Experimental Determination of the Rates of Nucleation and of Growth of Phase Transformation Centers*

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The processes of granulation by crystallization of molten droplets in the flow of a cooling agent (prilling) and on the cooled surfaces of the granulators are widely used in the chemical and allied industries. The process of granulation (crystallization) of melts and qualitative indicators of granular products, their marketability is determined by the transfer phenomena in the phases and by the kinetics of crystallization and enantiotropic polymorphic transformations in the crystalline phase. Quantitatively the latter are given in the form of dependences of the rate of nucleation and growth of centers of transformation. The processes kinetics is usually less studied, but it determines the structure of the formed crystal phase and the maximum rate of the process. Therefore, most attention is focused on its study. The description of the scheme, of developed experimental laboratory facilities for the study of the rates of nucleation and growth of crystallization centers in the polycrystalline front of the growing group of crystals, as is the case when crystallization occurs in devices in real conditions (constrained growth of crystals) and single crystals in a thin layer (unrestricted growth of crystals) is given. The transfer of heat in the measuring cell and the sample and possible errors of experimental results were estimated using the natural scale method.

Keywords: *nucleation, crystal growth, polymorphic phase transformations.*

Introduction

The dynamics of processes with the initial system restructuring (phase transformations), in particular, pellet formation, depends on the kinetics of crystallization and enantiotropic polymorphic transformations in the crystal phase and on transfer phenomena. It determines the maximum rate (intensity) of pellet formation [1–8]. This stage is least studied. So, the universality of an approach to the description of determination of kinetic parameters (the rate of nucleation ω_n and growth v_g of transformation centers) is based on the possibility of determining independently in one experiment the induction period τ_{ind} preceding the transformation start, and the time change of transformation degree. The first parameter is used to determine ω_n. Rate ω_n and the second parameter are used to determine v_g [1]. The technique was suggested, approved and is being used at N. I. Gelperin department of processes and apparatuses for chemical technology of MITHT [1, 5–8]. In particular, workers of the department developed, tested and use experimental units for the determination of rates of nucleation and crystal growth in melts and solutions in "constrained"

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conditions at high transformation degrees η (τ) ≥ 0.1–0.3 and in "unconstrained" conditions upon the formation and growth of single crystals with simultaneous data interpretation (for each experiment), including graphic images of the boundaries of the centers of the formed new phase and analytical ones, on the basis of suggested interpolation and extrapolation dependences with the use of software developed by us.

The rates of nucleation ω_n and growth v_g of transformation centers were calculated for the first time by processing indirect data. In particular, we calculated the rates of crystallization and enantiotropic transformations for NH_4NO_3 with fillers, for carbamide with fillers, for high- and low-molecular sulfur, for $Al_2(SO)_4$, and also for melts with high crystallization temperatures (300–400° C) (alkali metal hydroxides and nitrates) and for a number of organic substances. The article presents revealed descriptions of phase transformation models, as well as surface energy on the interface, activation energy of self-diffusion and frequency of nucleation in the listed melts. These magnitudes were determined by experimental data processing. For the first time the ratio of ω_n and v_g for crystals in "constrained" conditions (polycrystalline front) and in "unconstrained" conditions with a growth of single crystals was obtained experimentally with the use of a created installation.

Principles of creating new experimental unit and working procedure

Rates ω_n and v_g for single crystals were determined with the use of tools by directly watching the nucleation and growth of the single crystals followed by experimental data processing by the software developed by us [1, 5–8]. The installation [1, 5, 8] developed and described by us was modified to study high-temperature crystallization of melts of alkali metals hydroxides and nitrates. Direct determination of v_g in the "constrained" conditions for the polycrystalline front and the mediated study of ω_n in "unconstrained" conditions were carried out by crystallization in capillaries. Because of the high crystallization temperature of the studied melts we had to break away from using liquid thermostats and to replace them with air baths [1, 8].

In case of enantiotropic polymorphic transformations, crystallization of opaque melts, as well as other phase transformations and those formally similar to them (for example, powders granulation or formation of deposits on pore walls upon their obstruction, etc.) the determination was made indirectly [1, 5, 6, 8] according to time dependences of transformation degree $\eta(\tau)$ and kinetics $\omega_n = f(\Delta t)$. The kinetics of enantiotropic polymorphic transformations in hydroxides and nitrates of alkali metal and in NH_4NO_3 (with fillers) was studied by volumetry and DTA.

The installation for studying the kinetics of melts crystallization in capillaries allows determining at the same time the rates of "unconstrained" nucleation and the linear rate of growth of the "constrained" polycrystalline front. The scheme of the experimental unit is shown in Figure 1.

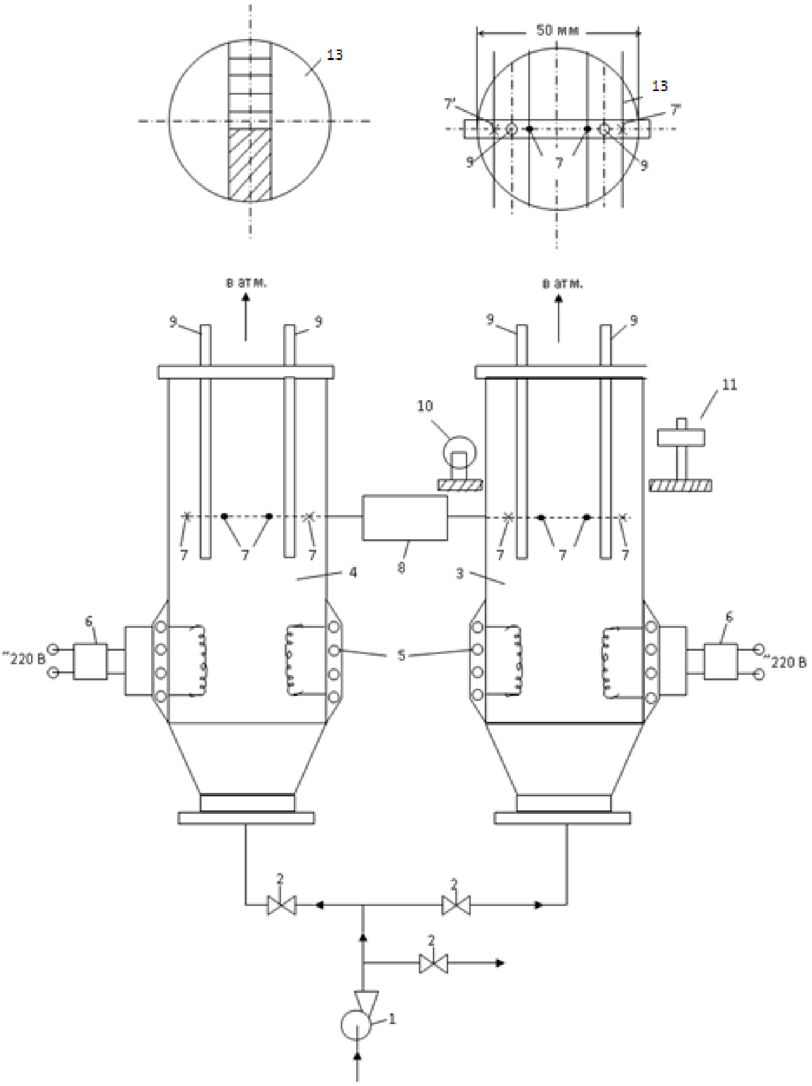

Figure 1. Scheme of experimental unit for studying the kinetics of melts crystallization in capillaries: 1 – laboratory blowers; 2 – valves; 3 and 4 – air thermostats of quartz glass, 5 – nichrome heating coils with thermal insulation; 6 – system for regulating and stabilizing voltage on the coils; 7, 7' – quick-response thermocouples and thermistors, respectively, for measuring the temperature of thermostatic air near the capillaries; 8 – unit for measuring, fixing and transforming signals from the thermocouples and thermistors; 9 – capillaries with the melt; 10 – source of directional light; 11 – measuring microscope with a scale interval of 0.1 mm (MIR-1); 12 –image observed in the microscope; 13 – scheme of arranging the capillaries of the thermocouples and thermistors in the thermostat.

