LITERATURE CITED

1. J. C. Slattery, Momentum, Energy, and Mass Transfer in Continua, McGraw-Hill (1972).
2. G. Wallis, One-Dimensional Two-Phase Flow, McGraw-Hill (1969).

DYNAMIC EQUATION OF STATE OF A GAS CONTAINING VAPORIZING DROPLETS

G. P. Yasnikov and V. S. Belousov

UDC 536.12

On the basis of the relaxational formalism of nonequilibrium thermodynamics, a differential equation is obtained relating the pressure and volume of a gas containing vaporizing droplets. The relaxation time is calculated.

The existing methods of calculating processes of gas compression with evaporative cooling are based, as a rule, on the methods of classical thermodynamics. This leads to the necessity of assuming thermal and phase equilibrium between the droplets and the vapor–gas mixture [1-3]. With a sufficiently high rate of the process, the temperature of the vapor T and the droplet T_D will differ from the saturation temperature T_S: $T-T_S = \xi_1$, $T_D-T_S = \xi_2$. As a result, the vapor concentration will also differ from the equilibrium value: $x-x_S = \xi_3$. The rigorous description of nonequilibrium, even with fixed parameters of the cooling medium, is an extremely complex problem, and leads to very cumbersome results [4, 5]. Therefore, it is of interest to consider some simplified models of the process of nonequilibrium compression with droplets. Thus, for example, for the practical realization of evaporative cooling in compressors, it is expedient to use small concentrations of finely dispersed moisture (~30 g per kg of air) [2, 6]. The behavior of this mixture will be associated with small deviations from the equilibrium state, which may be analyzed using linear nonequilibrium thermodynamics. Below, the nonequilibrium compression of gas with droplets is analyzed on the basis of the relaxational formalism of the thermodynamics of irreversible processes.

It is assumed that the vapor, gas, and droplets, with masses M_V, M_G, and M_D, respectively, form two local-equilibrium subsystems and, in accordance with the mass-conservation law, $M_V + M_D = M_M$, the mass of injected moisture. It is expedient to introduce the notation: $\mu = M_M/M_G$, $x = M_V/M_M$, $1-x = M_D/M_V$. In accordance with the well-known ideas of [7-9], it may be assumed that, in quasisteady conditions, the intensity of heat transfer and the rate of vaporization depend on the temperature difference between the subsystems $T-T_D$. The behavior of this system will be characterized by a single effective relaxation time τ_z. Further, following [10], the operator form of the effective thermodynamic derivatives is used, allowing the adiabatic modulus k and the polytropic index n to be represented in the form of operators

$$\begin{pmatrix} \hat{k} \\ \hat{n} \end{pmatrix} = \begin{pmatrix} k_\infty \\ n_\infty \end{pmatrix} + \left[\begin{pmatrix} k_0 \\ n_0 \end{pmatrix} - \begin{pmatrix} k_\infty \\ n_\infty \end{pmatrix}\right]\left(1 + \tau_V \frac{d}{dt}\right)^{-1}. \tag{1}$$

In this expression k_∞ and n_∞ depend solely on the properties of the vapor–gas mixture (without the particles) in the initial state, and characterize the process of instantaneous compression, in which the particles do not react to the perturbation. The indices k_0 and n_0 characterize the equilibrium compression of the mixture of the gas and the droplet. It depends on the instantaneous state of the system, and varies over time. Formally repeating the derivation in [10], a dynamic equation is obtained for the adiabatic and polytropic compression processes of the vapor–gas mixture with the droplets

$$\ddot{p}V + \dot{p}\left\{\left[\begin{pmatrix} k_\infty \\ n_\infty \end{pmatrix} + 1\right]\dot{V} + \frac{V}{\tau_V(t)}\right\} + p\begin{pmatrix} k_\infty \\ n_\infty \end{pmatrix}\left(\ddot{V} + \frac{\dot{V}}{\tau_p(t)}\right) = 0. \tag{2}$$

In deriving this equation, it is taken into account that $k_\infty k_0^{-1} = n_\infty n_0^{-1} = \tau_p \tau_V^{-1}$; a dot over a a quantity denotes the first derivative with respect to the time; two points denotes the sec-

---

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 43, No. 5, pp. 733-740, November, 1982. Original article submitted October 8, 1981.

