

TRANSPORT AND RELAXATION PHENOMENA IN POLYATOMIC GAS MIXTURES

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A closed system of equations is derived for the diffusion velocities, heat fluxes, and viscous stress tensor by using a method in which the distribution function is expanded in a series in generalized polynomials [6]. The equations differ from the familiar expressions [3] in that the form of some of the kinetic coefficients is simpler and that consistent allowance is made for the effect of viscous momentum transfer on diffusion of the components. The structure of the kinetic coefficients are analyzed for the cases of "easy" and "hindered" energy exchange between the translational and internal degrees of freedom of the molecules. The equations of energy relaxation of the components and the conditions under which an expression for the volume viscosity of the mixture can be derived are discussed.

1. INTRODUCTION

THE recently developed formal kinetic theory of polyatomic gases and gas mixtures [1-3] is based as a rule on a generalization of the Chapman-Enskog method [4-5]. A different approach to the theory of polyatomic gases, using the expansion of the distribution function in orthogonal polynomials and essentially a generalization of the Grad method [7], was proposed in [6]. Besides obtaining equations that are of more general (relaxation) character, an advantage of this method is that even in the usual 17-moment approximation (or 13-moment in the case of monatomic mixtures [8]) it is possible to obtain much simpler expressions for the kinetic coefficients in the diffusion equations and for the heat flow, corresponding to the complete second approximation in the expansion in Sonine polynomials [9]. The influence of the viscous momentum transport on the diffusion of the components is consistently accounted for here just as in [8].

In the present paper we extend the method used in [6] to include the case of polyatomic gas mixtures. It is possible to write down in the 17-moment approximation a closed system of transport equations for each of the mixture components. Linear relations for the diffusion rates, the heat fluxes, and the viscous-stress tensor follow from this system under the assumption that the macroscopic parameters of the gas change little within times and lengths on the order of the effective times and free paths of the molecules. The obtained relations are valid both in the case of an "easy" and "hindered" exchange of energy between the translational and internal degrees of freedom of the molecules under the condition that the deviations of the corresponding energies from their equilibrium values are small. The kinetic coefficients that enter in these relations can be simplified in many cases by linearization with respect to the small parameter $Z_{\alpha\beta}^{-1}$, which characterizes the degree of "hindrance" of the exchange [10]. In the conclusion we consider the equations of relaxation of the translational and internal energies of the components, which lead in the case of "easy" exchange to linear relations for the scalar additions to the partial pressure tensors; these relations justify the introduction of the second (volume) viscosity of the mixture.

2. TRANSPORT RELATIONS

The state of the α component of a polyatomic gas mixture is described by a distribution function $f_{\alpha i} = f_{\alpha}(\mathbf{v}, E_{\alpha i}, \mathbf{r}, t)$, which depends on the velocity \mathbf{v} and on the internal energy $E_{\alpha i}$ of the molecules of species α . Just as in [6], we expand $f_{\alpha i}$ in terms of the irreducible Hermite tensor polynomials $H_{\alpha r_1 \dots r_m}^{mn}(\mathbf{v})$ and the polynomials $P_{\alpha}^{(q)}(E_{\alpha i})$ proposed in [1]. The expansion coefficients can be expressed with the aid of the orthogonality relations for polynomials in terms of the generalized moments of the distribution function. In the case of a polyatomic gas mixture, a physical meaning is possessed by the following 17 moments:

$$\begin{aligned} \rho_{\alpha} &= m_{\alpha} n_{\alpha} = m_{\alpha} \sum_i \int f_{\alpha i} d\mathbf{c}, \\ \rho_{\alpha} \mathbf{w}_{\alpha} &= m_{\alpha} \sum_i \int \mathbf{c} f_{\alpha i} d\mathbf{c}, \\ n_{\alpha} E_{\alpha}^{\text{tr}} &= \frac{m_{\alpha}}{2} \sum_i \int c^2 f_{\alpha i} d\mathbf{c}, \quad n_{\alpha} E_{\alpha}^{\text{in}} = \sum_i \int E_{\alpha i} f_{\alpha i} d\mathbf{c}, \\ \pi_{\alpha rs} &= m_{\alpha} \sum_i \int (c_r c_s - \frac{1}{3} \delta_{rs} c^2) f_{\alpha i} d\mathbf{c}, \\ \mathbf{q}_{\alpha}^{\text{tr}} &= \frac{m_{\alpha}}{2} \sum_i \int c^2 \mathbf{c} f_{\alpha i} d\mathbf{c}, \\ \mathbf{q}_{\alpha}^{\text{in}} &= \sum_i \int E_{\alpha i} \mathbf{c} f_{\alpha i} d\mathbf{c}. \end{aligned} \tag{2.1}$$

