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OSCILLATORY AND MONOTONIC INSTABILITY AT THE BOUNDARY OF THE TRANSITION "MOLECULAR DIFFUSION–CONCENTRATION CONVECTION" IN TERNARY GAS MIXTURES

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It is shown by a linear analysis for stability that for partial Rayleigh numbers R_1 and R_2 that have different signs, there exist two anomalous regions with monotonic ($R_1 < 0$, $R_2 > 0$) and oscillatory ($R_1 > 0$, $R_2 < 0$) instability where the density at the bottom is higher than at the top. The experimental data obtained confirm the presence of these two regions of instability, and the position of the stability boundaries is well described by the given theory for mixtures with a linear distribution of the concentration. For systems with a pronounced nonlinearity in the distribution of the concentrations, agreement between theory and experiment is violated.

1. In binary mixtures for a specified geometry of the channel (Fig. 1) at a negative gradient of the density (the density at the top is lower than the density at the bottom), the force of gravity virtually does not affect the velocity of mixing of the components, since mechanical equilibrium of the inhomogeneous mixture is realized; this equilibrium becomes unstable with the opposite direction of the gradient of the density and, as a result, gravitational concentration convection arises. It seemed that the addition of a third component to the system should not lead to a qualitative change in its behavior compared to a binary mixture. However, experimental studies of mixing of the components showed that convective flows can arise in ternary mixtures under conditions of stable stratification when the density at the bottom is higher than at the top [1-4]. To understand the reasons for the occurrence of anomalous concentration convection, it was necessary to perform a linear analysis for stability [5-7]. But for isothermal multicomponent gas systems this analysis was performed only for the case of a plane horizontal layer, and within the framework of the chosen diffusion model it had an estimative character [8]. We consider the case of isothermal diffusion instability of ternary gas mixtures for a plane vertical channel (Fig. 1b), which does not always correspond to experiment, where a cylindrical capillary was also used, but the simple geometry of the channel allows one to obtain an analytical solution of the problem of the stability of the diffusion in the complicated situation where two "thermodynamic forces" and two independent gradients of the concentration act simultaneously. It should be assumed that the main features of diffusion instability and related effects will correspond to the experimental data (see, e.g., [1-4]).

2. According to [5, 9], we assume that the macroscopic motion of an isothermal ternary gas mixture is described by a general system of hydrodynamic equations that involves the Navier–Stokes equations of motion and the equations of continuity and mass transfer of the components. Considering the condition of independent diffusion, where $\sum_{i=1}^{3} \vec{j_i} = 0$, $\sum_{i=1}^{3} c_i = 1$, we have the following system of equations:

$$\rho \left[\frac{\partial \vec{u}}{\partial t} + (\vec{u} \nabla) \vec{u} \right] = - \nabla p + \eta \nabla^2 \vec{u} + \left(\frac{\eta}{3} + \xi \right) \nabla \operatorname{div} \vec{u} + \rho \vec{g},$$

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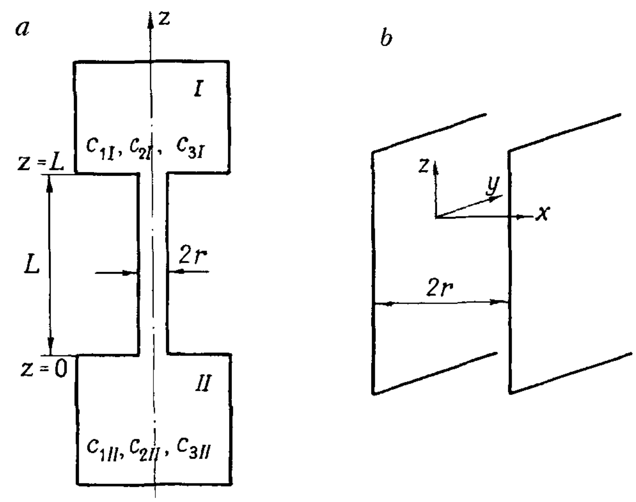

Fig. 1. Geometry of the problem: a) diffusion cell of a two-column apparatus; b) diffusion channel.

