NOTATION

d, d_{cb}, d_n, diameters of cylindrical part of chamber, of central body of swirler, and of minimum nozzle cross section; L_0, L, length of preconnected, thermally insulated section and distance from start of development of the dynamic boundary layer to the cross section under consideration; Φ, Φ_{enc}, Φ_{en}, value of the swirling intensity parameter in the cross section under consideration and its calculated and actual values at the exit from the swirler (at the entrance to the channel); P_c, c_p, T_f^*, pressure in the chamber and heat capacity and stagnation temperature of the gas; η_w, η_{oo}, dynamic coefficient of viscosity of the gas at the wall temperature T_w and at the stagnation temperature T_f^*; $q_w(x)$, local density of heat flux to the wall in the cross section under consideration; w_{xo}, maximum value of axial component of gas velocity in the boundary zone; ρ_o, gas density at the point where $w_x = w_{xo}$; Re_t^{**}, Reynolds number determined from the conditional thickness of energy loss δ_t^{**}; $m = (d_n/d)^2$, degree of diaphragming; w_x, w_φ, axial and circular components of gas velocity; Re_L, Reynolds number determined from the maximum value of the mass velocity in the cross section under consideration; x, distance from initial cross section of channel to the cross section under consideration.

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KINETICS OF THE PRECIPITATION OF A SUBSTANCE FROM A GAS MIXTURE

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The kinetics of the process of precipitation of a substance from a gas mixture is investigated. Problems connected with the capture of molecules of the noncondensing component by the growing layer of condensate of the readily condensing gas are discussed.

The problem of the condensation of multicomponent gas mixtures plays an important role in many technological processes (the deposit of layers of substances of an assigned composition, the separation of gas mixtures, the removal of gases from vacuum systems, etc.).

The phenomenon of cryocapture, the essence of which consists in the absorption of molecules of a gas which does not condense at the given temperature of the cryopanel during the precipitation of a readily condensing gas under conditions of their simultaneous supply [1], is widely used in cryogenic technology. Generally speaking, such absorption can occur in any process of precipitation of a substance from a multicomponent mixture (the presence of cryogenic temperatures is not an obligatory condition). A theory of the given process must be constructed on the basis of a molecular-kinetic approach. But the kinetics of the conden-

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sation of multicomponent gas mixtures, as noted in [1], has not yet been adequately studied.

On the other hand, in determining the concentrations of the components in the forming condensate one often uses either equations valid only for equilibrium conditions (when the number of evaporating molecules equals the number of condensing ones) or the other limiting case, when the evaporation of molecules of the admixed component from the condensate is not allowed for at all. But the actual conditions of condensation can lie between these limiting cases.

All the foregoing leads to the need to study the process of precipitation of a material from a gas mixture on the basis of a molecular-kinetic approach. Later we will consider a binary gas mixture for simplicity.

We write the expression for the density of the flux of molecules of component i into the condensate (we neglect transport phenomena in the presumably solid condensate itself, while we take the coefficients of sticking of molecules of both components to the condensate as equal to unity) [2, 3] as

$$J_i = N_i - \left(\frac{kT}{2\pi m_i}\right)^{1/2} n_i \exp\left\{-\frac{Q_i}{kT}\right\}, \tag{1}$$

where T is the temperature of the condensate, assumed to be known; N_i is the flux density of molecules of component i incident on the surface of the condensate, which, in the case of a Maxwellian distribution function for the incident molecules, has the form

$$N_i = n_{gi}\left(\frac{kT_g}{2\pi m_i}\right)^{1/2}.$$

Connecting the densities of the molecules in the condensate with the fluxes J_i, we can rewrite (1) in the form

$$J_i = N_i - \frac{J_i}{\sum\limits_s J_s} I_i, \tag{2}$$

where

$$I_i = A_i \exp\left\{-\frac{Q_i}{kT}\right\};\ A_i = n\left(\frac{kT}{2\pi m_i}\right)^{1/2};$$

n is the total density of molecules in the condensate.

We note that Eq. (2) includes the quantity N_i, which in general must be found from the solution of the external problem for the gaseous phase (with allowance for the Knudsen layer [4]). For this, however, one must know the fluxes of molecules of each component flying off from the surface of the condensate, which in turn depend on the concentrations of the components in the condensate. Thus, the problem of calculating the parameters in the gaseous phase must, generally speaking, be analyzed jointly with the problem of determining the concentrations of the components in the condensate. In the given case Eq. (2) can be treated as a boundary condition connecting the parameters of the condensate with the parameters of the external gas stream.

