

## SIZE DISTRIBUTION OF CRYSTALS FROM A BATCH CRYSTALLIZER

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Relations are derived for calculation of size distribution of product crystals from a batch crystallizer for two limiting conditions: crystallizer with constant nucleation rate during the whole operation and crystallizer with spontaneous nucleation taking place only at the beginning of the operation. Also a model is considered with nucleation in two successive waves. The obtained relations are verified by a set of laboratory experiments.

Though the batch crystallizers are very frequently used in chemical industry, very little attention has been paid so far to the size distribution of their products crystals. Larson<sup>1</sup> formulated some basic problems concerning the batch crystallizers but he did not receive results of any practical value according to which the size distribution of product crystals could be determined. Granulometric composition of the product from a batch crystallizer with seeding had been studied<sup>2</sup> but spontaneous nucleation had not been considered there. An attempt for calculation of the mean size of product crystals from a batch crystallizer had been made<sup>3</sup> for two conditions: constant nucleation rate and seeded solution with negligible nucleation.

Here, relations are derived for an improved model of a batch crystallizer with constant nucleation rate, for a batch crystallizer with spontaneous nucleation at the beginning of the operation and for a batch crystallizer with nucleation taking place in two waves. These models have been verified experimentally.

### THEORETICAL

*Batch crystallizer with constant nucleation rate.* From the supersaturation balance where the supersaturation rate  $s$  is for constant supersaturation  $\Delta q$  just compensated by the rate of crystal growth and nucleation we have<sup>1</sup>

$$s = k_G A \Delta q^g / V + k_N \Delta q^n. \quad (1)$$

The surface area of crystals  $A$  is not known in this equation and is of course a function of time

$$A/V = \int_0^t \dot{N}_0 \beta L^2 dt. \quad (2)$$

Number of crystals  $N_0$  originating in a unit amount of solution per unit of time *i.e.* the numerical nucleation rate may be expressed from the relation

$$\dot{N}_0 = k_N \Delta Q^n / (\alpha Q_c L_N^3) \quad (3)$$

which is also constant because of constant supersaturation. On the other hand the crystal size  $L$  is a function of time

$$L = L_N + \dot{L}t. \quad (4)$$

After substituting Eqs (3) and (4) into Eq. (2), relation for the surface area of crystals is obtained by integration

$$A/V = \frac{k_N \Delta Q^n \beta}{3\alpha Q_c \dot{L}} \left[ \left( \frac{L}{L_N} \right)^3 - 1 \right]. \quad (5)$$

On substituting Eq. (5) together with the earlier derived relation for linear growth rate  $\dot{L} = k_G \beta \Delta Q^n / (3\alpha Q_c)$  into Eq. (1), the following relation is obtained

$$s = k_N \Delta Q^n \left[ (\dot{L}t/L_N) + 1 \right]^3. \quad (6)$$

As for the saturation rate resulting from cooling of the solution holds  $s = -T \varepsilon dQ_{eq} : dT$ , the following relation can be written

$$\begin{aligned} (T_0 - T_t) \frac{dQ_{eq}}{dT} &= k_N \Delta Q^n \int_0^t \left( \frac{\dot{L}t}{L_N} + 1 \right)^3 dt = \\ &= k_N \Delta Q^n \frac{L_N}{4\dot{L}} \left[ \left( \frac{\dot{L}t}{L_N} + 1 \right)^4 - 1 \right]. \end{aligned} \quad (7)$$

An equivalent equation holds for final conditions of crystallization where  $t = t_e$  is the time of the batch operation and  $T = T_e$  is the final temperature. Ratio of both these relations gives

$$\frac{T_0 - T_t}{T_0 - T_e} = \frac{[(\dot{L}t/L_N) + 1]^4 - 1}{[(\dot{L}t_e/L_N) + 1]^4 - 1}, \quad (8)$$

where we have assumed that  $dQ_{eq}/dT = \text{const}$ . Since for the product holds  $(\dot{L}t_e + L_N) \gg L_N$ , relation (8) can be simplified to

