FORMAL CRYSTALLIZATION KINETICS

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Exponential equations of crystal growth applied in industrial crystallization are approximating well, in a narrow interval of supersaturations, the theoretically derived molecular crystallization equations. These relations are in limiting cases identical. So-called crystallization constant k_g and the formal reaction order of crystallization g are constant only in a narrow range of supersaturations. Values of g and k_g change when the limiting supersaturation is exceeded. Equations are derived for calculation of k_g from physical characteristics of the crystallization system. At dislocation crystal growth from solutions holds $1 \leqq g \leqq 2$ where greater values can be explained by disturbances in the growth regime.

In industrial application the formal kinetic equation[1] is usually applied for crystallization

$$(dG/d\tau) = k_g A(\Delta c)^g, \qquad (1)$$

where k_g is the so-called crystallization constant dependent on the relative velocity of liquid motion in respect to the crystal, temperature, concentration of other components present, perfectness of the crystal shape, and independent of supersaturation. Exponent g, called reaction order of crystallization, becomes $1 \leqq g \leqq 2$ according to the character of the matter and method of its crystallization. Eq. (1) is identical completely with the relation frequently used for evaluation of experimental data on the crystal growth[2]

$$L = dG/(A \, d\tau \varrho_c) = k'_g(\Delta c)^g, \qquad (2)$$

where

$$k'_g = k_g/\varrho_c. \qquad (3)$$

Eqs (1) and (2), based on the formalism of reaction kinetics, are in the case of crystallization more or less empirical relations.

If we consider crystallization as a two-stage process[3] we can write

$$dm/A \, d\tau = k_d(c - c_i) \quad \text{diffusion,} \qquad (4)$$

$$dm/A \, d\tau = k_i(c_i - c_0)^i \quad \text{surface reaction,} \tag{5}$$

$$dm/A \, d\tau = k_g(\Delta c)^g \quad \text{total crystallization rate.} \tag{6}$$

Eq. (6) is equivalent to Eq. (1) and thus the crystallization constant k_g as well can be defined as the mass which is in a unit of time built in a unit of crystal surface at the unit concentration gradient Δc (driving force of crystallization).

By elimination of the unknown concentration at the interphase boundary, k_g can be expressed as

$$k_g = (k_i/k_d^i)(\Delta c)^{g(i-1)} \left[(\Delta c)^{1-g} k_d - k_g\right]^i . \tag{7}$$

Analytical solution of Eq. (7) is possible for $g = i = 1$, $g = i = 2$, and $g = 1$, $i = 2$. In this way calculated k_g for $g = i = 1$ depends on Δc only through the function k_d, $k_i = f(\Delta c)$. In all other cases are in the relation for k_g contained Δc and k_g as well and thus it cannot be a constant characterizing how the crystallization proceeds.

In literature is usually applied for k_d the relation[4,5]

$$k_d = D/\delta , \tag{8}$$

where δ is best approximated by equation[6]

$$\delta = \left[\frac{2}{3}\left(\frac{\eta}{\varrho_s D}\right)^{\frac{1}{3}}\left(\frac{\varrho_s v}{\eta X}\right)^{\frac{1}{2}}\right]^{-1} . \tag{9}$$

As D, η and ϱ are functions of Δc, then according to Eq. (8) is k_d as well dependent on Δc. But this dependence is rather inexpressive and thus k_d can be considered constant in a reasonably wide interval of Δc. Some of information on values of the exponent g and the constant k_i can be get on basis of the molecular kinetic theories of crystal growth published e.g. by Burton, Cabrera and Frank[7] (BCF), Chernov[8] and Bennema[9] (dislocation theory). The volume diffusion model of the BCF theory assumes that the diffusive field in vicinity of crystals is established on basis of the surface reaction which is just as fast as the rate of mass removal by the crystal. According to this theory for the rate of growth of area L holds the relation

