

## THE EFFECT OF KINETIC PARAMETERS ON DISCONTINUOUS CRYSTALLIZATION PROCESS

J. NÝVLT

*Research Institute of Inorganic Chemistry, 40060 Ústí n. L.*

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The discontinuous crystallization process is simulated on a computer using various input kinetic parameters. The results of the simulation — the transient course of supersaturation and the crystal size distribution (CSD) of the product — markedly depend on kinetic parameters of nucleation and growth of the crystals. The CSD of the product can be expressed by semiempirical equations containing theoretically derived groups of system and process parameters. The transient course of supersaturation is expressed by a differential equation to which an empirical approximate solution is proposed.

The attempts to characterize discontinuous crystallization process have been numerous in the literature<sup>1-9</sup>. In some of these papers theoretical relations have been derived characterizing for instance CSD of the product under certain simplifying assumptions regarding either the supersaturation or the course of nucleation. These assumptions were made for the sake of making the pertaining equations amenable to mathematical methods of solution. On the other hand it is quite uncertain to what extent these assumptions are met in practical batchwise crystallization process. Nevertheless, the obtained equations do offer certain means of evaluation of the crystallization process and the possibility of assessing which of the quantities will affect the result of crystallization.

The aim of this work is to ascertain the extent to which individual kinetic constants characterizing the system in question may affect the crystallization process and to attempt correlation of the input parameters and the result of crystallization.

### THEORETICAL

#### *The Transient Course of Supersaturation*

The discontinuous crystallization process may be characterized by the following differential balance of supersaturation

$$d \Delta w / dt = s - k_G A \Delta w^{\mathbf{a}} - k_N \Delta w^{\mathbf{a}}, \quad (1)$$

where all terms are functions of time. If the temperature during crystallization follows

the course given by

$$\frac{T_0 - T_t}{T_0 - T_e} = \left(\frac{t}{t_e}\right)^X \quad (2)$$

the supersaturation rate may be written as

$$s = X(T_0 - T_e) t^{X-1} t_e^{-X}. \quad (3)$$

Neglecting the temperature dependence of the kinetic parameters one still has to specify the transient growth of the surface area of the crystals

$$A = \int_0^t \beta \dot{N}(t) L^2(t) dt \quad (4)$$

where  $\dot{N}(t)$  and  $L(t)$  are functions of supersaturation

$$\dot{N}(t) = k_N \Delta w^a(t) / \alpha \rho_c L_N^3, \quad (5)$$

$$L(t) = L_N + [k_G \Delta w^b(t) / 3\alpha \rho_c]. \quad (6)$$

Analytical solution to the above integro-differential equation has not been known<sup>3</sup> which has led to the proposal of a numerical solution by steps<sup>7</sup>. In order that we may approximate the resulting time dependence of supersaturation by empirical relations the whole process must be subdivided into two individual parts: The ascending and the descending one separated by a maximum at a time  $t_{\max}$ . Providing that we start from solutions of zero supersaturation and no seeding the formed supersaturation depends initially on time, namely

$$\Delta w = s dt \sim (t/t_{\max})^X. \quad (7)$$

With increasing supersaturation the crystals become more and more numerous and their surface area increases too, which ultimately causes the supersaturation to decrease

$$-d \Delta w / dt \sim X \Delta w. \quad (8)$$

This means

$$\Delta w \sim (t/t_{\max})^X \exp(-Xt/t_{\max}). \quad (9)$$

Let us therefore assume that the ascending part of the  $\Delta w - t$  curve may be generally

approximated by the following equation

$$\Delta w = at^x \exp(-bt), \quad (10)$$

where  $x$  may take arbitrary adjustable values.

From the condition for a maximum one obtains

$$b = x/t_{\max}, \quad (11)$$

$$a = (e^x/t_{\max}^x) \Delta w_{\max}. \quad (12)$$

Hence

$$\Delta w/\Delta w_{\max} = (t/t_{\max})^x e^{x(1-t/t_{\max})} \quad [t \leq t_{\max}]. \quad (13)$$

After some arrangement to obtain a form convenient for calculation we have

$$\log(\Delta w/\Delta w_{\max}) = x \cdot f(t) \quad [t \leq t_{\max}], \quad (14)$$

where  $f(t)$  is given by

$$f(t) = \log \frac{t}{t_{\max}} + \left(1 - \frac{t}{t_{\max}}\right)/2.303 \quad (15)$$

and takes the values shown in Table I.