The determination of the duration of the induction period preceding the start of crystallization τ_{ind}, the creation of overcooling in the capillaries and the measurement of the speed of the polycrystalline front movement υ_g were carried out with the use of the suggested temperature control system.

Thermostats 3 and 4 were used for heating (melting) and thermostating the capillaries. They had independent systems for voltage adjustment and stabilization 6, nichrome electric heating spirals for external heating and "open" spirals for internal heating isolated by a heat insulator 5. Air temperature near the capillaries was measured by quick-response thermistor 7’, thermocouple 7 of a wire 0.05 mm in diameter with a brazed seam diameter of 0.08 mm and by block 8 described below for measuring, recalculating, digitizing and inputting information into the computer. On the top of the thermostats, package 9 of two or three capillaries with a diameter of 1 mm and a length of 150 mm was installed. The capillaries had scale marks applied on them at intervals of 5 mm. The optimum capillary sizes are: diameter 1 mm, walls thickness 0.1 mm. The capillaries filling with the working melt by 30–100 mm with the use of vacuum and "sealing off" at one end were developed before [1, 2, 5–8].

Briefly, the technique of carrying out the experiments was as follows. Before the experiments the required air consumption was adjusted by releasing a part of the air into the atmosphere through valve 2. The required temperature in the thermostat for melting (thermostating) 4 and in the measuring cell 3 was also adjusted. A package of capillaries was thermostated for 5 min. (Thermostatting time, other parameters and the experiment technique were developed, proved and described in [1, 2, 5–8]). The melt condition in the capillaries was observed visually. Then the thermocouples package was transferred to measuring cell 3, where temperature t_c corresponding to the required fusion overcooling was maintained. A stop watch was turned on. The moment of crystallization start τ_{ind} in each capillary and the speed of the interface movement υ_g were visually observed. 30 experiments were made. Separate precision experiments at each overcooling were made with the use of one capillary with observation of the described phenomena by means of the microscope. The value of the external heat-transfer coefficient α_c was determined by solving the inverse problem [1, 14, 15] according to the experimental curves of time history of temperature in a filled capillary upon its cooling. The range of the studied overcooling values is presented in Table 1.

Table 1. Parameters of interpolation equations for the ascending branches of dependences of crystal nucleation rates $\omega_з = B_з \Delta t_S^{n_з}$ and growth rates $\upsilon_л = B_л \Delta t_s^{n_л}$

Substance	$B_\text{л}$, [m/(s·deg)]		$n_\text{л}$	
	In capillaries	Single crystal	In capillaries	Single crystal
NaOH	$(6.4\pm0.6)\cdot10^{-7}$	$(1.18\pm0.1)\cdot10^{-5}$	2.0±0.2	2.0±0.2
KOH	$(5\pm0.5)\cdot10^{-7}$	$(8.2\pm0.8)\cdot10^{-6}$	2.0±0.2	2.0±0.2
KNO_3	$(1.9\pm0.2)\cdot10^{-7}$	$(4.47\pm0.4)\cdot10^{-6}$	2.3±0.2	2.2±0.2
Substance	B_n, [m^3·s, deg)]$^{-1}$		$n_\text{з}$	
	In capillaries	Single crystal	In capillaries	Single crystal
NaOH	$(1.1\pm0.1)\cdot10^{4}$	$(1.1\pm0.1)\cdot10^{4}$	2.5±0.3	2.5±0.3
KOH	$(1.7\pm0.2)\cdot10^{4}$	$(1.7\pm0.2)\cdot10^{4}$	2.2±0.2	2.2±0.2
KNO_3	$(8.0\pm0.8)\cdot10^{3}$	$(8.0\pm0.8)\cdot10^{3}$	2.3±0.2	2.3±0.2

Comparing the rates of nucleation and growth of single crystals in the "boundless" volume of optically transparent melts (in the "unconstrained" conditions) and determining the same parameters of the polycrystalline layer formation and growth (in the "constrained" conditions) is of scientific and practical value. In order to determine the kinetic parameters of the substances (Table 1) installation [16] was used. In order to work with the substances with crystallization temperatures up to 400 °C (melts of alkali metal hydroxides and nitrates) a modernized installation (Figure 2) was applied [1, 5, 8].

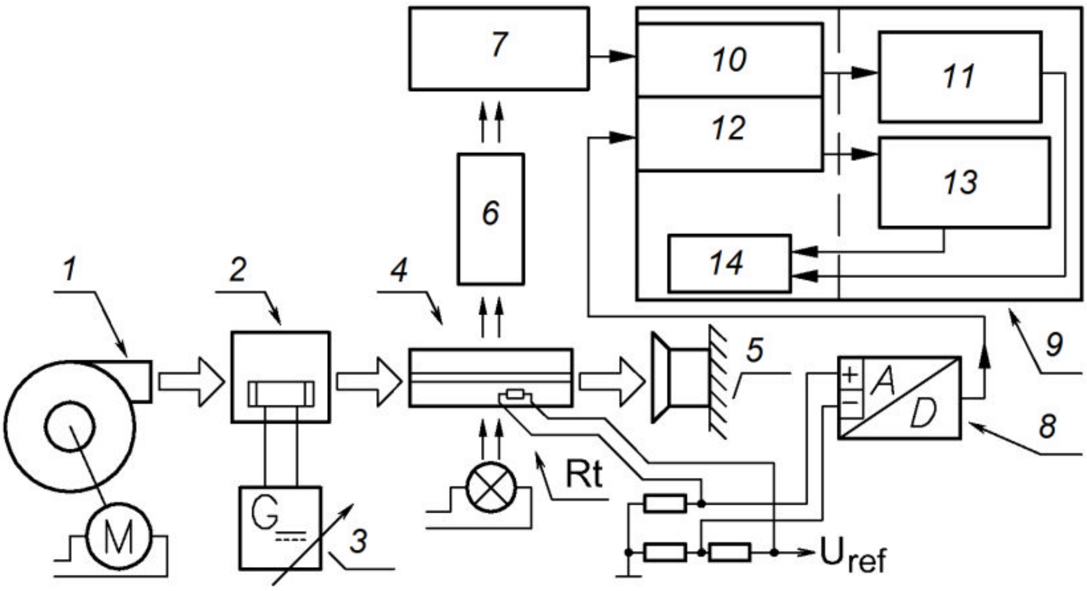

Figure 2. Schematic diagram of measuring installation for thin-layer crystallization: 1 – centrifugal fan, 2 – air duct with heater, 3 – adjustable power supply, 4 – measuring cell, 5 – air exhaust, 6 – microscope objective, 7 – video camera matrix, 8 – ADC (analog-digital converter), 9 – personal computer (personal computer), 10 – video capture card, 11 – video recording software, 12 – port for connecting ADC, 13 – temperature recording software, 14 – disk for data recording, Rt – thermistor (temperature sensor).