$$L = \frac{DN_0 a\Omega\sigma}{2x_0\varrho_{\text{crit}}[1 + (2\pi a/x_0 y_0)(\delta - y_0) + (2a/x_0)\ln(y_0/x_0)]} , \tag{10}$$

where the radius of the critical nucleus of a new layer on the crystal surface is

$$\varrho_{crit} = y_0/4\pi = \gamma a/[1 \ln (\sigma + 1)] . \tag{11}$$

For large σ is $(2\pi a)/(x_0 y_0) (\delta - y_0) \gg (2a/x_0) \ln (y_0/x_0)$ and Eq. (10) takes the form

$$L = (DN_0 \Omega \sigma)/\delta . \tag{12}$$

Introduced assumption $\delta \gg y_0$ is always fulfilled. For large σ thus holds $L \sim \sigma$.

For small σ the third term of the denominator in Eq. (10) is considerably greater than the first and second term. By arranging relation (10) and by use of Eq. (11) the following relation is obtained

$$L = \frac{DN_0 \mathbf{k} T \Omega \sigma^2}{4a\gamma \ln (4\pi\gamma/\mathbf{b}\mathbf{k}T\sigma)} . \tag{13}$$

For small σ is $L \sim \sigma^2$ as $\ln (4\pi\gamma/\mathbf{b}\mathbf{k}T\sigma)$ is not a very sensible function of σ. The transition from linear to the parabolic function takes place at supersaturation given by

$$\sigma_{transition} \sim (\gamma x_0)/(\mathbf{k}T\delta) . \tag{14}$$

At $\sigma < \sigma_{transition}$ is $g \sim 2$ and at $\sigma > \sigma_{transition}$ is $g = 1$. We have found out that the values of the exponent g in Eq. (6) can be equal only to 1 or 2. But we know from measurements of the crystallization rate that g can be of any value between 1 and 2. So the dislocation theory is applied which takes into consideration only the surface diffusion as the controlling operation of the crystal growth. The rate of crystal growth can be in this case determined by relation[9]

$$L = C(\sigma^2/B) \tanh (B/\sigma) , \tag{15}$$

where

$$B = (9\cdot5/\varepsilon) (\gamma/\mathbf{k}T) (a/\lambda_s) ; \tag{16}$$

and

$$C = (\mathbf{k}\sigma/h) \beta c_0' \Lambda \Omega N_0 \exp (-\Delta G_{deh}/\mathbf{k}\sigma) , \tag{17}$$

where

$$\Lambda = n_{s0}/N_{s0} \quad \text{and} \quad c_0' = (\lambda_s/x_0) \ln (2\lambda_s/1\cdot78a) .$$

As concerns the formalism of Eqs (4) to (6) it holds $k_d \gg k_i$ i.e. the rate of crystal growth is controlled by the slowest operation — the rate of surface reaction. In such case $c_i \sim c$, and the surface reaction takes place at the concentration difference $\Delta c = \sigma/c_0$.

If the effect of the volume and surface diffusions is simultaneously considered, according to Bennema[10] relations (4) and (5) are applied for $i = 1$ and in the stationary state by eliminating c_i the equation of growth is obtained

$$dm/A \, d\tau = [1/k_d + 1/k_i(\sigma)]^{-1} \, \Delta c = [1/c_0 k_d + 1/c_0 k_i(\sigma)]^{-1} \, \sigma$$

and

$$c_i = [k_d c + k_i(\sigma) c_0]/[k_d + k_i(\sigma)] . \tag{18}$$

As $dm/A \, d\tau \varrho_c = L$ we can write

$$L = [\varrho_c/c_0 k_d + \varrho_c/c_0 k_i(\sigma)]^{-1} . \tag{19}$$

By use of relation (8) together with $c_0 = N_0 M/N_A$ and $\Omega = M/N_A \varrho_c$ holds

$$c_0 k_d/\varrho_c = DN_0 \Omega/\delta . \tag{20}$$

The surface reaction takes place at the driving force

$$\sigma' = (c_i - c_0)/c_0 = K(\sigma) \, \sigma , \tag{21}$$

where

$$K(\sigma) = (c_i - c_0)/(c - c_0) = (\{[k_d c + c_0 k_i(\sigma)]/[k_d + k_i(\sigma)]\} - c_0)(c - c_0)^{-1} =$$
$$= [1 + k_i(\sigma)/k_d]^{-1} . \tag{22}$$

