Thus, the results of our analysis show that the dynamics of the cavitation zone must be taken into account when interpreting experimental profiles obtained for the velocity of contact surfaces in the study of separation phenomena in low-strength media. The influence of the cavitation zone on the dynamics of a free surface was first observed in [4].

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DIFFUSION KINETICS WITH CRYSTAL GROWTH FROM THE GAS PHASE

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A series of relations describing the flow of matter to the surface of a crystal, growing in a sealed cylindrical ampul from a gas—vapor medium, was derived in [1-3]. It was assumed that the growth process is governed by the diffusion kinetics, but the question of when this is valid was not studied. At the same time it is necessary to assess the conditions under which the transport of matter is the limiting stage. It is known that crystals which grow in the diffusion region are distinguished by the fact that they exhibit the highest perfection. In addition, the rate of growth and the character of the impurity distribution in the case of the diffusion kinetics depend directly on technological parameters, such as the temperature gradients, the dimensions of the system, the orientation of the system, the pressure, etc.; this enables efficient control of the growth process.

Diffusion kinetics is realized in cases when the characteristic transport time τ_v is much longer than the characteristic time of the phase or chemical transformation itself. In the case of growth with the help of gas-transport reactions the chemical transformations can be schematically represented in terms of stages: adsorption of gaseous reagents on the surface of the growing crystal, chemical reaction between adsorbed molecules, and desorption of the reaction products. We denote the duration of each stage by τ_a, τ_r, and τ_d, respectively. We shall assume that a reaction of the type

$$\nu_1 A_1(g) \rightleftarrows \nu_2 A_2(g) + \nu_3 A_3(s)$$

occurs on the solid surface. Here A_i designate the chemical elements; ν_i are the stoichiometric coefficients; g and s are gaseous and solid products.

According to [4, 5], the characteristic times of the adsorption stage τ_a and desorption stage τ_d are

$$\tau_{(i)} = \delta_{(i)} \sqrt{\frac{2\pi m_{(i)}}{kT}} \exp\left(\frac{U_{(i)}}{kT}\right) \quad (i = a,\ d), \tag{1}$$

where $m_{(i)}$ is the mass of the adsorbed molecule m_a or the desorbed molecule m_d; $U_{(i)}$ is the activation energy of the corresponding process; k is Boltzmann's constant; T is the tempera-

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ture; $\delta_{(i)} \simeq \sqrt{2\pi kT/\varphi_{(i)}}$ is the effective thickness of the surface layer; $\varphi_{(i)}$ is the second derivative of the energy of the molecule at the point of the minimum of the potential energy.

According to Eq. (1),

$$\frac{\tau_d}{\tau_a} = \frac{\delta_d}{\delta_a}\sqrt{\frac{m_d}{m_a}}\exp\left(\frac{U_d - U_a}{kT}\right).$$

Setting $\delta_d \simeq \delta_a$ and using the fact that $U_d > U_a$ [6], we verify that of these two stages the limiting stage is desorption of the reaction products, with the exception of the case when $m_d \ll m_a$.

The characteristic time τ_r of the chemical reaction is, in order of magnitude, $\tau_r \simeq 1/Z$ (Z is the number of collisions on the surface between adsorbed molecules A_i which terminate with chemical transformations). We shall assume that chemical transformations occur when the energy of the vibrational motion of the molecules is higher than the activation energy ε_0 of the chemical reaction. Then

$$Z = \int_{\varepsilon_0}^{\infty} \sigma v_s\, dn_\varepsilon,\quad v_s = \sqrt{\frac{2\varepsilon}{m_1}}\exp\left(-\frac{U_{d,1}}{kT}\right),$$
$$dn_\varepsilon = \frac{2n}{\sqrt{\pi (kT)^3}}\exp\left(-\frac{\varepsilon}{kT}\right)\sqrt{\varepsilon}\, d\varepsilon \tag{2}$$

(σ is the effective collision cross section in a two-dimensional gas). In writing Eq. (2) we took into account the fact that the velocity v_0 of the vibrational motion and the velocity of the motion along the surface are related by the relation $v_0 = v_s \exp(U_{d,1}/kT)$ ($U_{d,1}$ is the desorption energy of the molecules A_1).

We express the number n of adsorbed molecules of the component A_1 as

$$n = (P_1/kT)\delta_a \exp(U_{d,1}/kT) \tag{3}$$

where P_1 is the partial pressure of the given substance at the surface of the crystal. After substituting Eq. (3) into Eq. (2) and integrating we obtain

$$\tau_r = \frac{kT}{\sigma\delta_a P_1}\sqrt{\frac{m_1\pi}{2kT}}\,\frac{\exp(\varepsilon_0/kT)}{1+\varepsilon_0/kT}. \tag{4}$$

Estimates made using the formulas (1) and (4) show that as the crystals grow by means of chemical transport the slowest of the three stages studied is, as a rule, the chemical transformation itself on the solid surface. Thus, setting $\sigma \simeq \delta_a \simeq \delta_d = 10^{-8}$ cm, $m_a \simeq m_d$, $T = 10^3$ K, $U_d/kT = 10$, $\varepsilon_0/kT = 5$, we obtain $\tau_d/\tau_r \simeq 10^{-4} P_1$ (here P_1 is given in Pa), i.e., when $P_1 \lesssim 10^4$ Pa the transformation rate is limited by the chemical reaction.