0022-0841/82/4305-1207$07.50

ond derivative. Formally, Eq. (2) coincides with the dynamic equation of state for a mixture of gas with solid particles, but in the case of a droplet the equation includes the variable (because of the change in particle radius) relaxation times $\tau_p(t)$ and $\tau_V(t)$.

The calculation of these times is an independent problem, which may be solved by the general methods outlined in [11] and the calculation scheme in [12]. Assuming that the vapor–gas mixture is an ideal gas, the entropy-balance equation for the whole system is written in the form

$$dS = \begin{pmatrix} c_{V1} \\ c_{p1} \end{pmatrix} \frac{d\xi_1}{T(\xi_1)} + c_2 \frac{d\xi_2}{T_D(\xi_2)} + \mu\Delta\tilde{\mu} \frac{d\xi_3}{T_s} + \frac{1}{T} \begin{pmatrix} pdV \\ -Vdp \end{pmatrix}. \tag{3}$$

In view of the small moisture concentration ($\mu \ll 1$), the specific heat

$$c_{V1} = c_{V_G} + \mu x_s c_{1_V};\ c_{p1} = c_{pG} + \mu x_s c_{pV};\ c_2 = \mu(1 - x_s) c_D \tag{4}$$

may be regarded as constant and referred to the equilibrium state with a vaporized-moisture concentration x_s. All the specific quantities (c_{V1}, c_{p1}, $\Delta\tilde{\mu}$, V) in Eq. (3) relate to 1 kg of gas.

For the subsequent calculations, it is expedient to regard all three relaxation parameters ξ_1, ξ_2, ξ_3 as independent. The entropy production may be written in the usual form [11]

$$\dot{S} = -\vec{A} \cdot \dot{\vec{\xi}}. \tag{5}$$

The affinity between each of the relaxational processes is specified by the components of the vector $\vec{A} = T\hat{g} \cdot \vec{\xi}$. The elements of matrix $\hat{g}$ are the coefficients of the series expansion of the entropy in the vicinity of the equilibrium state with respect to the relaxation parameters, retaining terms of up to second order in smallness. They are easily calculated by differentiating the coefficients of the differential form in Eq. (3) with respect to ξ_1, ξ_2, ξ_3

$$\hat{g} = \left(\frac{\partial^2 S}{\partial\vec{\xi}\partial\vec{\xi}} \right)_{\vec{\xi}=0} = \begin{pmatrix} c_z T_s^{-2} & 0 & 0 \\ 0 & c_2 T_s^{-2} & 0 \\ 0 & 0 & a_{zT} \end{pmatrix};\ \vec{\xi} = \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix}, \tag{6}$$

where $a_{zT} = \frac{\mu}{T_s} \left(\frac{\partial\Delta\tilde{\mu}}{\partial x_s} \right)_{zT_s}$. The subscript z is introduced to abbreviate the notation. For isochoric conditions, z = V; for isobaric conditions, z = p. The kinetics of the relaxational processes are specified using Newton's laws for the heat transfer

$$c_{z1} \frac{dT}{dt} = -\alpha f (T - T_D), \tag{7}$$

$$c_2 \frac{dT_D}{dt} = \alpha f (T - T_D) \tag{8}$$

and the mass transfer

$$\frac{dx}{dt} = -\beta(x - x_s). \tag{9}$$

Expressing T, T_D, and x in terms of the relaxation parameters, the system in Eqs. (7)-(9) may be written in vector form

$$\dot{\vec{\xi}} = -\hat{L}' \cdot \vec{\xi}, \tag{10}$$

where $\hat{\mathbf{L}}'$ is the matrix of empirical phenomenological coefficients, of the form

$$\hat{L}' = \begin{pmatrix} -\alpha f c_{z1}^{-1} & -\alpha f c_{z1}^{-1} & 0 \\ -\alpha f c_2^{-1} & \alpha f c_2^{-1} & 0 \\ 0 & 0 & \beta \end{pmatrix}. \tag{11}$$

On the other hand, the linear phenomenological laws may be written in terms of the affinity of the process

$$\dot{\vec{\xi}} = -\hat{\mathbf{L}} \cdot \frac{\vec{A}}{T} = -\hat{\mathbf{L}} \hat{g} \vec{\xi} = -\hat{\mathbf{M}} \vec{\xi}. \tag{12}$$

