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Crystal growth of the calcium carbonate polymorph vaterite in distilled water

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Contents

1 Introduction

The objective of this laboratory exercise is to study the crystallization of the vaterite polymorph of calcium carbonate, and to determine the crystal growth order, g, and the growth rate constant, k_r, of the crystallization in distilled water at 25 °C and 40 °C. By measuring the variation of the concentration of calcium ions in the solution as a function of time, it is possible to plot the results in a logarithmic plot to determine g and k_r. The purpose of this exercise is to get a fundamental understanding of crystallization by supersaturation, and to see the correlation of the temperature and the growth order constant. This understanding is essential to manipulate the crystallization, so that it can be used for industrial purposes.

2 Theory

2.1 The growth rate constant and growth rate order

The linear growth rate, G, of a crystal is generally defined as the change of a characteristic crystal dimension with time. Vaterite crystals can be approximated as spheres, thus allowing the growth rate to be defined by the infinitesimally small changes in the crystal radius, dr, per unit time, dt:

$$G = \frac{dr}{dt} = k_r(S-1)^g \tag{1}$$

where k_r is the growth rate constant, S is the supersaturation ratio and g is the growth rate order which is given by the rate-determining growth mechanism. This mechanism may be transport (diffusion)/surface absorption ($g = 1$), surface integration ($g = 2$) or surface nucleation (polynuclear growth) ($g > 2$).

The crystallization of calcium carbonate is necessarily accompanied by a corresponding increase in the volume of the crystals formed. It follows that the infinitesimally small change in the crystal volume, dV, may be found from experimental data giving the decrease in calcium concentration, $d(C_{Ca^{2+}})$. The volume change is given by the following expression:

$$dV = \frac{-d(C_{Ca^{2+}})M_W}{\rho N} \tag{2}$$

where M_W is the molar weight of vaterite, ρ is the density of vaterite and N the number of seed crystals per unit volume. It is assumed that nucleation, agglomeration and particle breakage may be considered negligible in the growth experiments.

The volume of sample $n+1$ may be calculated from the volume of the previous sample n and the corresponding volume change is given by equation (2):

$$dV = V_{n+1} - V_n \iff V_{n+1} = V_n + dV \tag{3}$$

From this the crystal radius for sample $n+1$, r_{n+1}, may be found by using the volume formula for a sphere:

$$V_{n+1} = \frac{4}{3}\pi r_{n+1}^3 \iff r_{n+1} = \left(\frac{3V_{n+1}}{4\pi}\right)^{1/3} \tag{4}$$

For two samples collected in succession, the change in radius is then given by

$$dr = r_{n+1} - r_n \tag{5}$$

The first calculations, i.e. finding V_1 and r_1, are made using a given value for the initial seed volume, $V_0 = 1.36 \cdot 10^{-10}$ mL.

2.2 The supersaturation ratio

For calcium carbonate, as an example of a binary salt, the supersaturation ratio is defined as

$$S = \sqrt{\frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{sp}}} \tag{6}$$

In addition, the following empirical correlations have been found between the concentration of calcium and the supersaturation ratio at $T = 25$ °C and $T = 40$ °C respectively:

$$S_v = -0.0106c^4 + 0.1574c^3 - 0.9658c^2 + 4.4747c + 0.1459; \ T = 25 \text{ °C} \tag{7}$$

$$S_v = -0.0116c^4 + 0.1708c^3 - 1.0349c^2 + 4.6608 + 0.0548; \ T = 40 \text{ °C} \tag{8}$$

where c is the concentration of calcium in mmol/L. The correlations above are valid in the range between $c = 0.5$ mmol/L and $c = 5$ mmol/L.

2.3 Determining the growth rate constant and growth rate order from experimental data

As has been shown in the previous sections, the growth rate constant and growth rate order may be determined from measured values of the change in calcium concentration over time. The calcium concentrations are calculated from experimental data for the volume of EDTA, V_{EDTA}, added during titration of samples collected throughout the crystallization process. It is known that each molecule of EDTA will bind to one calcium ion. Assuming that the titration is ended at precisely the point at which the number of moles of EDTA added is equal to the number of moles of calcium initially present in solution, the concentration of calcium, $C_{Ca^{2+}}$, may be calculated from the following expression:

$$C_{Ca^{2+}} = \frac{C_{EDTA} V_{EDTA}}{V_s} \tag{9}$$

where C_{EDTA} and V_{EDTA} are the concentration and volume of EDTA respectively and V_s is the volume of the sample containing the calcium solution.

