

Process Engineering Laboratory II

Crystallization

Introduction

Crystallization is a separation process, widely applied in the chemical and pharmaceutical industry. The principle of crystallization is based on the limited solubility of a compound in a solvent at a certain temperature, pressure, etc. A change of these conditions to a state where the solubility is lower will lead to the formation of a crystalline solid. Although crystallization has been applied for thousands of years in the production of salt and sugar, many phenomena occurring during crystallization are still poorly understood. Especially the mechanisms of nucleation and crystal growth and the complex behavior of industrial crystallizers remain elusive.

One of the reasons for this is the lack of appropriate tools to measure and monitor crystallization processes. On the other hand, demands for consistent product quality (purity, crystal size, etc.) are ever increasing, thus creating a large interest in crystallization research.

The aim of this practicum is to refresh your theoretical knowledge on crystallization and to demonstrate the problems and challenges commonly occurring in crystallization. One of the goals of this practicum is also to write a good report which contains physically correct explanations for the phenomena you observed. In the following sections an outline of the theoretical concepts is presented, the experimental setup is explained and the practical tasks are discussed. The final section is about the report you are expected to hand in to pass the practicum. The report is an important part of the practicum as it trains your ability to present results in a scientific way.

The practicum will be conducted according to the timetable shown below.

| Phase: | Duration: | Activities: |
|--------|-----------------|--------------------------------------|
| 1 | 30 min | Introduction |
| | | Presenting the setup and equipment |
| | | Heating up of the crystallizer |
| 2 | 15 min | Heating up to start temperature |
| | | Start of temperature control program |
| | | Addition of seed crystals |
| 3 | 70 min | While crystallization is running: |
| | | Review of theory with the assistant |
| 4 | 30 min | Switching off the equipment |
| | | Filtration of the suspension |
| | | Drying of the crystals |
| | | Cleaning the equipment |
| 5 | after practicum | Measurement with Coulter Multisizer |
| | | Writing of report |

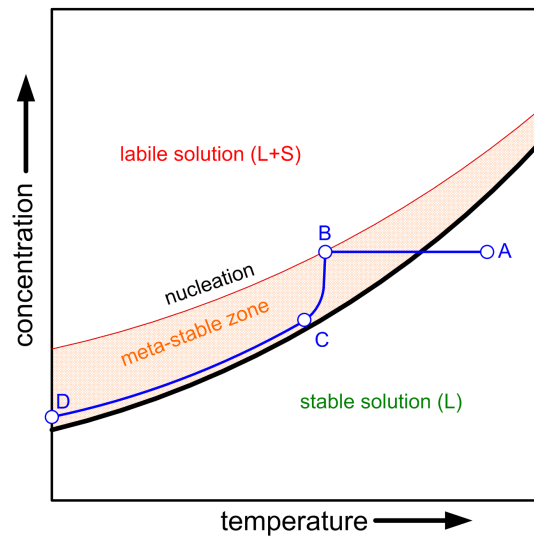


Figure 1: Solubility diagram and typical de-supersaturation profile of an unseeded crystallization.

Theoretical background

Crystallization is the process of forming a crystalline material from a liquid, gas or amorphous solid. The crystals thus formed have highly regular internal structure, the basis of which is called the crystal lattice. Since the formation of such a highly ordered structure prohibits foreign molecules from being incorporated into the lattice, a solid product of high purity is obtained. The simultaneous formation and purification of a solid product makes crystallization an important operation in the process industry.

All crystallization processes are aimed at creating a supersaturated solution or melt. The supersaturation is the driving force under whose influence new crystals are formed and present crystals grow. This is illustrated in figure 1 where a typical cooling crystallization experiment is shown together with the solubility line.

For most substances, the solubility increases with increasing temperature, with sodium chloride being a notable exception. Suppose we start at point A in the diagram, which is undersaturated. Any crystals added to a solution in this region would dissolve. If we now cool to a point between A and B, we enter the meta stable region where existing crystals will grow, but no new crystals are formed. Cooling further we obtain a labile solution at point B where spontaneous formation of new crystals, i.e. nucleation, takes place. This dramatically decreases the concentration and point C will be reached. Cooling further, the crystals formed between B and C grow and consume whatever supersaturation we create by cooling, so we stay in the meta stable region until we reach the end of the crystallization at point D.