It follows from Eqs. (6), (10), (11), and (12) that

$$\hat{\mathbf{L}} = \begin{pmatrix} \alpha f T_s^2 c_{z1}^{-2} & -\alpha f T_s^2 c_{z1}^{-1} c_2^{-1} & 0 \\ -\alpha f T_s^2 c_{z1}^{-1} c_2^{-1} & \alpha f T_s^2 c_2^{-2} & 0 \\ 0 & 0 & \beta a_{zT_s}^{-1} \end{pmatrix};$$

$$\hat{\mathbf{M}} = \hat{\mathbf{L}} \cdot \hat{g} = \begin{pmatrix} \alpha f c_{z1}^{-1} & -\alpha f c_{z1}^{-1} & 0 \\ -\alpha f c_2^{-1} & \alpha f c_2^{-1} & 0 \\ 0 & 0 & \beta \end{pmatrix}. \tag{13}$$

The isochoric and isobaric relaxation times are inverse quantities of the roots of the characteristic equation of the matrix $\hat{\mathrm{M}}$ [13]

$$r^3 - r^2 \mathrm{Sp}\, \hat{\mathbf{M}} + r \left\{ \begin{vmatrix} \alpha f c_{z1}^{-1} & -\alpha f c_{z1}^{-1} \\ -\alpha f c_2^{-1} & \alpha f c_2^{-1} \end{vmatrix} + \begin{vmatrix} \alpha f c_{z1}^{-1} & 0 \\ 0 & \beta \end{vmatrix} + \begin{vmatrix} \alpha f c_2^{-1} & 0 \\ 0 & \beta \end{vmatrix} \right\} + \mathrm{Det} \hat{\mathbf{M}} = 0. \tag{14}$$

In those cases where one of the relaxation times (of vaporization of heat transfer) is much less than the other, the last term in Eq. (14) may be neglected, and the relaxation time is determined from the relation

$$r = \frac{1}{\tau_z} = \mathrm{Sp}\, \hat{\mathbf{M}} = \alpha f \left(\frac{1}{c_{z1}} + \frac{1}{c_2} \right) + \beta. \tag{15}$$

Since Det $\hat{\mathrm{M}} = 0$, there is a linear relation between the relaxation times, which may be obtained from the condition $\delta S = 0$, thereby passing to one relaxation parameter ξ. This is also the basis for representing the adiabatic modulus and the polytropic index in the form in Eq. (1).

Finally, note that, in the case of a polytropic process, there is heat transfer with the surrounding medium. Then the entropy flux $d_e S$ must be included in Eq. (3); it is related to the heat flux as follows

$$dQ = T_s d_e S = c_n dT_s = T_s \left(\frac{\partial S}{\partial T} \right)_{\vec{\xi}, n} dT_s,$$

that is

$$dS = d_e S + d_i S = \left(\frac{\partial S}{\partial T_s} \right)_{\vec{\xi}, n} dT_s + \left(\frac{\partial S}{\partial \vec{\xi}} \right)_{T_s} d\vec{\xi}. \tag{16}$$

Since the matrix elements g_{ik} in Eq. (6) are calculated in the equation of state (T_s = const), the relaxation times τ_z defined by Eq. (15) may be used for both adiabatic and polytropic processes. In this case, the heat-transfer coefficient α and mass-transfer coefficient β may in principle be found using empirical dependences.

The relaxation times τ_z defined by Eq. (15) will now be considered in more detail. If an arbitrary phase of the compression process is chosen as the initial equilibrium state, with respect to which the deviation ξ is considered, the current drop radius is determined from the relation

$$\frac{R}{R_0} = (1 - x_s)^{1/3}. \tag{17}$$

Taking into account that the concentration of droplets in 1 kg of gas

$$N_0 = \frac{N_\mathrm{D}}{M_\mathrm{G}} = \frac{3\mu}{4\pi R_0^3 \rho_\mathrm{D}} \tag{18}$$