TABLE I  
Values of  $f(t)$  defined in Eq. (15)

$t/t_{\max}$	$-f(t)$	$t/t_{\max}$	$-f(t)$
0.1	0.6087	1.3	0.0165
0.2	0.3512	1.4	0.0278
0.3	0.2186	1.5	0.0413
0.4	0.1370	1.6	0.0568
0.5	0.0836	1.7	0.0739
0.6	0.0479	1.8	0.0925
0.7	0.0245	1.9	0.1125
0.8	0.0099	2.0	0.1338
0.9	0.0023	3.0	0.3925
1.0	0.0000	4.0	0.7022
1.1	0.0021	5.0	1.4749
1.2	0.0078	10.0	3.3478

The curve given by Eq. (13) or (14) is asymmetric and for  $t > t_{\max}$  approaches asymptotically  $\Delta w = 0$ . This course could obviously agree with the reality only in the absence of supersaturating the solution. At the supersaturation rate increasing according to Eq. (3), however, the supersaturation steadies down to reach the final value  $\Delta w_{\text{eq}}$  and for the end of the experiment one can write that

$$s_e = k_G A_e \Delta w_e^g. \quad (16)$$

The balance of supersaturation (1) then takes the following approximate form

$$d \Delta w / dt = k_G A_e (\Delta w^g - \Delta w_e^g) + k_N \Delta w_e^n. \quad (17)$$

Assuming that supersaturation  $\Delta w_e$  is sufficiently low to make nucleation negligible one obtains for the frequent case of  $g = 1$  that

$$\Delta w - \Delta w_e \sim \exp(-k_G A t), \quad (18)$$

$$\Delta w_{\max} - \Delta w_e \sim \exp(-k_G A t_{\max}), \quad (19)$$

$$\frac{\Delta w - \Delta w_e}{\Delta w_{\max} - \Delta w_e} \sim \exp(-k_G A t_{\max}(1 - t/t_{\max})). \quad (20)$$

Considering that the supersaturation rate varies with time according to Eq. (3) one can write with respect to Eq. (7) that

$$\frac{\Delta w - \Delta w_e}{\Delta w_{\max} - \Delta w_e} = \left(\frac{t}{t_{\max}}\right)^y e^{y(1-t/t_{\max})} \quad (t \geq t_{\max}) \quad (21)$$

or

$$\log \frac{\Delta w - \Delta w_e}{\Delta w_{\max} - \Delta w_e} = y \cdot f(t) \quad (t \geq t_{\max}) \quad (22)$$

and compare the last two equations with Eqs (13) and (14).

The equations of both curves are formally similar and differ only in the value of the exponent  $x$  or  $y$  and the limiting value  $\Delta w_e$ . Their characteristics are the position of the maximum ( $t_{\max}$ ,  $\Delta w_{\max}$ ) and other points such as the inflection point

$$t_i = t_{\max}(1 \pm x^{-1/2}), \quad (23)$$

$$\log(\Delta w_i / \Delta w_{\max}) = x / \log(1 \pm x^{-1/2}) \pm 0.4342x^{-1/2}. \quad (24)$$

The last equation may be approximated by

$$\Delta w_i / \Delta w_{\max} = 0.6 + 0.135x^{-1/2} \quad (t_i > t_{\max}). \quad (25)$$

### *The Crystal Size Distribution of the Product*

The relations describing the CSD of the product of a discontinuous crystallizer obtained under certain simplifying assumptions were summarized in the preceding paper<sup>4</sup>. On the assumption of constant rate of nucleation throughout the process we have obtained

$$(L_{\max}/L_N)^{1+3g/n} = B t_e^{1-g/n} m_c^{g/n}, \quad (26)$$

where

$$B = (4.5)^{g/n} k_G \beta / (3 / (3\alpha \varrho_c L_N k_N^{g/n})). \quad (27)$$

