the solid shrinks until it disappears while the reaction progresses. This process is shown in figure 2.1 (a).
- The soluble part of the solid reacts and produces an insoluble product whereby the reacting core shrinks while the particle does not change in size. This process is shown in figure 2.1 (b).
- The soluble part of the solid reacts, and a gelatinous and intermediate layer forms around the surface of the particle while the unreacted core shrinks. This process is shown in figure 2.1 (c).[2]



Figur 2.1: Different reaction pathways in the shrinking core model[2]

All leaching processes include both diffusion and surface reaction. However the overall kinetics may be dominated by only one of these, and thus the kinetics of leaching is divided into two different processes: reaction-controlled or diffusion-controlled. This is important when calculating the rate constants because the calculations are different for the two processes. The calculations are shown in appendix A.

2.3 UV-Vis spectrophotometer

A UV-Vis spectrophotometer measures the absorbance of an optically active species, which can then be quantified using the Beer-Lambert's law:

$$A = \epsilon l C, \tag{2.3}$$

here A is the absorbance, ϵ is the absorptivity of the species, l is travel length of the light, and C is the concentration of the species. Thus the law states that the quantity of light absorbed by the substance is proportional to the concentration of the substance and the path length of light travelling through the solution. However the formula can not be used directly to obtain the metal sulphate concentration in this experiment, because the molar absoptivity ϵ for the species is not known. Thus, a calibration curve must be used instead.

3 Experimental Procedure

In this experiment, reaction kinetics were studied. This was carried out by differing one experimental condition, while keeping the others constant to see how it affected the reaction rate.

There were two experiments executed, where the mixture of metal oxides and graphite differed. The parameters and compositions are shown in table 3.1

Tabell 3.1: Reaction data

Experiment	Solid/Liquid Ratio [g/L]	T [°C]	$C_{H_2SO_4}$ [mol L^{-1}]	CuO, Fe_2O_3, graphite [%]
1	20	25	0.1	60 + 20 + 20
2	20	25	0.1	30 + 40 + 30

3.1 Procedure

Prior to the experiments all glassware and magnets were cleaned, to assure accurate measures. Chemicals were also pre-measured to the correct amount, shown in table A.2. In addition, H_2SO_4 (250 mL, 0.1 [mol/L]) was prepared by diluting H_2SO_4 98%. 10 vials were prepared with deionized water (2.5 mL).

Tabell 3.2: Amounts of chemicals

Experiment	H_2O (DI) [mL]	H_2SO_4 [mL]	CuO [g]	Fe_2O_3 [g]	graphite [g]
1	248.64	1.36	3	1	1
2	248.64	1.36	1.5	2	1.5

3.1.1 Leaching and analysing samples

The glass reactor was placed on the stirring plate using clamps to secure it. Water outlets were joined from the water bath (25 °C) to the reactor jacket. The condenser was also attached to the reactor. The solid materials and H_2SO_4 (250 mL) were added to the reactor, while the stirring speed was set to 450 rpm, and a timer was set as soon as the H_2SO_4 was added. A sample of the mixture was taken at each time interval (10 samples in total), and added to a vial containing DI water in order to quench the reaction. The temperature of both the reaction and of the water bath were observed as the sample was extracted.

All 10 vials where consecutively filtered through 0.45 µm filter tips, and stored in cuvettes. The absorbance of all ten samples at 800 nm was measured with a UV/Vis spectrophotometer. Before the samples were analyzed a calibration curve was created, using known concentrations ranging from 0.03 mol L^{-1} to 0.12 mol L^{-1}, and plotting the absorbance as a function of the concentration.

The mixture left in the reactor after extracting all ten samples, were filtered using a Buncher funnel and filter paper. The filter cake was left over night to dry, then weighed the next day.

4 Results

4.1 Calculated conversion factor

Table 4.1 and 4.2 show the time points (t), the absorbance (A), the concentration (C), the volume (V) in the vessle before the sample was extracted, number of mols (n), and the conversion factor (X) for each sample from experiment 1[1] and 2. The two experiments had different compositions of metal oxides and graphite, shown in table 3.2.