and using Eq. (17), the quantity αf may be written in the form

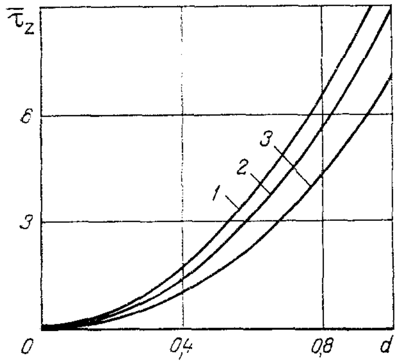

Fig. 1

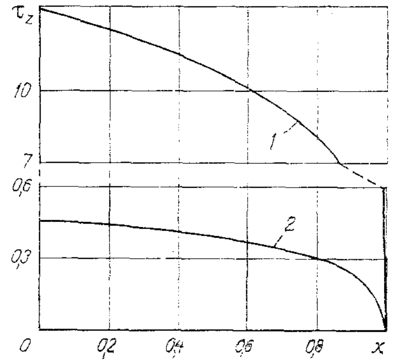

Fig. 2

Fig. 1. Dependence of the mean relaxation time $\bar{\tau}_z$ on the drop diameter d (mm): 1) $\mu = 0.005$; 2) 0.03; 3) 0.1.

Fig. 2. Dependence of the relaxation time τ_z on the degree of vaporization of the drop x: 1) $\mu = 0.005$, d = 1 mm; 2) 0.03, 2.

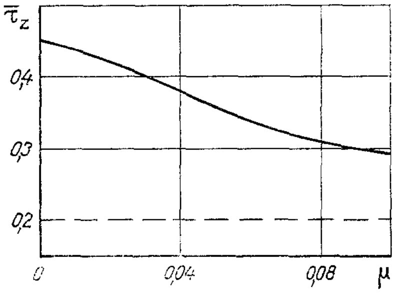

Fig. 3

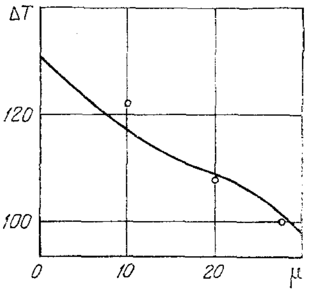

Fig. 4

Fig. 3. Dependence of the mean relaxation time $\bar{\tau}_z$ on the moisture concentration μ with a particle diameter d = 0.2 mm.

Fig. 4. Temperature rise in the compression of a vapor–gas mixture with droplets in a compressor with various droplet concentrations. The compression time $\tau_0 = 0.2$ sec, the drop diameter d = 0.2 mm, initial temperature $T_1 = 293$°K, degree of increase in pressure $p_2/p_1 = 3.65$. The points correspond to experimental results of [6].

$$\alpha f = 4\pi R^2 \alpha N_0 = \frac{3\mu\alpha}{R_0\rho_D}(1-x_s)^{2/3}. \tag{19}$$

Since the matrix element g_{33} in Eq. (6) is calculated at constant temperature, the law of drop vaporization in an isothermal medium may be used to determined β. In the simplest case, it takes the form [7]

$$\frac{dM_D}{dt} = -4\pi R D N_D (c_s - c). \tag{20}$$

In this expression, the concentrations c_s and c and the droplet mass M_D may be expressed in terms of the degree of vaporization x and the moisture concentration μ using the relation

$$c = \bar{\rho}_V(p,\ T)\, r_V = \bar{\rho}_V \frac{\mu x}{\frac{m_V}{m_G} + \mu x} = \frac{m_G}{m_V}\frac{p}{R_V T}\mu x = \mu x \frac{p}{R_G T} = \mu x \bar{\rho}_G(p,\ T). \tag{21}$$

Using Eqs. (21) and (18), Eq. (20) may be written in the form

$$\frac{d\xi_3}{dt} = -\frac{3\mu D \bar{\rho}_G}{R_0^2 \rho_D}(1-x_s)^{1/3}\xi_3 = -\beta\xi_3. \tag{22}$$

The factor preceding ξ_3 on the right-hand side of Eq. (22) is the coefficient β in Eq. (9). Using Eqs. (20) and (21), the relaxation times in Eq. (15) may be written in the form

$$\frac{1}{\tau_z}=\frac{3\mu\alpha}{R_0\rho_D}\left[\frac{(1-x_s)^{2/3}}{c_{zG}+\mu x_s c_{zV}}+\frac{1}{\mu(1-x_s)^{1/3}c_D}\right]+\frac{3\mu D\bar{\rho}_G(1-x_s)^{1/3}}{R_0^2\rho_D}. \tag{23}$$

If the initial state under the condition $x_s = 0$ is taken as the state at the start of the calculation, then the first two terms will characterize the thermal relaxation without mass transfer and the last the isothermal vaporization. This corresponds to the usual calculation scheme for the process of drop vaporization [4, 7]. Simultaneous thermal and diffusional relaxation was considered in [5]. The results of [4, 5] may be used to refine τ_z; however, they are so cumbersome as to require numerical calculation on a computer.

