

CALCULATION OF THE KINETICS OF CRYSTALLIZATION BASED ON A SINGLE BATCH EXPERIMENT

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The kinetics of crystal growth and nucleation in dependence on the supersaturation of a solution of KCl were evaluated based on a single batch crystallization experiment, where the supersaturation was monitored refractometrically and the product crystal size distribution was established at the end of the experiment. The crystal growth kinetic data obtained compare well with published values. For the nucleation data the agreement is less satisfactory.

Kinetic data of crystallization are routinely derived from model experiments using mixed suspension – mixed product removal (MSMPR) crystallizers¹. In the case of the experimentally simpler batch crystallization, we can confine ourselves to the approximate problem solution^{2,3} or to the determination of the kinetics of growth at a negligible nucleation⁴⁻⁸, or else the shift of the crystal size distribution during the batch experiment can be solved^{9,10}.

This paper describes a relatively simple method for the determination of the kinetic constants of crystallization based on a single batch experiment, where the supersaturation is monitored during the experiment⁸ and the back shift of the size distribution of the product crystals is measured¹⁰.

THEORETICAL

In the discontinuous crystallization experiment we start from a solution saturated at a temperature T_0 , which is seeded with several crystals of the substance and then cooled to a temperature T_f following a suitable temperature program. During the experiment, the temperature and the concentration are measured, the latter conductometrically, densimetrically, refractometrically or the like. After attaining temperature T_f , the constantly stirred suspension is allowed to reach the equilibrium, the crystals are collected and dried, and their size distribution is established.

So, ultimately we have available a series of time t (s) – temperature T (°C) – concentration w (kg per kg of free solvent) data, and the crystal size distribution, which can be expressed as¹¹

$$M(L) = w_1 M(z_1) + (1 - w_1) M(z_2), \quad (1)$$

where

$$M(z_i) = 100(1 + z_i + z_i^2/2 + z_i^3/6) \exp(-z_i) \quad (2)$$

$$z_1 = 3(L - L_N)(L_m - L_N)^{-1} \quad (3)$$

$$z_2 = 3(L - L_0)(L_m - L_N)^{-1} \quad (4)$$

or, for a simple single-peak distribution, only by Eqs (2) and (3). The total mass of the product is

$$m_c = m_o(w_0 - w_f), \quad (5)$$

where m_o is the mass of the free solvent in the batch. The number of crystals is

$$N_c = 2m_c[9\alpha\varrho_c L_m^3 f(z_N)]^{-1}, \quad (6)$$

where

$$f(z_N) = 1 + z_N + z_N^2/2 + z_N^3/6 \quad (7)$$

$$z_N = 3L_N(L_m - L_N)^{-1}. \quad (8)$$

Now, we divide the product into a sufficiently high number (k) of size fractions (for instance, $k = 100$); the number of crystals in the i -th fraction will be

$$N_{c(i)} = N_c[\exp(-z'_1) - \exp(-z'_2)], \quad (9)$$

where

$$z'_1 = 3(L_i - L_N)(L_m - L_N)^{-1} \quad (10)$$

$$z'_2 = 3(L_i - L_N + \Delta L)(L_m - L_N)^{-1} \quad (11)$$

and ΔL is the fraction width. The mass of crystals in this fraction is

$$m_{c(i)} = \alpha\varrho_c N_{c(i)} L_i^3. \quad (12)$$

The total mass of the crystals then is

$$m_{c(t)} = \sum_{i=1}^k m_{c(i)}. \quad (13)$$

For the individual time segments (counted from the end of the experiment), a loss in the crystal size y ,

$$y = L_{i(t)} - L_{i(t-1)}, \quad (14)$$

is then sought iteratively so that the total crystal mass (13) just corresponds to the

mass balance

$$m_{c(t)} = m_o(w_o - w_t). \quad (15)$$

The crystal growth rate is given by the relation

$$\dot{L} = (L_{i(t-1)} - L_{i(t)}) (\Delta t)^{-1} \quad (16)$$

and the nucleation rate is

$$\dot{N}_N = \Delta N (\Delta t m_o)^{-1}, \quad (17)$$

where

$$\Delta N = N_{c(t-1)} - N_{c(t)} \quad (18)$$

is the number of crystals in the vanished fractions, for which $L_{i(t-1)} \leq 0$.