Tabell 4.1: Data from experiment 1, with a solid/liquid ratio of 20, temperature of 25 °C, concentration of H_2SO_4 of 0.1 $\mathrm{mol\,L^{-1}}$, and a composition of 60% + 20% + 20% (CuO, Fe_2O_3, graphite)

Sample	t [s]	A [$\mathrm{L\,mol^{-1}\,cm^{-1}}$]	C [$\mathrm{mol\,L^{-1}}$]	V [L]	n [mol]	X
1	50	0.07829	0.0069	0.2500	0.0017	0.0430
2	120	0.16293	0.0138	0.2475	0.0039	0.0986
3	220	0.22660	0.0189	0.2450	0.0045	0.1137
4	290	-[1]	-	-	-	-
5	385	0.31877	0.0264	0.2400	0.0061	0.1542
6	460	0.34702	0.0287	0.2375	0.0066	0.1669
7	630	0.37517	0.0310	0.2350	0.0068	0.1719
8	890	0.41973	0.0346	0.2325	0.0075	0.1896
9	1205	0.43870	0.0361	0.2300	0.0076	0.1922
10	1810	0.48817	0.0401	0.2275	0.0082	0.2073

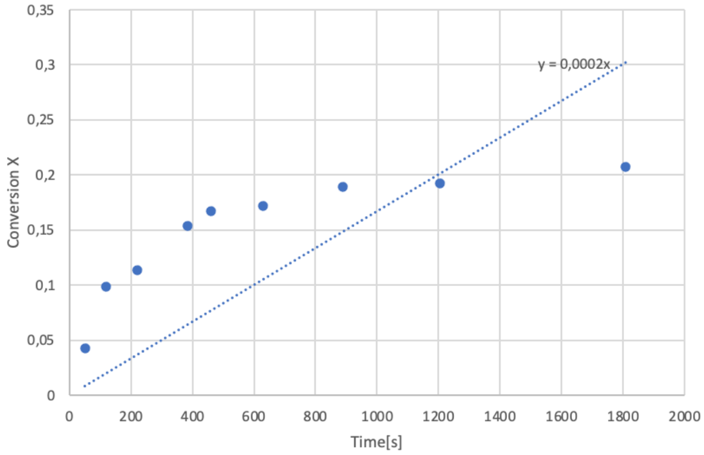
Tabell 4.2: Data from experiment 2, with a solid/liquid ratio of 20, temperature of 25 °C, concentration of H_2SO_4 of 0.1 $\mathrm{mol\,L^{-1}}$, and a composition of 30% + 40% + 30% (CuO, Fe_2O_3, graphite)

Sample	t [s]	A [$\mathrm{L\,mol^{-1}\,cm^{-1}}$]	C [$\mathrm{mol\,L^{-1}}$]	V [L]	n [mol]	X
1	40	0.06810	0.0061	0.2500	0.0015	0.0767
2	95	0.07825	0.0069	0.2475	0.0017	0.0870
3	155	0.12525	0.0107	0.2450	0.0026	0.1330
4	270	0.11810	0.0101	0.2425	0.0024	0.1228
5	360	0.12322	0.0106	0.2400	0.0024	0.1228
6	473	0.14101	0.0120	0.2375	0.0027	0.1381
7	592	0.15999	0.0135	0.2350	0.0030	0.1535
8	900	0.17683	0.0149	0.2325	0.0032	0.1637
9	1200	0.19656	0.0165	0.2300	0.0035	0.1790
10	1873	0.21984	0.0184	0.2275	0.0038	0.1944

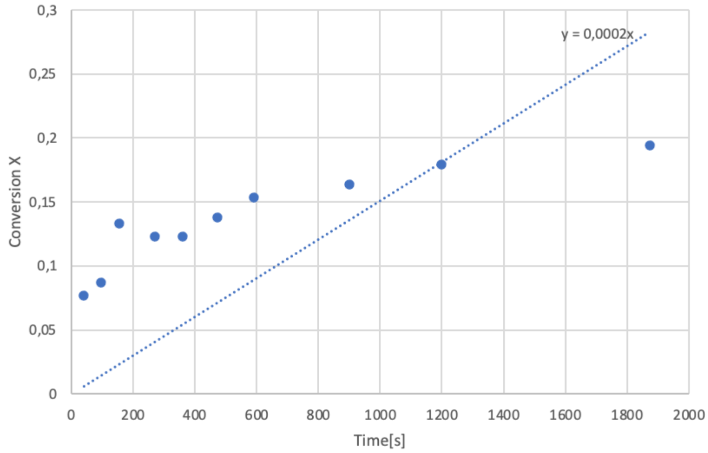
---

[1] Sample number 4 was accidentally spilled while being filtered using syringes and filter tips. Therefore this sample has no data.