The installation provided video as a tool recording of the two-dimensional image of crystal nucleation and growth in a thin (δ = 0.5 mm) layer of a melt (or a solution) using an optical microscope with $\times 10^3$ magnification. At the same time it recorded sample temperature. After digital processing each video frame contained numerical values of sample temperature and the corresponding time elapsed after the process start. The data were transferred to the computer and processed with the use of the suggested software.

The measuring installation (Figure 2) included (as in [16]) personal computer 9 with a video output card – video tuner 10 and blocks 11–14 that transformed and coordinated the image processing and recording, the sample temperature and the maintenance of this temperature by means of an air thermostat (Nos 1, 2, 3 included in the thermal block).

This block operates on the principle of dynamic stabilization of air flow temperature. It contains centrifugal fan 1 with adjustable (in contrast to [16]) consumption of pumped air. Inside the fan, a multispiral heater is installed. It provides air heating to 400°C and control of heating power by means of both hand control and automatic control due to the fact that measuring cell 4 is included in this contour. Then the heated air passes through measuring cell 4 and air exhaust 5.

In contrast to [16], the top and bottom sides of the measuring cell were made of two cover glasses, vacuum-processed and unsoldered, which provided good thermal insulation. The measuring cell had grooves for samples shift and fixation in the microscope field and for samples change. Samples consisted of two cover glasses with a layer of the studied substance between them. It was possible to observe samples both in reflected and in transmitted light, and the layer of the studied substance was in the microscope 6 objective focus. The image of the site of the studied substance layer was projected to the CCD matrix of the video camera 7, from which the video signal came to video tuner module 10 in the computer.

The installation allowed to record temperature directly in the sample by means of a quick-response thermocouple made of Pt-AuPd wires 0.05 mm in diameter tested in aggressive high-temperature melts (NH_4NO_3, NPK, KNO_3, KOH, NaOH, S [1, 5–8, 12, 16]) and used in MITHT in an installation for high-speed thermal analysis developed by E. A. Kazakova [12] and modified [1, 5–8, 16] to study melts crystallization. Usually, in order to speed up the work temperature was measured indirectly only by the control thermistor placed beside the microscope field of view. The thermistor case was made of glass with a thickness of ~ 0.1 mm, which corresponds to the thickness of the cover glasses of the sample. So, it is believed that qualitatively and quantitatively the dynamics of temperature change in the layer of the studied substance and in semi-conductor material of the thermistor was similar.

Temperature was recorded by digitizing signals from the measuring bridge (Figure 2), one of the branches of which contained a thermistor (thermocouple). A two-channel analog data digitizer of the integrating type operated by the computer was used.

The requirements to the studied substances, the technique of samples preparation, the estimation of the error of measuring temperature in the thermostatting air flow and in the sample material and methods of its minimization, the estimation of the possibility of heterogeneous nucleation on the glass wall of the sample and "creeping" growth of crystals on the glass wall surface were described in detail in [1, 5–8, 16] and are not presented here. An estimation of work parameters of the installation blocks (Figure 2) with the use of the natural scales method [9, 10] is presented below.

Estimation of parameters of installation blocks and characteristic of their work

1. *Determination of the length of the site of air flow stabilization in the flat channel at the measuring cell inlet* (Figure 3):

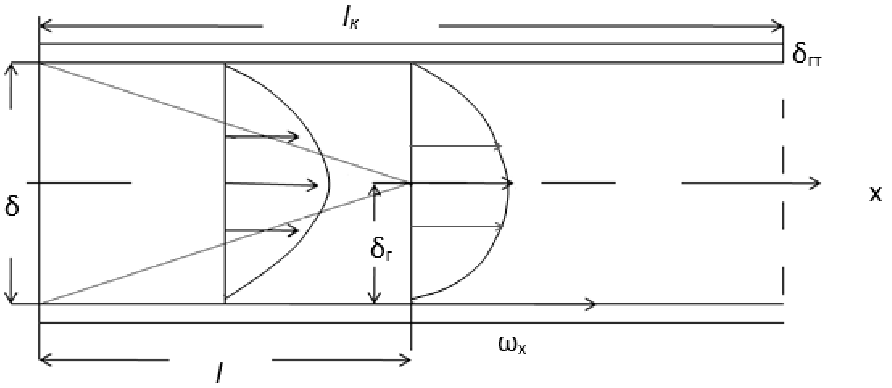

Figure 3. Site of air flow stabilization in the flat channel at the measuring cell inlet.

Channel parameters: l_k = 85 mm; δ_{gl} = 2 mm; λ_{gl} = 0.7 W/(m·deg) (glass); δ = 7 mm; ω = $\frac{1}{\delta}\int_0^{\delta}\omega dh$ = 1 m/s.

Using the known [17] expression for hydrodynamic layer thickness determination $\delta_{\Gamma}/l = 5{,}1/\sqrt{\mathrm{Re}}$ we obtain the expression for the length of the site of hydrodynamic stabilization:

l= 0.098 $\sqrt{\frac{\omega\delta^3}{\upsilon_{в}}} = 0{,}013$ m, which is in agreement with the amended estimates [18].

2. *Estimation of air cooling when passing the channel*:

– convective coefficient of heat transfer from the air flow to the channel wall $\alpha_{в}$:

$$\mathrm{Re} = \frac{\omega\delta}{\upsilon_{в}} = 368 \Rightarrow \text{оценки } \alpha_{в} = \begin{cases} \dfrac{2\lambda_{в}}{\delta} = 8\dfrac{вт}{м^2 град}\,снизу \\ \dfrac{3{,}66\lambda_{в}}{\delta} = 14{,}6\dfrac{вт}{м^2 град}\,оценка\,сверху \end{cases}.$$

– dummy factor of heat transfer in the channel wall $\alpha_{ст.}$:

$$\alpha_{ст.} = \frac{\lambda_{ст.}}{\delta_{ст.}} = 350\frac{вт}{м^2 град};$$

– effective coefficient of heat transfer from the air flow in the channel to the ambient environment (s):

$$\frac{1}{\alpha_{э}} = \frac{1}{\alpha_{в}} + \frac{1}{\alpha_{ст}} + \frac{1}{\alpha_{с.}} \Rightarrow \alpha_{э} = 7{,}8\frac{вт}{м^2 град}.$$

Determination of air temperature drop upon its movement along the channel Δt:

$$\Delta t = \frac{2l_k \alpha_э \left(t_в - t_с\right)}{\delta \rho_в c_в \omega} = 11,4°C.$$

An experimental test showed that the air flow changed its temperature from 150 °C at the inlet to 140 °C at the outlet. This confirms the reliability of the estimation.

3. *Determination of the length of the site of air flow stabilization in the measuring cell channel* (Figure 4):

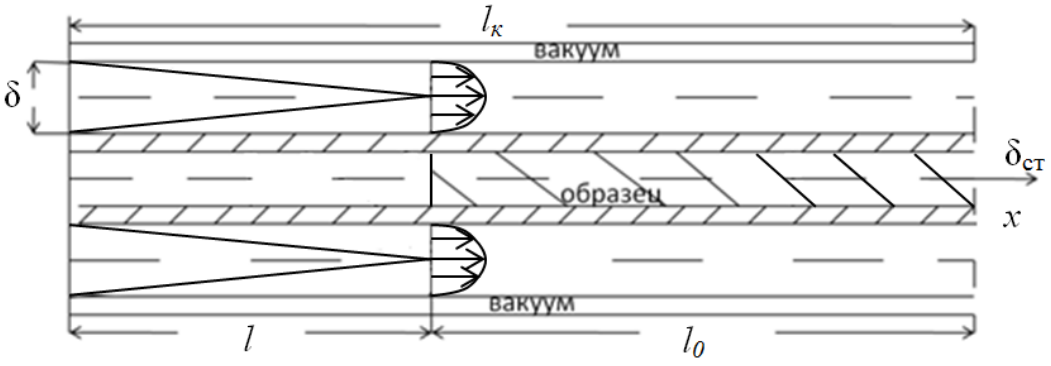

Figure 4. The site of air flow stabilization in the measuring cell channel.
[вакуум means vacuum; образец means sample; к means ch (chanel); ст means st (stabilization)]