The calcium concentrations are plotted against time and data from a fitted curve may be used to perform the necessary calculations of the supersaturation ratio, S, using the equations (7) and (8), and changes in crystal volume using (2). The corresponding change in crystal radius then allows the growth rate constant and growh rate to be determined by use of equation (1). Taking the logarithm of equation (1) then gives the equation

$$\ln G = g \ln(S - 1) + \ln k_r \tag{10}$$

As can be seen from equation (10), plotting $\ln G$ as a linear function of $\ln(S-1)$ will result in an equation of the form $y = ax + b$, where a is equal to the growth rate order and b to the natural logarithm of the growth rate constant, i.e. $g = a$ and $k_r = e^b$.

3 Experimental procedures

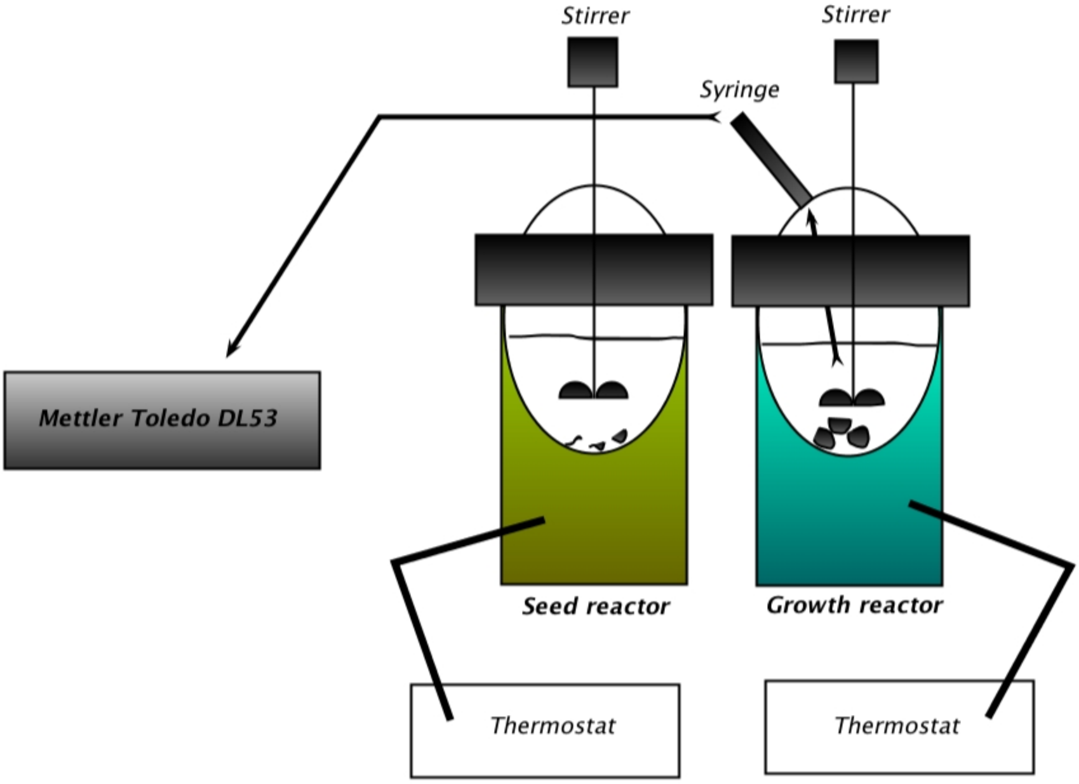


Figure 1: Experimental setup for the crystallization experiment. The seeds and growth solution are prepared and stirred in separate, thermostatically regulated reactors. Samples of the solution in the growth reactor are extracted throughout the experiment by using a syringe and then analyzed by EDTA-titration with a Mettler Toledo DL53.