For this case σ' appears in Eq. (15) instead of σ and thus

$$L = (C/B) \, K^2(\sigma) \, \sigma^2 \tanh (B/K(\sigma) \, \sigma) . \tag{23}$$

In steady state by comparison of Eqs (19) and (23) for $k_i(\sigma)$ the relation is obtained

$$k_i(\sigma) = (\varrho_c C K^2(\sigma) \, \sigma/c_0 B) \tanh (B/K(\sigma) \, \sigma) . \tag{24}$$

On substituting (24) and (20) into (19) we obtain

$$L = \{\delta/DN_0 \Omega + (C K^2(\sigma) \, \sigma/B) \tanh (B/K(\sigma) \, \sigma)]^{-1}\}^{-1} . \tag{25}$$

Eq. (25) gives the rate of crystal growth if the growth is affected both by the volume diffusion and the surface reaction. For $k_d \gg k_i$ relation (25) takes the form of Eq. (23) and for $k_i \gg k_d$ of Eq. (13).

Eq. (25) is thus the accurate expression of the frequently used Eq. (6). From it can be seen that the exponent g in the empirical Eq. (6) can actually have any value in the

range $1 \leqq g \leqq 2$ while the crystallization constant k_g is dependent also on supersaturation. The limiting cases can be obtained from Eq. (25)

1) $k_d \ll k_i$ and thus $c_i \sim c_0$

$$k_g = k_d = DN_0 \Omega \varrho_c / \delta c_0 = D/\delta \ . \tag{8a}$$

2) $k_d \gg k_i$ and thus $c_i \sim c$

$$k_g = k_i = (\varrho_c/c_0) \, c(\sigma/B) \tanh B/\sigma \ . \tag{26}$$

a) In the case of large B/σ is $\tanh B/\sigma \sim 1$ and then

$$k_g = k_i = (\varrho_c/c_0) \, C\sigma/B \ .$$

b) In the case B/σ is small is $\tanh B/\sigma \sim B/\sigma$ and thus

$$k_g = k_i = \varrho_c C/c_0 \ .$$

3) $k_i \sim k_d$, k_i is given by Eq. (24), k_d by Eq. (8) and

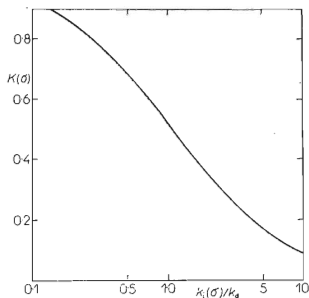$$k_g = f(k_d, k_i, \sigma) \ .$$

Fig. 1

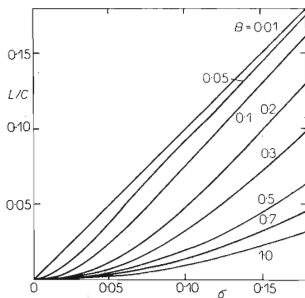Dependence of $K(\sigma)$ on $k_i(\sigma)/k_d$, Eq. (23)

Fig. 2

Rate of Growth of the Surface Area L in Dependence on Supersaturation for Various B for the Purely Surface Diffusive Mechanism

Estimate of Individual Constants

Width of diffusion layer. The quantity δ is defined at best by Eq. (9). On substituting the typical values for $\eta \sim 10^{-2}$ g/cm^2 s, $\varrho_s \sim 1$ g/cm^3, $D \sim 10^{-5}$ cm^2 s^{-1} we obtain $\delta = 1/57 (X/v)^{1/2} = 10^{-2} - 10^{-3}$ cm, for $X = 1$ cm and $v = 1 - 30$ cm/s. So estimated value of δ is in agreement with the expected values[27] for well stirred solutions $\delta \sim 10^{-3}$ and poorly stirred solutions $\delta \sim 10^{-2}$ cm.

