AN UNDERGRADUATE LABORATORY EXERCISE FOR STUDYING KINETICS OF BATCH CRYSTALLIZATION

Marjatta Louhi-Kultanen, Bing Han, Annikka Nurkka, Henry Hatakka
Lappeenranta University of Technology • Lappeenranta, Finland

Industrial crystallization is a unit operation used to obtain pure solid chemicals of a certain size, usually from multicomponent solutions. It can be considered as a method belonging to the fields of particle, purification, and material science. Process control of crystallization principally consists of control of the driving force, *i.e.*, control of supersaturation. The fundamentals of industrial crystallization can be found from various crystallization handbooks such as the *Handbook of Industrial Crystallization*, edited by Myerson,[1] Mullin's *Crystallization*,[2] the *Crystallization Technology Handbook*, edited by Mersmann,[3] and Davey and Garside's *From Molecules to Crystallizers*.[4] Teaching of industrial crystallization fundamentals has covered crystallization applications for both inorganic and organic compounds. Kinetic study of crystal growth from melt in the case of polymer spherulites was introduced by Marentette and Brown,[5,6] and Singfield, *et al*.[7] Fernández-Torres, *et al*.,[8] used a solved problem to illustrate the eutectic freeze crystallization method. García-Ruiz, *et al*.[9] developed a teaching method to obtain large protein crystals by precipitation with the aid of gels.

Crystallization kinetics has a great influence on crystalline product properties such as crystal size distribution and mean crystal size. Thus, crystallization kinetics data is essential for process simulation and design of industrial crystallizers. In addition to conventional off line measurement methods, crystallization kinetic data can be obtained by real-time Process Analytical Technology (PAT) methods. Real-time process monitoring has developed greatly since the 1990s and many sophisticated methods are now available.

The laboratory exercise introduced in the present work was first implemented at Lappeenranta University of Technology in the early 2000s and has slowly evolved to its current form. The laboratory exercise aims to enhance understanding of what the nucleation rate (generation rate of nuclei, *i.e.*, the increasing number of zero-sized crystals over time) and crystal growth rate mean in practice. In the exercise, a counter-type

Marjatta Louhi-Kultanen *is a professor (chemical engineering, especially separation technology) in the Laboratory of Separation Technology at Lappeenranta University of Technology (LUT) and a docent in industrial crystallization at LUT. She teaches courses on the fundamentals of mass transfer and unit operations. Her research interests focus on purification and separation of inorganic and organic compound systems by industrial crystallization. She is a member of the Working Party of Crystallization, European Federation of Chemical Engineering (EFCE).*

Bing Han *gained her M.Sc. from Tianjin Key Laboratory of Marine Resources and Chemistry at Tianjin University of Science and Technology. After completing her M.Sc. degree, she continued her studies as a double-degree doctoral student at Lappeenranta University of Technology (LUT) and Tianjin University of Science and Technology. Industrial crystallization is her main research subject. The research topics in her doctoral thesis are multi-phase phenomena and process monitoring in industrial crystallization processes.*

Annikka Nurkka*, quality system manager, M.Sc. (Ed.), has worked in higher education and university pedagogy. She has taught pedagogy to university personnel, coordinated development projects in education (e.g., e-learning projects, accreditation of degree programs) and has worked together with teachers in the development of teaching activities and the publication of articles on the impact of changes in teaching processes.*

Henry Hatakka*, D.Sc. (Tech.), is a post-doctoral researcher at LUT. He received his doctorate in chemical engineering from LUT. His research interests include industrial crystallization, solid-liquid separation, and advanced oxidation processes in water treatment.*

inline particle size analyzer is used to monitor and illustrate how the number of crystals increases when nucleation takes place. In addition, the crystal growth kinetics are determined based on a desupersaturation model and by measuring the initial seed crystal size and the crystal size of the final product. The use of chemical engineering calculations and empirical work incorporates elements of constructivist learning, and the use of group work encourages collaborative learning and development of the perspectives of chemical engineering practices.