From (2) it is easy to obtain expressions for the concentrations $c_i = J_i/\sum_s J_s$ of the components in the condensate and for the coefficient of capture β, defined as the ratio of the resultant flux of molecules of component i into the condensate to the incident flux of molecules. In the future, we will assume that the resultant flux of molecules of one of the components into the condensate is far larger than the resultant flux of molecules of the second component, i.e., $J_1 \gg J_2$. In this case the concentration of admixture molecules in the condensate and the coefficient of capture of admixture molecules can be written in the form

$$c_2 = N_2/(J_1 + I_2), \tag{3}$$

$$\beta = J_1/(J_1 + I_2), \tag{4}$$

where $J_1 = N_1 - I_1$.

It is seen from (4) that the probability of capture of molecules of the admixture component by the growing layer of condensate ($J_1 > 0$), and hence the resultant flux of admixture molecules into the condensate, is greater than zero.

It follows from (3) that when $J_1 \ll I_2$ one can consider the conditions of equilibrium for the admixture component as satisfied, while when $J_1 \gg I_2$ one can neglect evaporation of admixture molecules from the condensate (for these limiting cases the coefficients of capture of admixture molecules are close to zero and one, respectively).

With the help of the equations obtained let us investigate some phenomena connected with the capture of admixture molecules by the growing layer of condensate during free-molecule flow of the gas. We will consider the process of removal from some volume V of molecules of a noncondensing component with the help of the precipitation of a readily condensing gas.

We can write the following balance equations for the densities n_{gi} of the components in the gaseous phase in the volume under study:

$$\begin{aligned} V\frac{dn_{g1}}{dt} &= b_1(n'_{g1}-n_{g1})-\left[n_{g1}\left(\frac{kT_g}{2\pi m_1}\right)^{1/2}-I_1\right]S, \\ V\frac{dn_{g2}}{dt} &= b_2(n'_{g2}-n_{g2})-n_{g2}\left(\frac{kT_g}{2\pi m_2}\right)^{1/2}S\beta, \end{aligned} \tag{5}$$

where b_i is a quantity characterizing the transmissive capacity of the channel through which the component i flows into the volume (for free-molecule flow of a gas through a long cylindrical channel $b_i = \pi r^2 D_{ki}/L$); n'_{gi} is the density of component i in the gaseous phase outside the volume; S is the surface area of the cryopanel onto which the gas precipitation occurs.

In the steady state we have from (5)

$$\begin{aligned} n_{g2} &= \frac{b_2 n'_{g2}}{b_2+S\left(\frac{kT_g}{2\pi m_2}\right)^{1/2}\frac{J_1}{J_1+I_2}}, \\ J_1 &= \frac{b_1 n'_{g1}+SI_1}{b_1+S\left(\frac{kT_g}{2\pi m_1}\right)^{1/2}}\left(\frac{kT_g}{2\pi m_1}\right)^{1/2}-I_1. \end{aligned} \tag{6}$$

It follows from (6) that during the precipitation of the readily condensing gas ($J_1 > 0$) the density n_{g2} in the volume decreases in comparison with the density which there would have been in the volume without condensation of the first component.

The capture of molecules of the noncondensing component will also occur for internal flows of gas mixtures in channels on whose walls the condensation of one of the components occurs. This leads to a decrease in the probability W of the passage of molecules of the noncondensing component through the channel, defined as the probability that a molecule going into one end of the channel reaches its other end (without allowance for the possibility of its return to the channel after intermolecular collisions in the volume adjacent to the exit cross section) [5].

In investigating internal problems of precipitation of gas mixtures in a channel we will consider that stage of the process when, in the quasisteady approximation used here, the concentrations of the components in the condensate, which covers the entire inner surface of the channel, can be considered as independent of time. We take the thickness h of the layer of condensate as sufficiently small in the course of the entire process, so that $h/r \ll 1$ and the variation of the channel geometry due to the growth of the thickness of the condensate can be neglected.

With allowance for the assumptions made and for Eq. (2) we can write the following equation for the density of the flux of molecules of component i into the condensate for a cylindrical channel:

$$J_i(x) = \int_0^1 I_i(x')\frac{J_i(x')}{\sum\limits_s J_s(x')}K_1(|x-x'|)\,dx' + N_i(0)K(x) + N_i(1)K(1-x) - \frac{J_i(x)}{\sum\limits_s J_s(x)}I_i(x), \tag{7}$$

where $N_i(0)$ and $N_i(1)$ are the densities of the fluxes of molecules of component i entering the channel at $x = 0$ and $x = 1$ ($x = X/L$); K_1 and K are functions characterizing the probabilities of a molecule from one surface element reaching another surface element [6].