The parameters of the cell and of the sample placed into it:

$l_k = 47$ mm; $l_0 = 24$ мм; $\delta_{ст.} = 0{,}1$ mm; $\lambda_{ст.} = 0{,}7 \frac{Вт}{м \cdot град}$ (glass); $\delta = 1$ mm;

Air speed in the cell channel $\omega_1; \omega_1 \cdot 2 = \omega \cdot 7 \Rightarrow \omega = \frac{7}{2} = 3{,}5 м/с.$ The length of the stabilization site:

$$l = 0{,}098 \sqrt{\frac{\omega_l \delta^3}{\upsilon_в}} = 0{,}0013 = 1{,}3 \text{ mm}; \ (l_k - l_0)/2 = 11{,}5 \text{ mm},$$

i.e., the sample is blown by a stabilized air flow. Estimation of the value of the thermostatic air cooling upon passing the measuring cell channel:

$\alpha_в = \frac{2\lambda_в}{\delta} = 56 \frac{вт}{м^2 град}; \alpha_{ст.} = \frac{\lambda_{ст.}}{\delta_{ст.}} = 7000 \frac{вт}{м^2 град}; \alpha_{вак} \to 0$ – heat-exchange coefficient through the vacuumized wall.

Experimental test showed that the air flow upon passing the cell in the stationary mode changes temperature by 0.15 °C, which is in accordance with the made estimation.

4. *Using the natural scales method for estimating the course of heat transfer in the measuring cell and in the sample* (Figure 5):

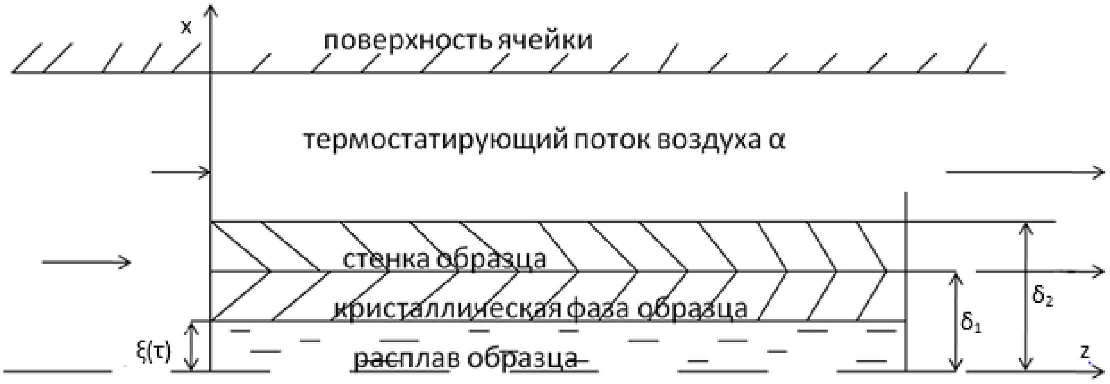

Figure 5. Scheme of the sample position in the measuring cell (z is a symmetry axis). [поверхность ячейки means cell surface; термостатирующий поток воздуха α means thermostatting air flow α; стенка образца means sample wall; кристаллическая фаза образца means sample crystalline phase; расплав образца means crystal melt]

The possible error of the processes occurring in the measuring cells of experimental units for kinetic parameters determination is estimated by the natural scales method [10].

Heat transfer in a sample at the approximation of consecutive transformation and isotropy of the environment parameters found experimentally is described by the known system of heat transfer equations [1, 8].

Natural scales $\left(t_0, \tau_0, x_0, \upsilon_{ло}\right)$ were introduced, and the variables were made dimensionless. A system of heat transfer equations with dimensionless variables was written. A chain of determinantal equations was written, the signs at the corresponding derivatives being left. Estimates of natural scales of heat transfer in the sample are described by the system of resulting equations.

Heat transfer in the cover glass:

$x_{02} = \dfrac{\lambda_2}{\alpha} = \dfrac{0{,}7}{56} = 0{,}0125$ m; $\delta_{ст.} = \delta_2 - \delta_1 = 0{,}0001$ m – the wall practically does not show thermal resistance to heat transfer as compared to thermal resistance of convective heat transfer in the coolant (thermostatting air).

The relaxation times of the temperature layer in the glass and the time of the process course are close. The process is almost stationary:

$$\tau_{ok} = \frac{\lambda_k C_k \rho_k}{\alpha^2} = \frac{0{,}2 \cdot 1{,}3 \cdot 10^3 \cdot 1 \cdot 1 \cdot 10^3}{56^2} = 91 \text{ c} \approx \tau_{проц} \geq 60 \text{ s}$$

The process in the crystalline phase is almost stationary.

Heat transfer in the melt:

$$Ki = \frac{L}{C_k\left(t_{kp} - t_c\right)} = \frac{199 \cdot 10^3}{1.6 \cdot 10^3 \cdot \left(320 - 310\right)} = 12,4.$$

$$x_{ож} = \lambda_{ж} /[\alpha(Ki - 1)] = \frac{0,9}{56(12,4 - 1)} = 0,0014 \text{ m} \qquad \xi(\tau) < \frac{\delta}{2} = 0,0005 \text{ m}$$

The melt layer does not show thermal resistance. The relaxation time of the temperature field in the melt is much less than the process duration. The process is almost stationary:

$$\tau_{ож} = \frac{\lambda_{ж} C_{ж} \rho_{ж}}{\alpha^2 (Ki - 1)^2} = \frac{0,9 \cdot 2,19 \cdot 10^3 \cdot 1696}{56^2 \cdot (12,4 - 1)^2} = 8,2 \text{ c } \tau_{проц} \geq 60 \text{ s.}$$

The scale of linear rate of crystal growth υ_g:

$\upsilon_{ол} = B_{л} \Delta t_S^{пл} = \dfrac{\alpha}{c_k \rho_k} = \dfrac{56}{1,6 \cdot 10^3 \cdot 1696} = 0,00002$ m/s; $\upsilon_{л} \cong 8 \cdot 10^{-3}$ m/s – much less than the speed of the crystallization front movement in the experiments. Therefore, the difference of temperatures at the crystallization front t_s (front warming-up) and in the thermostatting air t_c. should be considered.

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5. *Estimation of phase transformation temperature at the interface* (Figure 6):

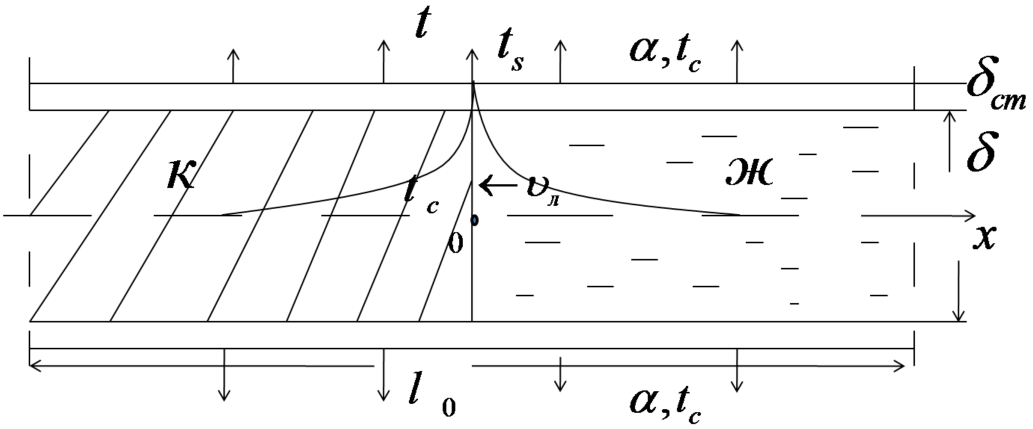

Figure 6. Phase transformation at the interface.