The distribution function of the size of the crystals is described by

$$M(L) = 100[1 - (L/L_{\max})^4]. \quad (28)$$

For the case of a spontaneous nucleation at the onset of the crystallization process we have derived

$$(L_{\max}/L_N)^2 [(L_{\max}/L_N) - 1] \approx \frac{2}{3}(n+1)(T_0 - T_c)/\Delta T_{\max} \quad (29)$$

and for the distribution function of the crystal size

$$M(L) \approx 100(1 + z + z^2/2 + z^3/6) \exp(-z), \quad (30)$$

where

$$z = (L - L_N)/(k_L \dot{L} t_e). \quad (31)$$

If the approximations

$$m_c \approx (T_0 - T_c) \cdot (dw_{eq}/dT), \quad (32)$$

$$m_N \approx 2(n+1)^{-1} \Delta T_{\max} \cdot (dw_{eq}/dT) \quad (33)$$

used in the derivation of Eq. (29) are substituted back together with

$$L_{\max} - L_N = k_L \dot{L} t_e = k_L \cdot (k_G \beta \Delta w^g / 3\alpha \varrho_c) t_e \quad (34)$$

one obtains

$$(L_{\max}/L_N)^2 (k_G \beta \Delta w^g t_e k_L / 3\alpha \varrho_c L_N) = \frac{4}{3}(m_c/m_N). \quad (35)$$

The distribution function can be shown to take then the form

$$m_c \approx \frac{2}{9}(3/k_L)^3 N\alpha\varrho_c L_{\max}^3 \quad (36)$$

and since

$$m_N = N\alpha\varrho_c L_N^3 \quad (37)$$

one obtains

$$k_G\beta \Delta w^g t_e k_L / 3\alpha\varrho_c L_N \approx 8L_{\max}/k_L^3 L_N. \quad (38)$$

From the viewpoint of the kinetics of nucleation the average supersaturation may be approximated from

$$m_N \approx k_N \Delta w^n t_e \quad (39)$$

and with regard to Eqs (36) and (37) one can write

$$\Delta w \approx \left( \frac{4 \cdot 5 m_c (L_N/L_{\max})^3}{k_N t_e (3/k_L)^3} \right)^{1/n}. \quad (40)$$

On substituting into Eq. (38) and after some arrangement we have

$$(L_{\max}/L_N)^{1+3g/n} \approx k_L^{3(1+g/n)} / (2^3 \cdot 6g/n) B m_c^{g/n} t_e^{1-g/n}. \quad (41)$$

Comparing the result with Eq. (26) derived for entirely different conditions one finds that the two equation differ only by the coefficient. It may be therefore expected that for other so far uninvestigated conditions of batchwise crystallization the following equation would hold

$$(L_{\max}/L_N)^{1+3g/n} = f(B, m_c, t_e, g/n). \quad (42)$$

### Simulation of Experimental Data

A series of discontinuous crystallization experiments was simulated on a Minsk computer using the program described in the preceding communication<sup>7</sup>. Similarly as in the earlier communication the system was characterized by the following constants:

$$\alpha = 0.45; \quad \beta = 3.8; \quad \varrho_c = 1985.0; \quad c_a = 4.15 \cdot 10^6;$$

$$E_s = 8\,624.7; \quad L_N = 1 \cdot 10^{-4} \text{ m}; \quad g = 1.0; \quad E_G = 3000; \quad E_N = 0.$$

Other constants of the system ( $k_G, k_N, n$ ) were varied in such a manner as to ascertain their effect on the course of crystallization. The nucleation order was varied simultaneously with the constant of nucleation so as to keep the rate of nucleation  $\dot{m}_N = k_N \Delta w^n$  approximately constant. The values of the selected parameters are summarized in Tables II and III.