The important phenomena that occur during crystallization can be described by the following quantities:

- the nucleation rate B [$\#/(m^3s)$]; the number of new crystals formed per unit time and volume of suspension
- the growth rate G [m/s]; the rate at which the size of the crystals increases

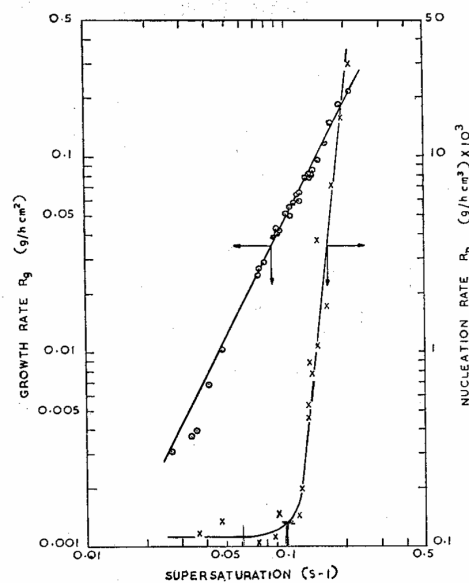


Figure 2: Growth and nucleation rates of potassium sulphate in water as a function of supersaturation [1].

- both B and G are influenced by the supersaturation S [-], where $S = c/c_s$, with c [kmol/m³] the current solute concentration and c_s the equilibrium concentration at the same temperature.

For potassium sulphate, the dependence of B and G on S is shown in figure 2.

A further differentiation of nucleation can be made by the way new crystals are formed. Secondary nucleation can take place at low supersaturations when crystals are already present. Small parts of the existing crystals are washed off and form new nuclei that can grow. As such, secondary nucleation is severely affected by the stirring rate. Primary nucleation usually takes place in the absence of previously formed crystals (though this is not a necessity) when solute molecules meet and form clusters that can grow further to form crystals. This is a stochastic process, and as such, nucleation can be somewhat unpredictable.

The formation of stable nuclei only happens if the increase in interfacial energy resulting from the formation of a solid–liquid interface is offset by a decrease in energy released by the formation of a (thermodynamically favored) solid. At low supersaturations, the energy required to form a solid–liquid interface is bigger than the energy released upon formation of a cluster which are consequently unstable resulting in a very low nucleation rate. Only when the supersaturation is high enough, i.e. when we enter the labile region, stable solid particles will form. This is generally a very sharp transition, which can also be seen from the steep increase in nucleation rate for a certain supersaturation in figure 2.

The unpredictable nature of nucleation, coupled with its dramatic effect on the crystal size distribution, indicate that this a process we can poorly control. As such, in industrial crystallization, we mostly add small, previously produced crystals. These crystals will consume whatever supersaturation we create by growing, thus ensuring we stay within the meta stable region. This is called seeded crystallization, a technique often applied if a consistent product quality is important.

In cooling crystallization, the supersaturation is created by a decrease in temperature. Depending on how the solution is cooled, a different end product is obtained. The simplest way of performing a cooling crystallization is to let a warm solution cool to the surrounding room temperature (curve i in figure 3(a)). Obviously, the cooling rate will be highest in the beginning, when there is a large temperature difference between the solution and its surroundings, and it will be lowest at the end of the crystallization. The seed crystals will not be able to grow fast enough to consume the supersaturation created in the beginning. As a consequence, we are likely to shoot into the labile region and have nucleation. Therefore, we can expect our end product have a rather wide distribution of crystal sizes.

Alternatively, we can cool linearly with the help of a thermostat (curve ii in figure 3(a)). This will reduce the initial supersaturation, but since the solubility curve is steepest at high temperature, we will still create the highest supersaturation in the beginning we therefore still risk having nucleation.

A more sophisticated cooling would ensure that the supersaturation remains constant throughout the whole crystallization. This requires knowledge on the growth rate, the nucleation rate, the solubility and the seed crystals, but with some mathematical effort, it is possible to compute a cooling curve that results in a constant supersaturation.

In figure 3(b), the evolution of the supersaturation for each of these cooling strategies is shown.

