THEORY OF NUCLEATION IN BINARY SYSTEMS

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A method of calculating the rate of nucleation in phase transformations in binary mixtures is proposed.

Of special interest among the processes of new-phase nucleation are nucleation processes in multicomponent systems, which are encountered much more often than phase transformations in pure materials. Such processes include the condensation of gas mixtures and the formation of aerosols, fogs, and smogs.

Nucleation in a multicomponent system is represented as a series of elementary events of addition and cleavage of molecules of all the components; the composition of the nucleating material is determined here not only by the composition of the mixture but also by the mobility of molecules of different types, and also by the mutual solubility of the components in the new phase. Growth of such a nucleus may be described, as for a single-component system, by kinetic equations of Fokker—Planck type:

$$\frac{\partial}{\partial t} f(\xi, t) = -\operatorname{div} \mathbf{J}. \tag{1}$$

The size distribution function of the nuclei $f(\xi, t)$ is a function of the time and the multidimensional vector ξ

$$\xi = (n_1, n_2, \ldots, n_m), \tag{2}$$

determining the component composition of the nucleus. The number n_i determines the number of molecules of the i-th component in the nucleus. Thus, each nucleus is characterized by a definite set of numbers n_i and corresponds to a definite point in m-dimensional space. At each point of this space, the flux vector of the nucleus is defined:

$$\mathbf{J} = -R\nabla f - Rf\nabla G. \tag{3}$$

The solution of this problem for a two-component system was first obtained in [2]. Under the assumption that matrix R is diagonal and the dependence of the kinetic coefficients on the dimension of the nucleus may be neglected, Eq. (1) for the two-component system A + B transforms to the following form in the case of an established (steady) flow of nuclei:

$$R_A \frac{\partial^2 \varphi}{\partial n_A^2} + R_B \frac{\partial^2 \varphi}{\partial n_B^2} - R_A \frac{\partial \varphi}{\partial n_A} \frac{\partial G}{\partial n_A} - R_B \frac{\partial \varphi}{\partial n_B} \frac{\partial G}{\partial n_B} = 0. \tag{4}$$

The distribution function must satisfy the boundary conditions

$$\begin{gathered} \varphi(n_A, n_B) \to 0 \quad \text{as} \quad n_A + n_B \to \infty, \\ \varphi(n_A, n_B) \to 1 \quad \text{as} \quad n_A + n_B \to 0, \end{gathered} \tag{5}$$

following from the physical meaning of the function [2].

The most significant factor which must be taken into account in solving the given problem is that, close to the point $\xi^* = (n^*_A, n^*_B)$ determined by the equations

$$\frac{\partial G(n_A, n_B)}{\partial n_A} = 0, \quad \frac{\partial G(n_A, n_B)}{\partial n_B} = 0, \tag{6}$$

the surface $G = G(n_A, n_B)$ is a hyperbolic paraboloid, i.e., ξ^* is a saddle point of the surface.

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If the total flux of nuclei is defined as

$$J_{\text{tot}} = \int\limits_{L} |\mathbf{J} \times d\mathbf{l}|, \tag{7}$$

where L is an arbitrary curve intersecting all the current lines of the vector J (which, in particular, may also pass through the point ξ^*), the greatest contribution to the integral in Eq. (7) will be made by the region close to this point. The method of solution proposed in [2] and then developed in [3, 4] is as follows. It is assumed that, in some region close to the saddle point ξ^*, the current lines of the vector J may be regarded as parallel. Then, from physical considerations, the direction of the vector J at the saddle point is chosen so as to simplify Eq. (4). Thus, for example, in [2], the direction of J coincides with the direction of most rapid descent of the surface G at the saddle point, while in [3, 4] this choice was shown to be invalid and it was proven that the direction must be chosen not only on the basis of the curvature of surface G but also so as to take account of the kinetic coefficients R_A and R_B.

In the present work, another approach to the solution of this problem is proposed, with no need to make any assumptions regarding the direction of the vector J.