TABLE II  
Summary of Simulated Experiments without Seeding

No	$t_e$	$k_G$	$k_N$	$n$	$B$	$L_{\max}/L_N$
1	240	5.48	1.65	3.71	101.8	10.3
2	240	0.548	1.65	3.71	10.18	6.1
3	240	54.8	1.65	3.71	1 018.0	23.5
4	240	5.48	0.165	3.71	189.6	12.7
5	240	5.48	16.5	3.71	54.8	8.6
6	240	5.48	0.103	1.71	707.9	8.0
7	240	5.48	0.413	2.71	187.3	9.3
8	240	5.48	6.6	4.71	71.6	10.9
9	240	5.48	26.4	5.71	57.0	11.5
11	120	5.48	1.65	3.71	101.8	4.7
12	120	0.548	1.65	3.71	10.18	2.0
13	120	54.8	1.65	3.71	1 018.0	16.0
14	120	5.48	0.165	3.71	189.6	6.7
15	120	5.48	16.5	3.71	54.8	4.0
16	120	5.48	0.103	1.71	707.9	4.0
17	120	5.48	0.413	2.71	187.3	4.3
18	120	5.48	6.6	4.71	71.6	5.0
19	120	5.48	26.4	5.71	57.0	5.3

The crystallization process was characterized by the following numerical constants:

$$X = 3; \quad t_e = 120 \quad \text{or} \quad 240 \text{ min}; \quad T_0 = 40.0; \quad T_c = 30.0.$$

No seeding was considered except for one test series of experiments when we took:  $m_0 = 0.005$ ;  $L_0 = 5 \cdot 10^{-4}$  m. The length of the time step was taken 12 s, which proved in the preceding runs<sup>7,9</sup> to be satisfactory from the standpoint of the stability of numerical solution.

The results of the runs are plotted in Figs 1 through 5 and some of the data are given in Tables II and III.

## DISCUSSION

All computer runs were carried out with the same cooling program given by Eq. (2) with  $X = 3$ . It is not therefore surprising that the transient development of supersaturation exhibits a very similar course. The extent to which the curve follows Eqs (13) and (22) can be assessed from Fig. 3 plotting  $\Delta w/\Delta w_{\max}$  as a function of  $t/t_{\max}$  for the data from the run 11 and compared with the theoretical curves (13) and (22) for condition that

$$\Delta w_e = \Delta w_i/2.$$

TABLE II  
(continued)

$t_{\max}$	$\Delta w_{\max}$	$10^3 L_{\max}$ (43)	$10^3 L_{\max}$ (44)	$\Delta L_{\max}$ (43)	$\Delta L_{\max}$ (44)
104	0.109	0.96	1.02	0.07	0.01
132	0.182	0.26	0.54	0.35	0.09
76	0.049	3.43	1.92	1.08	-0.43
116	0.168	1.36	1.21	-0.09	0.06
88	0.067	0.68	0.86	0.18	0.00
84	0.048	0.81	0.84	-0.01	-0.04
96	0.081	0.90	0.74	0.03	-0.01
104	0.130	1.02	1.07	0.07	0.02
112	0.147	1.06	1.12	0.09	0.00
60	0.152	0.48	0.47	-0.01	0.00
76	0.242	0.14	0.25	0.06	-0.05
44	0.072	1.72	0.89	-0.12	+0.71
68	0.239	0.68	0.56	-0.01	0.11
52	0.091	0.34	0.40	0.06	0.00
54	0.084	0.40	0.40	0.00	0.00
56	0.124	0.45	0.44	-0.02	-0.01
60	0.172	0.51	0.49	-0.01	0.01
62	0.187	0.53	0.51	0.00	0.02

TABLE III  
Summary of Simulated Experiments with Seeding

No	$t_e$	$k_G$	$k_N$	$n$	$L_{\max}/L_N$	$t_{\max}$	$\Delta w_{\max}$
21	240	5.48	1.65	3.71	10.2	100	0.106
22	240	0.548	1.65	3.71	6.2	140	0.182
23	240	54.8	1.65	3.71	24.8	84	0.028
24	240	5.48	0.165	3.71	12.5	120	0.160
25	240	5.48	16.5	3.71	8.7	92	0.066
26	240	5.48	0.103	1.71	8.0	88	0.047
27	240	5.48	0.413	2.71	9.3	100	0.080
28	240	5.48	6.6	4.71	11.0	112	0.127
29	240	5.48	26.4	5.71	11.4	116	0.143



As may be apparent the simulated experimental data are satisfactorily fitted by the above equations for the values of the adjustable parameters  $x = 12$  and  $y = 45$  with that the times closer to  $t_{\max}$  are better described by higher  $x$  and  $y$  while the times close to zero are better described in the limit by the value  $x = X = 3$ . For times  $t \gg t_{\max}$  the optimum value of  $y$  would be also lower than the mean 45. Similarly one could correlate also the other curves. Owing to the character of Eqs (13) and (22) being only very rough approximation it would not be sensible to attempt to correlate  $x$  or  $y$  with the system parameters.