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \vec{u}) = 0, \quad \rho \left(\frac{\partial c_i}{\partial t} + \vec{u} \nabla c_i \right) = - \operatorname{div} \vec{j_i}, \tag{2.1}$$

$$\vec{j_i} = - \rho \left(D^*_{11} \nabla c_1 + D^*_{12} \nabla c_2 \right), \quad \vec{j_2} = - \rho \left(D^*_{21} \nabla c_1 + D^*_{22} \nabla c_2 \right),$$

The quantities D^*_{ij} and the coefficients of diffusion of the binary gas mixtures are related as

$$D^*_{11} = \frac{D_{13} \left[c_1 D_{32} + (c_2 + c_3) D_{12} \right]}{c_1 D_{23} + c_2 D_{13} + c_3 D_{12}}, \quad D^*_{12} = - \frac{c_1 D_{23} (D_{12} - D_{13})}{c_1 D_{23} + c_2 D_{13} + c_3 D_{12}},$$

$$D^*_{22} = \frac{D_{23} \left[c_2 D_{13} + (c_1 + c_3) D_{12} \right]}{c_1 D_{23} + c_2 D_{13} + c_3 D_{12}}, \quad D^*_{21} = - \frac{c_2 D_{13} (D_{12} - D_{23})}{c_1 D_{23} + c_2 D_{13} + c_3 D_{12}}.$$

Expressions (2.1) are supplemented by the equation of state of the medium

$$\rho = \rho (c_1, c_2, p), \quad T = \text{const}, \tag{2.2}$$

which makes it possible to relate the thermodynamic parameters in (2.1).

The system of equations (2.1)-(2.2) describes a class of problems that consider isothermal concentration convection, including the gas-mixture motion arising in a gravity field in the presence of spatial nonuniformity of the density caused by inhomogeneity of the composition. The indicated phenomena have much in common with the effects observed in thermal convection, where they are described within the framework of the Boussinesq approximation [5, 6].

We assume that the thermodynamic variables – the concentration of the i-th component c_i and the pressure p – have the form

$$c_i = \langle c_i \rangle + c_i', \quad p = \langle p \rangle + p',$$

where $\langle c_i \rangle$ and $\langle p \rangle$ are the constant mean values, taken as a reference point; c_i' and p' are the disturbed characteristics. The variation in density caused by the nonuniformity of the pressure is small compared to the variations caused by the inhomogeneity of the composition and is in conformity with the fact that the pressure should not vary strongly along the gas mixture. Considering the smallness of the nonstationary disturbances, neglecting the square terms with respect to the disturbances, we finally obtain (the primes on the disturbed quantities are omitted)

$$\frac{\partial \vec{u}}{\partial t} + \vec{u}\nabla\,\vec{u} = -\frac{1}{\rho_0}\nabla p + \nu\,\nabla^2\,\vec{u} + g\,(\beta_1 c_1 + \beta_2 c_2)\,\vec{\gamma},$$

$$\frac{\partial c_1}{\partial t} + \vec{u}\nabla\, c_1 = D_{11}^*\,\nabla^2\,c_1 + D_{12}^*\,\nabla^2\,c_2\,,$$

$$\frac{\partial c_2}{\partial t} + \vec{u}\nabla\, c_2 = D_{21}^*\,\nabla^2\,c_1 + D_{22}^*\,\nabla^2\,c_2\,, \tag{2.3}$$

$$\operatorname{div}\vec{u} = 0\,,$$

where $\nu = \eta/\rho$; $\beta_i = -\frac{1}{\rho_0}\left(\frac{\partial\rho}{\partial c_i}\right)_{P,T,c_j\neq c_i}$; $\vec{\gamma}$ is the unit vector directed vertically upward.

The boundary conditions are standard for the velocity on the surface of the plane S and are related to the vanishing of the normal component of the material flow at the boundary, i.e.,

$$\vec{u} = 0\,;\quad \frac{\partial c_i}{\partial n} = 0\,.$$

Here n is the normal to the boundary.