3.1 List of equipment and chemicals

- Calcium chloride dihydrate
- Sodium carbonate
- Distilled water
- Ammonium buffer solution
- Concentrated hydrochloric acid
- 0.01 M EDTA (for Mettler Toledo DL53)
- Two reactors
- Thermostat
- Beakers for the preparation of solutions

- Light microscope
- Precise weighing scale
- Syringe
- Plastic hose
- Titrator (Mettler Toledo DL53)
- 0.22 µm filter for syringe
- Volumetric flasks
- Automatic pipette

3.2 Seed preparation

1. Vaterite seed were made by adding 250 mL of 0.2 M calcium chloride dihydrate to 250 mL of 0.2 M sodium carbonate at 30 °C while being stirred with 1500 rpm for 15 minutes. The stirring speed was then changed to 500 rpm.
2. The solutions were made by dissolving 7.35 g calcium chloride dihydrate in 250 mL distilled water, and 5.3 g sodium carbonate in 250 mL distilled water.

3.3 Growth experiments

1. The experiment was performed by adding the seed solution (15 mL) to an aqueous growth solution (500 mL) with different concentrations of calcium carbonate depending on the temperature of the solution. All of the solutions were stirred at 500 rpm all the time.
2. When the temperature of the solutions were 25 °C and 40 °C, the concentrations of calcium were 2 mM and 1.5 mM respectively. The 2 mM solution was prepared by dissolving 106 mg sodium carbonate and 147 mg calcium chloride dihydrate in 500 mL of distilled water. The 1,5 mM was prepared by solving 80 mg sodium carbonate and 110 mg calcium chloride dihydrate in 500 mL distilled water.
3. The seed solution was added right after the growth solution was made, so that the growth solution should not nucleate by itself.
4. During the next 20 minutes of crystal growth, 9 samples were taken: one directly after the seed solution were added, six during the next 10 minutes and two during the last 10 minutes. These samples were filtered through a 0.22 µm filter, weighed, diluted with distilled water and then titrated.
5. About 1 mL of an ammonium buffer solution and a few droplets of concentrated HCl were added to the samples, and the concentration of calcium in the samples was determined by titration.
6. The seed crystals and product crystals were examined by light microscopy.

7. The experiment was performed twice; once at 25 °C and once at 40 °C.

4 Results and discussion

4.1 Results

All calculations involved in determining the growth rate constant, k, and the growth rate order, g, from the experimental data is explained in section 2.3. All the results in this section are based on the second series of data collected during the experiment, i.e. with calcium concentration $C_{\mathrm{Ca}^{2+}} = 1.5$ M and temperature $T = 40$°C. The reason for this is elaborated in Section 4.2.

Data for the graphical presentation of calcium concentration, $C_{\mathrm{Ca}^{2+}}$, as a function of time, t, can be found in Table 1 and the resulting graph can be found in Figure 2.

Table 1: Calcium concentration in reactor, $C_{\mathrm{Ca}_2^+}$, measured at chosen time points, t.

Measurement #	t [s]	$C_{\mathrm{Ca}^{2+}}$ [mmol/s]
1	12	0.854
2	130	0.600
3	194	0.453
4	320	0.374
5	481	0.334
6	577	0.310
7	647	0.296
8	907	0.286
9	1201	0.294

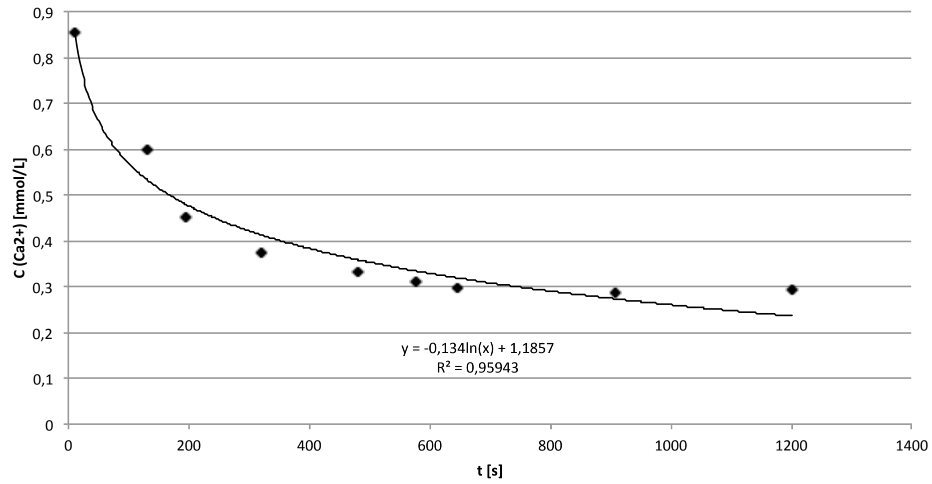


Figure 2: Graphical presentation of calcium concentration, $C_{\mathrm{Ca}^{2+}}$, as a function of time, t. A fitted logarithmic curve found by regression is shown with its equation.