As we educate students of chemical engineering, at Master's degree level, our aim as teachers is to provide the ability and skills to design and size various unit operation equipment, in addition to developing an understanding of the fundamentals of unit operations. The crystallization laboratory exercise combines direct experimental measurements and theoretical approaches in which modeling is done based on experimentally obtained data. The results obtained at laboratory scale can be used for industrial scale calculations.

Pedagogical approach

The laboratory exercise on kinetics of batch crystallization is based on principles of constructive alignment[10] and collaborative learning.[11] The basic concept is that competencies are generated through cooperation between the students and teachers, and the teachers' primary role is to facilitate learning.

Constructive alignment is an outcomes-based approach to education that attempts to connect the elements of learning outcomes, teaching methods, and student assessment.[10] It is claimed that by making sure that all of the elements work toward the same goal, institutions can ensure that students' efforts are appropriate and efficient. When developing the laboratory work, alignment between the intended learning outcomes and student activities was an important aim.

Current engineering education, it has been claimed, does not support learning of many of the skills required of engineers, for example, communication and group working skills.[12,13] The laboratory exercise aims to address this issue through an approach based on collaborative learning.[11] Thus, the success of one student can help other students to be successful. Collaborative learning fosters students' development of critical thinking through discussion, clarification of ideas, and evaluation of others' ideas. It is especially beneficial in enhancing critical thinking and problem-solving skills, which are crucial also in understanding complicated chemical processes that are not readily comprehended at a conceptual level.

Course overview

The industrial crystallization part of the Chemical Engineering Unit Operation II course is intended for students in the first year of their Master's level studies and consists of the following parts: theory, operation, and design of crystallizers; mass transfer of dissolution; and Process Analytical Technology (PAT) in crystallization processes. Learning outcomes of the industrial crystallization part of the course are such that on completion of the module a student can: explain the fundamentals of industrial crystallization (kinetics, solid-liquid equilibrium, population density, crystal size distributions, polymorphism, solvate and hydrate formation, mass transfer in crystallization and dissolution, and real-time process monitoring); list and describe the operation of the most important industrial crystallizers; and estimate the preliminary size of an MSMPR crystallizer. Student learning is assessed by written examination and the laboratory exercise report compiled by each student group. The written examination covers the whole content of the Chemical Engineering Unit Operation II course. Improved examination answers suggest that the laboratory exercise has enhanced students' understanding of the fundamentals of crystallization kinetics.

In the industrial crystallization module, the teaching methods comprise lectures (8 hours), calculation exercises (12 hours), and the laboratory exercise (4 hours of laboratory measurements, data treatment, and reporting as independent study).

Instructors assist the students in carrying out the crystallization experiments. Instructions given in the supporting information for the course in Appendix 1 provide further guidance on obtaining crystallization kinetics models by treating the empirical data obtained. Groups of four to five students simultaneously carry out two experimental sets: nucleation rate measurements and crystal growth rate measurements. First, two to three students from the group focus on crystal growth measurements and the other two to three students on nucleation measurements. After completing a number of experiments, the students swap tasks so that every student carries out both nucleation and growth rate measurements and all students investigate both nucleation kinetics and growth kinetics. Each group prepares a report, which is checked by the teacher. To obtain statistically more reliable results, the teacher collects the experimental data acquired by about five groups and distributes all the results back to the groups for further data treatment. A broader range of experimental data enables the obtained data to be treated in a more analytical and critical way. In addition, clearly divergent experimental results can be seen and treated appropriately.

The laboratory exercise is closely linked to other teaching methods used in the course, *i.e.*, crystallization lectures and calculation exercises. The calculation exercises include initial data giving kinetic models of the nucleation rate and crystal growth rate. However, quite often these kinetic data are not available for a specific compound and crystallization system. Therefore, the kinetic data are required to be determined experimentally. The laboratory exercise illustrates a methodology to obtain kinetic data required for crystallizer design. Furthermore, the introduced laboratory exercise can be used efficiently with moderate teaching load for crystallization courses with a relatively high number of participating students.