The integral term in (7) characterizes the flux of molecules of component i which have evaporated from the condensate over the entire length of the channel and reached the vicinity of point x, while the second and third terms on the right side of (7) characterize the fluxes of molecules of component i which have entered through the end of the channel and reached the vicinity of point x. The last term determines the flux of evaporated molecules. We take the temperature of the surface of the phase transition as constant. Taking $N_1(0) = N_1(1) = N_1$ and $J_1 >> J_2$, with an exponential approximation of $K_1(x)$ and $K(x)$ [6, 7], for J_1 we obtain from (7)

$$J_1 = \frac{1}{2}(N_1 - I_1)(\exp\{-xl\} + \exp\{-l(1-x)\}) = \frac{1}{2}(N_1 - I_1)\varphi(x). \qquad (8)$$

Introducing the new variable $f - (I_2/J_1)J_2$, from (7) with allowance for (8) we obtain an equation for f:

$$f(x) = \int_0^1 f(x')K_1(|x-x'|)\,dx' + N_2(0)K(x) + N_2(1)K(1-x) - \frac{1}{2}\,\frac{N_1 - I_1}{I_2}\,\varphi(x)f(x). \qquad (9)$$

Then, taking the dimensionless parameter $\varepsilon = (N_1 - I_1)/I_2$ as much smaller than unity (physically this means a small departure from equilibrium for the admixture component), we seek the solution of (9) in the form of a series with respect to ε:

$$f = f_0 + \varepsilon f_1 + \varepsilon^2 f_2 + \ldots \qquad (10)$$

Substituting (10) into (9) and equating terms with equal powers of ε, for f_0 we obtain the equation

$$f_0(x) = \int_0^1 f_0(x')K_1(|x-x'|)\,dx' + N_2(0)K(x) + N_2(1)K(1-x). \qquad (11)$$

With the exponential approximation for K_1 and K the solution of (11) has the form

$$f_0 = D - Bx, \qquad (12)$$

where

$$D = N_2(0)\,\frac{l+1}{l+2} + N_2(1)\,\frac{1}{l+2};\; B = [N_2(0) - N_2(1)]\,\frac{l}{l+2}.$$

From (9), (10), and (12) we get the following equation for f_1:

$$f_1(x) = \int_0^1 f_1(x')K_1(|x-x'|)\,dx' - \frac{1}{2}\varphi(x)(D - Bx). \qquad (13)$$

In the same approximation the solution of (13) has the form

$$f_1 = \frac{B}{l}\exp\{-(1-x)l\} - \frac{B}{l}\exp\{-lx\} + Gx + H, \qquad (14)$$

where

$$G = \frac{l}{l+2}\,B\left(1 + \frac{1}{l}\exp\{-l\} - \frac{3}{l}\right);\; H = \frac{G}{l} + \frac{3B}{2l} - \frac{B}{2l}\exp\{-l\} - D.$$

The resultant flux of molecules of the noncondensing component emerging from the channel is determined from the equation

$$N_r = \pi r^2\left[N_2(0)K_2(1) + 2l\int_0^1 f(x)K(1-x)\,dx\right], \qquad (15)$$

where

$$2lK = -\frac{dK_2}{dx}.$$

Being confined to two terms of the expansion (10) in the expression for f and allowing for the definition given above for the probability W of passage of a molecule [in accordance with which $N_2(1) = 0$], using (15) we obtain

$$W = \frac{2}{2+l}\left[1 - \varepsilon\,\frac{2l + \exp\{-l\} - 1}{2+l}\right]. \qquad (16)$$

The second term of (16) characterizes the decrease in the probability of passage of a molecule of the noncondensing component through the channel owing to its capture by the growing layer of condensate.

We note that (16) has a sufficiently good accuracy for short channels. But its accuracy is degraded for long channels owing to the exponential approximation of the functions K, K_1, and K_2 [6, 7]. We can improve the result somewhat if we use exact rather than approximate values of the functions K and K_2 in (15) (leaving the expression for f(x) as before, however).