An attempt to correlate  $\Delta w_{\max}$  with  $L_{\max}/L_N$  yielded a very interesting dependence shown in Fig. 4. Undoubtedly the points corresponding to the runs with the same  $k_G$  lie very closely on straight lines characterized by the time of duration of the batch

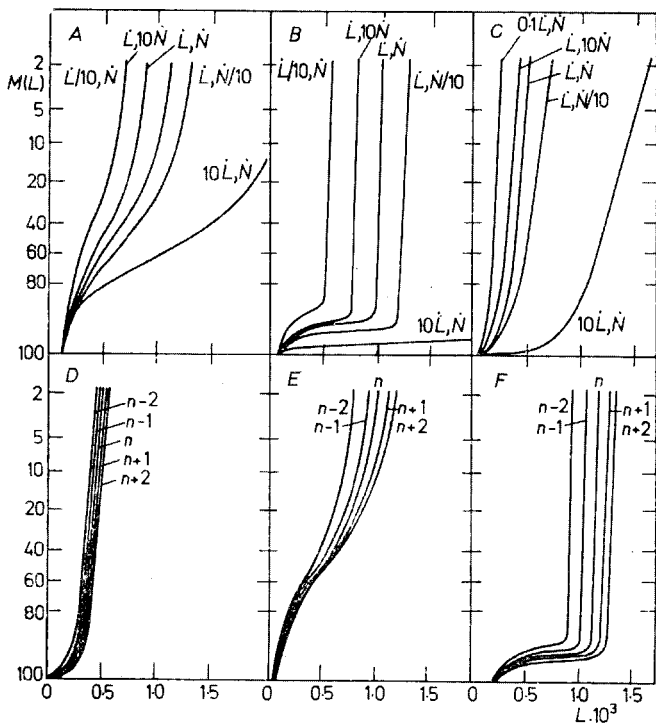


FIG. 1

#### The Effect of Kinetic Parameters on the Transient Course of Supersaturation

The curves correspond to runs A 2, 4, 1, 5, 3; B 9, 8, 1, 7, 6; C 22, 24, 21, 25, 23; D 29, 28, 21, 27, 26; E 19, 18, 11, 17, 16; F 12, 14, 11, 15, 13.

process,  $t_c$ . Surprisingly enough, on the same straight lines ( $t_c = 240$ ) appear the points from the runs both with and without seeding. As definite outliers appear the experiments with different value of  $k_G$  interconnected by broken line.

Processing the data of  $L_{\max}$  using Eq. (42) revealed that a correlation with  $B^{1/2}$  (Fig. 5) gives a better fit than the anticipated correlation of  $(L_{\max}/L_N)^{1+3g/n}$  with  $B$ . A multiple regression according to Eq. (42) for both alternatives yielded

$$(L_{\max}/L_N)^{1+3g/n} = B(t_c/120)^{1+3g/n} m_c^{-2.7(1+3g/n)}, \quad (43)$$

$$(L_{\max}/L_N)^{1+3g/n} = B^{1/2}(t_c/100)^{1.2+3g/n} m_c^{0.6-g/n}. \quad (44)$$

The results of the calculation using the last two equations are summarized in Table II