The condition of mechanical equilibrium is defined as

$$-\frac{1}{\rho_0}\nabla p_0 + g\,(\beta_1 c_{10} + \beta_2 c_{20})\,\vec{\gamma} = 0\,,$$

$$D_{11}^*\nabla^2 c_{10} + D_{12}^*\nabla^2 c_{20} = 0\,, \tag{2.4}$$

$$D_{21}^*\nabla^2 c_{10} + D_{22}^*\nabla^2 c_{20} = 0\,.$$

In this case, the horizontal components of the gradient of the concentration are equal to zero:

$$\frac{\partial c_{i0}}{\partial x} = \frac{\partial c_{i0}}{\partial y} = 0$$

(the plane specified by the x and y axes is perpendicular to z), and then the concentration of the component c_{i0} is determined only by the vertical coordinate z. Here, the linear dependence of the concentration on the height follows from Eqs. (2.4):

$$c_{10} = -A_1 z + B_1\,,\quad c_{20} = -A_2 z + B_2\,.$$

The gradients of the concentrations of the components at all points of the gas mixture are vertical and have the values

$$\nabla c_{10} = -A_1\vec{\gamma},\quad \nabla c_{20} = -A_2\vec{\gamma}.$$

We rewrite expressions (2.3) in dimensionless form. We take the following scales of measurement units: the characteristic linear dimension of the cavity d for distance; d^2/ν for time; D_{22}^*/d for velocity; $A_i d$ for the concentration of the i-th component; $\rho_0 \nu D_{22}^*/d^2$ for pressure. Converting, by means of the indicated units, to dimensionless quantities and assuming, by analogy with [5], that $u_x = u_y = 0$, $u_z = u(x)$, $c_i = c_i(x)$, and $\nabla p = 0$, we obtain the system of equations for the disturbances

$$\mathrm{P}_{22}\frac{\partial c_1}{\partial t} - u = \tau_{11}\frac{\partial^2 c_1}{\partial x^2} + \frac{A_2}{A_1}\tau_{12}\frac{\partial^2 c_2}{\partial x^2},$$

$$\mathrm{P}_{22}\frac{\partial c_2}{\partial t} - u = \frac{A_1}{A_2}\tau_{21}\frac{\partial^2 c_1}{\partial x^2} + \frac{\partial^2 c_2}{\partial x^2}, \tag{2.5}$$

$$\frac{\partial \vec{u}}{\partial t} = \frac{\partial^2 u}{\partial x^2} + \mathrm{R}_1\tau_{11}c_1 + \mathrm{R}_2 c_2,$$

where $\mathrm{P}_{ii} = \nu/D^*_{ii}$; $\mathrm{R}_i = g\beta_i A_i d^4/\nu D^*_{ii}$; $\tau_{ij} = D^*_{ij}/D^*_{22}$.

3. The solution of (2.5) has the form

$$\{c_1, c_2, u\} = \{c_1^0, c_2^0, u^0\}\sin\left[(n+1)\frac{\pi}{2}x\right]\exp[-\lambda t], \tag{3.1}$$

where $n = 1, 3, 5, \ldots$ are the characteristic odd modes of the disturbances. The choice of (3.1) is dictated by the occurrence of at least two countercurrents – ascending and descending – in the experiments [1-4].

The boundary conditions assume the vanishing of the velocity and the disturbances of the concentrations of the components c_i on the vertical planes bounding the layer of the gas mixture:

$$u = c_1 = c_2 = 0, \quad x = \pm 1.$$

Substituting (3.1) into system (2.5) and eliminating successively the concentration and velocity amplitudes, we obtain a cubic equation with respect to λ that determines the characteristic roots for any n as a function of the parameters – the partial Rayleigh numbers, τ_{ij}, and the Prandtl numbers – in the form

$$p\lambda^3 + q\lambda^2 + r\lambda + s = 0, \tag{3.2}$$

where

$$p = \mathrm{P}_{22}^2, \quad q = \mathrm{P}_{22}\left[(n+1)\frac{\pi}{2}\right]^2[-\mathrm{P}_{22} - 1 - \tau_{11}],$$

$$r = \left[(n+1)\frac{\pi}{2}\right]^4\{\mathrm{P}_{22}[1+\tau_{11}] + \tau_{11} - \tau_{12}\tau_{21}\} - \mathrm{P}_{22}(\mathrm{R}_1\tau_{11} + \mathrm{R}_2),$$

$$s = \left[(n+1)\frac{\pi}{2}\right]^6\left[\tau_{12}\tau_{21}\left[(n+1)\frac{\pi}{2}\right]^2 - \tau_{11}\right] +$$

$$+\left[(n+1)\frac{\pi}{2}\right]^2\left[\left(1 - \frac{A_2}{A_1}\tau_{12}\right)\mathrm{R}_1\tau_{11} + \left(\tau_{11} - \frac{A_1}{A_2}\tau_{21}\right)\right].$$