Supersaturation in time t is determined as

$$\Delta w = w_t - w_{eq,t}, \quad (19)$$

solubility w_{eq} being calculated by means of the relations¹²

$$\log x = A + B(T + 273.15)^{-1} + C \log (T + 273.15) \quad (20)$$

$$w = [18.015/M_{hyd}(1/x - 1) + M_{anh}/M_{hyd} - 1]^{-1}. \quad (21)$$

The \dot{L} and \dot{N}_N points calculated for the individual time segments then are fitted by curves using the relations

$$\dot{L} = k'_G \Delta w^g \quad (22)$$

$$\dot{N}_N = k'_N \Delta w^n \quad (23)$$

EXPERIMENTAL

The apparatus is shown schematically in Fig. 1. It consists of a duplicated glass crystallizer C fitted with a two-paddle agitator A and a baffle B. Its temperature is controlled by a thermostat TH and a pump P, a resistance thermometer T and heating H; the thermostat is activated by a temperature programmer TP by which the starting temperature T_0 and the cooling rate can be adjusted. The temperature of the solution in the crystallizer is measured with the resistance thermometer T, and via the bridge TB the signal is fed to a line recorder LR. The concentration of the solution is measured continuously by means of a recording immersion refractometer^{13,14,20}, working on the principle of measurement of light passed through a bent glass rod (light guide) dipped in the suspension; the signal is fed also via the bridge RB to the line recorder LR.

Calibration of the refractometer was performed using pure water and aqueous solutions of KCl saturated at 20°C. Refractive index values of KCl solutions at 30°C were taken from ref.¹³ The data are summarized in Table I. Measurements with water gave the dependences

$$E(T) = 2.048 - 34.2T \quad (24)$$

$$E(n) = 2.3584 \Delta n, \quad (25)$$

TABLE I
Calibration of refractometer

T °C	w^a	n^b	$\Delta n \cdot 10^4$	E mV
Temperature calibration				
20	—	1.3330	—	1 360
30	—	1.3319	—	1 040
40	—	1.3305	—	660
50	—	1.3289	—	340
60	—	1.3272	—	0
Concentration calibration				
30	0	1.3320	0	0
30	0.1	1.3458	138	3 607.6
30	0.2	1.3595	275	6 754.1
30	0.3	1.3732	412	9 435.5
30	0.35	1.3801	481	10 601.9

^a Concentration of KCl, in kg per kg free solvent; ^b $n(\text{H}_2\text{O})$ for temperature calibration measurements, $n(\text{KCl})$ at 30°C for concentration calibration measurements^{1,3}.

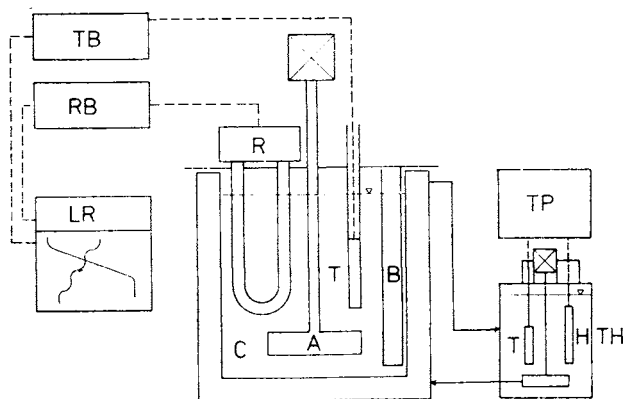


FIG. 1
Layout of the apparatus used

measurements with solutions of KCl led to the following concentration dependences:

$$E(w) = 38\,441w - 23\,253w^2 \quad (26)$$

$$\Delta w = 2.411 \cdot 10^{-5} \Delta E + 16.4 \cdot 10^{-10} \Delta E^2. \quad (27)$$

The effect of temperature on the output signal can be determined from Eq. (24) as

$$\Delta E(T) = -34.2(T - T_0). \quad (28)$$

Similarly, Eq. (26) in conjunction with the relation

$$\Delta E(w) = E(w) - E(w_0) \quad (29)$$

determines the concentration dependence of the output signal. The subscript 0 denotes reference values at which the bridge RB gives a zero signal. The corrected value of the signal for the calculation of supersaturation from Eq. (27) then is obtained from the relation

$$\Delta E = \Delta E(\text{exper}) - \Delta E(T) - \Delta E(w). \quad (30)$$

The model experiment was performed using a solution of KCl at a concentration of $w_0 = 0.4700$ kg/kg₀, which is saturated at 64°C. This solution was cooled until crystals separated, and then heated to 60.6°C. The amount of the solution in the crystallizer was such that the mass of water in it was $m_0 = 550$ g. The suspension was cooled at a rate of 20 K/h to $T_f = 28.9^\circ\text{C}$ and then held at this temperature for 20 min; thereafter the crystals were collected, dried and subjected to sieve analysis. The temperature and the signal from the refractometer were recorded during the experiment. In a preliminary experiment, the dependence

$$T = 12.25 + 0.01074E \quad (31)$$

was found.