TABLE 1

Obtained parameter values fitted from experimental data of nucleation kinetics

dN/dt #/s	Calculated B #/s m^3	Initial temperature ˚C	Final temperature ˚C	ΔT ˚C	Δc kg KDP/kg H_2O	log(Δc)	log(B)
0.25	2.48×10^5	23.0	15.0	8	0.035	-1.46	5.39
0.18	1.81×10^5	23.2	17.2	6	0.027	-1.57	5.26
0.12	1.20×10^5	23.0	18.0	5	0.023	-1.65	5.08
0.10	1.04×10^5	23.0	19.0	4	0.018	-1.74	5.02

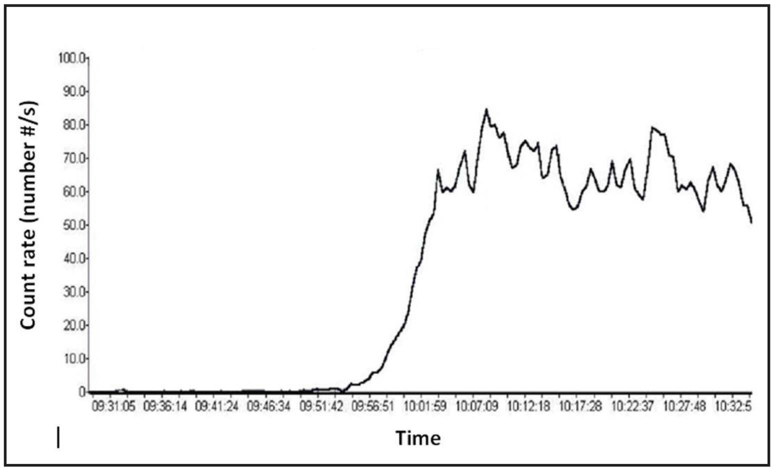

Figure 1. *Count rates (number /s) of KDP crystals monitored by the MTS PSyA laser reflection particle size analyzer over time with subcooling of 5 °C.*

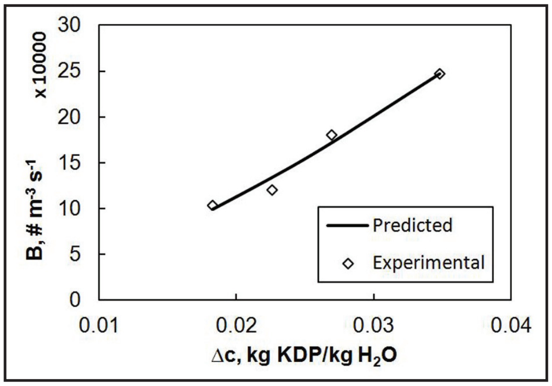

Figure 2. *Experimental and fitted nucleation rate as a function of supersaturation.*

In our courses, the student number has varied typically between 20 and 30 students and all the laboratory exercises of the groups have been carried out within one week.

EXPERIMENTAL PROCEDURE

A harmless inorganic salt—potassium dihydrogen phosphate (KDP)—is used as the model compound and water is the solvent. The crystallization temperatures are close to room temperature, so there is no risk that students may handle hot samples. KDP is crystallized by cooling from an aqueous solution, because the salt is relatively soluble in water and its solubility is higher at higher temperatures. The laboratory exercise focuses on nucleation and crystal growth kinetics: how the nucleation rate and crystal growth rate can be determined in laboratory scale systems.

Nucleation rate models

Nucleation rate study is based on online count number measurements by an MTS PSyA laser reflection particle size analyzer. Particle size analyzers are the most expensive equipment used in the laboratory exercise at a price of roughly € 50 000 per unit. A curve of nucleus count numbers with time can be obtained for a known subcooled degree. An example is shown in Figure 1. In the exercise, each student group uses a different undercooling degree, which means supersaturation differs and more data are available, enabling more accurate parameter fitting. Based on data from all groups with a subcooled rate between 4 and 8 ˚C, parameters k_B and i can be estimated by fitting the data to Eq. (1).