Coefficient of mass transfer by diffusion k_d. This coefficient k_d is defined by Eq. (8). By substituting for δ and $D \sim 10^{-5}$ cm^2/s we obtain $k_d = 10^{-2} - 10^{-3}$ cm/s.

Constant B. Into definition equation (16) are substituted corresponding values $\varepsilon = 2 - 5$, $a/\lambda_s = a/(10a - 100a) = 0 \cdot 1 - 0 \cdot 01$. $T = 300$ K, $kT = 4 \cdot 14 \cdot 10^{-14}$ erg, $B = (0 \cdot 02 - 0 \cdot 5) (\gamma/kT)$, where γ is the free surface energy corresponding to 1 growth unit and γ' the free surface energy of 1 cm^2. As γ is not known the approximate relation $\gamma z = \gamma'$ is used, where z is the number of growth units per 1 cm^2 $z = 1/a^2$.

For the considered solubility 1 mol/1 $- 30$ mol/1 the corresponding γ' should be[11] $\gamma' \sim \sim 1 - 30$ erg/sm^2. For $a = 5 - 10 \cdot 10^{-8}$ cm is $\gamma/kT = 0 \cdot 06 - 7$. The expected value of constant B is then $B = 10^{-3} - 5$. Value of the experimentally determined[9,10,26] B is in the range $10^{-3} - 5 \cdot 10^{-1}$.

Constant C defined by Eq. (18) includes some quantities which are very hard to estimate. Nevertheless, at least an estimate of the order of magnitude of the value of this constant is made. By substituting $kT/h \sim 10^{13}$ s^{-1}, $\beta = 1$, $c_0 = 1$, $N_0 = 10^{19} - 10^{21}$ particles/cm^3, $\Omega = 10^{-22}$ cm^3/particle, $A = 10^{-7}$, $\Delta G_{deh} = 10 - 13$ kcal/mol, and $C = 10^{-6} - 10^{-2}$.

Constant $K(\sigma)$ defined by Eq. (22) is dependent on values of k_d and $k_i(\sigma)$ in the given system and is thus in some cases also dependent on σ. The curve $K(\sigma)$ for $10^{-1} < k_i(\sigma)/k_d < 10$ is plotted in Fig. 1.
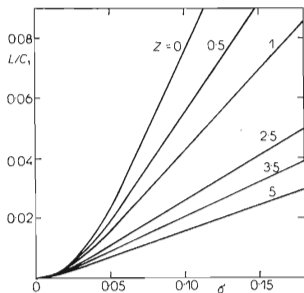
FIG. 3

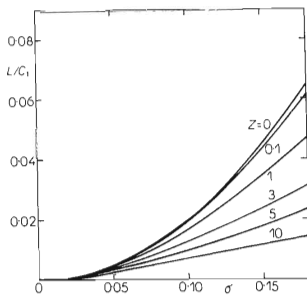Dependence of L on σ for $B_1 = 0 \cdot 1$ and Various Z

FIG. 4

Dependence of L on σ for $B_1 = 0 \cdot 5$ and Various Z

Rate of Growth of Surface Area of Crystals

Rate of growth of surface area of crystals has already been expressed by Eqs (*15*) and (*25*). In Fig. 2 is Eq. (*15*) evaluated for $B = 10^{-3}$; 10^{-2}; $5 . 10^{-2}$; $0·1$; $0·2$; $0·3$; $0·5$; $0·7$; and $1·0$ in the range $\sigma = 0·01 - 0·20$ which comes into consideration in experimental measurements.

For values of B greater than 1 is $\tanh B/\sigma \approx 1$ and Eq. (*15*) becomes a purely parabolic dependence.