The flux in Eq. (7) is found from Eq. (4), by means of a series of transformations. The following change of variables is introduced: $n_A - n_A^* = u\sqrt{R_A}$, $n_B - n_B^* = v\sqrt{R_B}$; this gives the result

$$\frac{\partial^2\varphi}{\partial u^2} + \frac{\partial^2\varphi}{\partial v^2} - \frac{\partial G}{\partial u}\frac{\partial\varphi}{\partial u} - \frac{\partial G}{\partial v}\frac{\partial\varphi}{\partial v} = 0. \tag{8}$$

Expanding G(u, v) in the vicinity of the saddle point

$$G(u, v) = G^* + G_{11}u^2 + G_{22}v^2 + 2G_{12}uv,$$

$$G_{11} = \frac{1}{2}\frac{\partial^2 G}{\partial u^2} \equiv \frac{1}{2}R_A D_{11},$$

$$G_{22} = \frac{1}{2}\frac{\partial^2 G}{\partial v^2} \equiv \frac{1}{2}R_B D_{22},$$

$$G_{12} = \frac{1}{2}\frac{\partial^2 G}{\partial u \partial v} \equiv \frac{1}{2}\sqrt{R_A R_B}\, D_{12}, \tag{9}$$

where $D_{11} = \partial^2 G/\partial n_A^2$, $D_{22} = \partial^2 G/\partial n_B^2$, $D_{12} = \partial^2 G/\partial n_A \partial n_B$, the quadratic form in Eq. (9) may be reduced to canonical form by rotating the coordinate system

$$G - G^* = -px^2 + qy^2, \quad p > 0, \quad q > 0, \tag{10}$$

where $-p$ and q are eigenvalues of the matrix g:

$$g = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix},$$

$$p = -\frac{G_{11} + G_{22}}{2} + \sqrt{\frac{(G_{11} - G_{22})^2}{4} + G_{12}^2}, \tag{11}$$

$$q = \frac{G_{11} + G_{22}}{2} \sqrt{\frac{(G_{11} + G_{22})^2}{4} + G_{12}^2}.$$

Equation (8) is invariant relative to rotations of the coordinate system; therefore, it takes the following form:

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + 2px\frac{\partial\varphi}{\partial x} - 2qy\frac{\partial\varphi}{\partial y} = 0. \tag{12}$$

It may be shown that the total flux in the new coordinate system is

$$J_{\text{tot}} = -\sqrt{R_A R_B} \int\limits_{-\infty}^{+\infty} f_0(x, y)\frac{\partial\varphi}{\partial x}\, dy, \tag{13}$$

where $f_0(x, y) = f_0(x = 0, y = 0)\exp(-qy^2 + px^2)$.

The value of the integral in Eq. (13) may be obtained from Eq. (12), by introducing the function

$$\chi(x)=\int_{-\infty}^{+\infty}\varphi(x,\ y)\exp(-qy^2)\,dy. \tag{14}$$

It is a solution of the equation

$$\frac{d^2\chi}{dx^2}+2px\,\frac{d\chi}{dx}=0, \tag{15}$$

which is easily obtained if Eq. (12) is multiplied by exp $(-qy^2)$ and integrated, term by term, with respect to y. The general solution of Eq. (15) is

$$\chi(x)=C_1\int_{0}^{x}\exp(-p\tau^2)\,d\tau+C_2. \tag{16}$$

The constants C_1 and C_2 are found using the boundary conditions in Eq. (5), rewritten in the form

$$\begin{aligned}&\varphi(x,\ y)\to 1,\ x\to-\infty;\\&\varphi(x,\ y)\to 0,\ x\to+\infty,\end{aligned} \tag{17}$$

since $x\to-\infty$ corresponds to $n_A+n_B\to 0$, and $x\to+\infty$ corresponds to $n_A+n_B\to+\infty$. As in [2, 4], it is assumed here that the boundary conditions in Eq. (5) are sufficiently well satisfied in some vicinity of the saddle point in which Eq. (9) holds. Substituting Eq. (17) into Eq. (14), it is found that

$$\chi(-\infty)=\sqrt{\frac{\pi}{q}},\ \chi(+\infty)=0.$$

Thus, $C_1=-\sqrt{p/q}$, $C_2=(1/2)\sqrt{\pi/q}$, and the final expression for the nucleation rate is obtained using Eqs. (13) and (14):

$$J_{\text{tot}}=-\sqrt{R_AR_B}\,f_0(n_A^*,\ n_B^*)\exp(px^2)\,\frac{d\chi}{dx}=\sqrt{R_AR_B}\,f_0^*\sqrt{\frac{p}{q}}=f_0^*\sqrt{R_AR_B\frac{\sqrt{(D_{11}-rD_{22})^2+rD_{12}^2}-D_{11}-rD_{22}}{\sqrt{(D_{11}-rD_{22})^2+rD_{12}^2}+D_{11}+rD_{22}}}\,.$$

An explicit dependence of the nucleation rate on the kinetic and thermodynamic parameters of the system is obtained. Equation (18) has a clear physical meaning, since the quantities p and q appearing there are inversely proportional to the square root of the characteristic dimensions of the saddle-point region of surface G. The maximum variation in G in this region is 1; i.e., the variation in the work of nucleus formation in this region is no greater than the magnitude of the thermal energy.