Examples of experimental and predicted results are shown in Table 1 and Figure 2. An expression for nucleation rate B obtained by fitting measured data of an earlier laboratory exercise for KDP is shown in Eq. (1):

$$B = 2.92 \cdot 10^7 \Delta C^{1.42} \tag{1}$$

where B is the nucleation rate and ΔC is the supersaturation degree based on the difference between the actual salt concentration and the equilibrium concentration of the saturated solution taken from solubility data.

Crystal growth rate models

Crystal growth can be illustrated by measuring crystal size distribution over time directly during the batch process. In this system, the supersaturation level varies to some extent over time. An indirect desupersaturation curve method can be used for estimation of the crystal growth rate at different supersaturation degrees versus time. The model of the desupersaturation curve derived by Garside, e*t al*.[14] consists of the terms shown in Eqs. (A5)–(A10) in Appendix 1.

RESULTS

Based on available literature, solubility data, and experimental data obtained by crystal size measurement and desupersaturation method by all groups with a subcooling range between 3.5 and 6 ˚C, Eqs. (A5)–(A10) are used and parameter values are obtained by least square method. Parameter values for the models of crystal growth rate are given in Table 2.

Two crystal growth models, explained in more detail in Appendix 1, are used to investigate crystal growth mechanisms[1,15]:

A. The crystal growth rate mechanism dominated by surface nucleation based birth and spread (B+S) [Eq. (A3)]:$G_{B+S} = A_{B+S}(S-1)^{5/6}\exp[-B_{B+S}/(S-1)]$

B. Burton-Cabrera-Frank (BCF) model (screw dislocations on the crystal surface as the crystal growth step) [Eq. (A4)]:

$$G_{BCF} = A_{BCF}\left\lfloor (S-1)^2 / B_{BCF}\right\rfloor \tanh\left\lfloor B_{BCF} / (S-1)\right\rfloor \qquad (A4)$$

The student groups use Eqs. (A3) and (A4) to draw conclusions about the crystal growth mechanism. Better fitting shows if crystal growth is taking place by birth and spread mechanism or via screw dislocation mechanism. The experimental and predicted results by the two methods are shown in Table 2 and Figures 3. Based on the differences between experimental and modeling results in Figure 3A and Figure 3B, it can be seen that the deviations by desupersaturation method are smaller in Figure 3B. Therefore, it can be concluded that better crystal growth rate data as a function of supersaturation are obtained by desupersaturation method than by direct crystal growth rate measurements. Moreover, based on sum values of squared residuals obtained by BCF and birth and spread growth models, BCF model is concluded to be a slightly more appropriate expression for crystal growth of potassium dihydrogen phosphate.

TABLE 2

Obtained parameter values from the birth and spread (B +S) model and Burton-Cabrera-Frank (BCF) model

Parameters	ΔL/Δt	Desupersaturation
k_{G1}	1.68×10^{-6}	2.74×10^{-5}
g1	0.68	1.06
A_{B+S}	7.18×10^{-7}	3.60×10^{-6}
B_{B+S}	-0.0142	0.0124
A_{BCF}	-1.28×10^{-6}	4.67×10^{-6}
B_{BCF}	-1×10^{-5}	4.39×10^{-9}

Course feedback of students was collected via Webropol online survey software when the course was over. Aspects of the course were graded on a scale 1 to 6 (1 – poor; 6 – excellent). Average values from 24-25 feedback responses were: “Instructions of the laboratory work were clear and understandable” – 4.04; “Guidance during crystallization measurements was good” – 4.71; “The laboratory work impacted my learning of crystallization kinetics fundamentals” – 4.24; “The teamwork was useful” – 4.28; and “Process Analytical Technology based in-line process monitoring (count rate measurements with MTS PSyA)” – 4.42. As can be seen from the feedback, the students gave the highest grade for guidance during the laboratory work and learning of Process Analytical Technology was considered useful. As a summary, in the eyes of the students, the laboratory exercise has proven to enhance learning of fundamentals of industrial crystallization and the students feel that they can use appropriate analysis methods in practice.