here $\mathbf{c} = \mathbf{v} - \mathbf{u}$, where \mathbf{u} —average gas velocity of the mixture, m —mass of the molecules of species α , ρ_{α} and $\mathbf{w}_{\alpha} = \mathbf{u}_{\alpha} - \mathbf{u}$ —mass density and average diffusion velocity of the molecules of the α -component, $\pi_{\alpha rs}$ —partial tensor of viscous stresses; E_{α}^{tr} , $\mathbf{q}_{\alpha}^{\text{tr}}$, E_{α}^{in} , $\mathbf{q}_{\alpha}^{\text{in}}$ —average energies and heat fluxes corresponding to the translational and internal degrees of freedom of molecules of species α .

For the distribution function we have in the 17-moment approximation

$$\begin{aligned} f_{\alpha i} &= f_{\alpha i}^{(0)} \left[1 + \gamma_{\alpha}^{1/2} \mathbf{w}_{\alpha} \xi_{\alpha} + \frac{1}{3} \frac{n_{\alpha} \Delta E_{\alpha}^{\text{tr}}}{p_{\alpha}} (\xi_{\alpha}^2 - 3) \right. \\ &+ \frac{k}{c_{\alpha}^{\text{in}}} \frac{n_{\alpha} \Delta E_{\alpha}^{\text{in}}}{p_{\alpha}} (\epsilon_{\alpha i} - \langle \epsilon_{\alpha} \rangle) + \frac{1}{2} \frac{\pi_{\alpha rs}}{p_{\alpha}} (\xi_{\alpha r} \xi_{\alpha s} - \frac{1}{3} \xi_{\alpha}^2 \delta_{rs}) \\ &\left. + \frac{1}{5} \frac{\gamma_{\alpha}^{1/2}}{p_{\alpha}} \mathbf{h}_{\alpha}^{\text{tr}} \xi_{\alpha} (\xi_{\alpha}^2 - 5) + \frac{k}{c_{\alpha}^{\text{in}}} \frac{\gamma_{\alpha}^{1/2}}{p_{\alpha}} \mathbf{h}_{\alpha}^{\text{in}} \xi_{\alpha} (\epsilon_{\alpha i} - \langle \epsilon_{\alpha} \rangle) \right], \end{aligned} \tag{2.2}$$

where

$$\begin{aligned} f_{\alpha i}^{(0)} &= n_{\alpha}(\gamma_{\alpha}/2\pi)^{3/2}Q_{\alpha}^{-1}\exp(-\xi_{\alpha}^2/2 - \epsilon_{\alpha i}), \\ \xi_{\alpha} &= \gamma_{\alpha}^{1/2}\mathbf{c}, \quad \epsilon_{\alpha i} = E_{\alpha i}/kT, \quad \gamma_{\alpha} = m_{\alpha}/kT, \\ Q_{\alpha} &= \sum_i \exp(-\epsilon_{\alpha i}). \end{aligned}$$

Here

$$\begin{aligned} \Delta E_{\alpha}^{\text{tr}} &= E_{\alpha}^{\text{tr}} - E_{\alpha 0}^{\text{tr}}, & \Delta E_{\alpha}^{\text{in}} &= E_{\alpha}^{\text{in}} - E_{\alpha 0}^{\text{in}}, \\ \mathbf{h}_{\alpha}^{\text{tr}} &= \mathbf{q}_{\alpha}^{\text{tr}} - 1/2 p_{\alpha} \mathbf{w}_{\alpha}, & \mathbf{h}_{\alpha}^{\text{in}} &= \mathbf{q}_{\alpha}^{\text{in}} - \langle \epsilon_{\alpha} \rangle p_{\alpha} \mathbf{w}_{\alpha}, \\ c_{\alpha}^{\text{in}} &= (\partial E_{\alpha 0}^{\text{in}} / \partial T)_V = k(\langle \epsilon_{\alpha}^2 \rangle - \langle \epsilon_{\alpha} \rangle^2), \end{aligned} \quad (2.3)$$

where

$$E_{\alpha 0}^{\text{tr}} = 3/2 kT, \quad E_{\alpha 0}^{\text{in}} = \langle \epsilon_{\alpha} \rangle kT, \quad p_{\alpha} = n_{\alpha} kT,$$