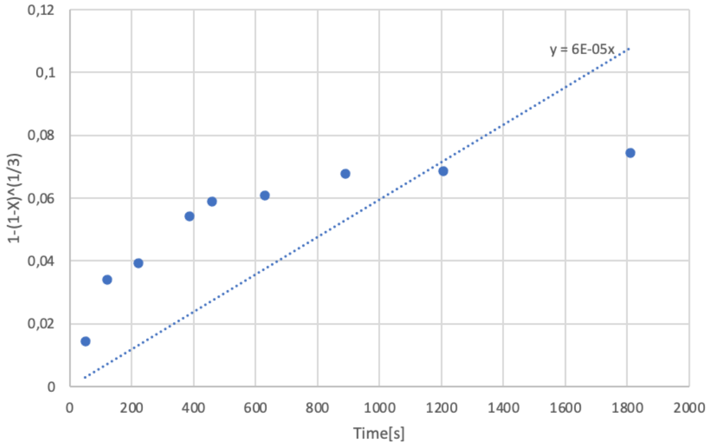
4.2 Plots and rate constants



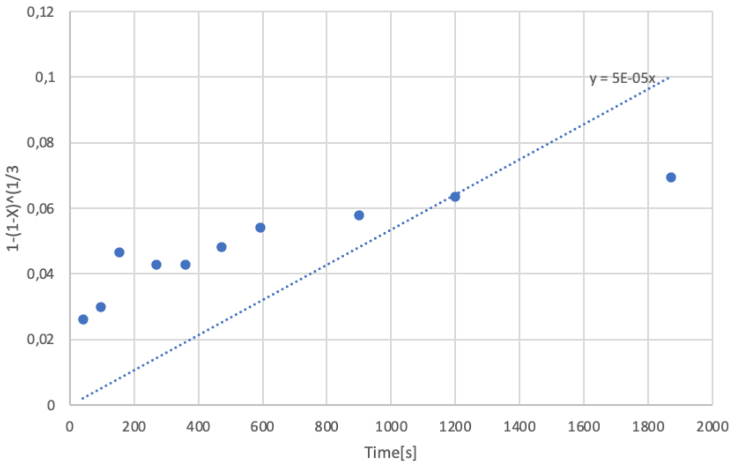
Figur 4.1: Conversion X as a function of time for experiment 1



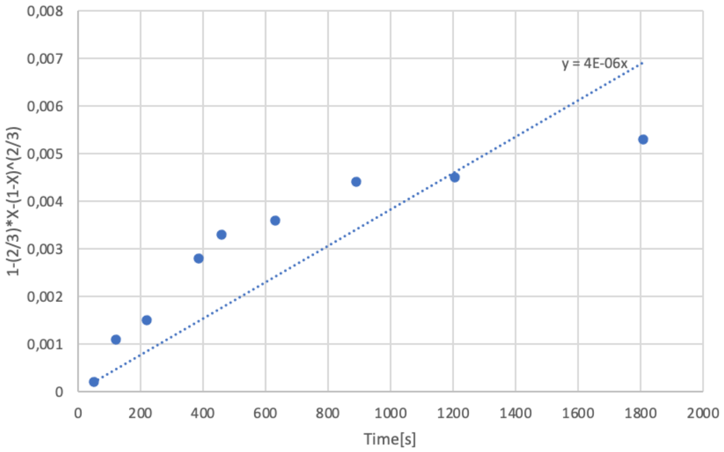
Figur 4.2: Conversion X as a function of time for experiment 2