CONCLUSIONS

A laboratory exercise for learning crystallization kinetics was introduced. The students carried out the studies in student groups of four to five students, which allowed the whole course group of 20- 30 students to undertake empirical investigations, which were further utilized in data treatment calculations to estimate crystallization kinetics models.

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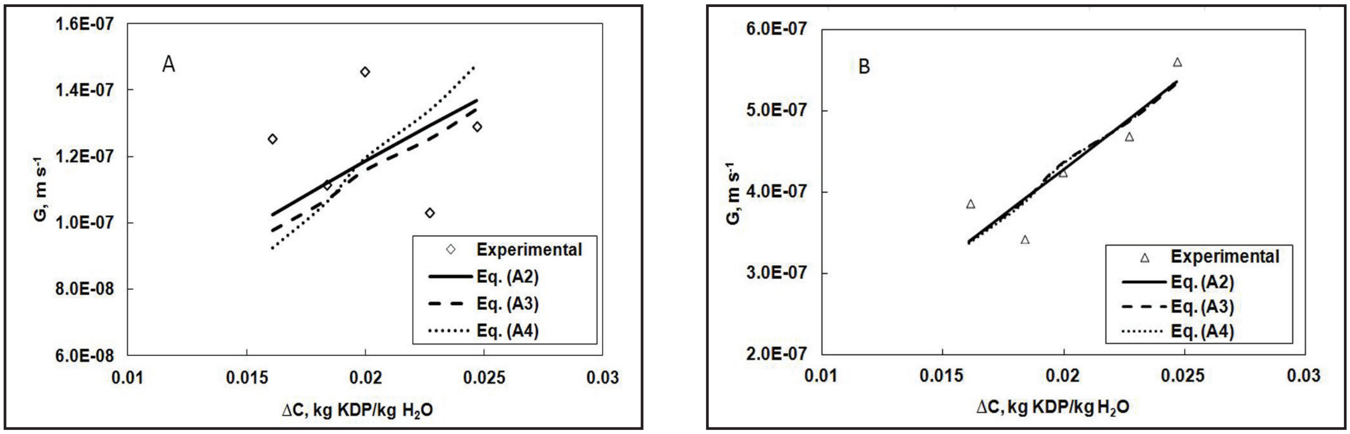

Figures 3. *Comparison of experimental and predicted results with crystal size measurement method (**A**) and desupersaturation method (**B**).*

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APPENDIX 1. SUPPORTING INFORMATION: INSTRUCTIONS FOR LABORATORY WORK

Introduction

Crystallization kinetics data can be used for design and sizing of industrial crystallizers and for selection of the operational conditions of a crystallization process. Crystal size distribution and the shape of the final crystalline product (the quality of the product) are mainly determined by the nucleation rate and crystal growth rate.

The laboratory exercise introduces a methodology to determine crystallization kinetics. Crystallization is initiated when nuclei (cluster of molecules of visible or detectable size) are formed in a supersaturated solution. This process is referred to as nucleation. The formed nuclei grow larger as long as the solution, *i.e.*, mother liquor, is supersaturated. The exercise comprises two parts; nucleation kinetics and crystal growth kinetics. The crystallization method used is cooling crystallization.