$\langle \rangle$ denotes averaging with a Boltzmann factor $Q_{\alpha}^{-1} \exp(-\epsilon_{\alpha i})$.

When (2.2) is used, the parameters determining the state of the polyatomic gas mixture are ρ_{α} , \mathbf{u} , T , $\rho_{\alpha} \mathbf{w}_{\alpha}$, $\pi_{\alpha RS}$, $n_{\alpha} \Delta E_{\alpha}^{\text{tr}}$, $n_{\alpha} \Delta E_{\alpha}^{\text{in}}$, $\mathbf{h}_{\alpha}^{\text{tr}}$, and $\mathbf{h}_{\alpha}^{\text{in}}$. Out of these, 17N quantities are independent (N—number of mixture components), since the following conditions are satisfied

$$\sum_{\alpha} \rho_{\alpha} \mathbf{w}_{\alpha} = 0, \quad \sum_{\alpha} n_{\alpha} (\Delta E_{\alpha}^{\text{tr}} + \Delta E_{\alpha}^{\text{in}}) = 0, \quad (2.4)$$

which follow from the definition of the mean mass velocity of the mixture \mathbf{u} and the temperature T .

A closed system of differential equations for the quantities under consideration can be obtained by multiplying the kinetic equation for the polyatomic mixture^[3] by the corresponding polynomials with subsequent integration with respect to velocity and summation with respect to i . Owing to the complexity of these equations, we shall not write them out here completely¹⁾, since we are interested principally in the case when the following conditions are satisfied

$$L \gg \lambda_0, \quad \tau_L \gg \tau_0, \quad (2.5)$$

where L and τ_L are the characteristic linear and temporal scales of variation of the macroscopic quantities, and λ_0 and τ_0 are the average free-path length and time of the molecules.

We note that summation of the first three equations with respect to α leads to the equations for ρ , \mathbf{u} , and T ; these correspond to the ordinary equations of continuity, motion, and energy of a polyatomic gas mixture (see, for example,^[5]). The right sides of the equations for the remaining quantities contain the moments relative to the collision integrals, which can be expressed, in accordance with the approximation (2.2) used for $f_{\alpha i}$, in terms of the same macroscopic parameters of the polyatomic gas. We confine ourselves in their calculation, as usual, to the terms that are linear in the moments. An analysis of the obtained expressions shows that the order of magnitude of the coefficients at the moments in the right sides of the equations for $\rho_{\alpha} \mathbf{w}_{\alpha}$, $\pi_{\alpha RS}$, $\mathbf{h}_{\alpha}^{\text{tr}}$, and $\mathbf{h}_{\alpha}^{\text{in}}$ is determined primarily by the values of $\tau_{\alpha\beta}^{-1}$ and $(c_{\alpha}^{\text{in}}/k)\tau_{\alpha\beta}^{-1}$ and the values of $Z_{\alpha\beta}^{-1}\tau_{\alpha\beta}^{-1}$, which are encountered simultaneously with them. Here $\tau_{\alpha\beta}$ —characteristic colli-

sion time for the molecules α and β , defined by the relation

$$\tau_{\alpha\beta}^{-1} = n_{\beta} kT / \mu_{\alpha\beta} n [D_{\alpha\beta}]_1,$$

where $\mu_{\alpha\beta}$ is the reduced mass and $[D_{\alpha\beta}]_1$ corresponds to the first approximation and to the coefficient of mutual diffusion in the mixture of molecules α and β . Obviously $\tau_{\alpha\beta} \sim \tau_0$. The parameter $Z_{\alpha\beta}$ characterizes the ratio of the frequency of the elastic and inelastic collisions of the molecules α and β . It is known that inelastic collisions accompanied by energy transfers between the translational and internal degrees of freedom occur as a rule less frequently than elastic collisions. In particular, if rotational degrees of freedom are excited, then $Z \sim 5-20$ (exception for light gases, when $Z \sim 10^2$ ^[11]). Upon excitation of the vibrational degrees of freedom, $Z \sim 10^3-10^4$.