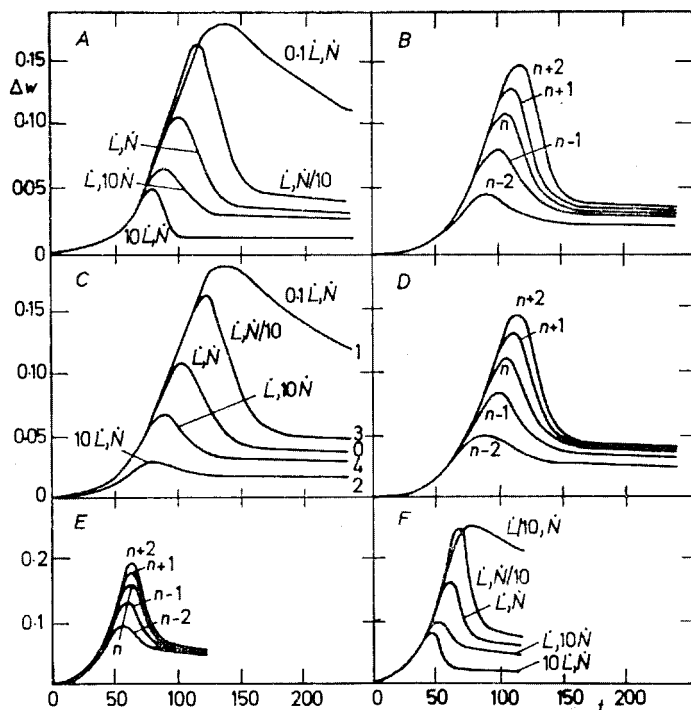


FIG. 2

#### The Effect of Kinetic Parameters on Granulometric Composition of the Product

The curves correspond to runs A 2, 5, 1, 4, 3; B 22, 25, 21, 24, 23; C 12, 15, 11, 14, 13; D 16, 17, 11, 18, 19; E 6, 7, 1, 8, 9; F 26, 27, 21, 28, 29.

and compared with the simulated experimental values. The equations fit the experimental data with the following average deviations of  $L_{\max}$ :

	Eq. (43)	Eq. (44)
Run 1-9	$0.22 \cdot 10^{-3}$	$0.07 \cdot 10^{-3}$
Run 11-19	$0.03 \cdot 10^{-3}$	$0.10 \cdot 10^{-3}$
Run 1-19	$0.12_5 \cdot 10^{-3}$	$0.09 \cdot 10^{-3}$

Clearly, Eq. (43) provides an excellent fit for experiments with a shorter time  $t_e$ , but a rather poor fit on  $k_G$  for experiments with  $t_e = 240$ . In contrast, Eq. (44) fits both experimental runs with comparable accuracy.

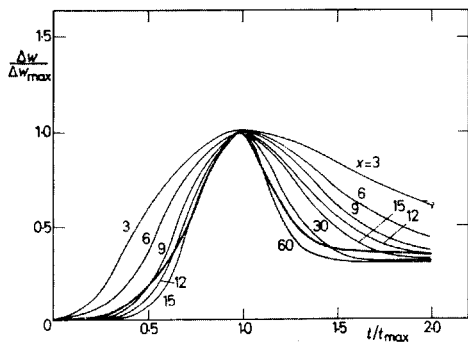


FIG. 3

Comparison of the Transient Course of Supersaturation (Run 11) with Theoretical Curves Computed from Eqs (13) and (22)

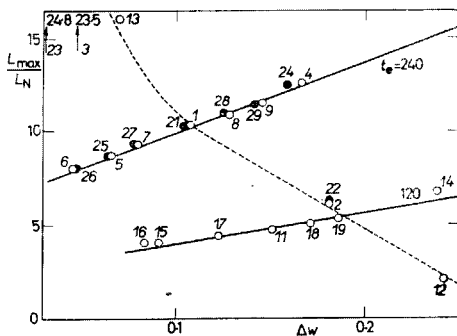


FIG. 4

Size of the Largest Crystals of the Product as a Function of Maximum Supersaturation

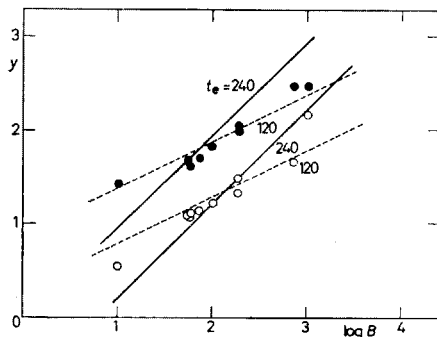


FIG. 5

Plot of  $y = \log(L_{\max}/L_N)^{1+3g/n}$  versus  $\log B$

Solid straight lines have the expected slope equal unity; broken straight lines have a satisfactory slope equal 0.5.