We shall now estimate the conditions under which the diffusion kinetics is valid. The characteristic time of the transport process is $\tau_v = x_+/v$ (x_+ is the distance between the evaporation and precipitation surfaces and v is the velocity of the vapor–gas medium, which is equal in magnitude to the flow velocity of the active component onto the surface of the crystal).

We shall now analyze two limiting cases: 1) no natural convection, and 2) turbulent convection.

In the absence of natural convection [1]

$$v = \frac{D}{x_+}\,\frac{2H}{2-H},\quad H = \frac{c_+ - c_-}{1 - c_-} \tag{5}$$

(c_+ and c_- are the concentrations of the active component at the surfaces of the source and the sink and D is the diffusion coefficient). Taking into account Eq. (5) we have

$$\tau_v = \frac{x_+^2}{D_0}\,\frac{P}{P_0}\left(\frac{T}{T_0}\right)^{1,8}\frac{2-H}{2H}. \tag{6}$$

In writing Eq. (6) we employed the formula $D = D_0(P_0/P)(T/T_0)^{1.8}$, recommended in [7], where $P_0 = 10^5$ Pa and $T_0 = 273$ K. For most transport systems $D_0 \simeq 10^{-5}$ m^2/sec.

Comparing Eqs. (4) and (6), we can see that as the temperature increases the probability that a process whose rate is limited by the rate of the chemical reaction will occur increases, and as the pressure increases the rate is limited by the transport velocity. The pressure and temperature at which the diffusion regime is established depends on, apart from other factors, the length of the mass-transfer zone. In general, as $x_+ \to \infty$ the rate of growth is always determined by the velocity of transport of the matter, and as $x_+ \to 0$ it is determined by the rate of the phase or chemical transformations themselves. For example, in the case of iodide transport of germanium ($U_d/kT \simeq 10$, $\varepsilon_0/kT \simeq 5$, $T_0 \simeq 10^3$ K, $D_0 \simeq 10^{-5}$ m^2/sec, $H = 10^{-2}$-10^{-1}) we obtain from Eqs. (4) and (6) that $\tau_r/\tau_v > 1$ for $P < (1 - 10)/x_+$ Pa. Setting $x_+ = 0.1$ m we find that the diffusion regime starts at pressures $P > 10$-10^2 Pa. This agrees with the experimental data of [6].

In the case of developed turbulent natural convection in a vapor–gas medium the flow of the active component onto the surface of the crystal is determined by the relation [2, 3]

$$v \simeq br_0^2 \sqrt{g\beta\,(\partial T/\partial x)}\,\beta\,(\partial T/\partial x).$$

Here r_0 is the radius of the ampul; β is the thermal expansion coefficient; g is the acceleration due to gravity; b = 0.03 for vertical and 0.008 for horizontal ampuls. Setting $\beta = 1/T_-$ and $\partial T/\partial x \simeq (T_+ - T_-)/x_+$ (T_+ and T_- are the temperatures in the evaporation and deposition zones), we obtain

$$\tau_v = \frac{x_+^{5/2}}{br_0^2\sqrt{g}}\left(\frac{T_-}{T_+ - T_-}\right)^{3/2}.$$

From here it follows that in a developed turbulent regime the characteristic transport time is independent of the pressure in the system. In addition, it should be kept in mind that turbulent convection starts for certain values of the Grashof numbers [8], which in turn are functions of the pressure in the system. In this connection, when the pressure changes the turbulent and laminar regimes can alternate. However, for conditions under which developed turbulent natural convection is realized, τ_v remains independent of the pressure.

We note that in the turbulent regime τ_v depends strongly on the radius of the ampul: $\tau_v \sim r_0^{-2}$. As a result, by changing only the transverse dimensions of the system and leaving all other conditions unchanged, it is in principle possible to influence the kinetics of the process, transferring from diffusion kinetics to kinetics controlled by the rate of the chemical reaction, and vice versa. This must be kept in mind when comparing the rate of growth of crystals in ampuls with different transverse dimensions. Turning once again to the case of iodide transport of germanium in the system GeI_2–GeI_4 (the conditions of growth are the same as previously) we find that if for $r_0 = 0.2$ cm the ratio $\tau_v/\tau_r \simeq 500$, then for $r_0 = 2$ cm the duration of both stages is now comparable.

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