RESULTS AND DISCUSSION

The KCl crystal size distribution from the model experiment is given in Table II and shown in Fig. 2. The data give $L_N = 0.06$ mm, $L_m = 0.576$ mm $((L_m - L_N)/3 =$

TABLE II
Size distribution of product crystals

L_i mm	$M(L_i)$ wt. %	L_i mm	$M(L_i)$ wt. %
1.20	14.20	0.40	91.81
1.00	23.50	0.30	96.99
0.75	31.89	0.20	99.35
0.60	46.29	0.10	99.78
0.50	79.35	0.08	100.00

= 0.172 mm). The solubilities were calculated for the molecular mass $M = 74.551$ from Eqs (20) and (21) using the constants $A = 6.75911$, $B = -604.3346$ and $C = -2.357042$. The data are given in Table III. The kinetics of crystallization was evaluated by using Eqs (5)–(19), inserting $\alpha = 1$, $\beta = 6$, $\rho_c = 1.989 \text{ kg m}^{-3}$. The results are summarized in Table IV. The $m_c(L)$ dependence for the various time segments is shown in Fig. 3.

In relation to the linear growth rate data, the fact that they are polythermal over the range of 30–60°C must be taken into account. To eliminate the temperature dependence of the crystal growth rate we can start from the theoretical relation¹⁵

$$(d \ln \dot{L}) / (d \ln w_{eq}) \approx [d \ln (Dw_{eq})] / [d (1/T)]. \quad (32)$$

TABLE III
Calculation of supersaturation

t min	T °C	w_{eq} kg kg_0^{-1}	E mV	$\Delta w \cdot 10^3$ kg kg_0^{-1}
140	28.9	0.3685	630	0
120	32.5	0.3793	600	1.766
100	37.4	0.3939	560	3.958
80	42.0	0.4074	520	5.698
60	47.0	0.4219	500	7.884
40	51.7	0.4354	430	8.364
20	56.3	0.4484	380	9.021
0	60.6	0.4605	340	9.556

TABLE IV
Evaluation of crystallization kinetics

t min	T °C	$\Delta w \cdot 10^5$ kg kg_0^{-1}	N_c kg_0^{-1}	$m_c \cdot 10^2$ kg	$\dot{L} \cdot 10^8$ m s^{-1}	\dot{N}_N $\text{kg}_0^{-1} \text{ s}^{-1}$	$\dot{L}_{30} \cdot 10^8$ m s^{-1}
140	28.9	0	649 879	5.58	0.08	0	0.08
120	32.5	177	649 879	4.89	0.75	0	0.75
100	37.4	396	649 879	3.97	3.00	0	2.90
80	42.0	570	478 093	3.13	3.42	260	3.19
60	47.0	788	351 716	2.21	5.00	191	4.52
40	51.7	836	221 928	1.44	6.08	197	5.34
20	56.3	902	120 108	0.69	10.60	154	9.06

If D and w_{eq} depend on temperature in roughly the same manner, we can write

$$(\text{d} \ln \dot{L})/(\text{d} \ln w_{\text{eq}}) = 0.5. \quad (33)$$

The corresponding correction provided \dot{L} values transformed to a temperature of 30°C, which are included in Table IV. Correlation according to Eq. (22) gave the following result:

$$\dot{L} = 1.58 \cdot 10^{-5} \Delta w^{1.19}. \quad (34)$$

Since we have

$$\dot{L} = k'_G \Delta w^g = k_G [\beta/(3\alpha Q_c)] \Delta w^g, \quad (35)$$

we can derive the growth rate constant value of $k_G = 1.57 \cdot 10^{-2}$. From published data¹⁵ reported for concentrations given in the relative supersaturation values $\sigma' = \Delta w/w_{\text{eq}}$, it follows that $k''_G = 2.59 \cdot 10^{-6}$, $g = 1$. Converting with respect to the supersaturation units, $k'_G = k''_G/w_{\text{eq}} = 2.59 \cdot 10^{-6}/0.38 = 6.82 \cdot 10^{-6}$, we obtain the relation

$$\dot{L} = 6.82 \cdot 10^{-6} \Delta w, \quad (36)$$

which compares very well with the results of the present work, as Fig. 4 demonstrates.