[к means c (crystal); ж means l (liquid); л means l (linear), ст means st (stabilization)]

The mathematical description of heat transfer upon stationary movement of the interface at speed $\upsilon_{л}$ and stationary heat transfer in a rather extended sample $\delta << l_0$ in the case when heat transfer in the sample cross-section is limited only by the thermal resistance to heat removal into the coolant (thermostatting air) has the appearance of quasistationary convective equation (1):

$$\frac{d^2 t_i}{dx^2} \pm \frac{\upsilon_{л}}{\alpha_i}\frac{dt_i}{dx} - \frac{\alpha П}{\lambda_i S}(t_i - t_c) = 0,\ -\infty < x < \infty, \tag{1}$$

i = Ж, К; П, S;

[Ж means L (Liguid), К means C (Crystal); П means P (sample Perimeter, S – sample Section];

with boundary conditions:

$$t_i(\infty) = t_c; \frac{dt_i(\infty)}{dx} = 0$$

$$t_i(0) = t_s$$

$$-\lambda_k \frac{dt_k(0)}{dx} - \lambda_{ж} \frac{dt_{ж}(0)}{dx} = L\rho_k \upsilon_{л}$$

This task describes the stationary movement of the polycrystalline front in the capillary and of the growing monocrystal in the flat preparation. In general, α can be used to take into account the thermal resistance to heat removal into the thermostatting flow $1/\alpha'$ and the thermal resistance of the preparation walls $-\lambda_{cm}/\delta_{cm}$ of the capillary (cover glass) and $2\lambda_i/\delta$ – the layer of the crystallizing substance. For the capillary $П/S = 4/d_k, d_k$ – the internal diameter of the capillary; for the plate $П/S = 2/\delta, \delta$ – the thickness of the crystallizing layer of the substance.

System (1) was rewritten by introducing dimensionless temperature $\theta_i = (t_i - t_c)/(t_s - t_c)$:

Equation (1`) characteristic for equation (1) took the following form:

$$m^2 \pm \frac{\upsilon_{л}}{a_i} m - \frac{\alpha П}{\lambda_i S} = 0, \tag{1`}$$

Where th roots had the following values:

$$m_{1,2} = -\frac{\upsilon_{л}}{2a_{ж}} \pm \sqrt{\left(\frac{\upsilon_{л}}{2a_{ж}}\right)^2 + \frac{\alpha П}{\lambda_{ж} S}} \text{ и } m_{1,2} = \frac{\upsilon_{л}}{2a_k} \pm \sqrt{\left(\frac{\upsilon_{л}}{2a_k}\right)^2 + \frac{\alpha П}{\lambda_k S}}. \tag{2}$$

The general solution of the equation:

$$\theta_i = C_1 e^{m_1 x} + C_2 e^{m_2 x}. \tag{3}$$

According to the condition of temperatures limit $x \to \infty; -\infty$ only the following solutions are usable:

$$\theta_{\text{ж}} = C_1 \exp\left[\left(-\frac{\upsilon_{\text{л}}}{2a_{\text{ж}}} - \sqrt{\left(\frac{\upsilon_{\text{л}}}{2a_{\text{ж}}}\right)^2 + \frac{d\Pi}{\lambda_m S}}\right)x\right] \tag{4}$$

$$\theta_k = C_1 \exp\left[\left(\frac{\upsilon_{\text{л}}}{2a_k} - \sqrt{\left(\frac{\upsilon_{\text{л}}}{2a_k}\right)^2 + \frac{\alpha\Pi}{\lambda_k S}}\right)x\right] \tag{5}$$

From the boundary condition $x = 0 \Rightarrow C_1 = 1$.

Let us substitute the expressions for temperatures in phases (4, 5) in Stefan condition at the mobile interface at $x = 0$:

$$\lambda_k\left[-\frac{\upsilon_{\text{л}}}{2a_k} + \sqrt{\left(\frac{\upsilon_{\text{л}}}{2a_{\text{к}}}\right)^2 + \frac{\alpha\Pi}{\lambda_{\text{к}} S}}\right] + \lambda_{\text{ж}}\left[\frac{\upsilon_{\text{л}}}{2a_{\text{ж}}} + \sqrt{\left(\frac{\upsilon_{\text{л}}}{2a_{\text{ж}}}\right)^2 + \frac{\alpha\Pi}{\lambda_{\text{ж}} S}}\right] = \frac{L\rho_k\upsilon_{\text{л}}}{t_s - t_c} \tag{6}$$

Using experimentally found $\upsilon_{\text{л}}$ we find from equation (6) t_s – temperature at the interface, and, therefore, also the real overcooling (overheat) of the metastable phase upon the movement of the stable phase granules in it.

Results of experimental determination of kinetic parameters and their discussion

In case of homogeneous nucleation (when there are no centers of a size larger than critical in the a metastable phase) stationary distribution of nucleation centers of subcritical size is described by Frenkel equation [1–4]:

$$\omega_{\text{З}} = C\exp\left(-\frac{a}{T}\right)\exp\left[-\frac{b}{T(T_{\Phi} - T)^2}\right] = C\exp\left[-\frac{a}{T}\right]\exp\left[-\frac{b}{T\Delta t_S^2}\right]. \tag{7}$$

Because nucleation upon crystallization and enantiotropic polymorphic transformations is of probabilistic nature [1–4], nucleation rate is defined as the most probable number of nucleation centers $M(\tau)$ formed in the unit volume of a metastable phase V in unit time τ:

$$\omega_{\text{З}} = \frac{1}{V}\frac{dM(\tau)}{d\tau}. \tag{8}$$

The number of expected events (the formation of nucleation centers of critical size) is much less than the number of elementary acts. Therefore, the probability $P(k, \tau)$ of the formation of k phase transformation centers can be described by Poisson distribution [1, 5, 6]:

$$P(k,\tau) = \frac{M(\tau)^k}{k!}\exp[-M(\tau)];\ \ k \geq 0. \tag{9}$$

The probability of fixation of the transformation start (the formation of one and more transformation centers) is equal to:

$$P(k,\tau) = 1 - \exp[-M(\tau)];\ \ k \geq 1. \tag{10}$$

It was determined experimentally by calculating the empirical expectation function of the transformation start $F(\tau)$:

$$P(k,\tau) = F(\tau) = \frac{n(\tau)}{n_{\Sigma}+1} = 1 - \exp[-M(\tau)]; \; k \geq 1, \tag{11}$$

where $n(\tau)$ is the number of experiments where the transformation start at time τ was recorded; n_{Σ} is the total number of experiments. Using dependences (8) and (11) it is possible to calculate nucleation rate using the equations written in the differential and difference forms:

$$\omega_з = -\frac{1}{V}\frac{d\{\ln[1-F(\tau)]\}}{d\tau}, \tag{12}$$

$$\omega_з = -\frac{1}{V}\frac{\Delta\ln[1-F(\tau)]}{\Delta\tau}. \tag{13}$$

When determining nucleation rate, increments $\Delta\ln[1-F(\tau)]$ and $\Delta\tau$ are used. Therefore, is not important to fix exactly the time of the emergence of a critical nucleation center. The technique allows determining ω_n in an isothermal and non-isothermal samples upon the formation of one or k nucleation centers [1, 5, 6, 11]. The adequacy of the technique of determining ω_n in the course of the real process is proved by the satisfactory agreement of the calculated and independent experimental durations of the induction periods preceding the start: of crystallization (obtained by high-speed thermal analysis (HSTA)); sedimentation of melt drops in transparent liquid coolants; polymorphic transformation (obtained by DTA, volumetry, HSTA for NH_4NO_3 (divergence no more than 10±2% with a probability of 90%) [1–5].