Depending on the values of p, q, r, and s, Eq. (3.2) yields either three real roots (monotonic disturbances) or one real and two complex-conjugate roots (oscillatory disturbances). Following [5, 8], we represent $\lambda = \delta + i\omega$, and then (3.2) leads to the following system of equations for the real and imaginary parts of the decrement δ and ω:

$$p(\delta^3 - 3\delta\omega^2) + q(\delta^2 - \omega^2) + r\delta + s = 0, \tag{3.3}$$

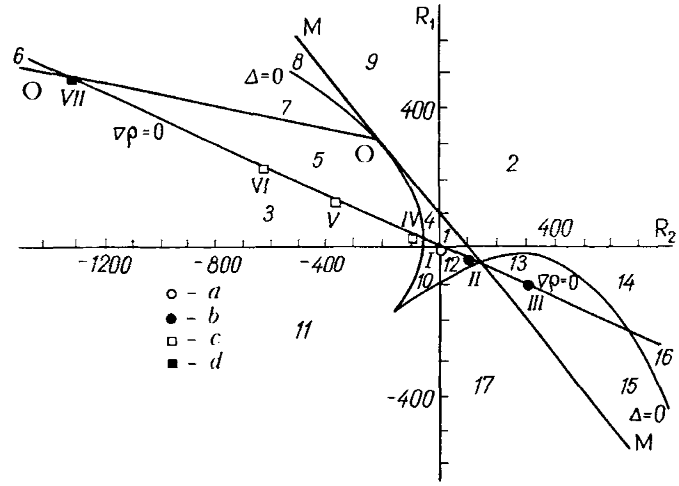

Fig. 2. Characteristic regions (1-17) of diffusion mixing for the ternary system 0.3409 He (1) + 0.6591 Ar (2) – N_2 (3) at T = 298 K and neutral lines of monotonic MM and oscillatory OO disturbances, zero gradient of the density $\nabla\rho = 0$, and the discriminant curve $\Delta = 0$; points a, b) experimental data determining stable and unstable states in diffusion of the binary mixture to the pure component; c, d) obtained for the case of stable and unstable mixing of the pure component with the binary mixture; the conditions were varied by changing the pressure: I) 0.58; II) 1.56; III) 2.54 MPa for points *a* and *b* and IV) 1.56; V) 3.04; VI) 4.03; VII) 5.7 MPa for points *c* and *d*.

$$\omega\,[p\,(3\delta^2 - \omega^2) + 2\delta q + r] = 0\,. \tag{3.4}$$

Hence, we can obtain the spectrum of decrement surfaces determined on the plane of the partial Rayleigh numbers $\lambda_n = \lambda_n(R_1, R_2)$ for fixed values of n and the characteristic set of frequencies $\omega_n = \omega_n(R_1, R_2)$.

To determine the boundaries of stability, we set $\delta = 0$ in (3.3), (3.4) and obtain the critical lines $R_1(R_2)$ for monotonic and oscillatory disturbances and the frequency of neutral oscillations ω at the boundary of oscillatory instability in the form

$$\tau_{11}\left(1 - \frac{A_2}{A_1}\tau_{12}\right)R_1 + \left(\tau_{11} - \frac{A_1}{A_2}\tau_{21}\right)R_2 = \left[(n+1)\frac{\pi}{2}\right]^4(\tau_{11} - \tau_{12}\tau_{21})\,, \tag{3.5}$$

$$\tau_{11}\left(-\frac{A_2}{A_1}\tau_{12} - P_{22} - \tau_{11}\right)R_1 + \left(-\frac{A_1}{A_2}\tau_{21} - P_{22} - 1\right)R_2 = \left[(n+1)\frac{\pi}{2}\right]^4 \times$$
$$\times\left[\frac{1}{P_{22}}\langle P_{22}(1 + \tau_{11}) + \tau_{11} - \tau_{12}\tau_{21}\langle(-P_{22} - 1 - \tau_{11}) - \tau_{21}\tau_{12} + \tau_{11}\right]\,, \tag{3.6}$$

$$\omega^2 = \frac{\left[(n+1)\frac{\pi}{2}\right]^4[\tau_{12}\tau_{21} - \tau_{11}] + \left(1 - \frac{A_2}{A_1}\tau_{12}\right)R_1\tau_{11} + \left(\tau_{11} - \frac{A_1}{A_2}\tau_{21}\right)R_2}{P_{22}(-P_{22} - 1 - \tau_{11})}\,. \tag{3.7}$$

Expression (3.7) imposes limitations on (3.6) that are associated with the fact that a straight line has the meaning of a neutral line for oscillatory disturbances only on the portion where $\omega^2 > 0$ [5].