$$(T_0 - T_t)/(T_0 - T_e) \approx (t/t_e)^4 \quad (9)$$

which is the equation of the cooling curve corresponding to the condition of constant nucleation rate. The product mass crystallized in the time  $t$  is given by Eq.  $m_c = (T_0 - T_1) \varepsilon dQ_{cq}/dT$ , where the factor  $\varepsilon$  results from the material balance  $\varepsilon = (M_{anh}/M_{hyd} - \rho/\rho_1)^{-1}$ . With these relations Eq. (7) can be then simplified for the condition  $t = t_e$  to

$$m_c = k_N \Delta Q^n (L_N/4L) [(\dot{L}_e + L_N)/L_N]^4 \quad (10)$$

in which  $\dot{L}_e + L_N = L_{max}$  can be taken as the size of largest crystals in the product. The mean mass of crystals for the condition of constant supersaturation is

$$\bar{m} = (1/n_{L_0} t_e) \int_0^{t_e} \alpha Q_c n_{L_0} L^3 dt \quad (11)$$

which together with Eq. (4) and condition  $L \gg L_N$  may be simplified to

$$\bar{m} \approx \frac{1}{4} \alpha Q_c L_{max}^3. \quad (12)$$

For the balance of number of crystals then holds

$$(4m_c / \alpha Q_c L_{max}^3) = (k_N \Delta Q^n t_e / \alpha Q_c L_N^3) \eta_N, \quad (13)$$

where  $\eta_N$  is the ratio of the actual and theoretical nucleation rates which is dependent on the arrangement of the experimental device. In ideal case  $\eta_N = 1$ . From Eq. (13)  $\Delta Q$  may be expressed and substituted into Eq. (10) so that we get

$$(L_{max}/L_N)^{1+3g/n} = (4^{g/n}/\varepsilon) B m_c^{g/n} t_e^{1-g/n} \eta_N^{1-g/n}, \quad (14)$$

where  $B = k_G \beta / (3\alpha Q_c k_N^{g/n} L_N)$ .

The system constant  $\sigma$  has been earlier<sup>4</sup> defined for continuous crystallizers

$$\sigma = 3(9/2)^{g/n} L_N^{3g/n+1} B. \quad (15)$$

By its use Eq. (14) can be arranged into the final form

$$L_{max}^{1+3g/n} = \frac{(8/9)^{g/n}}{3\varepsilon} \sigma t_e^{1-g/n} m_c^{g/n} \eta_N^{1-g/n}. \quad (16)$$

For the size distribution of crystals according to this model Eq. (11) may be solved for the over-all mass of crystals

$$m_c = \frac{1}{4} \alpha_{Q_c} n_{L_0} L_{\max}^4 \quad (17)$$

Similarly, for mass of the oversize fraction we may write

$$m^+ = \int_L^{L_{\max}} \alpha_{Q_c} n_{L_0} L^3 dL = \frac{1}{4} \alpha_{Q_c} n_{L_0} (L_{\max}^4 - L^4) \quad (18)$$

so that for the mass of oversize product crystals holds

$$M(L) = 100m^+/m = 100[1 - (L/L_{\max})^4] \quad (19)$$

*Batch crystallizer with spontaneous nucleation at the beginning of crystallization.* At the beginning of crystallization operation, when only saturated solution with negligible amount of solid phase is present in the crystallizer, supersaturation increases proportionally with the supersaturation rate

$$\Delta Q = \varepsilon^{-1} st, \quad (t \leq t_{\max}) \quad (20)$$

until  $t = t_{\max}$  when the boundary of metastable region  $\Delta Q_{\max}$  is reached. Nucleation takes place in the region of supersaturations close to  $\Delta Q_{\max}$ , so that supersaturation is not increasing more and sufficient crystallization area is formed for its removal from the solution. The time dependence of supersaturation is schematically plotted in Fig. 1. If the nucleation rate is expressed by Eq. (3), the number of crystals spontaneously formed at the beginning of the operation may be written

$$N = 2 \int_0^{t_{\max}} [k_N (\varepsilon^{-1} st)^n / (\alpha_{Q_c} L_N^3)] dt = 2\varepsilon \Delta Q_{\max} / [(n+1) \alpha_{Q_c} L_N^3], \quad (21)$$