Regression gave a logarithmic curve described by the equation

$$y = -0.134 \ln x + 1.1857 \tag{11}$$

A power function was also applied to the experimental data, but equation (11) gave the best fit and was therefore chosen. A graph can be seen in Figure 2. Here y is the concentration of calcium ions as a function of time, which here is denoted by x. The values for the calcium concentration found by inserting the time values from Table 1 into Equation (11) were used instead the experimental values in the subsequent calculations.

A logarithmic plot of the linear growth rate, G, against $(S-1)$ can be found in Figure 3. Data for this graphical presentation is given in Table 2. The fitted curve found shown in the graph was found by linear regression and is described by the equation

$$y = 1.7501x - 20.875 \tag{12}$$

Here y is the linear growth rate, G, and x is $S-1$. From this, the growth rate order was determined to $g = 1.7501$ and the growth rate constant to $k_r = 0.8592$ nm/s.

Table 2: Data for G, $S-1$ and their natural logarithms, $\ln G$ and $\ln(S-1)$. G is the linear growth rate and S is the supersaturation ratio.

Measurement #	G [m/s]	$\ln G$ [-]	$(S-1)$ [-]	$\ln(S-1)$ [-]
1	$3.39 \cdot 10^{-8}$	-17.2	2.38	0.866
2	$1.45 \cdot 10^{-9}$	-20.4	1.27	0.240
3	$4.25 \cdot 10^{10}$	-21.6	1.07	0.0687
4	$2.6 \cdot 10^{-10}$	-22.0	0.81	-0.206
5	$1.6 \cdot 10^{-10}$	-22.5	0.60	-0.513
6	$1.24 \cdot 10^{-10}$	-22.8	0.50	-0.691
7	$1.06 \cdot 10^{-10}$	-23.0	0.44	-0.823
8	$8.36 \cdot 10^{-11}$	-23.2	0.25	-1.37
9	$6.09 \cdot 10^{-11}$	-23.5	0.097	-2.33

At the end of the experiment, the seed and growth solutions were examined by light microscopy. Three images of crystals in the seed solution at increasing magnification are shown in Figure 4.