Model compound

Potassium dihydrogen phosphate, KH_2PO_4 and water as a solvent are used as the model system. The solubility data of KDP in water at different temperatures is needed to determine the driving force degree, *i.e.*, supersaturation, usually expressed by the difference between actual concentration and equilibrium concentration. KDP crystals are assumed to be cubic, the density of KDP crystals is 2340 kg/m^3, and the solubility of KDP can be taken from the literature.[2]

Nucleation rate

Nucleation rate B is a kinetic parameter presenting the generation rate of zero-sized nuclei per unit volume. The nucleation rate depends on supersaturation, mixing conditions in the stirred tank and the suspension density, *i.e.*, kg crystals per unit volume. In this laboratory exercise we investigate the nucleation rate of the cooling crystallization system as a function of supersaturation, Δc, as shown in Eq. (A1)[2]:

$$B = k_B \Delta c^i \qquad (A1)$$

where

k_B	constant
Δc	supersaturation, which is the difference between concentration c and solubility c*
i	constant
B	nucleation rate, number of nuclei m^{-3} s^{-1}

Crystal growth rate

The growth rate of a crystal is affected by many factors, such as supersaturation, mixing conditions, impurities present in the solution and additives. The section below shows commonly used equations and models for the crystal growth rate.

Kinetics of crystal growth can be described with a semi-empirical equation shown in Eq. (A2)[2]:

$$G = k_{G1} \Delta c^{g1} \qquad (A2)$$

where

G	linear crystal growth rate, m s^{-1}
k_{G1}, g1	constants

A model of the crystal growth rate mechanism has been introduced for crystal growth systems dominated by surface nucleation based the birth and spread model (B+S model). This model allows the spreading of nuclei at a finite constant rate that is assumed to be independent of crystal size. It also assumes that nuclei can form at any location, including in incomplete layers, and that there is no inter growth between the nuclei. The simplified expression of this model is[*1, 15*]:

$$G_{B+S} = A_{B+S}(S-1)^{5/6} \exp\left[-B_{B+S}/(S-1)\right] \qquad (A3)$$

A_{B+S}, B_{B+S}	constants
S	supersaturation ratio, $(=c/c^*)$, –
G_{B+S}	crystal growth rate based on B+S model

The following model has proven to be appropriate for crystallization systems in which crystal growth rate is dominated by screw dislocations on the crystal surface. According to the Burton-Cabrera-Frank (BCF) model, screw dislocations in the crystal are the source of new growth steps and crystal growth from these steps can occur continuously. In this model, surface diffusion is assumed to be the determining rate. The simplified expression can be described as[1, 15]:

$$G_{BCF} = A_{BCF}\left\lfloor (S-1)^2 / B_{BCF} \right\rfloor \tanh\left\lfloor B_{BCF} / (S-1) \right\rfloor \qquad \text{(A4)}$$

where

A_{BCF},B_{BCF}	constants
G_{BCF}	crystal growth based on BCF model

The crystal growth rate as a function of supersaturation can be determined by the batchwise desupersaturation curve technique introduced in the *Handbook of Industrial Crystallization*[1] and by Garside, *et al*.,[14] who presented a detailed description of the evaluation of crystal growth kinetics from a desupersaturation curve, shown in Figure A1, using initial derivatives. Only size-independent growth is considered. Growth rate dispersion is assumed to be negligible, and crystallization conditions are taken to be isothermal. For a batch crystallizer, mass deposition as a result of nucleation is negligible. The crystal growth kinetics can be computed with Eqs. (A5) to (A10).

$$G = \frac{R_G \beta}{3\alpha\rho_c} \qquad \text{(A5)}$$

$$R_G = k_{G2}\Delta c^{g2} \qquad \text{(A6)}$$

$$g2 = \frac{2\beta\Delta c_0}{3\alpha\rho_c \bar{L} A_T} + \frac{\Delta c_0 \Delta\ddot{c}_0}{\Delta\dot{c}_0^2} \qquad \text{(A7)}$$

$$k_{G2} = -\frac{\Delta\dot{c}_0}{A_T\left(\Delta c_0\right)^{g2}} \qquad \text{(A8)}$$

$$A_T = \frac{6m_{seed}\left[c^*\left(T_0\right)+1\right]}{\rho_c \bar{L} m_{solution}} \qquad \text{(A9)}$$

$$\Delta c = a_o + a_1 t + a_2 t^2 \qquad \text{(A10)}$$

where the values of $\Delta c_0 = a_o$, $\Delta\dot{c}_0 = a_1$, and $\Delta\ddot{c}_0 = 2a_2$ can be obtained from the fitted equation of the desupersaturation curve. Descriptions and units of the symbols are as follows:

A_T is the total crystal surface area at zero time, [$m^2\ kg^{-1}$ solvent], c^* the solubility [$kg\ kg^{-1}$ solvent], Δc the concentration driving force [kg/kg solvent], g2 the growth order [-], G the linear growth rate [$m\ s^{-1}$], k_{G2} the growth rate coefficient [$kg\ m^{-2}\ s^{-1}$ ($kg\ kg^{-1}$ solvent)^{g2}], $\bar{L}$ the average seed crystal size [m], R_G the growth rate [$kg\ m^{-2}\ s^{-1}$], $m_{solution}$ the mass of solution [kg], m_{seed} the mass of solution [kg], t the time [s], T_0 the initial temperature of solution [K], α the volume shape factor [-], β the surface area shape factor [-], and ρ_c the crystal density [kg/m^3]. The values of $\Delta c_0 = a_o$, $\Delta\dot{c}_0 = a_1$, and $\Delta\ddot{c}_0 = 2a_2$ can be obtained from the fitted equation of the desupersaturation curve in Figure A1.

Experimental measurements

Nucleation kinetics

An MTS PSyA laser reflection particle size analyzer is used to characterize the nucleation rate. It is assumed that the number of nuclei is directly proportional to the count rate increase of the PSyA analyzer, and the sampling volume of the analyzer is 1 ml. Nucleation kinetics of potassium dihydrogen phosphate, KH_2PO_4 (KDP) from water is studied. A saturated solution of KDP at room temperature is used in the experiments. Mixing intensity, which is supported by an up-pumping 4-pitched-blade turbine, is kept constant during the crystallization operation.

The experimental procedure is as follows:

1) Add 2.5 liter saturated KDP solution to a jacketed mixing tank.
2) Heat the solution 4°C above the saturation temperature. Keep the temperature constant for 10 min.
3) Cool the solution __˚C below the saturation temperature and initiate nucleation by adding 0.2 g KDP seeds to the solution.
4) Measure the count rate by MTS PSyA online probe until a constant level is reached.
5) Each group should measure a single data point. All data points obtained by the different groups are used in the calculations.

By assuming the count rate increase of the PSyA analyzer, dN (number/s) is directly proportional to the number of nuclei in the solution, and the analysis volume is 1 ml, the nucleation rate B (number $m^{-3}\ s^{-1}$) can be calculated as: $B = [(dN/dt)/V_{anal}]$. After obtaining the nucleation rate at different supersaturation

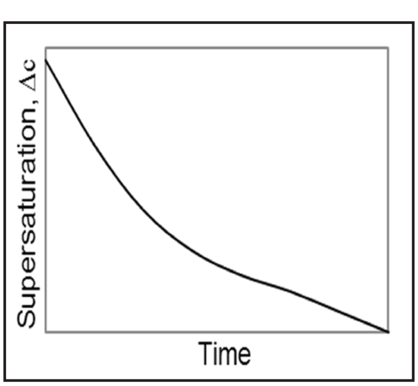

Figure A1. *Desupersaturation curve.*

levels, the parameters in Eq. (A1) can be obtained by fitting the measured data to the equation.

Crystal growth rate

Crystal size measurement (batch crystallization)

A saturated solution of KDP at room temperature is also used for investigating kinetic growth of KDP from water. Mixing is provided by an up-pumping 6-pitched-blade turbine, and the mixing intensity is kept constant for all experiments.