Eq. (*25*) is arranged into the form

$$L = C_1 \sigma / \{ Z + [(\sigma/B_1) \tanh B_1/\sigma]^{-1} \} , \qquad (25a)$$

where $C_1 = CK(\sigma)$, $B_1 = B/K(\sigma)$ and $Z = C_1 \delta / DN_0 \Omega$. Equation (*25a*) is evaluated for $B_1 = 0·1$; $0·5$ and $1·0$ for values of $Z = 0·1 - 20$. The effect of increasing value of Z is obvious from Figs 3, 4 and 5.

Reaction Order of Crystallization

The formal reaction order of crystallization g with regard to Eq. (*6*) can be determined from the shape of curves plotted in Figs 2 to 5. By plotting the growth rate L in dependence on supersaturation in logarithmic coordinates for individual parts of this dependence straight lines can be used which in a limited range of σ satisfactorily

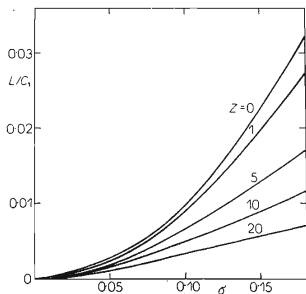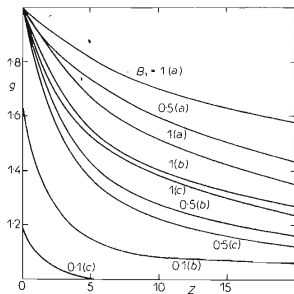

Fɪɢ. 5

Dependence of L on σ for $B_1 = 1·0$ for Various Z

Fɪɢ. 6

Reaction Order of Crystallization g in Dependence on Z for $B = 0·1$; $0·5$; $1·0$ for Intervals: σ $a = 0·01 - 0·05$, $b = 0·05 - 0·10$, $c = 0·10 - 0·20$

approximate the actual dependence. Slope of the straight line is then giving the reaction order g and the intercept on the axis y the value of the crystallization constant k_g. For $Z = 0$, *i.e.* for the mechanism of surface reaction where volume diffusion is negligible g, are given in Table I for individual values of B

With the change in the reaction order k_g changes as well. In case the volume diffusion is not negligible, g is again determined by the graphical method. The dependence $L - \sigma$ (25a) is approximated by straight lines in the intervals $\sigma = 0.01$ to 0.05; $0.05 - 0.1$ and $0.1 - 0.2$. The corresponding reaction orders in dependence on Z are given in Fig. 6.

DISCUSSION

It is obvious from the made analysis that Eqs *(1)* or *(2)* are only valid in limited intervals of supersaturations. If surface reaction is the controlling operation of the growth, k_i can be expressed on basis of physical characteristics of the operation *(26)*. The reaction order g is here determined only by the value of constant B and the considered interval of supersaturation (Table I). In the case surface reaction is the controlling operation of crystallization in the whole interval of supersaturations, $g = 2$ for $B \geqq 0.5$ and $g = 1$ for $B \leqq 0.005$. Corresponding crystallization constants k_g are thus constant as well. In these limiting cases Eqs *(1)* or *(2)* are satisfied in the whole interval of supersaturations (it is not reasonable to assume for the growth measurements $\sigma > 0.20$). For $0.005 < B < 0.5$ the values of the formal reaction order are between 1 and 2 which change moreover with changing supersaturation. This means that both Eqs *(1)* and *(2)* are valid only in a certain range of σ and after exceeding the limiting supersaturation both g and k_g do change.

In the case the crystal growth is controlled by the mechanism of diffusion only, the volume diffusive model BCF can be applied according to which for $\sigma < \sigma_{\text{transition}}$ is $g = 2$ and

$$k_g = \varrho_c D N_0 k T \Omega / \left[c_0^2 \, 4\gamma a \, \ln \left(4\pi\gamma / bkT\sigma \right) \right] .$$

For $\sigma > \sigma_{\text{transition}}$ is $g = 1$ and k_g is given by the relation *(8a)*. As $\sigma_{\text{transition}}$ is situated in the region of supersaturation which can be studied only by use of special techniques $(\sigma_{\text{transition}} \sim 7 \cdot 10^{-3} - 10^{-5})$ it is out of question for consideration in industrial measurements and thus Eqs *(1)* or *(2)* can be considered to be valid in the whole range of possible supersaturations, also in the case when volume diffusion is the controlling operation.