An advantage of the suggested technique is its universality (applicability for the experimental determination of nucleation and growth rates in various phase transformations) and cost effectiveness. In each experiment, the following values were recorded simultaneously: the induction period durations (in order to determine ω_n) and the time change of transformation degree $\eta = f(\tau)$ (for opaque environments) or the rate of the formed interface movement (for transparent environments), i.e., $\upsilon_л$ was recorded at once. In the latter case it is necessary to recalculate temperature at the interface, which differs from temperature of the thermostatting environment (equation (6)) using the formulas given in [1, 5, 6]. Then dependences should be plotted: $\omega_з = f(\Delta t_s)$, $\upsilon_л = f(\Delta t_s)$ of kinetic parameters vs driving force (for the mentioned processes, vs overcooling (overheating) of the metastable phase – Δt_s):

$$\lambda_k\left[-\frac{\upsilon_л}{2a}+\left(\frac{\upsilon_л^2}{4a_k^2}+\frac{a_c P}{\lambda_k S}\right)^{1/2}\right]+\lambda_{ж}\left[-\frac{\upsilon_л}{2a_{ж}}+\left(\frac{\upsilon_л^2}{4a_{ж}^2}+\frac{a_c P}{\lambda_{ж} S}\right)^{1/2}\right]=\frac{L\rho_k\upsilon_л}{t_s - t_c}$$

In the first case, the linear rate of transformation centers growth $\upsilon_{\text{л}}$ was determined indirectly by recording the time dependence of transformation degree. Having determined previously nucleation rate ω_n we used this dependence to calculate the linear rate of growth $\upsilon_{\text{л}}$ [1, 5–8]. The calculation was based on the time dependences of volume transformation degree $\eta(\tau)$ at homogeneous and heterogeneous nucleation, respectively, derived in [1, 8]:

$$\eta(\tau_k)=\int_{\tau}^{\tau_k}\beta\left[\upsilon_{\text{л}}(\tau')d\tau'\right]^{n}\omega_{\text{з}}(\tau)\left[\eta_{\max}-\eta(\tau)\right]d\tau+\frac{\beta}{V}\left[\int_{\tau_{\text{инд}}}^{\tau_k}\upsilon_{\text{л}}(\tau')d\tau'\right]^{m} \tag{14}$$

$$\eta(\tau_k)=N_{\text{уд}}\beta\left[(r+\int_{0}^{\tau_k}\upsilon_{\text{л}}(\tau')d\tau')^{n}-r^{n}\right]+\int_{\tau_{\text{инд}}}^{\tau_k}\beta\left[\int_{\tau}^{\tau_k}\upsilon_{\text{л}}(\tau')d\tau'\right]^{n}\omega_{3}(\tau)\left[\eta_{\max}-\eta(\tau)\right]d\tau+\frac{\beta}{V}\left[\int_{\tau_{\text{инд}}}^{\tau_k}\upsilon_{\text{л}}(\tau')d\tau'\right]^{n} \tag*{(15),}$$

where β is the shape factor of the growing nucleation centers, β = 4/3π for spheres; $1 \le n \le 3$ is the dimensionality of nucleation centers growth; $\tau_{\text{инд}}, \tau_k$ are the times of the process start and end; $\eta_{\max} \le 1$ is the maximum transformation degree; $N_{\text{уд}}$ is the quantity of heterogeneous nucleation centers in a unit volume of the metastable phase; *r* is the heterogeneous nucleation center radius.

For practical calculations of $\upsilon_{\text{л}}$ with the use of experimental $\eta = f(\tau)$ dependences in case of "unconstrained" $\upsilon_{\text{л}} \ne f(\eta)$ and "constrained" $\upsilon_{\text{л}} = f(\eta)$ growth differential analogs of equations (14) and (15) were used. In case of spherical nucleation centers they are given by:

$$\eta(\tau_k)=\frac{3}{4}\pi\left[\sum_{i=1}^{N_1}\left[\sum_{j=1}^{N_2}\upsilon_{\text{л}j}\Delta\tau_i\right]^{3}\omega_{3i}\left[\eta_{\max}-\eta(\sum_{i=1}^{N_1}\Delta\tau_i)\right]\Delta\tau_i+\frac{1}{V}\left[\sum_{i=1}^{N_1}\upsilon_{\text{л}i}\Delta\tau_i\right]^{3}\right] \tag{16}$$

$$\eta(\tau_k)=N_{\text{уд}}\frac{3}{4}\pi\left[\left(r+\sum_{k=1}^{N_3}\upsilon_{\text{л}k}\Delta\tau_k\right)^{3}-r^{3}\right]+\frac{3}{4}\pi\left[\sum_{i=1}^{N_1}\left[\sum_{j=1}^{N_2}\upsilon_{\text{л}j}\Delta\tau_i\right]^{3}\omega_{3i}\left[\eta_{\max}-\eta(\sum_{i=1}^{N_1}\Delta\tau_i)\right]\Delta\tau_i+\frac{1}{V}\left[\sum_{i=1}^{N_1}\upsilon_{\text{л}i}\Delta\tau_i\right]^{3}\right] \tag{17}$$

where $N_1=\dfrac{\tau_k-\tau_{\text{инд}}}{\Delta\tau_{ij}}, N_2=\dfrac{(\tau_k-i\Delta\tau_i-\tau_{\text{инд}})}{\Delta\tau_i}$;

$$\Delta\tau_j=\begin{cases}0.5\Delta\tau_i \\ \Delta\tau_i\end{cases} \text{при } j=1;\ N_3=\tau_k/\Delta\tau_i;\ \Delta\tau_k \ne \Delta\tau_j .$$

The choice of a calculation equation is determined the by existence or absence of $\tau_{\text{инд}}$. In practice [1, 2, 4–8], $\tau_{\text{инд}} \ne 0$. That is, it is necessary to use equations (14), in practice (16). Then *vg*$_i$ is found step by step in time by taking into account the known interrelation between η_i and τ_i by minimizing functional $\sum_{i=1}^{N_i}\left|\eta_i^{\partial}-\eta_i^{p}\right|\xrightarrow{\upsilon_{\text{л}i}}\min$ by one-parametrical optimization [1, 5–8]. It was found that crystal growth upon crystallization (of sulfur, carbamide, NH_4NO_3, KNO_3, KOH, NaOH, acetone anil etc.) to $\eta \leq 0{,}3 - 0{,}4 \pm 0.05$ is "unconstrained" [1, 5, 6, 8]. The growth of areas of the formed modifications at enantiotropic polymorphic transformation in NH_4NO_3, KNO_3, KOH, NaOH to $\eta = 0.4 \pm 0.05$ is also "unconstrained". The suggested technique allows considering at each step $\Delta\tau_i$ in time and the change of shape factor β of the growing center if additional information about this (visual, X-ray diffraction, optical etc.) is available. In order to facilitate the calculation of $\upsilon_л$ on the basis of equations (14, 15) a number of simplified partial dependences were obtained at fixed assumptions in [1, 5, 6, 8].