where approximation<sup>3</sup>  $s = k_N \Delta Q_{\max}^n$  was used. So formed crystal nuclei have formed a crystal area  $A = N\beta L^2$ , where the size of crystals  $L$  is given by Eq. (4). As supersaturation relatively quickly decreases to a steady value, further nucleation may be neglected and balance (1) is simplified to the form  $sV = k_G A \Delta Q^g$ , which on substituting for  $A$  or  $N$  together with the definition relation  $\dot{L} = k_G \beta \Delta Q^g / (3\alpha_{Q_c})$  gives

$$s = [2\varepsilon \Delta Q_{\max} / (n+1)] (3\dot{L}/L_N) (1 + \dot{L}t/L_N)^2 \quad (22)$$

From Eq. (9), it can be written for the highest cooling rate at the end of the crystallization experiment

$$s_{\max} = \varepsilon \frac{dQ_{\text{eq}}}{dT} \frac{4(T_0 - T_c)}{t_c} \approx \frac{4m_c}{t_c} \quad (23)$$

so that for condition  $t = t_c$  from Eqs (22) and (23) with approximation  $\varepsilon d\varrho_{eq}/dT \approx m_c/(T_0 - T_e)$  and  $L = (L_{max} - L_N)/t_e$  the final relation is obtained

$$\left(\frac{L_{max}}{L_N}\right)^2 \left(\frac{L_{max}}{L_N} - 1\right) \approx \frac{3}{2} \frac{(n+1)(T_0 - T_e)}{\Delta T_{max}} \quad (24)$$

Granulometric product composition can be expressed on the basis of following considerations: The over-all mass of crystals at the end of crystallization is given by

$$m_c = \int_0^{L_{max}} \alpha_{Qc} n_L L^3 dL \quad (25)$$

If supersaturation of the solution decreases exponentially down to the steady value (Fig. 1) after reaching the boundary of metastable region, the nucleation rate decreases analogically so that for the probability density of exit crystals  $n_L$  may be written  $n_L = n_{L0} \exp(-kt)$ , where  $k$  is an adjustable constant corresponding to the conditions of the experiment. From the simplifying condition  $L \approx \dot{L}t$  we then obtain

$$m_c = \alpha_{Qc} n_{L0} \int_0^{t_0} \dot{L}(\dot{L}t)^3 \exp(-kt) dt \quad (26)$$

which is an equation similar to that for a continuous ideally agitated crystallizer<sup>6</sup>.

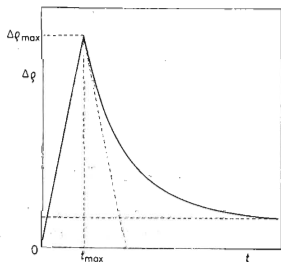


FIG. 1

Dependence of Supersaturation on Time at the Beginning of Batch Crystallization with Spontaneous Nucleation (schematically)

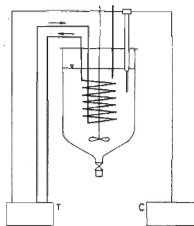


FIG. 2

Laboratory Model of Batch Crystallizer

For granulometric composition may be thus written

$$M(L) \approx 100(1 + z + z^2/2 + z^3/6) \exp(-z), \quad (27)$$

where  $z$  is the dimensionless crystal size defined by

$$z = (L - L_N)/(k_L \dot{L} t_c). \quad (28)$$

The value of constant  $k_L$  may be chosen  $k_L = 9$  which corresponds to the value  $M(L) = 2\%$  and which is characterizing with sufficient accuracy the size of the largest crystals  $L_{\max}$ . Granulometric product composition from a batch crystallizer with spontaneous nucleation at the beginning of the operation may be linearized similarly as the granulometric product composition from a continuous crystallizer<sup>7</sup>, therefore.