The relaxation times τ_p and τ_V calculated from Eq. (23) under the assumption that Nu = 2 [7] are found to be practically identical and proportional to the surface area of the particles, i.e., compression will be almost equilibrium for very finely disperse systems and like the compression of a pure gas for coarsely disperse systems ($\tau_z \to 0$ as $d \to 0$ and $\tau_z \to \infty$ as $d \to \infty$). The dependence of the mean relaxation time on the diameter is shown in Fig. 1.

The dependence of τ_z on the degree of vaporization is shown in Fig. 2 and the dependence of $\bar{\tau}_z$ on the drop concentration μ in Fig. 3. In the limit as $\mu \to 0$, $\tau_z \to \infty$, and compression in the absence of droplets occurs, as would be expected, like compression of a pure gas. The averaging of the relaxation times in Figs. 1 and 3 is taken over the degree of vaporization x. In the calculations, the following parameter values are assumed: $c_{pG} = 1010$ J/kg°K; $c_{VG} = 720$ J/kg·°K; $c_{pV} = 2000$ J/kg·°K; $c_{VG} = 1600$ J/kg·°K; $c_D = 4200$ J/kg·°K; $D = 2.2\cdot10^{-5}$ m^2/sec; $\lambda = 2.5\cdot10^{-2}$ W/m·°K; $\rho_D = 1000$ kg/m^3; $\rho_G = 1.3$ kg/m^3.

From the known mean relaxation times, the polytropic index may be estimated for the mixture of gas with vaporizing droplets [10]

$$n=n_\infty+\frac{n_0-n_\infty}{1+\dfrac{\tau_V}{\tau_0}} \tag{24}$$

and the temperature rise ΔT in the compression of this mixture in the cylinder of a compressor may be calculated

$$\Delta T=T_1\left[\left(\frac{p_2}{p_1}\right)^{(n-1)/n}-1\right]. \tag{25}$$

Comparison of the results of calculation with the experimental data of [6] is shown in Fig. 4, where the points correspond to the experimental results. The discrepancy between the calculational and experimental data does not exceed 6%.

If n relaxational processes occur simultaneously in the system, then the expression for the susceptibility [13] may be used to write the polytropic index in the form

$$\hat{n}=n^\infty+\sum_i\frac{\delta n_i}{1+\tau_i\hat{D}}, \tag{26}$$

where

$$n^\infty=-\frac{V}{p}\left(\frac{\partial p}{\partial V}\right)_{\vec{\xi}};\ \delta n_i=n_{0i}-n^\infty;$$

$$n_{0i}=-\frac{V}{p}\left(\frac{\partial p}{\partial V}\right)_{\substack{A_j,\\ A_i=0}};\quad \tau_i=-\left[L\left(\frac{\partial A_i}{\partial \xi_i}\right)\right]_{\xi_j}^{-1},\ i\neq j.$$

Then the corresponding dynamic equation of state will be of order n + 1. For two relaxational processes (the case considered in the present work)

$$\hat{n}=n^\infty+\frac{\delta n_1}{1+\tau_1\hat{D}}+\frac{\delta n_2}{1+\tau_2\hat{D}} \tag{27}$$

and the dynamic equation of state takes the form

$$\dddot{p}V\tau_1\tau_2+\ddot{p}[\dot{V}(2+n^{\infty})\tau_1\tau_2+V(\tau_1+\tau_2)]+\dot{p}\{\ddot{V}(2n^{\infty}+1)\tau_1\tau_2+\dot{V}[n^{\infty}(\tau_1+\tau_2+\delta n_1\tau_2+\delta n_2\tau_1)+\tau_1+\tau_2]+V\}+$$
$$+p[\dddot{V}n^{\infty}\tau_1\tau_2+\ddot{V}n^{\infty}(\tau_1+\tau_2+\delta n_1\tau_2+\delta n_2\tau_1)+\dot{V}(n^{\infty}+\delta n_1+\delta n_2)]=0. \quad (28)$$

Writing the characteristic Eq. (14) in terms of the relaxation times

$$\tau^2-(\tau_1+\tau_2)\tau+\tau_1\tau_2=0 \quad (29)$$

and neglecting the last term of this equation in the limiting cases $\tau_1\tau_2 \ll (\tau_1+\tau_2)^2$, it is found that $\tau = \tau_1 + \tau_2$, where $\tau_1=[\alpha f(c_{z1}^{-1}+c_2^{-1})]^{-1}$, $\tau_2=\beta^{-1}$ are the relaxation times of the processes of heat transfer and vaporization, respectively. Then Eq. (28) reduces to the dynamic equation of state obtained above, Eq. (2).