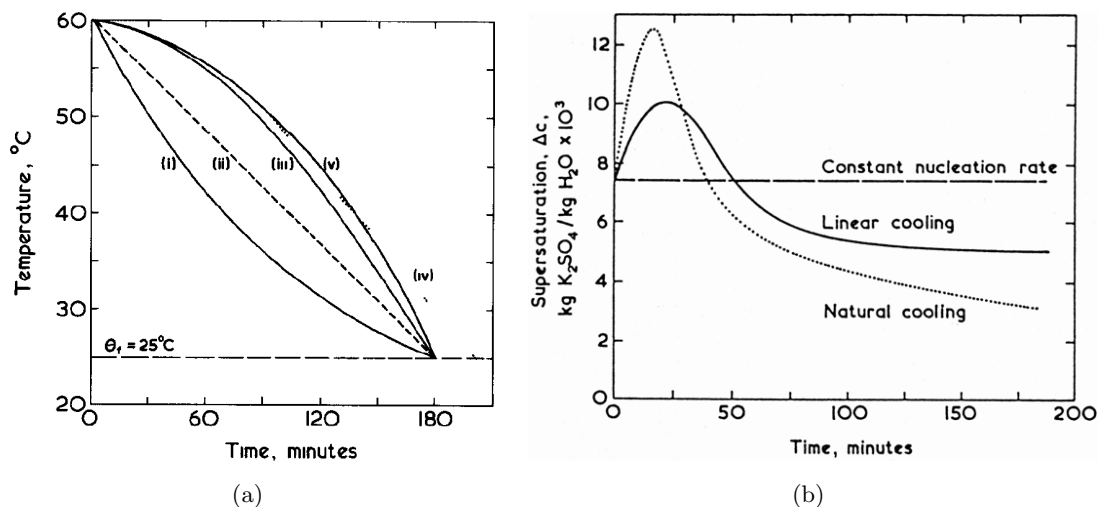


Figure 3: Different cooling curves (a) and the resulting evolution of the supersaturation as a function of process time (b).

To calculate the cooling curve for constant supersaturation, the following assumptions are made:

- we perform a batch crystallization
- the supersaturation S is constant throughout the whole process
- the supersaturation S is small enough to prevent nucleation from happening
- the seed crystals are mono disperse, i.e. all seed crystals have the same size

The balance equation for such a process is as follows:

$$\frac{d\Delta c}{dt} = r - k_g A \Delta c^n - k_n \Delta c^m \quad (1)$$

where $\Delta c = c - c_s$ is the difference between actual and saturation concentration (sometimes called supersaturation as well) and r is the increase in the supersaturation due to the decreasing temperature. The second term of the right hand side is the decrease of the supersaturation due to crystal growth and the third term is the decrease due to nucleation.

The crystal area per unit mass of solvent can, if nucleation is neglected ($k_n=0$), be calculated as follows:

$$A(t) = \beta N L(t)^2 \quad (2)$$

where β is an area shape factor and $L(t)$ is the crystal size:

$$L(t) = L_0 + \int_0^t G(\theta(t), L(t)) dt \quad (3)$$

N is the number of seed crystals:

$$N = \frac{W_0}{\alpha \rho L_0^3} \quad (4)$$

W_0 is the mass of seed crystals per unit mass solvent and α is a volume shape factor. The crystal growth rate can be described as follows:

$$G(\theta(t), L(t)) = \frac{k_g \beta}{3\alpha \rho} \Delta c^n \quad (5)$$

Since for r , we can write:

$$r = \frac{d\Delta c_s}{dt} = \frac{d\Delta c_s}{d\theta} \frac{d\theta}{dt} \quad (6)$$

the balance equation can be simplified by assuming $\frac{d\Delta c}{dt} = 0$.

$$\frac{d\theta(t)}{dt} = \frac{3W_0 G(\theta(t), L(t))}{\frac{dc_s}{d\theta} L_0} \left(1 + \frac{1}{L_0} \int_0^t G(\theta(t), L(t)) dt \right)^2 \quad (7)$$

This general equation can now be applied to the potassium sulphate system. This requires certain substance specific data to be known. The measurement of these is often very difficult and extremely time consuming. For potassium sulphate, a well known substance, these data can be found in literature [2].

$$\begin{aligned} \frac{\beta}{3\alpha \rho} &= 1.01 \times 10^{-3} \\ k_g &= -0.1 + 3.25 \times 10^{-2} \theta(t) + 5 \times 10^2 L(t) \\ c_s(\theta) &= -3.294 \times 10^{-6} \theta^2 + 2.044 \times 10^{-3} \theta + 7.11 \times 10^{-2} \\ n &= 2 \end{aligned} \quad (8)$$

Substituting the above in equation 7, we obtain a differential equation that cannot be solved explicitly. With the help of some software, we can however solve the equation numerically. Using the following parameters: $W_0 = 1.5 \times 10^{-2}$ kg seed crystals per kg solvent, $L_0 = 113 \times 10^{-6}$ m, $T_0 = 70^\circ\text{C}$, $T_1 = 30^\circ\text{C}$ and $\delta c = 4 \times 10^{-3}$ kg/kg a simulation can be performed in MATLAB to obtain the ideal cooling profile. The syntax for the program `temp.m` is: `temp(0.015,0.000113,70,30)`.