NOTATION

$f(\xi,\ t)$, distribution function of the nuclei, determining the number of nuclei with composition ξ per unit volume at time t; $R=\begin{pmatrix}R_A & R_{AB}\\ R_{BA} & R_B\end{pmatrix}$, matrix of kinetic coefficients, determining the probability of addition of a specified type of molecule to the nucleus; $G=G(n_A,\ n_B)$, dimensionless ratio of the work of formation of nucleus of composition $(n_A,\ n_B)$ to the temperature, expressed in energy units; $f_0=\text{const}\exp(-G)$, equilibrium distribution function; $\varphi=f/f_0$, dimensionless distribution function.

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NITROGEN CONDENSATION IN A HYPERSONIC NOZZLE

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We will investigate the numerical calculations and the experimental study of homogeneous nitrogen condensation in a hypersonic nozzle at $M \gtrsim 20$.

Saturation conditions are often achieved when gases expand in the nozzles of hypersonic aerodynamic equipment [1-4]. If this occurs at a sufficiently low pressure (for nitrogen and air, less than $4 \cdot 10^{-3}$ bar) and the impurity content of the gas is low, then significant supercooling of the flow occurs [1-3]. It then becomes important to determine the range of braking parameters at which gas flow in the nozzle occurs without the condensation process having a significant effect. Theoretical prediction of conditions for the onset of condensation presents a number of difficulties in principle, so that, as a rule, it is necessary to commence from experimental results. As has been shown in [3-7], in interpreting the experimental results obtained, fairly good results may be obtained by classical homogeneous-condensation theory, if we specially select the coefficients in the expressions which extrapolate the dependences of the condensed-phase parameters to the temperature range below the triple point. In the present study numerical calculations will be performed on the basis of classical theory to generalize experimental data on nitrogen condensation in a hypersonic nozzle [8]. The results of the study show that when the dependence of condensed-phase surface tension coefficient on droplet radius is considered, classical homogeneous-condensation theory can be used to predict conditions for the commencement of condensation in apparatus with high value breaking parameters.

Experimental data on nitrogen condensation in a hypersonic tube were obtained for the following conical nozzle parameters: critical-section diameter 1 mm, half-aperture angle 9°, output-section diameter 220 mm. The braking pressure was measured behind the direct shock wave in the working portion of the device while the temperature was decreased in the gas forechamber as the pressure therein was maintained constant. As the braking temperature T_0 was decreased, the braking pressure behind the shock wave P_0' first remained constant at its isentropic level, after which, at some braking temperature T_{0c} it began to decrease and then behaved irregularly with further decrease in T_0. As careful measurements [1, 2] reveal, the static pressure in the working section P begins to increase with reduction in T_0, with deviation from the isentropic value of P commencing at approximately the same temperature T_{0c}. In comparing the numerical calculation results to experimental data it is assumed that deviation of P and P_0' from their isentropic values occur at one and the same braking temperature T_{0c}. Nonsteady-state processes in the experiments may be neglected, since the characteristic time for change in T_0 comprised ~ 10 sec, while the characteristic time for flow establishment in the nozzle was $\sim 10^{-3}$ sec.

The value of T_{0c} was measured for three values of braking pressure P_0. For variant No. 1 $P_0 = 106.75$ bar, $T_{0c} = 1143$°K, $M = 22.8$; No. 2, $P_0 = 71.92$, $T_{0c} = 943$°K, $M = 22.2$; No. 3, $P_0 = 51.66$, $T_{0c} = 900$°K, $M = 21.8$. M is the Mach number in the working section of the device in the absence of condensation, which can be calculated from the measured ratio P_0'/P_0 and expressions for isentropic nitrogen flow. The gas pressure in the forechamber was monitored by an 0.16 accuracy class manometer, and remained constant within 0.81 bar. The braking temperature T_0 was measured by a PP-1 thermocouple 0.1 mm in diameter with systemic error no greater than 1%. The braking pressure at the compression discontinuity was measured by a

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