The foregoing considerations allow us to neglect, if conditions (2.5) are satisfied, the time derivatives of the quantities $\rho_{\alpha} \mathbf{w}_{\alpha}$, $\pi_{\alpha RS}$, $\mathbf{h}_{\alpha}^{\text{tr}}$ in the left parts of the equations for these quantities, compared with the corresponding terms in the right sides, as well as the nonlinear terms²⁾, i.e., the fluxes and the energy deviations multiplied by the gradients of n , \mathbf{u} , and T . As a result we arrive at the following linear system of equations for the diffusion rates, heat fluxes, and viscous-stress tensors:

$$\begin{aligned} \sum_{\beta} \frac{n_{\alpha} n_{\beta} kT}{n [D_{\alpha\beta}]_1} (w_{\alpha r} - w_{\beta r}) &= -p \frac{\partial y_{\alpha}}{\partial x_r} - \left(y_{\alpha} - \frac{\rho_{\alpha}}{\rho} \right) \frac{\partial p}{\partial x_r} \\ &\quad - \frac{2}{3} \left(\frac{\partial n_{\alpha} \Delta E_{\alpha}^{\text{tr}}}{\partial x_r} - \frac{\rho_{\alpha}}{\rho} \frac{\partial n \Delta E^{\text{tr}}}{\partial x_r} \right) \\ &\quad - \left(\frac{\partial \pi_{\alpha RS}}{\partial x_s} - \frac{\rho_{\alpha}}{\rho} \frac{\partial \pi_{RS}}{\partial x_s} \right) - \sum_{\beta} \frac{m_{\beta}}{m_{\alpha} + m_{\beta}} \frac{n_{\alpha} n_{\beta} kT}{n [D_{\alpha\beta}]_1} \\ &\quad \times \left(\frac{6}{5} C_{\alpha\beta}^* - 1 \right) \left(\frac{h_{\alpha r}^{\text{tr}}}{p_{\alpha}} - \frac{m_{\alpha}}{m_{\beta}} \frac{h_{\beta r}^{\text{tr}}}{p_{\beta}} \right) \\ &\quad - \sum_{\beta} \frac{n_{\alpha} n_{\beta} kT}{n [D_{\alpha\beta}]_1} \left[E_{\alpha\beta}^* \frac{h_{\alpha r}^{\text{in}}}{n_{\alpha} c_{\alpha}^{\text{in}} T} - E_{\beta\alpha}^* \frac{h_{\beta r}^{\text{in}}}{n_{\beta} c_{\beta}^{\text{in}} T} \right], \end{aligned} \quad (2.6)$$

$$-2y_{\alpha} \epsilon_{rs} - \frac{4}{5p} \left\{ \frac{\partial q_{\alpha r}^{\text{tr}}}{\partial x_s} \right\} = \sum_{\beta} a_{\alpha\beta} \frac{\pi_{\beta RS}}{y_{\beta}}, \quad (2.7)$$

$$\begin{aligned} -y_{\alpha} \frac{\partial T}{\partial r} - \frac{T}{p} \left(\frac{2}{5} \frac{\partial \pi_{\alpha RS}}{\partial x_s} + \frac{2}{3} \frac{\partial n_{\alpha} \Delta E_{\alpha}^{\text{tr}}}{\partial x_r} \right) \\ - \frac{T}{p} \sum_{\beta} \frac{n_{\alpha} n_{\beta} kT}{m_{\alpha} + m_{\beta}} \frac{1}{n [D_{\alpha\beta}]_1} \left(\frac{6}{5} C_{\alpha\beta}^* - 1 \right) (w_{\alpha r} - w_{\beta r}) \\ = \sum_{\beta} b_{\alpha\beta} \frac{h_{\beta r}^{\text{tr}}}{y_{\beta}} + \sum_{\beta} \frac{k}{c_{\beta}^{\text{in}}} b_{\alpha\beta} \frac{h_{\beta r}^{\text{in}}}{y_{\beta}}, \end{aligned} \quad (2.8)$$