In the last and the most frequent case both the surface reaction and diffusion in the solution participate on the growth. In this case the reaction order depends not only on supersaturation and the value of constant B but also on the contribution of volume diffusion characterized by the constant Z. In such case Eqs *(1)* or *(2)* are valid only for concrete conditions and in a narrow interval of supersaturations.

The contribution of volume diffusion on the value of the reaction order g was experimentally determined for $KAl(SO_4)_2$ (ref.[19]), where at increasing velocity $v = 0$ to $100\ cm/s$ the reaction order has increased continuously in the range from 1·25 to 1·62. Since in the used experimental arrangement both σ and B were constant, changes in the values of g were the result of changes in the quantity Z only. The determined dependence $g-v$ is in agreement with the theoretical dependence $g-Z$ because with increasing v decreases δ, and thus Z as well and with decreasing Z continuously increases the reaction order g (Fig. 6).

In equations for the growth of crystals there appears also the interfacial tension crystal–solution γ' in the constant B. The approximate value of B can be in some cases determined on basis of experimental measurements and γ' then calculated for the considered compound. The interfacial tension is an important quantity which determines the size of the metastable region of the supersaturated solution of the compound[13] and its nucleation characteristics[12].

The comparison of the formal reaction kinetics to the molecular kinetic equations proves that it is necessary to be very cautions in making conclusions on the nature of the controlling operation in the crystal growth on basis of the knowledge of the reaction order g. It is obvious that for $g = 2$ surface reaction is always the controlling operation if we neglect the insignificant range of supersaturation in which $g = 2$ also in the volume diffusion model. But for $g = 1$ it is not clear whether surface reaction of diffusion in the solution is the controlling operation as this value is admissible for both mechanisms. Nor in the case $1 < g < 2$ can be stated that diffusion and surface reaction contribute to the growth simultaneously as the order which is not a whole number is also possible in the case of an effective surface reaction alone. Conclusions on the controlling mechanism of crystallization can be made only when the dependences $L - \sigma$ and $L - v$ at $\sigma = $ const. are known.

TABLE I

Formal Reaction Order of Crystallization Controlled by the Surface Reaction

B	g	Interval σ	B	g	Interval σ
>1	2	0·01—0·20	0·1	2	0·01 —0·05
0·7	2	0·01—0·20		1·64	0·05 —0·12
0·5	2	0·01—0·20		1·20	0·12 —0·20
0·3	2	0·01—0·07	0·5	2	0·01 —0·035
	1·92	0·07—0·20		1·37	0·035—0·09
0·2	2	0·01—0·7		1·05	0·09 —0·20
	1·82	0·07—0·20	0·01	1·3	0·01 —0·25
				1	0·03 —0·20
			≦0·005	1	0·01 —0·20

Another problem[14] is related to the value of $K(\sigma)$. From the few information, available in literature results that solution in contact with the growing surface area is always supersaturated, nevertheless the concentration at the surface is smaller than that in the surrounding solution[25]. The supersaturation of solution varies on the surface area of the crystal[16], so $K(\sigma)$ is variable. The problem of distribution of concentration along the area of crystal surface has been discussed[17] several times with the result that it is necessary to consider only the average controlling concentration difference. From this point of view $K(\sigma)$ is also constant for the whole surface area (e.g. Bennema[16] assumes $K(\sigma) = 1$).

The values of $K(\sigma)$, calculated on basis of the experimental measurements of the drop in concentration of solution toward the growing surface area of crystals in a stationary system[18], and the data[19] are given in Table II.