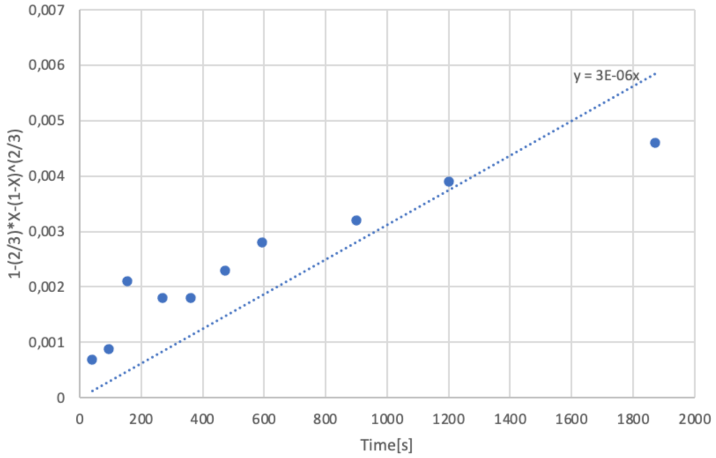
Figur 4.3: $1-(1-X)^{\frac{1}{3}}$ as a function of time for experiment 1



Figur 4.4: $1-(1-X)^{\frac{1}{3}}$ as a function of time for experiment 2



Figur 4.5: $1-\frac{2}{3}X-(1-X)^{\frac{2}{3}}$ as a function of time for experiment 1



Figur 4.6: $1-\frac{2}{3}X-(1-X)^{\frac{2}{3}}$ as a function of time for experiment 2

The rate constants k_c and k_d are given by the slope values in figures 4.3-4.6. The values are given in table 4.3:

Tabell 4.3: Rate constants from experiment 1 and 2

	k_c	k_d
Experiment 1	$6 \cdot 10^{-5}$	$4 \cdot 10^{-6}$
Experiment 2	$5 \cdot 10^{-5}$	$3 \cdot 10^{-6}$

4.3 Efficiency

The efficiency of the leaching is found with equation (2.2). The mass of the solid mixture and the dried filter cakes, as well as the calculated efficiencies, are shown in table 4.4:

Tabell 4.4: Measured weights and calculated efficiencies for experiment 1 and 2

	$m_{solidmixture}$ [g]	$m_{driedcake}$ [g]	Efficiency [%]
Experiment 1	5.1446	2.7436	46.7
Experiment 2	5.1315	3.3633	34.5

5 Discussion

5.1 Rate constants

The rate constants k_c and k_d were calculated for both experiments. The calculated values are given in table 4.3. The R^2-values for each of the linear regressions were also found, and shown in table B.1 in the appendix. These values show how well the regression predictions approximate the real data points, and can therefore be used to determine whether the reaction is reaction-controlled or diffusion-controlled. Because $R^2(k_d) > R^2(k_c)$, the reaction in this experiment is diffusion-controlled. This means that the overall kinetics are dominated by diffusion reaction, as opposed to surface reaction, although all leaching reactions include both reaction types.

5.2 Efficiency

The efficiencies were calculated to be 46.7% and 34.5% for reaction 1 and 2 respectively. These show how well the sulphuric acid was able to dissolve the copper oxide. The difference in efficiency between experiment 1 and 2 could be due to difference in the time between taking out the samples, and filtering and analysing them. This is because the sulphuric acid might have continued dissolving the copper oxide, even after the samples were taken out of the reactor. The difference in efficiencies is also a result of the different parameters in experiment 1 and 2, namely that experiment 1 had twice as much CuO in the solid mixture. Since the CuO is the only leachable component, more of the solids dissolved in the liquid, resulting in a lighter filter cake, and therefore a higher efficiency.

In the case of using leaching in recycling of battery waste, efficiencies equal to the ones obtained in the experiment, would make a fairly good amount of valuable copper sulphate. However there would still be quite a lot of waste left that could possibly be harmful to the environment. Therefore the efficiencies are not ideal.

5.3 Experimental parameters

The varying parameter between experiment 1 and 2 was the weight percentage of the metal oxides. In experiment 1, CuO was 60 % of the mixture, while in experiment 2, it was 30 %. As explained in section 5.2, this had an effect on the efficiencies, as CuO is the only leaching component. However, the change in weight percentage had little effect on the rate constants, as they were quite similar in both experiments. This is because the conversion factor is independent of the amount added, due to the fact that the number of moles reacted is divided by the number of moles fed.