$$\begin{aligned} -y_{\alpha} \frac{c_{\alpha}^{\text{in}}}{k} \frac{\partial T}{\partial x_r} - \frac{T}{p} \frac{\partial n_{\alpha} \Delta E_{\alpha}^{\text{in}}}{\partial x_r} \\ - \frac{T}{p} \sum_{\beta} \frac{n_{\alpha} n_{\beta} kT}{n [D_{\alpha\beta}]_1} E_{\alpha\beta}^* (w_{\alpha r} - w_{\beta r}) \\ = \sum_{\beta} g_{\alpha\beta} \frac{h_{\beta r}}{y_{\beta}} + \sum_{\beta} \frac{k}{c_{\beta}^{\text{in}}} g_{\alpha\beta} \frac{h_{\beta r}^{\text{in}}}{y_{\beta}}. \end{aligned} \quad (2.9)$$

Here $y_{\alpha} = n_{\alpha}/n$ —molar concentration of the α -component in the mixture, and the mixture parameters ρ , n , p , $n \Delta E^{\text{tr}}$, and π_{RS} are determined by summing the corresponding partial quantities over α . In writing

¹⁾The corresponding equations for a monatomic gas mixture and for a simple polyatomic gas are given in [8] and [6].

²⁾The time derivatives of n , \mathbf{u} , and T are first eliminated from these equations with the aid of the first three conservation equations.

down (2.7), we used the symbols

$$\{L_r M_s\} = \frac{1}{2}(L_r M_s + M_s L_r) - \frac{1}{3}\delta_{rs} M_l L_l, \quad \varepsilon_{rs} = \{\partial u_r / \partial x_s\}.$$

The coefficients $a_{\alpha\beta}$, $b_{\alpha\beta}$, $b'_{\alpha\beta}$, $g_{\alpha\beta}$, and $g'_{\alpha\beta}$ are defined by the following expressions:

$$a_{\alpha\alpha} = \frac{y_{\alpha}^2}{|\eta_{\alpha\alpha}|} + \sum_{\gamma \neq \alpha} \frac{2y_{\alpha} y_{\gamma}}{(m_{\alpha} + m_{\gamma})n[D_{\alpha\gamma}]_1} \left(1 + \frac{3}{5} \frac{m_{\gamma}}{m_{\alpha}} A_{\alpha\gamma}^*\right), \quad (2.10)$$

$$a_{\alpha\beta} = -\frac{2y_{\alpha} y_{\beta}}{(m_{\alpha} + m_{\beta})n[D_{\alpha\beta}]_1} \left(1 - \frac{3}{5} A_{\alpha\beta}^*\right), \quad \beta \neq \alpha;$$

$$b_{\alpha\alpha} = \frac{4}{15} \frac{m_{\alpha} y_{\alpha}^2}{k|\eta_{\alpha\alpha}|} \left(1 + \frac{5}{6} \frac{c_{\alpha}^{\text{in}}}{k} Z_{\alpha\alpha}^{-1}\right) + \frac{4}{25} \sum_{\gamma \neq \alpha} \frac{y_{\alpha} y_{\gamma}}{(m_{\alpha} + m_{\gamma})^2 k n [D_{\alpha\gamma}]_1} \times \left[\frac{15}{2} m_{\alpha}^2 + \left(\frac{25}{4} - 3B_{\alpha\gamma}^*\right) m_{\gamma}^2 + 4A_{\alpha\gamma}^* \left(1 + \frac{5}{6} \frac{c_{\alpha}^{\text{in}}}{k} Z_{\alpha\gamma}^{-1}\right) m_{\alpha} m_{\gamma}\right],$$

$$b_{\alpha\beta} = -\frac{4}{25} \frac{m_{\alpha} m_{\beta} y_{\alpha} y_{\beta}}{(m_{\alpha} + m_{\beta})^2 k n [D_{\alpha\beta}]_1} \left[\frac{55}{4} - 3B_{\alpha\beta}^* - 4A_{\alpha\beta}^* \left(1 + \frac{5}{6} \frac{c_{\alpha}^{\text{in}}}{k} Z_{\alpha\beta}^{-1}\right)\right], \quad \beta \neq \alpha; \quad (2.11)$$