Description of the crystallization setup

The crystallization is conducted in a thermostated, 250 ml jacketed glass reactor (see figure 4(a)) equipped with a stirrer. A thermostat pumps a mixture of glycol and water through the jacket and uses a Pt100 thermocouple positioned in the reactor to control the reactor temperature. We will use a so called Coulter Multisizer to measure the particle size distribution of the crystals.

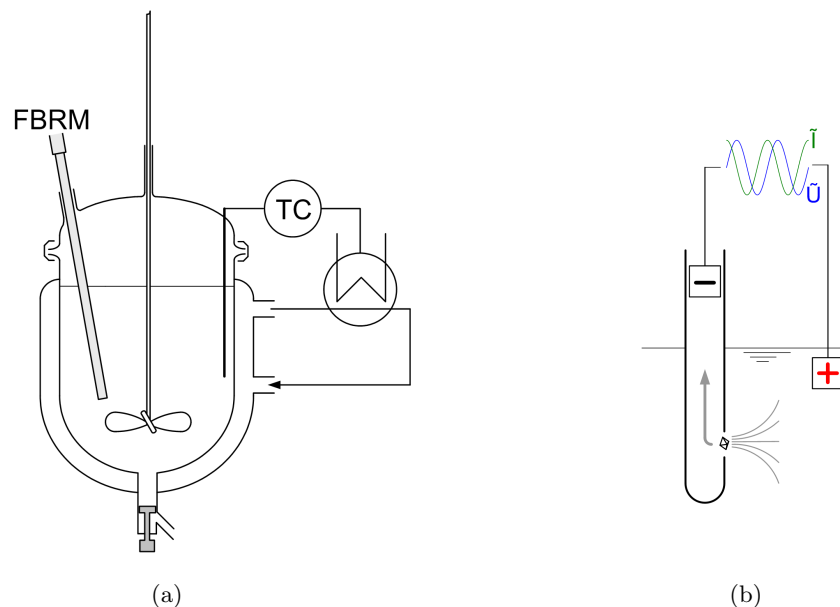


Figure 4: Schematic drawing of the crystallizer (a). The crystals are analyzed by a Coulter Multisizer which measures the change in impedance as a crystal enters the aperture tube and displaces a small volume of liquid (b).

The principle of the Coulter Multisizer is explained in figure 4(b). A small sample of the crystals obtained at the end of the experiment is added to a particle-free, saturated solution. In this solution, an electrode is positioned as well as a small glass tube which has a small opening or aperture on the side. A pump inside the device will create a low pressure which will cause the suspension to flow through this small opening in the glass tube to another tank. In this tank, a second electrode is positioned to which an AC-current is applied. If a particle passes through the aperture, the impedance of this circuit momentarily changes. This change is registered by the machine. Since this change is proportional to the particle volume, the impedance fluctuations can be converted to a particle volume distribution.

Experimental Tasks

- Fill the reactor with 150 gr of particle-free de-ionized water and add 29 gr of potassium sulphate to the water.
- Prepare 1.5 gr of seed crystals with a size between 90 and 125 μm .
- Use a sensible stirring speed during the crystallization. Usually the stirrer is rotated at a speed which just suffices to keep all crystals suspended. In this experiment, around 450 rpm is recommended.
- Heat the reactor up such that the reactor medium is at 70°C and that all crystals are dissolved. Ensure the thermostat medium does not heat up beyond 100°C.
- Once the reactor is heated up, start the temperature-control program. The program ensures the system first goes to the correct start temperature and then follows the ideal cooling curve, i.e. the cooling curve resulting in a constant supersaturation.
- The current reactor temperature is shown in the display on the thermostat. Once a temperature of 70°C has been reached and all the solid has dissolved, the solution has obtained the required supersaturation and the seed crystals can safely be added using a glass funnel.
- The crystallization will now run automatically to the end temperature of 30°C.
- At the end of the experiment the stirrer should be stopped and the suspension should carefully be drained through the bottom valve of the reactor.
- Using a Büchner-funnel, the suspension is vacuum-filtrated and the crystals are dried in an oven.
- Meanwhile, the setup should be flushed thoroughly with de-ionized water.
- After drying the crystals, the total crystal mass should be weighed and its particle size distribution should be measured using the Coulter Multisizer.