1. Weigh 300 g saturated solution into a 250-ml glass vessel. Heat the solution 4 °C above the initial temperature.
2. Cool the solution __°C below the saturation temperature following the teacher's instructions. The solution should be clear and primary nucleation before seeding has to be avoided.
3. Weigh 0.3 g seeds of KDP. Add the seeds to the supersaturated solution. Let the crystals grow for 30 min. Simultaneously, measure the electrical conductivity as a function of time. (Record the conductivity at every minute.)
4. Filter the crystals.
5. Measure the crystal size distribution of the seeds and final crystals with the Beckman Coulter LS 13320 laser diffraction analyzer. The background solution is ethanol. (KDP is poorly soluble in ethanol.)
6. Each group should measure a single data point. All data points obtained by the different groups are used in the calculations.

Crystal growth rate based on desupersaturation method

Derive the desupersaturation curve from the measured conductivity data. Here, it is assumed that the electric conductivity is linearly dependent on concentration over the studied concentration range. In addition, the initial and final concentration of the solution is assumed to be the saturated concentration at room temperature and the corresponding subcooled temperature. The parameters

$$y = ax + b \tag{A11}$$

where y is concentration and x is conductivity, can be obtained from the initial and final measured conductivity values and from the studied concentration range. The concentration range can be obtained from the used temperature range and solubility data. The whole supersaturation profile can then be computed with Eq. (A11).

Data treatment of obtained results

Data treatment for nucleation rate

Kinetic parameters k_B and i in Eq. (A1) are calculated by parameter fitting (method of least squares). Obtained results of experimental data and parameter fitting are shown in Figure 2 and Table 1.

Data treatment for crystal growth rate

Two different methods are used to find crystal growth rate as a function of supersaturation; ΔL/Δt-method and desupersaturation method. Methods are described in detail below. Obtained results of experimental data and parameter fitting are shown in Table 2 and Figure 3.

ΔL/Δt-method

In the ΔL/Δt-method, average size change over time is measured. ΔL is the difference between seeds and sample cumulative size distribution (median size at 50% of cumulative size distribution), and Δt is the measurement time. The method does not take into account the decrease of supersaturation during the measurement.

Desupersaturation method

The measured conductivity is converted to concentration and further supersaturation by linear fitting. Crystal growth rates are calculated from the fitted equation of the desupersaturation curve.

Report

Each group prepares a report that includes a description of the experimental procedure, testing equipment and experimental data, processing of the test data and results of measurements, and a conclusion and discussion. The teacher will assess the report and demand corrections if necessary.

The following elements form the major parts of the report.

1) Description of the experimental setting.
2) Solubility of KDP as a function of temperature.
3) Measured results:
    i. Supersaturations as concentration difference.
    ii. Nucleation rates with different supersaturations.
    iii. Measured growth rates for different supersaturations and crystal sizes.
4) Calculations:
    i. Find B = f(Δc) and fit parameters k_B and i in Eq.(A1).

TABLE A1

ΔL/Δt method and desupersaturation method of calculating crystal growth rate

ΔL/Δt	Desupersaturation method
ΔL is the difference between the seeds and the sample cumulative size distribution (median size).	Conductivity is translated to concentration by linear fitting $\varkappa(t_0,T_x) = c^*(T_{init})$ and $\varkappa(t_{end},T_x) = c^*(T_x)$. Then the desupersaturation curve can be obtained by calculation according to the linear equation.
Δt is the measurement time.	$\varkappa$ is conductivity, t_0 and t_{end} are initial time and ending time, and T_{init} and T_x are initial and final temperature, respectively.

ii. Find G = f(Δc) with two different methods, that is, the crystal size method (ΔL/Δt) and the desupersaturation method (see Table A1) and compare the results. Any method for parameter fitting can be used, however use of the least square method is recommended. Fit the obtained data of concentration as a function of time to the desupersaturation model. Fit the obtained data of crystal growth rates as a function of supersaturation to Eqs. (A3) and (A4). Compare the obtained fitting results to determine the crystal growth mechanism. ❐