So far no comparison was carried out of crystal nucleation and growth rates obtained (for example, in capillaries) in "constrained" conditions (as in a real process) with the values of these kinetic parameters for single crystals in "unconstrained" conditions. All the theoretical dependences of crystal nucleation and growth rates were obtained and are true only for the last case, and their equality is postulated by default [1, 4–8]. Without detailed analysis of this, reliable calculations of the course of crystallization and polymorphic transformations are impossible [1–4, 7, 8]. Experimental determination of nucleation and growth rates for the transformation centers is possible at rather small overcooling (or overheating in case of reverse enantiotropic polymorphic transformations). This is usually true for the ascending branch of $\omega_з = f(\Delta t_s)$ and $\upsilon_л = f(\Delta t_s)$ dependences. It is suggested to extrapolate experimental data $\upsilon_л = f(\Delta t_s)$ to the area of large Δt_s using the known dependence for theoretical calculation $\upsilon_л = f(\Delta t_s)$ [1, 2, 4–8]:

where C, D = const, $d = D\sigma$, $a = \frac{U}{R}$; U, σ are the activation energy of self-diffusion and superficial energy at the interface, respectively. The good coincidence of U values (with an error no more than 10±3% and probability 90%) obtained by processing independent experimental data $\omega_з = f(\Delta t_s)$ and $\upsilon_л = f(\Delta t_s)$ according to equations (7), (18) and to the dependence of melt viscosity on temperature, respectively, indirectly indicates the adequacy of the suggested procedure of determining the dependences in the course of the real process [1, 5–8]. This is indicated also by the coordination of the extrapolation data and the results of direct experiments as applied to a number of substances that are difficult to crystallize (acetone anil, sulfur with a high content of polymeric sulfur etc.) (Figure 7). The obtained experimental data (the ascending branches of dependences (7) and (18), respectively) for a wide range of substances with an error of 10±2% and probability of 90% $\omega_з = f(\Delta t_s)$ and $\upsilon_л = f(\Delta t_s)$ were interpolated by exponential dependences $\omega n = B_з \Delta t_s^{n_з}$, where B_3 = const, and $1 \leq n_л \leq 2$ respectively, which is in a good agreement with the theory [1, 2, 4–8].

$$\upsilon_л = C'\exp\left(-\frac{a}{T}\right)\exp\left[-\frac{d}{T(|T_Ф - T|)}\right] = C'\exp\left[-\frac{a}{T}\right]\exp\left[-\frac{d}{T(|T\Delta t_s|)}\right]. \qquad (18)$$

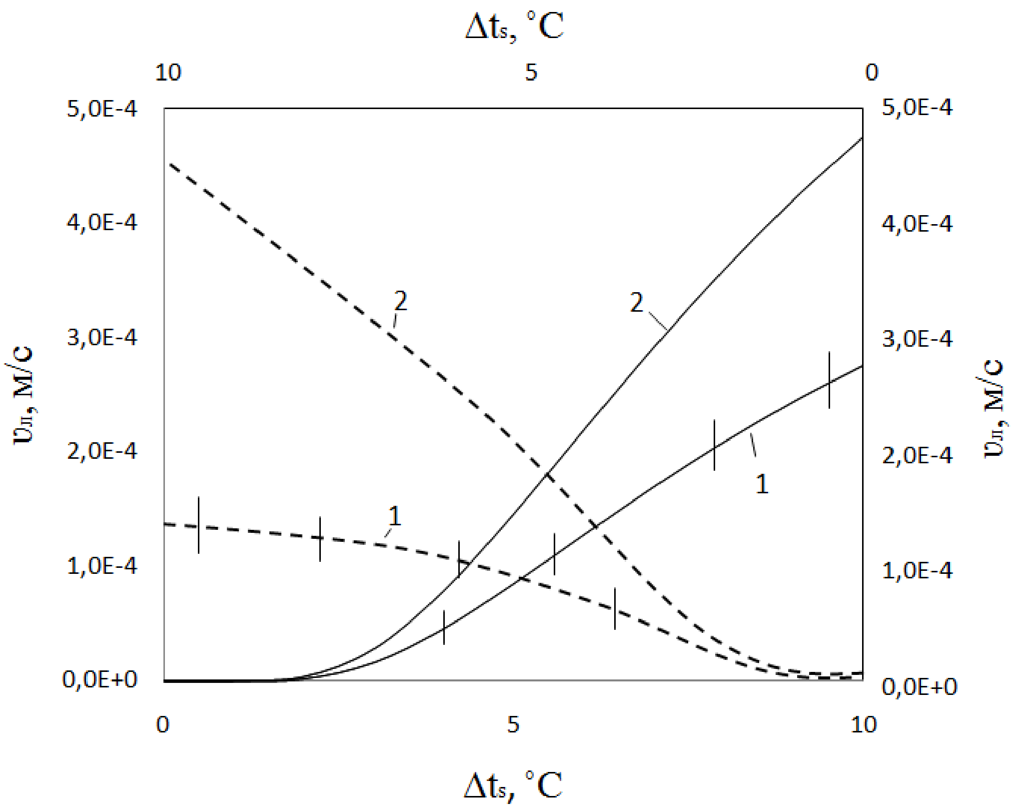

Figure 7. Dependences of the linear rate of crystal growth υg of sulfur (solid lines) and carbamide (dashed lines) on overcooling Δt_s: 1 –obtained experimentally and related to $\Delta t_s = t_{кр} - t_c$ calculated by temperature of the thermostatting environment t_c (the vertical strokes indicate the confidential interval of experimental data measurement with a probability of 90%); 2 – obtained experimentally and related to $\Delta t_s = t_{кр} - t_c$ calculated by temperature at the interface calculated taking into account Stefan's condition.

[л means l (linear); м/с means m/s]

As compared to [16], the software of the installation (Figure 2) was complemented with the possibility of determining ω_n not only by the quantity of nucleation centers formed by a certain timepoint, but also by processing the massif of $\tau_{инд}$ using equations (7–18) with the application of the above algorithm. This allowed comparing two approaches to the determination of nucleation rate and confirming their adequacy to the real process. Besides, the software allowed choosing sites of the growing crystal surface, to calculate the rate of their growth, and, as information on the linear rate of crystal growth was accumulated, depending on overcooling – to process the obtained massifs described by interpolation $\upsilon_g = B_л \Delta t_s^{n_л}$ and extrapolation (18) dependences.

The same was done with respect to the experimental data on nucleation rate depending on melt overcooling after processing them by interpolational $\omega_n = B_з \Delta t_s^{n_з}$ and extrapolational (7) dependences. Besides, the experimental dependences ω_n, $\upsilon_g = f(\Delta t_s)$ were processed with the use of the program to determine the activation energy of self-diffusion U calculated according to independent data $\omega_n = f(\Delta t_s)$, $\upsilon_g = f(\Delta t_s)$. The agreement of the latter values with themselves and with the data obtained according to the dependence of the melt viscosity on temperature was checked. This was additional indirect evidence of the correctness of the work done and of its adequacy to the real process [1] compared. Besides, the values of superficial energy at the interface σ, nucleation frequency ν* included in constants *C* and *C′* (equations 7 and 18) were determined. The obtained data are presented in Table 2.