The presented model is based on the assumption that nucleation takes place only at the beginning of the operation. Preliminary calculations according to the model of batch crystallizer by the computer have however demonstrated that the nucleation waves can be periodically repeated in the batch process similarly as in the continuous crystallizer<sup>8</sup>. In such case the granulometric product composition would be formally represented by an equation of the type

$$M(L) = 100 \sum_{i=1}^{i=\nu} w_i (1 + z_i + z_i^2/2 + z_i^3/6) \exp(-z_i), \quad (29)$$

where  $\nu$  is the number of nucleation waves and  $w_i$  is the mass fraction of the corresponding crystals in the product. Example of graphical plot of such granulometric composition for two nucleation waves is given in Fig. 3 (mixture of products from the first nucleation wave with  $L_1 = 0.7$  mm and from the second nucleation wave with  $L_2 = 0.3$  mm). The resulting plot, which represents the granulometric composition of the mixed product, is not linear any more.

## EXPERIMENTAL

The used laboratory crystallizer is schematically given in Fig. 2. Glass crystallizer of volume about 2 l is equipped with a propeller mixer, a cooling coil which simultaneously serves as a difuzor, contact and control thermometers. Temperature in the crystallizer is controlled by use of a programmed cooling controller<sup>9</sup> C and thermostat T and is simultaneously measured by an ordinary thermometer.

A saturated solution prepared in the crystallizer was slightly undercooled and then cooled according to a given programme. At the beginning of the programmed cooling several larger crystals were seeded into the solution so that nucleation took place in the presence of the solid phase. At the end of cooling the crystals were separated from the mother liquor and dried and their sieve analysis was made. According to the used programmed cooling, the temperature decrease in dependence on time corresponded to Eq. (9). The model experiments were made for

aqueous solutions of 8 substances:  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ,  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ , urea and  $\text{K}_2\text{SO}_4$ . In all the experiments the cooling was made for  $\Delta T = 20^\circ\text{C}$  according to the cooling curve given by Eq. (9) with the first three experiments made in 2 h with different initial undercooling and other two experiments in cooling times  $t_c = 4$  and 8 h.

## RESULTS AND DISCUSSION

Results of the model experiments are summarized in Table I. The sieve analyses are demonstrated in Fig. 4. According to the results given in Table I, the studied substances may be roughly subdivided into two groups: a) substances with the size of crystals increasing with the length of experiment. This may be expected from the theory because longer time of experiment means slower cooling rate *i.e.* a narrower metastable region and thus less crystals formed at the beginning of the operation. Into this group fall  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{FeSO}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{SO}_4$ ; b) substances with the size of crystals decreasing with the length of experiment, where mechanical disintegration of crystals took place due to the action of the propeller: here belong  $\text{CuSO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and also partially urea.

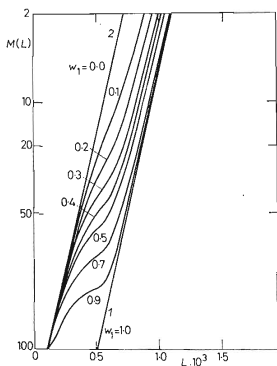


FIG. 3

Example of Granulometric Product Composition from a Batch Crystallizer with Two Nucleation Waves During Crystallization

$\bar{L}_1 = 0.7 \text{ mm}$ ,  $\bar{L}_2 = 0.3 \text{ mm}$ . Scale  $M(L)$  corresponds to Eq. (27).

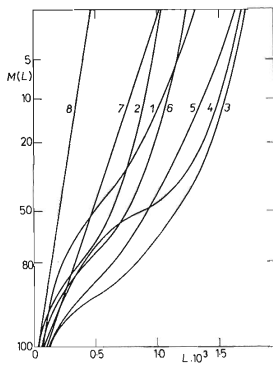


FIG. 4

Sieve Analysis of Product from Model Experiments (Numbers of the curves correspond to those of substances in Table I)

Scale  $M(L)$  corresponds to Eq. (27).

The shape of curves in Fig. 4 in majority of cases uniquely proves that nucleation took place at least in two separate waves (in respect to time). The experimental curves (Fig. 4) are very similar to the curves calculated (Fig. 3) which demonstrate the suitability of the model presented in the theoretical part of this study. For simplicity and with regard to the approximative character of the model, the experimental data were evaluated according to Eq. (24) where for the value  $L_{\max}$  was,

TABLE I

## Results of Model Crystallization Experiments

*a* Calculated from model experiments, *b* from granulometric composition of model experiments *c* by optical analysis.