5.4 Improvement of experiment

As the samples were filtered using syringes and filter tips, sample number 4 in experiment 1 was accidentally spilled, which in resulted in only 9 measured absorbances. Therefore the regression line for experiment 1 only has 9 data points. However it is unlikely that this would have made a huge difference, since one point missing won't affect the linear regression much.

Comparing the two experiments, there might be an inaccuracy in the time passed from the samples were extracted until its absorbance was measured. The samples in experiment 1 were set aside for some time before they were filtered, whereas in experiment 2, they were continuously measured immediately after extraction. It is then likely to assume that the samples in experiment 1 then had more time to continue the reaction, even though the sample was diluted with DI water. Therefore the two experiments can not be compared as accurately as desired.

6 Conclusion

In this experiment, the efficiencies of the reaction were calculated in two different experiments, with varying weight percentage of CuO. The calculated efficiencies differed somewhat between the two experiments. The main reason for this was because experiment 1 had more added CuO. The rate constants k_c and k_d were also calculated for the two different experiments. It was found that R^2 for k_d was bigger than R^2 for k_c, and thus the kinetics of this experiment was mainly diffusion-controlled. The biggest source of error in the experiment was found to be that the time passed from the samples were extracted until their absorbances were measured, did not stay the same for all samples, and differed a lot from experiment 1 to 2. Therefore the two experiments could not be compared as accurately as desired.

Trondheim, 30. september 2021

Referanser

[1] Leaching theory and kinetics. `http://wiki.biomine.skelleftea.se/wiki/index.php/Leach_kinetics`, 2008. Hentet 08.09.2021.

[2] Katharina Zürbes. St9: Leaching kinetics of oxides from battery waste. URL `https://folk.ntnu.no/preisig/HAP_Specials/Felles_lab/Experiments/ST9_battery_waste.pdf`.

[3] W14A The Shrinking Core Model. `http://websites.umich.edu/~elements/5e/14chap/expanded_ch14_A.pdf`. Hentet 08.09.2021.

[4] Gøril Flatberg. Detailed risk report, 2020. Hentet 08.09.21 .

A Calculations prior to experiment

A.1 Volume of H_2SO_4

The sulphuric acid used in the experiment was 98% concentrated, which gives a molarity of 18.4 mol/L. Using this principle, $C_1 \cdot \mathrm{V}_1 = C_2 \cdot \mathrm{C}_2$, gives the following expression.

$$X_{H_2SO_4} \cdot 18.4\frac{mol}{L} = 0.250L \cdot 0.1\frac{mol}{L} \tag{A.1}$$

$$X_{H_2SO_4} = \frac{0.250L}{18.4mol/L} \cdot 0.1\frac{mol}{L} H_2SO_4 = \underline{\underline{1.36mL}} \tag{A.2}$$

A.2 Mass of CuO, Fe_2O_3 and graphite

The volume of H_2sO_4 is 0.25 L, and the S/L ratio is 20. The total weight of all the solids is therefore:

$$S = 20 \cdot L = 20 \cdot 0.25 = \underline{5g} \tag{A.3}$$

The percentages of the mixed metal oxides and graphite differ from experiment 1 and 2, and are given in table 3.1. The mass of each component in both experiments is given in table A.1

Tabell A.1: Theoretical masses of all components

	$\mathrm{m}_{CuO}[g]$	$\mathrm{m}_{\mathrm{Fe_2O_3}}[g]$	$\mathrm{m}_{graphite}[g]$
Experiment 1	3	1	1
Experiment 2	1.5	2	1.5

The actual masses used in the experiment are given in table:

Tabell A.2: Measured masses of all components

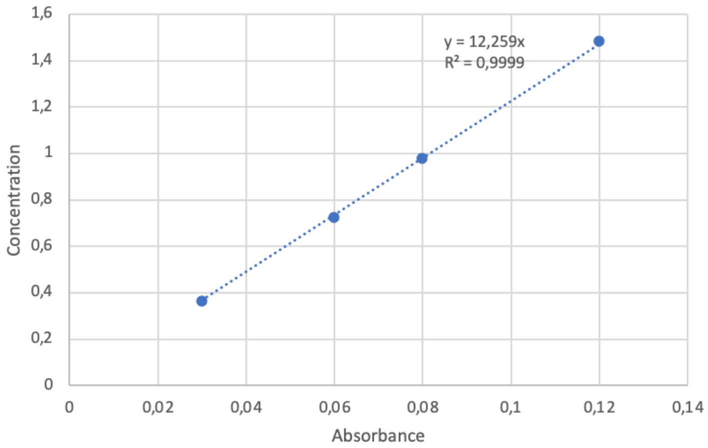
	$\mathrm{m}_{CuO}[g]$	$\mathrm{m}_{\mathrm{Fe_2O_3}}[g]$	$\mathrm{m}_{graphite}[g]$
Experiment 1	3.1461	0.9962	1.0023
Experiment 2	1.5554	2.0797	1.4964

B Calculations for results

B.1 Conversion factor

All the values used in the following calculations are given in tables 4.1 and 4.2.

First, a calibration curve was made by measuring the absorbance of samples with known concentrations of $CuSO_4$, and using linear regression. The calibration curve is shown in figure B.1:



Figur B.1: The calibration curve made by measuring the absorbance of samples with known concentrations of $CuSO_4$

The expression for this curve is:

$$y = 12.259x \tag{B.1}$$

This equation was used to find the concentration $C_{\mathrm{CuSO_4}}$ of the samples using the measured absorbances.

The number of moles reacted, n, was then found by:

$$n = C \cdot V \tag{B.2}$$

The number of moles fed, n_0 is given by:

$$n_0 = \frac{m_{CuO}}{Mm_{CuO}}, \tag{B.3}$$

where m_{CuO} is the mass of the CuO, given in table A.2. and Mm_{CuO} is the molar mass of CuO, which is 79.545 $\mathrm{g\,mol^{-1}}$. n_0 for experiment 1 and 2 respectively, are:

$$n_{0,1} = \frac{3.1461}{79.545} = 0.03955 mol \tag{B.4}$$

$$n_{0,2} = \frac{1.5554}{79.545} = 0.01955 mol \tag{B.5}$$

The conversion factor, X, was then found by:

$$X = \frac{n}{n_0} \tag{B.6}$$

B.2 Rate constants

The kinetic equations for the shrinking core model for reaction controlled process and diffusion controlled process are shown in equation (B.7) and (B.8) respectively:

$$1-(1-X)^{\frac{1}{3}}=k_c t \tag{B.7}$$

$$1-\frac{2}{3}X-(1-X)^{\frac{2}{3}}=k_d t \tag{B.8}$$

Here are k_c and k_d the rate constants for reaction controlled process and diffusion controlled process respectively. k_c was found by plotting $1-(1-X)^{\frac{1}{3}}$ as a function of the time, and k_d is found by plotting $1-\frac{2}{3}X-(1-X)^{\frac{2}{3}}$ as a function of the time. The values are given in table 4.3.

B.3 Linear regression

Figures 4.3-4.6 were used to find the values for k_c and k_d. To determine which rate constant, and thus which type of reaction, was the dominating in this experiment, the R^2 values were compared. These are shown in table B.1:

Tabell B.1: R^2 from the linear regressions used to find k_c and k_d

	R^2 (k$_c$)	R^2 (k$_d$)
Experiment 1	0.8062	0.9025
Experiment 2	0.7559	0.8994

C Risk analysis

This experiment has some risk associated with aspects like spillage of hot solution, burn injuries and wounds from broken glass. However these risks are fairly unlikely and/or have small consequences. The biggest risks for this experiment involve handling of the different chemicals, and the most dangerous component is sulphuric acid.[4] The hazards associated with each chemical are shown in table C.1:

Tabell C.1: The hazards associated with each chemical in this experiment [4]

Chemical	Hazards
Sulphuric acid	**Danger** May be corrosive to metals Causes severe skin burns and eye damage
Copper sulfate	**Warning** Harmful if swallowed Causes skin irritation Causes serious eye irritation Very toxic to aquatic life with long lasting effects
Copper(II) oxide	**Warning** Very toxic to aquatic life with long lasting effects
Iron(III) oxide	Not a hazardous substance
Graphite powder	Not a hazardous substance