From the condition of vanishing of the discriminant of Eq. (3.2) $\Delta(R_1, R_2) = 0$ the expression

$$27p^2s^2 - 18pqrs + 4q^3s + 4pr^3 - q^2r^2 = 0\,, \tag{3.8}$$

which describes a third-order curve on the plane (R_1, R_2) (Fig. 2), follows. In the sectors above it, all the three roots of Eq. (3.2) are real, and below it there are one real and two complex-conjugate roots (the disturbances oscillate).

The vanishing of the density gradient of the mixture with account for the determination of the partial Rayleigh numbers (2.5) allows one to obtain the equation of a line on the plane (R_1, R_2):

$$\tau_{11}R_1 = -R_2\,. \tag{3.9}$$

4. To compare the theory with experimental data, we number the components of the mixture: the lightest gas (by density) – 1, the heaviest gas – 2, the gas occupying an intermediate position – 3. We consider isothermal mixing in the system 0.3409 He (1) + 0.6591 Ar (2) – N_2 (3) (the figures before the chemical element give the concentration of the component in mole fractions) at $T = 298$ K, which is characterized by the same density of the binary mixture and the pure component. The experiments were carried out on a setup that implements the two-column method by a standard technique [1-4] with the binary mixture being present in both the upper and lower columns [1-3, 10]. The columns were connected by a cylindrical channel of radius $r = 2\cdot10^{-3}$ m and length $L = 7\cdot10^{-2}$ m. Instability was detected in each case, but at different pressures. Here, in accordance with (2.17), the partial Rayleigh numbers can be transformed to the form

$$R_1 = \frac{gnr^4\,\Delta m_1\,\Delta c_1}{\rho\nu D^*_{11}L}\,, \quad R_2 = \frac{gnr^4\,\Delta m_2\,\Delta c_2}{\rho\nu D^*_{22}L}\,,$$

$$n = \frac{p}{kT}\,, \quad \Delta c_1 = c_{1\mathrm{I}} - c_{1\mathrm{II}}\,, \quad \Delta c_2 = c_{2\mathrm{I}} - c_{2\mathrm{II}}\,, \quad \Delta m_1 = m_1 - m_3\,, \quad \Delta m_2 = m_2 - m_3\,.$$

Figure 2 shows lines of monotonic (MM) and oscillatory (OO) instability and the zero gradient of the density ($\nabla\rho = 0$), the discriminant curve ($\Delta = 0$), and experimental data on the mixture He + Ar – N_2. The coordinate axes and the lines divide the plane (R_1, R_2) into 17 regions with certain characteristics of the mode of mixing.

For the first quadrant ($R_1 > 0$, $R_2 > 0$), the condition $\nabla\rho > 0$ is met, under which monotonic disturbances are observed; these disturbances are damped in region 1 and increase in region 2.

The second quadrant ($R_1 < 0$, $R_2 > 0$) is divided into seven main regions. Region 3, $\nabla\rho < 0$, is characterized by one monotonic and two oscillatory disturbances; all the disturbances are damped. In sectors 4 and 5, $\nabla\rho > 0$, but this does not violate the conditions of stability. In region 6, in spite of the negative values of $\nabla\rho$ (stable stratification), the oscillatory disturbances acquire an unstable character (anomalous instability). Region 7, $\nabla\rho > 0$, is characterized by one diminishing monotonic disturbance and two increasing oscillatory disturbances. In sector 8 the oscillatory disturbances disappear, and in region 9 a monotonic disturbance manifests itself.

The third quadrant corresponds to stable stratification ($\nabla\rho < 0$), in region 11 the disturbances may be both monotonic and oscillatory, and in region 10 they are only monotonic, but all the disturbances in this quadrant are diminishing.