NOTATION

T, T_D, T_s, vapor, droplet, and saturation temperature, respectively; ξ_1, ξ_2, ξ_3, relaxation parameters; M_V, M_G, M_D, vapor, gas, and droplet mass; m, molecular mass; x, degree of dryness of the vapor; μ, moisture concentration; τ_p, τ_V, isobaric relaxation time; k, n, adiabatic modulus and polytropic index; p, pressure; V, volume; S, entropy; $\tilde{\mu}$, chemical potential; $\bar{\rho}_G$, $\bar{\rho}_V$, density of gas and vapor at the mixture pressure and temperature; ρ_D, density of the droplet; A, affinity of the process; α, heat-transfer coefficient; β, mass-transfer coefficient; λ, thermal conductivity of the gas; D, diffusion coefficient; R, drop radius; f, surface area of droplet; Nu, Nusselt number. Indices: 1, G, gas; 2, V, vapor; D, droplets; 0, equilibrium; p, isobaric conditions, p = const; V, isochoric conditions, V = const; s, saturation; ∞, instantaneous compression; a dot over a quantity denotes differentiation with respect to time; the symbol ^ over a quantity denotes an operator.

LITERATURE CITED

1. M. A. Mikhailovskii, Thermodynamic Calculations of Processes in Vapor–Gas Mixtures [in Russian], Mashgiz, Leningrad (1962).
2. L. I. Slobodyanik and Yu. N. Gogin, "Compressor cooling by water injection into the cylinder," Izv. Vyssh. Uchebn. Zaved., Energ., No. 9, 62-66 (1961).
3. L. G. Gal'perin, Yu. V. Kuznetsov, S. L. Magrachev, and G. P. Yasnikov, "Polytropic index of the compression of moist gas," Inzh.-Fiz. Zh., 12, No. 6, 817-819 (1967).
4. M. V. Vuikov and S. S. Dukhin, "Diffusional and thermal relaxation of a vaporizing droplet," Inzh.-Fiz. Zh., No. 3, 80-87 (1962).
5. Yu. A. Buevich, "Diffusional and thermal relaxation at the plane surface of a vaporizing drop," Inzh.-Fiz. Zh., 8, 314-348 (1965).
6. G. A. Pirogov, S. L. Magrachev, and Yu. V. Kuznetsov, "Experimental characteristics of a piston compressor with a mixture of moisture and air," in: Reliability and Efficiency of Compressor Machinery [in Russian], No. 200, Izd. UPI, Sverdlovsk (1971), pp. 61-75.
7. N. A. Fuks, Vaporization and Growth of a Drop in a Gaseous Medium [in Russian], Izd. Akad. Nauk SSSR, Moscow (1958).
8. R. Dean, Dickinson, and J. R. Marshall, "The rates of evaporation of sprays," A.I.Ch.E. J., 4, 541-552 (1968).
9. A. V. Lykov, Heat and Mass Transfer (Handbook) [in Russian], Énergiya, Moscow (1972).
10. G. P. Yasnikov and V. S. Belousov, "Effective thermodynamic functions of a gas with solid particles," Inzh.-Fiz. Zh., 34, No. 6, 1085-1089 (1978).
11. S. R. De Groot and P. Mazur, Non-Equilibrium Thermodynamics, Elsevier (1962).
12. G. P. Yasnikov and V. S. Belousov, "Dynamic equation of state of a mixture of gas with solid particles," Inzh.-Fiz. Zh., 34, No. 5, 834-838 (1978).
13. G. Bauer, "Phenomenological theory of relaxational phenomena in gases," in: Properties of Gases, Liquids, and Solutions. Physical Acoustics [Russian translation], Mir, Moscow (1968), pp. 61-154.