Having obtained Eq. (9) for f(x), it is also easy to determine the total number M of admixture molecules captured per unit time along the entire length of the channel:

$$M = 2\pi r L \int_0^1 J_2(x)\,dx = 2\pi r L \int_0^1 \frac{f(x)\,J_1(x)}{I_2}\,dx.$$

Using Eq. (7) we can find the distribution of the admixture in a uniform layer of condensate deposited on the inner surface of a cylindrical channel. As shown in [8], uniformity of the deposit of condensate can be achieved through a certain temperature distribution along the channel. Here it turns out that the distribution of the admixture in the condensate essentially depends on the ratio of the quantities I_2 and J_1 characterizing the intensity of evaporation of admixture molecules from the condensate and the rate of condensation of the main material. For example, with $I_2/J_1 >> 1$ in the case when $N_1(0) = N_1(1) = N_1$ and $N_2(0) = N_2(1) = N_2$ we obtain

$$c_2 = \frac{N_2}{A_2\left[\frac{J_1}{A_1}\left(\frac{N_1}{J_1} - 1 - \frac{l}{2} - \frac{l^2}{2}\,x(1-x)\right)\right]^{Q_2/Q_1}}\,. \tag{17}$$

It follows from (16) that the maximum amount of the admixture will be at the center of the channel. In the opposite case, when $I_2/J_1 \to 0$, for c_2 we have

$$c_2 = \frac{1}{2}\,\frac{N_2}{J_1}\,[\exp\{-xl\} + \exp\{-(1-x)\,l\}], \tag{18}$$

i.e., the concentration of the admixture reaches the maximum value at the ends of the channel.

In conclusion, we make some comments about the coefficient of sticking. It was taken as equal to unity in the expressions presented above. It was thereby assumed that each molecule of the gas mixture incident on the condensate is adsorbed while there are no molecules reflected elastically. If the probability of reflection is not neglegibly small, then Eq. (2) takes the form

$$J_i = \alpha_i N_i - \frac{J_i}{\sum_s J_s}\,I_i, \tag{19}$$

where α_i is the coefficient of sticking of a molecule of component i. According to [9], the coefficient of sticking can be represented in the form

$$\alpha = 1 - \exp\left\{-\frac{E_s}{E}\right\}, \tag{20}$$

where E_s is the specific energy of interaction of the gas molecule with the solid phase; E is the energy of the gas molecule. Here the quantity E_s remains constant, while E includes the energy E_v of vibrational excitation ($E = E' + E_v$, where E' is the energy of an unexcited molecule).

When $J_2 << J_1$ we obtain the following expressions from (19) for the concentration of admixture molecules in the condensate and for the coefficient of capture:

$$c_2 = \frac{\alpha_2 N_2}{\alpha_1 N_1 - I_1 + I_2}\,, \tag{21}$$

$$\beta = \frac{(\alpha_1 N_1 - I_1)\,\alpha_2}{\alpha_1 N_1 - I_1 + I_2}\,. \tag{22}$$

It follows from (20)-(22) that the quantities c_2 and β depend in principle on whether or not there is nonequilibrium vibrational excitation of the gas molecules, which can be achieved, in particular, through the action of laser radiation on the gas [9].

NOTATION

k, Boltzmann's constant; T_g, gas temperature; m_i, n_i, Q_i, mass of a molecule, density of molecules in the condensate, and heat of evaporation of a molecule, respectively, of component i; n_{gi}, density of molecules of component i in the gaseous phase; L, r, length and radius, respectively, of the cylindrical channel; $l = L/r$; D_k, Knudsen coefficient of diffusion of component i; x, dimensionless coordinate.

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INTERNAL RELAXATION IN PHASE INTERACTION IN A DISPERSED SYSTEM

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Corrections have been made to the relaxation times for heat and mass transfer between phases in dispersed systems, which incorporate the thermal conduction and diffusion within the particles.

The relaxation formalism in the thermodynamics of irreversible processes has been developed most fully by Meixner [1] and leads to expressions of the form

$$\chi^{\omega} = \chi^{\infty} + \frac{\chi^{0} - \chi^{\infty}}{1 + i\omega\tau}, \tag{1}$$

which allow one to calculate the generalized susceptibility χ^{ω} for a thermodynamic system in relation to the frequency of variation of the parameters and the values of the susceptibility in two limiting states: equilibrium χ^0 and frozen-in χ^{∞} together with the relaxation times for the corresponding process.

Recently, the relaxation approximation has been fairly widely used to describe the behavior of dispersed systems subject to external perturbations [2-5]. One then obtains formally expressions of the type of (1) with the following assumptions: a) the dispersed system is a single-phase medium with internal degrees of freedom that describe the exchange between phases; b) each of the phases is in internal equilibrium, even if there is no equilibrium between the phases; and c) it is assumed in calculating the relaxation time that the thermal or diffusion Biot number is negligibly small, and that this is caused not by smallness in the heat or mass transfer coefficients but by large values of the thermal conductivity or diffusion coefficients for the particles. Clearly, assumptions b and c are related.

In fact, the thermal conduction or thermal diffusion within the particles may be the rate-limiting processes, particularly for relatively large particles. In the relaxation approximation, this does not alter the general form of (1) but influences the relaxation time

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