The fourth quadrant involves regions of anomalous instability 15 and 16, where $\nabla\rho < 0$, but they lie above the line of monotonic instability MM. In regions 13 and 14, $\nabla\rho > 0$, and the mixture is unstable, and in 17 and 12, $\nabla\rho < 0$, and stable diffusion is noted. All the oscillatory disturbances in the fourth quadrant are diminishing.

Figure 2 also presents experimental points obtained at different pressures. To obtain experimental points in the second and fourth quadrants similarly to the foregoing we investigated two versions of position-

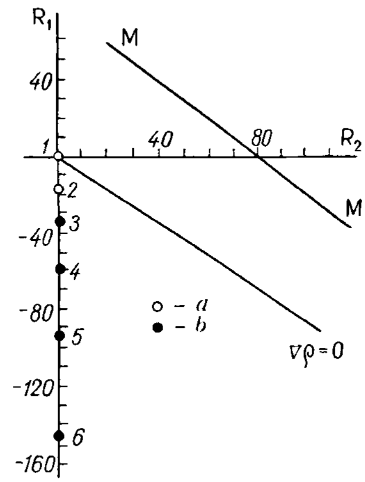

Fig. 3. Regions of stable and unstable diffusion for ternary mixtures and lines of monotonic MM disturbances and zero gradient of the density $\nabla\rho = 0$; a, b) experimental data determining stable and unstable states; the system 0.5134 He (1) + 0.4857 Ar (2) – 0.5184 CH_4 (3) + 0.4852 Ar (2); the conditions were varied by changing the pressure, the variations correspond to the values: 1) 0.58; 2) 1.07; 3) 1.54; 4) 2.05; 5) 2.54; 6) 3.05 MPa.

ing: 1) the binary mixture is at the top (the fourth quadrant); 2) the binary mixture is at the bottom (the second quadrant). The points corresponding to stable diffusion are light, and those for the case of convection are dark. It is seen from Fig. 2 that the experiment confirms theoretical predictions about the position of the regions of stability and indicates that the instabilities corresponding to the two anomalous regions 6 and 15 can be observed with one and the same mixture.

Figure 3 gives theoretical lines of stability and experimental data [11] for the mixture 0.5134 He (1) + 0.4857 Ar (2) – 0.5184 CH_4 (3) + 0.4852 Ar (2). Since the concentration of the heavy gas – argon – is virtually the same in both columns, the Rayleigh number $R_2 = 0$. It is seen that a transition to an unstable state occurs in an obviously stable region from the theoretical point of view. The reason for this discrepancy is probably a considerable difference in the distribution of the component concentration in this mixture from a linear one [12], assumed in (2.5).

Thus, it is shown that in isothermal mixing of ternary systems there exist two types of anomalous instability: one at $R_1 > 0$, $R_2 < 0$ and the other at $R_1 < 0$, $R_2 > 0$. Experiments with a mixture of He + Ar – N_2 with the same density in the columns confirm the presence of these two regions of instability and are well described by the theory from the point of view of the location of the boundaries of stability.

However, fundamental disagreement between experiment and theory is observed in systems with a substantially nonlinear distribution of the concentrations of the components along the length of the diffusion channel. Therefore, to describe mass transfer in these systems, one must develop an appropriate approach to the determination of the "true" values of the gradients of the component concentrations with account for the substantial nonlinearity of their distribution.

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NOTATION

c_i, concentration of the i-th component; D^*_{ij} and D_{ij}, "practical" coefficient of diffusion and coefficient of mutual diffusion of gases i and j; g, acceleration of gravity; $\vec{j_i}$, density of the diffusion flow of the i-th component; k, Boltzmann constant; L, length of the diffusion channel; m, mass of the molecule; n, normal to the boundary, mode of the disturbances; P_{ii}, Prandtl number; p, pressure; R_i, Rayleigh number; r, characteristic scale, radius of the diffusion channel; T, temperature; t, time; $\vec{u}$, velocity; η, coefficient of shear viscosity; λ, time decrement of the disturbances; ν, kinematic viscosity of the mixture; ξ, coefficient of volumetric viscosity; ρ and ρ_0, density and mean density; τ_{ij}, parameter characterizing the relationship between the "practical" coefficients of diffusion; ω, frequency of the neutral oscillations.

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