No	Compound	$t_e$	$L_{\max} \cdot 10^3$	$L_N \cdot 10^3$			$L_N^{(a)}$
				<i>a</i>	<i>b</i>	<i>c</i>	$L_N^{(b)}$
1	CuSO <sub>4</sub> ·5 H <sub>2</sub> O	2	1.43	0.336	0.050	0.060	6.72
		4	1.08	0.253			5.06
		8	1.00	0.235			4.70
2	NaNO <sub>3</sub>	2	1.02	0.236	0.058	0.040	4.07
		4	1.28	0.296			5.10
		8	1.19	0.275			4.74
3	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2	1.78	0.545	0.174	0.120	3.13
		4	2.55	0.781			4.49
		8	2.71	0.830			4.77
4	FeSO <sub>4</sub> ·7 H <sub>2</sub> O	2	1.66	0.372	0.060	0.040	6.20
		4	1.74	0.390			6.50
		8	2.14	0.480			8.00
5	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5 H <sub>2</sub> O	2	2.47	0.571	0.096	0.055	5.95
		4	1.89	0.437			4.55
		8	1.66	0.384			4.00
6	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2 H <sub>2</sub> O	2	1.14	0.272	0.076	0.095	3.58
		4	1.59	0.380			5.00
		8	1.43	0.342			4.50
7	(NH <sub>2</sub> ) <sub>2</sub> CO	2	0.83	0.159	0.060	0.055	2.65
		4	0.64	0.123			2.05
		8	0.81	0.156			2.60
8	K <sub>2</sub> SO <sub>4</sub>	2	0.75	0.265	0.031	0.035	8.55
		4	1.00	0.353			11.39
		8	1.23	0.435			14.03



in agreement with the assumption made in the theoretical part, taken from graph such size of crystals for which  $M(L) = 2\%$ . Values of maximum undercooling  $\Delta T_{\max}$  for the temperature closest to the initial crystallization temperature and for the lowest cooling rate  $2^\circ/\text{h}$  were taken from the earlier published papers<sup>10,11</sup> and values of  $L_N$  were calculated back from experimental data. Results of calculation are also given in Table I (column *a*) and are compared with values read off from the graph of linearized sieve analysis (column *b*): this is because from Eq. (28) for  $L = L_N$  holds  $z = 0$  and thus  $M(L_N) = 100\%$ . For further comparison the optical determination of  $L_N$  (column *c*) from a series of experiments with a nonprogrammed cooling was also made. In these experiments, the solution was first saturated at a temperature about  $10-15^\circ\text{C}$  higher than was the room temperature and then it was quickly cooled down to the temperature of about  $25^\circ\text{C}$ . As soon as the first turbidity of crystals appeared, the suspension was agitated for another 2 minutes so that the separation of crystals by filtration was easier. The crystals were then separated by filtration and washed by a saturated solution so as to remove last traces of the supersaturated mother liquor. After separation and drying the crystals were analyzed optically; as the basis was taken the crystal length. The optical size spectrum was then recalculated to mass fractions and from the granulometric composition in a graphical form were read off sizes of the smallest crystals for  $M(L_N) = 100\%$ . An example of such sieve analysis for urea is given in Fig. 5 from which it is obvious that for a very quick cooling the nucleation took place during the whole experiment because the sieve analysis corresponds to the Eq. (19).

It is obvious from data of Table I that the agreement of values  $L_N$  obtained by the direct optical measurement and of  $L_N$  from the sieve analysis of products of model

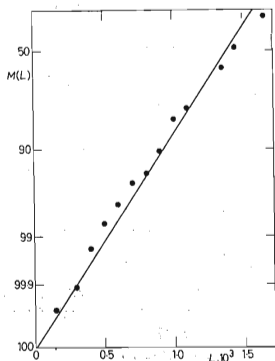


FIG. 5  
Sieve Analysis of Urea Crystals Obtained  
by Quick Cooling of Solution  
Scale  $M(L)$  corresponds to Eq. (19).