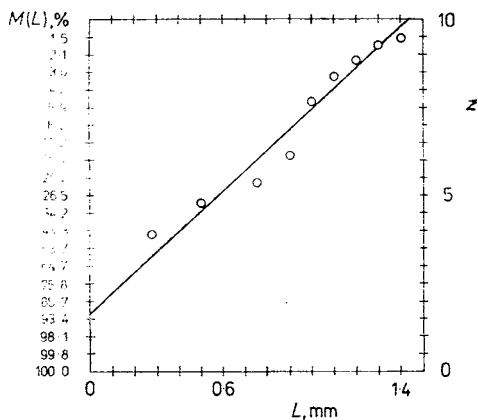


FIG. 2
Product crystal size distribution

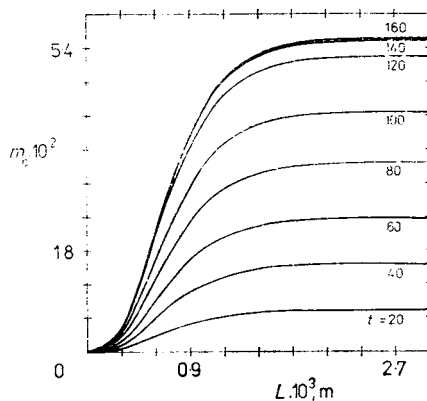


FIG. 3
Development of crystal size distribution —
cumulative distribution in dependence on
time (min)

The nucleation data correlation is considerably poorer because of their high variance. Assuming the validity of Eq. (23) we obtain

$$\dot{N}_N = 7.8 \cdot 10^7 \Delta w^{2.76}. \quad (37)$$

The nucleation exponent values reported in the literature^{15,16} are rather spread, viz. $n = 6.54$ and $n = 3.56$. Since these values have been derived based on the metastable region width, whereas in the model experiment in this work secondary nucleation took place, a lower n value can be expected. The coefficient of secondary nucleation, defined as¹⁵

$$\sigma = 1 - n/n^* \quad (38)$$

takes here the values of 0.22 and 0.58, respectively. Correlation (37) and the curves corresponding to the published nucleation exponents are shown in Fig. 5.

Published kinetic data of crystallization are frequently reported in the form of the equation

$$\log \dot{N}_N = \text{const} + (n/g) \log \dot{L}. \quad (39)$$

Data reported in this work provide the relation

$$\log \dot{N}_N = 19.029 + 2.32 \log \dot{L}, \quad (40)$$

whereas the relations given in refs^{18,19} correspond to the equations

$$\log \dot{N}_N = 21.390 + 2.55 \log \dot{L} \quad (41)$$

and

$$\log \dot{N}_N = 40.065 + 4.99 \log \dot{L}, \quad (42)$$

respectively. These kinetic data have been derived from model experiments on a continuous MSMPR crystallizer. Relations (40)–(42) are compared in Fig. 6.

Finally, Fig. 7 shows the course of supersaturation in the model experiment, calculated from the kinetic data by successively solving the equations

$$\Delta w(t) = \Delta w(t-1) + s - k_G A_c \Delta w^g - k_N \Delta w^n \quad (43)$$

$$A_c = N_c(t) \beta L(t)^2 \quad (44)$$

$$L(t) = L(t-1) + \dot{L}(t-1) \quad (45)$$

$$N_c(T) = k'_N \Delta w^n \quad (46)$$

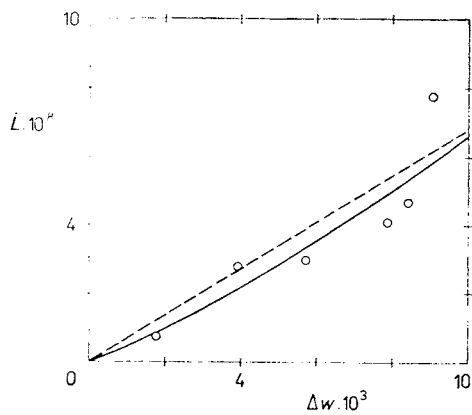


FIG. 4
Linear growth rate of crystals as a function of supersaturation. — this work, --- ref.¹⁵