Report

A report has to be written containing all the important information of the experiments carried out. The report should include, but is not limited to, the following items: **Remember: quality is important, not quantity. Limit your report to 5 pages of text.**

- title page: the title page includes a title (obviously), your names, your email addresses, the date you handed the report in and a small abstract (max. 20 lines).
- introduction: a small introduction that explains what experiment you are doing and what insight you want to gain.

- theory section: the theory section includes all the equations you are going to use to interpret your results. Derivations **do not** have to be included, but you should shortly state the principle behind the equations used. If assumptions have to be made for an equation to be valid, they have to be stated.
- theory section: Explain the differences between linear, natural and controlled cooling and qualitatively draw the final particle size distribution for each of these cases, for a seeded crystallization.
- theory section: As was mentioned before, not all substances can be crystallized by cooling crystallization. Can you come up with 2 different ways of crystallizing a substance from solution?
- experimental part which includes **what** you did, **why** you did it and **how** you did it.
- results and discussion: in this part your results are included. Your measurement results have to be explicitly given, so that any calculations are reproducible. The following plots, tables and discussions **are the minimum required**:
 1. The exact masses of water, potassium sulphate (both what you added and what you obtained) and seed crystals must be listed, so that your calculations can be verified.
 2. How does the difference between the amount of potassium sulphate you added in the beginning and that what you obtained in the end relate to the solubility data? Is it what you expected?
 3. Calculate the number-based particle size distribution q_0 and the volume-based particle sized distribution q_3 of the seed and of the final particles as well as the cumulative distributions Q_0 and Q_3 . Determine the median of both the number and the volume-based distributions, i.e. the $L_{50,0}$ and the $L_{50,3}$. The distributions are defined as follows:

$$q_0 = \lim_{\Delta L_i \rightarrow 0} \frac{1}{\Delta L_i} \frac{N_i}{\sum N_i} \quad (9)$$

$$q_3 = \lim_{\Delta L_i \rightarrow 0} \frac{1}{\Delta L_i} \frac{N_i L_i^3}{\sum N_i L_i^3} \quad (10)$$

$$Q_k(L) = \int_0^L q_k(L) dL \quad (11)$$
 with N_i being the number of particles per size interval ΔL_i . q_0 and q_3 are normalised, which means that $Q_k(L_{max}) = 1$.
 4. Plot the volume-based particle size distribution q_3 of both the seed crystals and the final particles. Discuss and explain the results: has there been nucleation and did the distribution widen during the process? What could be the causes of this?
 5. Compare the setpoint and the actual temperature during the experiment. Is the supersaturation constant throughout the crystallization process?

6. Determine the effect of seed crystal mass and size on process time and final particle size using MATLAB programme `temp.m`.

This part also includes the discussion of your results. In the discussion you state if the results you obtained were expected. If they were not expected, give explanations why they are not what you expect. This section is the most important section of your report because it gives the indication if you understood what you were doing. All the figures you are implementing in the report have to be commented (**what** can be seen and **why** do you think it is important to show?). Reports that give no or physically impossible explanations for the observed phenomena will be rejected or have to be corrected.

You have three weeks time to hand in a report that meets these standards, which includes possible corrections you have to make. Therefore, it is recommended to hand in the first version of the report earlier, so that you have time to correct possible mistakes. The time the assistant takes to correct your report is **not** included in the three weeks. The report can be handed in either digitally or as hard copy directly at the assistant's office.

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References

- [1] Mullin, J.W., Gaska, C.: *"The growth and dissolution of potassium sulphate crystals in a fluidized bed crystallizer"*, Can. J. Chem. Eng. 47 (1969) 47, 483-489.
- [2] Jones, A. G., Mullin, J.W.: *"Programmed cooling crystallization of potassium sulphate solutions"*, Chem. Eng. Sci. 29 (1974) 1, 105-118.