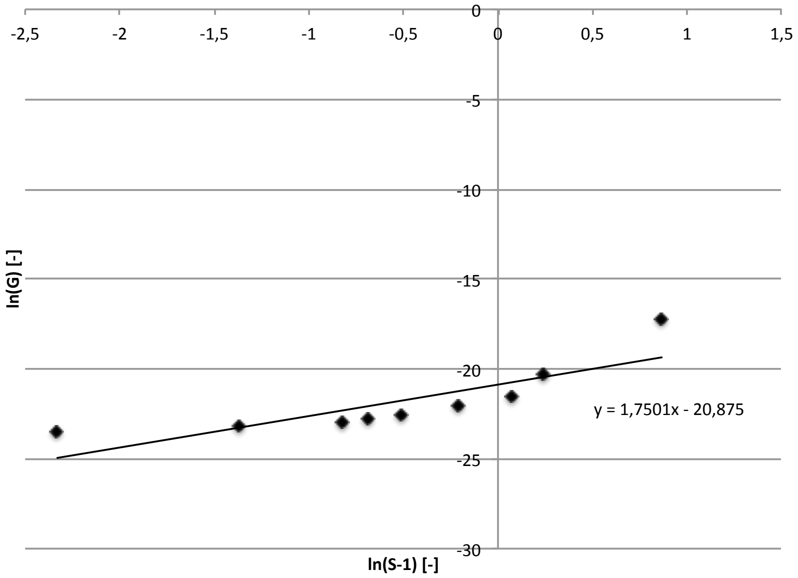
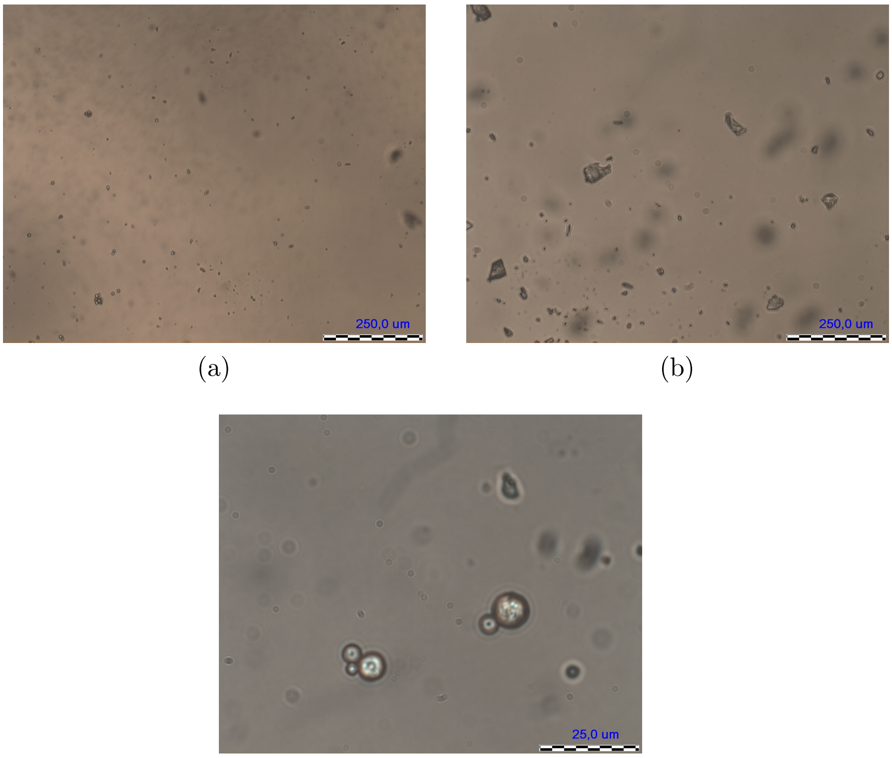


Figure 3: Logarithmic plot of the linear growth rate, G, against $(S-1)$. A fitted curve found by regression is shown with its equation.



(a)

(b)

(c)

Figure 4: Crystals in the seed solution at increasing magnification. (a) The vaterite seeds can be seen vaguely with most being recognizable as approximate spheres. Some crystals are gathered in clusters. (b) Collection of non-spherical crystals. (c) Small clusters of spherical seeds.

4.2 Discussion

As explained in the introduction (Section 1), the experiment was supposed to be performed at two different temperatures; 25 °C and 40 °C. During the experiment performed at 25 °C, the automatic titrator used to determine the concentration of calcium ions failed catastrophically, so that the titration curves did not show any equivalence points. This makes it impossible to determine how much EDTA that was used, and thus makes it impossible to determine the concentration of calcium in the solution. Therefore there are no reported results for the experiment that was supposed to be performed at 25 °C.

During the light microscopy of the different solutions with crystals, we experienced problems with the designated computer and software. After the solutions were disposed of, it was discovered that many of the picture files were corrupted and not saved properly. The only pictures that turned out to be fine were those with the seed solution. These are therefore used as a reference point for the appearance of vaterite crystals.

As seen in the graphical presentations, the linear regression gave the results $g = 1.7501$ and $k_r = 0.8592$ nm/s. These results indicate that the rate determining growth mechanism may be surface integration[1] since $g \approx 2$. The results conform to the values found in the literature[2] with some deviances.

There are several sources of errors that may have resulted in deviations from values found in the literature. There are uncertainties in the measuring devices used to make the solutions that lead to non-exact concentrations. This systematic error can affect the reaction kinetics results. Even though the batch reactor is continuously stirred, the solution may not be homogenous at all times. A non-homogenous solution results in concentration gradients throughout the solution that may affect the crystallization.

The crystallization may have started before the seed solution was added, so that the initial concentration of calcium ions, $C^0_{\mathrm{Ca}^{2+}}$, at recorded time $t = 0$ may have been too low. One of the approximations made in the calculations is that the vaterite crystals are spherical, and that only vaterite crystals are formed. From the light microscopy images (see Figure 4) it is obvious that some of the crystals are non-spherical. Some calcite crystals were also observed in the seed solution and this necessarily results in an error in the calculations.