Generally it may be concluded that increased rate constant of growth leads to smaller values of supersaturation and a substantial increase of the crystals of the product. A similar though less conspicuous effect exercises a decrease of the nucleation constant. Decreased nucleation order brings about smaller supersaturation as well as smaller crystals of the product.

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## LIST OF SYMBOLS

$A$	surface area of crystals ( $\text{m}^2/\text{kg}_0$ )
$A_c$	surface area of crystals at the end of charge ( $\text{m}^2/\text{kg}_0$ )
$a$	constant defined by Eq. (12)
$B$	system constant defined by Eq. (27)
$b$	constant defined by Eq. (11)
$c_a$	constant characterizing solubility <sup>7</sup>
$E_G$	activation energy of growth (kcal/mol)
$E_N$	activation energy of nucleation (kcal/mol)
$E_s$	energy parameter characterizing temperature dependence of solubility (kcal/mol)
$f$	function defined by Eq. (42)
$f(t)$	function defined by Eq. (15)
$g$	exponent in kinetic equation of growth
$\text{kg}_0$	kg of free solvent
$k_G$	rate constant of growth ( $\text{kg}^{1-g} \text{kg}_0^g \text{min}^{-1} \text{m}^{-2}$ )
$k_N$	rate constant of nucleation ( $\text{kg}/\text{kg}_0)^{1-n} \text{min}^{-1}$ )
$k_L$	coefficient in Eq. (31)
$L$	size of crystals (m)
$L_{\max}$	size of the largest crystals (m)
$L_0$	size of seeds (m)
$L_N$	initial size of crystals (m)
$M(L)$	cummulative distribution function of crystal size (% oversize)
$m_c$	mass of crystals ( $\text{kg}/\text{kg}_0$ )
$m_N$	mass of initial crystals ( $\text{kg}/\text{kg}_0$ )
$m_0$	mass of seeds ( $\text{kg}/\text{kg}_0$ )
$N$	number of crystals
$\dot{N}$	numerical rate of nucleation ( $\text{kg}_0^{-1} \text{min}^{-1}$ )
$n$	exponent of kinetic equation of nucleation
$s$	supersaturation rate ( $\text{kg}/\text{kg}_0 \text{min}$ )
$s_c$	supersaturation rate at the end of run ( $\text{kg}/\text{kg}_0 \text{min}$ )
$T$	temperature ( $^{\circ}\text{C}$ )
$T_0$	initial temperature ( $^{\circ}\text{C}$ )
$T_c$	final temperature ( $^{\circ}\text{C}$ )
$\Delta T_{\max}$	maximum undercooling (K)
$t$	time (min)
$t_c$	duration of run (min)
$t_{\max}$	time coordinate of maximum supersaturation (min)

$t_i$	time coordinate of inflection point on supersaturation curve (min)
$w$	concentration (kg/kg <sub>0</sub> )
$\Delta w$	supersaturation (kg/kg <sub>0</sub> )
$w_{eq}$	solubility (kg/kg <sub>0</sub> )
$\Delta w_e$	steady state supersaturation (kg/kg <sub>0</sub> )
$\Delta w_i$	supersaturation at time $t_i$ (kg/kg <sub>0</sub> )
$\Delta w_{max}$	maximum supersaturation (kg/kg <sub>0</sub> )
$X$	exponent characterizing the course of cooling
$x$	adjustable parameter
$a$	adjustable parameter
$z$	dimensionless size of crystals defined by Eq. (31)
$\alpha$	volume shape factor
$\beta$	surface shape factor
$\rho_c$	density of crystals (kg/m <sup>3</sup> )

## REFERENCES

1. Nývlt K., Václavů V.: Chem. Prům. 14, 79 (1964).
2. Nývlt J., Skřivánek J.: This Journal 33, 1788 (1968).
3. Mullin J. W., Nývlt J.: Chem. Eng. Sci. 26, (3), 369 (1971).
4. Nývlt J., Kočová H., Černý M.: This Journal 38, 3199 (1973).
5. Nývlt J.: Chem. Prům. 23, 343 (1973).
6. Nývlt J.: Chem. Prům. 24, 179 (1974).
7. Nývlt J.: This Journal 39, 3463 (1974).
8. Nývlt J., Wurzelová J., Čípová H.: This Journal, in press.
9. Nývlt J.: This Journal, in press.

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