experiments is very good with a slightly better agreement for substances for which the dependence of  $M(L)$  on  $L$  was linear (this is comprehensible since in extrapolation to the zero value a smaller error is involved). On the contrary, values  $L_N$  calculated from the model experiments according to the relation (24) are in average by 5.5 times higher than the smallest size of crystals determined by the direct method. Due to the approximative character of the model also this systematic and rather constant deviation can be considered acceptable and Eq. (24) can thus be arranged into the form

$$\left(\frac{L_{\max}}{5.5L_N}\right)^2 \left(\frac{L_{\max}}{5.5L_N} - 1\right) \approx \frac{(n+1)(T_0 - T_e)}{\Delta T_{\max}} \quad (30)$$

and used for calculation of the granulometric product composition from a batch crystallizer with a spontaneous nucleation at the beginning of crystallization.

#### LIST OF SYMBOLS

$A$	surface area of crystals ( $\text{m}^2$ )
$B = \dot{L}(L_N \dot{m}_N^g)^{-1}$	system constant
$g$	order of kinetic equation of crystal growth
$k$	empirical constant dependent on conditions of experiment ( $\text{h}^{-1}$ )
$k_G$	kinetic constant of crystal growth ( $\text{kg}^{1-g} \text{m}^3 \text{g}^{-2} \text{h}^{-1}$ )
$k_L$	empirical constant in Eq. (28) characterizing $L_{\max}$
$k_N$	kinetic nucleation constant ( $\text{kg}^{1-n} \text{m}^3 \text{h}^{-3} \text{h}^{-1}$ )
$L$	crystal size (m)
$L_N$	size of smallest product crystals (m)
$L_{\max}$	size of largest product crystals (m)
$\dot{L}$	linear crystal growth rate ( $\text{m h}^{-1}$ )
$m_e$	over-all mass of crystals (kg)
$\bar{m}$	mean crystal mass (kg)
$m^+$	mass of crystals with the size larger than a certain size $L$ (kg)
$\dot{m}_N$	nucleation rate ( $\text{kg m}^{-3} \text{h}^{-1}$ )
$M_{\text{anh}}$	molecular weight of anhydrous substance ( $\text{kg mol}^{-1}$ )
$M_{\text{hyd}}$	molecular weight of hydrate ( $\text{kg mol}^{-1}$ )
$M(L)$	cumulative oversize fraction (mass %)
$n$	order of kinetic equation of nucleation
$\dot{N}_0$	numerical nucleation rate ( $\text{m}^{-3} \text{h}^{-1}$ )
$N$	number of crystals
$n_{L0}$	population density of crystal nuclei ( $\text{m}^{-1}$ )
$n_L$	population density of crystals of size $L$ ( $\text{m}^{-1}$ )
$s$	supersaturation rate ( $\text{kg m}^{-3} \text{h}^{-1}$ )
$t$	time (h)
$t_e$	over-all time of batch crystallization (h)
$t_{\max}$	time in which $\Delta \varrho_{\max}$ is reached (h)
$T$	temperature (K)
$T_0$	initial temperature (K)
$T_e$	final temperature (K)

$T_1$	temperature in time $t$ (K)
$\Delta T_{\max}$	maximum allowable undercooling (K)
$-\dot{T}$	cooling rate ( $\text{K h}^{-1}$ )
$V$	volume of crystallizer ( $\text{m}^3$ )
$w_1$	mass fraction of the corresponding product portion
$z$	dimensionless crystal size defined by Eq. (28)
$\alpha$	volume shape factor (—)
$\beta$	surface shape factor (—)
$\epsilon$	factor resulting from the material balance (—)
$\eta_N$	ratio of the actual and theoretical nucleation rates (—)
$\nu$	number of nucleation waves (—)
$\rho$	concentration ( $\text{kg m}^{-3}$ )
$\Delta\rho$	supersaturation ( $\text{kg m}^{-3}$ )
$\Delta\rho_{\max}$	maximum supersaturation ( $\text{kg m}^{-3}$ )
$\rho_{\text{eq}}$	solubility ( $\text{kg m}^{-3}$ )
$\rho_1$	density of solution ( $\text{kg m}^{-3}$ )
$\rho_c$	density of crystals ( $\text{kg m}^{-3}$ )
$\sigma$	system constant defined by Eq. (15)

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