5 Summary and conclusions

The growth rate constant was determined to be $k_r = 0.8592$ nm/s at calcium concentration $C_{\mathrm{Ca}^{2+}} = 1.5$ M and temperature $T = 40$°C. The growth rate order was determined to be $g = 1.7501$ under the same conditions. The value of the growth rate order indicates that the rate determining growth mechanism may be surface integration.

No results were obtained from the experiment performed at $T = 25$°C and $C_{\mathrm{Ca}^{2+}} = 2$ M and it was therefore not possible to draw any conclusions regarding the effect of temperature on the growth rate constant and growth rate order.

Trondheim, October 19, 2011.

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6 References

[1] *Crystal growth of the calcium carbonate polymorph vaterite in distilled water*, 2011, viewed 7 October 2011, `http://www.nt.ntnu.no/users/preisig/Repository/TKP_4110_Felles_Lab/experiment%20descriptions/5_crystallization%20%20exercise%202011.pdf`

[2] Olderøy, M.Ø.; Xie, M.; Strand, B.L.; Flaten, E. M.; Sikorski, P.; Andreassen, J.-P.: Growth and Nucleation of Calcium Carbonate Vaterite Crystals in Presence of Alginate. *Crystal Growth & Design, Vol. 9, No. 12.* **2009**, p. 5180.

A Preparation of solutions

A.1 Solutions for seed preparation

The necessary amounts of calcium chloride dihydrate and sodium carbonate, $m_{\mathrm{CaCl_2 \cdot H_2O}}$ and $m_{\mathrm{Na_2CO_3}}$, were calculated as follows using the given concentrations and table data for the compounds' molar weight:

$$\begin{aligned} m_{\mathrm{CaCl_2 \cdot H_2O}} &= V_{tot} C_{\mathrm{CaCl_2 \cdot H_2O}} M_{\mathrm{CaCl_2 \cdot H_2O}} \\ &= 0.250 \text{ L} \cdot 0.2 \text{ M} \cdot 147.03 \text{ g/mol} = 7.35 \text{ g} \end{aligned}$$

$$\begin{aligned} m_{\mathrm{Na_2CO_3}} &= V_{tot} C_{\mathrm{Na_2CO_3}} M_{\mathrm{Na_2CO_3}} \\ &= 0.250 \text{ L} \cdot 0.2 \text{ M} \cdot 106.0 \text{ g/mol} = 5.3 \text{ g} \end{aligned}$$

Here V_{tot} denotes the total volume of the solution. $C_{\mathrm{CaCl_2 \cdot H_2O}}$ and $C_{\mathrm{Na_2CO_3}}$ are the concentrations of calcium chloride dihydrate and sodium carbonate respectively.

A.2 Solutions for growth experiments

The necessary amounts of calcium chloride dihydrate and sodium carbonate were again calculated using the given concentrations and table data for the compounds' molar weight. This was done as follows:

$$\begin{aligned} m_{\mathrm{CaCl_2 \cdot H_2O},1} &= V_{tot} C_{\mathrm{CaCl_2 \cdot H_2O},1} M_{\mathrm{CaCl_2 \cdot H_2O}} \\ &= 0.250 \text{ L} \cdot 4 \cdot 10^{-3} \text{ M} \cdot 147.03 \text{ g/mol} = 147 \text{ mg} \end{aligned}$$

$$\begin{aligned} m_{\mathrm{Na_2CO_3},1} &= V_{tot} C_{\mathrm{Na_2CO_3},1} M_{\mathrm{Na_2CO_3}} \\ &= 0.250 \text{ L} \cdot 4 \cdot 10^{-3} \text{ M} \cdot 106.0 \text{ g/mol} = 106 \text{ mg} \end{aligned}$$

$$\begin{aligned} m_{\mathrm{CaCl_2 \cdot H_2O},2} &= V_{tot} C_{\mathrm{CaCl_2 \cdot H_2O},2} M_{\mathrm{CaCl_2 \cdot H_2O}} \\ &= 0.250 \text{ L} \cdot 3 \cdot 10^{-3} \text{ M} \cdot 147.03 \text{ g/mol} = 110 \text{ mg} \end{aligned}$$

$$\begin{aligned} m_{\mathrm{Na_2CO_3},2} &= V_{tot} C_{\mathrm{Na_2CO_3},2} M_{\mathrm{Na_2CO_3}} \\ &= 0.250 \text{ L} \cdot 3 \cdot 10^{-3} \text{ M} \cdot 106.0 \text{ g/mol} = 80 \text{ mg} \end{aligned}$$