The dependence of $K(\sigma)-\sigma$ cannot be derived on basis of these values due to considerable inaccuracy in the measured concentrations. According to Eq. (22) of KDP, ADP, Sacharose and $KAl(SO_4)_2$ in an unstirred solution holds

$$k_i(\sigma)/k_d \sim 0.2-2$$

which means that $k_i(\sigma) \sim k_d$. In the case of $NaClO_3$ and $MgSO_4$ we obtain

$$k_i(\sigma)/k_d \sim 30-150$$

and thus $k_i(\sigma) > k_d$.

In all these cases, growth in an unstirred solution is controlled both by diffusion of the compound from the surrounding toward the crystal as well as by the proper operation on the crystal surface. Thus the rate of growth of these matters must

TABLE II
Values of $K(\sigma)$ Calculated from the Interferometric Measurements[19]

Compound	$\sigma\%$	$K(\sigma)$	Compound	$\sigma\%$	$K(\sigma)$
$NaClO_3$	0.66	0.007	KDP	8 1	0.31
	0.94	0.05	ADP	5.5	0.68
	1.49	0.04		9.6	0.69
	4.2	0.3		13.5	0.69
$KAl(SO_4)_2$	2.9	0.50	$MgSO_4$	4.6	0.03
	5.8	0.51	Sucrose	2.6	0.30
	10.0	0.35		6.3	0.80

change in dependence on mixing which was for all the mentioned compounds with the exception of KDP and ADP experimentally proved: Sacharose[20], $KAl(SO_4)_2$ (ref.[21]), $MgSO_4$ (ref.[22]) and $NaClO_3$ (ref.[23]). But in literature contradictory results can also be found *e.g.* according to[24] the growth of $KAl(SO_4)_2$ and $NaClO_3$ does not depend on mixing. These discrepancies can be easily explained as the lowest mixing rates applied in the study[24] were above the limiting velocity of liquid motion.

In some studies the formal reaction order g has been found greater than 2. So *e.g.* for the rate of growth of β-methylnaphthalene[25-27] from the solution of ethylalcohol the value of $g = 3·5$. From the foregoing analysis it is obvious that g cannot be greater than 2 for the dislocation growth. If the experimentally determined $g > 2$ some other mechanisms must take part at the growth *i.e.* not only the dislocation growth, *i.e.* growth on disrupted (flawed) F areas, contribution of growth on planes S and K is significant, attachement of macroscopic units to the growing plane, irregular growth at the origin of inclusions *etc.*

LIST OF SYMBOLS

A	surface area of G grams of crystals
a	distance of adjoining units in the crystal
c, c_0	concentration of supersaturated, saturated solution
c_i	concentration on the boundary crystal–solution
$\Delta c = c - c_0$	concentration gradient
c'_c	factor determining the form of spiral growth
D	coefficient of diffusion of the compound in solution
E	activation energy
g	formal reaction order of crystallization
G	mass of crystals in a unit of suspension
k	Boltzman's constant
k'_g	crystallization constant
k_g	crystallization constant
k_d	coefficient of mass transfer by diffusion
k_i	rate constant of the surface reaction
L	rate of growth of the surface area of crystals
m	mass of one crystal
M	molecular weight
N_A	Avogadro number
N_0	concentration of construction units in a saturated solution
N_{s0}	number of growth units in absorption layer per 1 cm^2
n_{s0}	number of growth units in absorption layer per 1 cm^2
T	temperature
v	liquid velocity
X	characteristic crystal dimension
x_0	distance of adjoining kinks in the step
y_0	distance of successive steps
Z	constant (Eq. (25a))

β	retardation factor of the growth unit at its inlet into the kink
δ	width of transition layer
γ	free energy of the edge per growth unit
λ_s	free diffusion path of a molecule on the crystal surface
n	viscosity of solution
ϱ_s	density of solution
ϱ_c	density of crystals
$\sigma = \Delta c/c$	relative supersaturation
ϱ_{crit}	radius of the critical nucleus
Ω	volume of the construction unit of crystal

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