Table 2. The values of parameters in the extrapolational equations for the determination of crystal nucleation and growth rates.
(The confidential intervals are specified with a probability of 90%)

Parameter	NaOH		KOH		KNO_3	
	Single crystal	In capillary	In capillary	Single crystal	In capillary	Single crystal
c, $(m^3\cdot s)^{-1}$	$3.6\cdot10^{7}\pm3\cdot10^{6}$	$3.3\cdot10^{8}\pm1.2\cdot10^{7}$	$2.2\cdot10^{9}\pm2\cdot10^{8}$	$9.2\cdot10^{8}\pm2.2\cdot10^{7}$	$1.7\cdot10^{9}\pm1.5\cdot10^{8}$	$1.1\cdot10^{6}\pm1.2\cdot10^{5}$
a, K	$1.6\cdot10^{3}\pm0.2\cdot10^{2}$	$1.6\cdot10^{3}\pm1.5\cdot10^{2}$	$2.9\cdot10^{3}\pm2\cdot10^{2}$	$2.9\cdot10^{3}\pm3\cdot10^{2}$	$2.2\cdot10^{3}\pm2\cdot10^{2}$	$2.2\cdot10^{3}\pm2\cdot10^{2}$
U, J/kgmol	$1.8\cdot10^{7}\pm2\cdot10^{6}$	$1.8\cdot10^{7}\pm1.9\cdot10^{6}$	$6.2\cdot10^{7}\pm5\cdot10^{5}$	$6.2\cdot10^{7}\pm4\cdot10^{5}$	$1.9\cdot10^{7}\pm2\cdot10^{6}$	$1.9\cdot10^{7}\pm2\cdot10^{6}$
b, K^3	$1.1\cdot10^{5}\pm1.2\cdot10^{4}$	$1.1\cdot10^{5}\pm1\cdot10^{4}$	$1.2\cdot10^{5}\pm1.1\cdot10^{4}$	$1.2\cdot10^{5}\pm1.2\cdot10^{4}$	$3.1\cdot10^{5}\pm2\cdot10^{4}$	$3.1\cdot10^{5}\pm3\cdot10^{4}$
σ, J/kgmol	$1.9\cdot10^{5}\pm1.5\cdot10^{4}$	$1.9\cdot10^{5}\pm1.5\cdot10^{4}$	$2.0\cdot10^{5}\pm1\cdot10^{4}$	$2.0\cdot10^{5}\pm2\cdot10^{4}$	$3.9\cdot10^{5}\pm4\cdot10^{4}$	$3.9\cdot10^{5}\pm4\cdot10^{4}$
$T(\omega_{з}^{max})$, K	555±50	555±50	593±5	593±55	557	557
ω_{nucl}^{max} $(m^3\cdot s)^{-1}$	$1.5\cdot10^{7}\pm1.2\cdot10^{6}$	$1.6\cdot10^{7}\pm1.5\cdot10^{6}$	$1.4\cdot10^{7}\pm1.3\cdot10^{6}$	$1.2\cdot10^{7}\pm1.1\cdot10^{5}$	$2.7\cdot10^{7}\pm2.5\cdot10^{6}$	$2.4\cdot10^{7}\pm2\cdot10^{5}$
$\frac{T(\omega_{зl}^{max})}{T_{cryst}}$	0.93±0.1	0.93±0.1	0.94±0.1	0.94±0.1	0.92±0.1	0.92±0.1
c', m/s	0.3±0.05	16.4±1.4	$1.1\cdot10^{2}\pm1\cdot10^{1}$	1.8±0.15	$1.4\cdot10^{2}\pm15$	2.0±0.15
a, K	$1.6\cdot10^{3}\pm1.5\cdot10^{2}$	$1.6\cdot10^{3}\pm1.5\cdot10^{2}$	$2.9\cdot10^{3}\pm2.5\cdot10^{2}$	$2.9\cdot10^{3}\pm3\cdot10^{2}$	$2.2\cdot10^{3}\pm2.1\cdot10^{2}$	$2.2\cdot10^{3}\pm2\cdot10^{2}$
U, J/kgmol	$1.8\cdot10^{7}\pm1.9\cdot10^{6}$	$1.8\cdot10^{7}\pm1.5\cdot10^{6}$	$6.2\cdot10^{7}\pm5\cdot10^{6}$	$6.2\cdot10^{7}\pm5\cdot10^{6}$	$1.9\cdot10^{7}\pm2\cdot10^{6}$	$1.9\cdot10^{7}\pm2\cdot10^{6}$
d, K^2	$1.7\cdot10^{4}\pm1.5\cdot10^{3}$	$1.7\cdot10^{4}\pm1.5\cdot10^{3}$	$1.9\cdot10^{4}\pm1.6\cdot10^{3}$	$1.9\cdot10^{4}\pm1.5\cdot10^{3}$	$3.1\cdot10^{4}\pm3\cdot10^{3}$	$3.1\cdot10^{4}\pm3\cdot10^{3}$
D, K^2 $\frac{кг\cdot моль}{Дж}$	$8.9\cdot10^{-2}\pm9\cdot10^{-3}$	$8.9\cdot10^{-2}\pm9\cdot10^{-3}$	$9.5\cdot10^{-2}\pm9\cdot10^{-3}$	$9\cdot10^{-2}\pm1.5\cdot10^{-3}$	$7.9\cdot10^{-2}\pm7\cdot10^{-3}$	$7.9\cdot10^{-2}\pm7\cdot10\text{-}^{3}$
$T(\upsilon_{л}^{max})$, K	525±50	525±50	573±50	573±50	527±50	527±50
$\upsilon_{л}^{max}$ (м/с)	$9.7\cdot10^{-3}\pm9\cdot10^{-4}$	$0.5\cdot10^{-4}\pm0.6\cdot10^{-5}$	$3.8\cdot10^{-4}\pm4\cdot10^{-5}$	$6.2\cdot10^{-3}\pm7\cdot10^{-4}$	$1.1\cdot10^{-3}\pm1\cdot10^{-4}$	$1.5\cdot10^{-2}\pm1\cdot10^{-3}$
$\frac{T(\upsilon_{л}^{max})}{T_{cryst}}$	0.88±0.09	0.88±0.09	0.91±0.09	0.91±0.09	0.87±0.09	0.87±0.08

Conclusion:

1. A theoretically reasonable fundamental universal technique for direct and indirect determination of nucleation and growth rates (in particular, for a crystal phase) is described. The technique was developed by the authors at N. I. Gelperin department of processes and apparatuses for chemical technology of MITHT of the Moscow technological university.
2. A scheme description, a possible structure of the created universal experimental laboratory units for the determination of rates of nucleation and growth of crystallization centers in the polycrystalline front of a growing collective of crystals were presented. These processes take place during the operation of crystallization devices in actual practice ("constrained" crystal growth) and in single crystals in a thin layer ("unconstrained" crystal growth). The latter data are necessary to estimate the mechanisms of crystal growth and kinetic coefficients that are difficult to determine. For the first time it was established that if the difference between the nucleation rates in the "constrained" and "unconstrained" conditions is small (10 – 20 ± 2% with a probability of 90%), the difference between crystal growth rates is considerable (several-fold). Perhaps this explains the irreproducibility of the results obtained by different authors in different conditions. Thus, physicochemical and crystallographic parameters, coefficients, for example, of superficial energy in crystal-melt systems, activation energy of self-diffusion, nucleation frequencies upon crystal surface formation should be determined by experimental data for single crystals. In contrast, the calculation of the dynamics of a new phase formation, the movement of interfaces and other engineering calculations should be performed using the considerably smaller rate of constrained crystal growth. The above is probably also true in case of other types of transformations with restructuring of the initial system.
3. Heat transfer in the measuring cell and in the sample, as well as possible errors of experimental results are estimated with the use of natural scales method.

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