Here V_{tot} denotes the total volume of the solution. $C_{\mathrm{CaCl_2 \cdot H_2O}}$ and $C_{\mathrm{Na_2CO_3}}$ are the concentrations of calcium chloride dihydrate and sodium carbonate respectively, with the subscripts 1 and 2 being used to distinguish between data for the two different concentrations. Subscript 1 is added to data for the 2 mM solution and subscript 2 to data for the 1.5 mM solution.

B Spreadsheet used in calculations

Forsøk 1

#	t [s]
1	12
2	130
3	194
4	320
5	481
6	577
7	647
8	907
9	1201
10	1299

T1 [°C]	T2 [°C]	ρ(s,T1)* [g/mL]	ρ(s,T2)* [g/mL]	M(s)* [g/mol]
25	40	0,997	0,992	18,016

C(EDTA) [mol/L]	N (# seeds per volumenhet)** [L^(-1)]	C0(Ca2+,2) [mmol/L]	C0(Ca2+,2) [mmol/L]	V0** [mL]
0,010019	4,50E+08	2	1,5	1,36E-10

*data for vann fra SI
**data fra oppgaven

Forsøk 2

#	t [s]	m(s) [g]	V(s) [mL]	V(EDTA,eq) [mL]	C(Ca2+,eksp) [mmol/L]	C(Ca2+,regr) [mmol/L]	S [-]	dC(Ca2+) [mmol/L]
1	12	29,3	29,53629032	2,518	0,85413035	0,852722509	3,376426811	-0,647277491
2	130	29,31	29,54637097	1,768	0,599518365	0,533450384	2,271593459	-0,319272125
3	194	29,29	29,52620968	1,334	0,452660404	0,479807007	2,07108679	-0,053643377
4	320	29,11	29,34475806	1,094	0,373517682	0,412744987	1,813890977	-0,06706202
5	481	29,08	29,31451613	0,976	0,33357344	0,358133786	1,598908603	-0,054611201
6	577	29,06	29,29435484	0,906	0,309862226	0,333749136	1,501267733	-0,02438465
7	647	28,72	28,9516129	0,856	0,296227503	0,318405597	1,439298748	-0,01534354
8	907	28,98	29,21370968	0,834	0,286024818	0,273140912	1,254061441	-0,045264685
9	1201	29,36	29,59677419	0,868	0,293832427	0,235518084	1,09729368	-0,037622828
10	1299	29,66	29,89919355					

dV [mL]	V(n+1) [mL]	r(n+1) [m]	dr [m]	dt [s]	G [m/s]	ln(G) [-]	S-1 [-]	ln(S-1) [-]
5,90E-11	1,95E-10	4E-06	4,07211E-07	12	3,39343E-08	-17,19884018	2,376426811	0,86559802
2,91E-11	2,24E-10	4E-06	1,70747E-07	118	1,44701E-09	-20,35376468	1,271593459	0,240270806
4,89E-12	2,29E-10	4E-06	2,72113E-08	64	4,25176E-10	-21,57851706	1,07108679	0,068673824
6,11E-12	2,35E-10	4E-06	3,34786E-08	126	2,65703E-10	-22,04864217	0,813890977	-0,205928857
4,98E-12	2,40E-10	4E-06	2,68367E-08	161	1,66687E-10	-22,51490091	0,598908603	-0,512646276
2,22E-12	2,42E-10	4E-06	1,18632E-08	96	1,23575E-10	-22,81417354	0,501267733	-0,690614923
1,40E-12	2,44E-10	4E-06	7,42752E-09	70	1,06107E-10	-22,96656869	0,439298748	-0,822575578
4,13E-12	2,48E-10	4E-06	2,17475E-08	260	8,36444E-11	-23,20444693	0,254061441	-1,370179146
3,43E-12	2,51E-10	4E-06	1,7893E-08	294	6,08606E-11	-23,52243571	0,09729368	-2,330021241