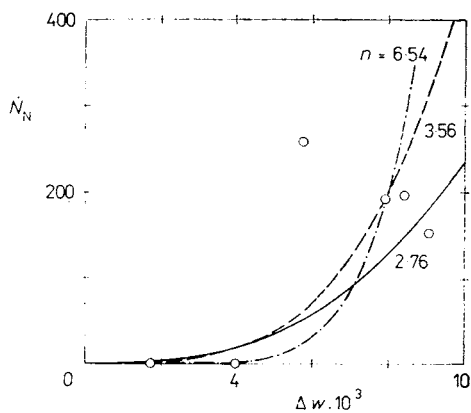


FIG. 5
Rate of nucleation as a function of supersaturation. The numbers indicate nucleation exponent values

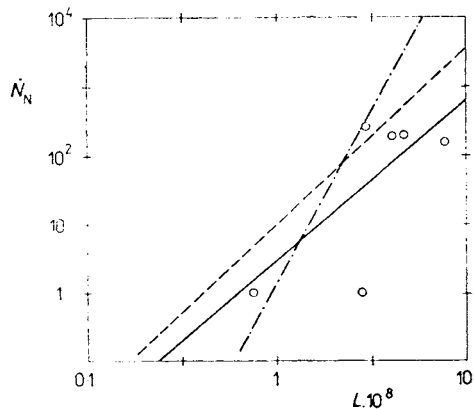


FIG. 6
Interdependence of the rate of nucleation and the linear growth rate (in logarithmic coordinates; curve labelling as in Fig. 5)

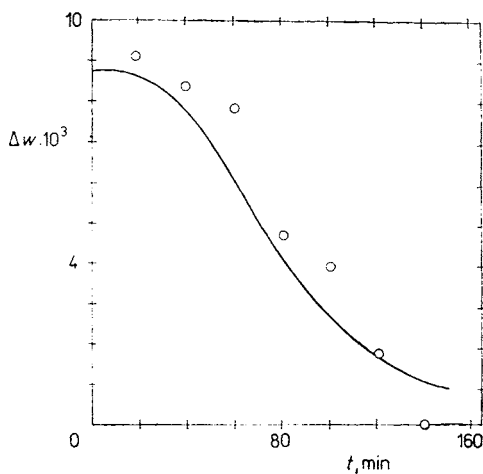


FIG. 7
Course of supersaturation calculated from model equations

as has been described in detail previously¹⁷. The points in the plot are experimental values of the $\Delta w/\Delta w_{\max}$ ratio.

LIST OF SYMBOLS

A, B, C	constants in Eq. (20)
E	output signal, mV
f	function defined by Eq. (7)
g	growth kinetics order
i	summation subscript
k	number of crystal fractions
k_G	growth rate constant, $\text{kg}^{1-\theta} \text{kg}_0^\theta \text{m}^{-2} \text{s}^{-1}$
k'_G	growth rate constant, m s^{-1}
k_N	nucleation rate constant, $\text{kg}^{1-n} \text{kg}_0^{n-1} \text{s}^{-1}$
k'_N	nucleation rate constant, $\text{kg}_0^{-1} \text{s}^{-1}$
L	crystal size, m
L_0	smallest crystal size in coarse fraction
L_N	initial crystal size
\dot{L}	linear growth rate of crystals, m s^{-1}
$M(L)$	oversize crystal fraction, wt. %
M_{anh}	molecular mass, kg kmol^{-1}
M_{hyd}	molar mass of hydrate, kg kmol^{-1}
m_c	mass of crystals separated, kg
m_o	mass of solvent, kg
N_c	number of crystals in batch
\dot{N}_N	rate of nucleation, $\text{kg}_0^{-1} \text{s}^{-1}$
n	kinetic order of nucleation
n	refraction index (Table I)
T	temperature, °C
t	time, s
w	concentration, kg kg_0^{-1}
w_{eq}	solubility, kg kg_0^{-1}
w_1	mass fraction of fine crystal fraction
Δw	supersaturation, kg kg_0^{-1}
x	mole fraction
y	crystal size decrease, m
z	dimensionless crystal size
z_N	dimensionless initial crystal size
α	volume shape factor
β	surface shape factor
ρ_c	crystal density, kg m^{-3}
σ	coefficient of secondary nucleation
σ'	relative supersaturation

Subscripts

0	starting
f	final

m mean value
t in time t

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