$$b_{\alpha\alpha'} = g_{\alpha\alpha} = -\frac{\pi}{3} \frac{m_{\alpha} y_{\alpha}^2}{k|\eta_{\alpha\alpha}|} \frac{c_{\alpha}^{\text{in}}}{k} Z_{\alpha\alpha}^{-1} - \sum_{\gamma \neq \alpha} \frac{m_{\gamma} y_{\alpha} y_{\gamma}}{(m_{\alpha} + m_{\gamma})k n [D_{\alpha\gamma}]_1} \times \left[\frac{4}{5} \frac{m_{\alpha}}{m_{\gamma}} \frac{c_{\alpha}^{\text{in}}}{k} A_{\alpha\gamma}^* (L_{\alpha\gamma}^* + M_{\alpha\gamma}^*) Z_{\alpha\gamma}^{-1} - F_{\alpha\gamma}^*\right], \quad (2.12)$$

$$b_{\alpha\beta'} = g_{\beta\alpha} = -\frac{m_{\beta} y_{\alpha} y_{\beta}}{(m_{\alpha} + m_{\beta})n k [D_{\alpha\beta}]_1} \times \left[\frac{4}{5} \frac{c_{\alpha}^{\text{in}}}{k} A_{\alpha\beta}^* (L_{\beta\alpha}^* + M_{\alpha\beta}^*) Z_{\alpha\beta}^{-1} + F_{\beta\alpha}^*\right], \quad \beta \neq \alpha;$$

$$g_{\alpha\alpha'} = \frac{y_{\alpha}^2}{k n [D_{\alpha\alpha}]_1} \left(\frac{c_{\alpha}^{\text{in}}}{k} + G_{\alpha\alpha}^* - H_{\alpha\alpha}^*\right) + \frac{\pi}{2} \frac{m_{\alpha} y_{\alpha}^2}{k|\eta_{\alpha\alpha}|} \frac{c_{\alpha}^{\text{in}}}{k} Z_{\alpha\alpha}^{-1} + \sum_{\gamma \neq \alpha} \frac{y_{\alpha} y_{\gamma}}{k n [D_{\alpha\gamma}]_1} \left(\frac{c_{\alpha}^{\text{in}}}{k} + \frac{6}{5} \frac{m_{\alpha}}{m_{\gamma}} \frac{c_{\alpha}^{\text{in}}}{k} A_{\alpha\gamma}^* L_{\alpha\gamma}^* Z_{\alpha\gamma}^{-1} + G_{\alpha\gamma}^*\right), \quad (2.13)$$

$$g_{\alpha\beta'} = \frac{y_{\alpha} y_{\beta}}{k n [D_{\alpha\beta}]_1} \left(\frac{6}{5} \frac{c_{\alpha}^{\text{in}}}{k} A_{\alpha\beta}^* M_{\alpha\beta}^* Z_{\alpha\beta}^{-1} - H_{\alpha\beta}^*\right), \quad \beta \neq \alpha.$$

Here

$$[\eta_{\alpha\alpha}]_1 = 5kT / 8\Omega_{\alpha\alpha}^{22}, \quad [D_{\alpha\beta}]_1 = 3kT / 16n\mu_{\alpha\beta}\Omega_{\alpha\beta}^{11}, \\ A_{\alpha\beta}^* = \Omega_{\alpha\beta}^{22} / 2\Omega_{\alpha\beta}^{11}, \quad B_{\alpha\beta}^* = (5\Omega_{\alpha\beta}^{11} - \Omega_{\alpha\beta}^{13}) / 3\Omega_{\alpha\beta}^{11}, \quad (2.14) \\ C_{\alpha\beta}^* = \Omega_{\alpha\beta}^{12} / 3\Omega_{\alpha\beta}^{11}.$$

The quantities $\Omega_{\alpha\beta}^{\text{tr}}$, which are a generalization of the known Chapman-Cowling integrals^[4], are written in the form

$$\Omega_{\alpha\beta}^{11} = \langle \zeta^2 - \zeta\zeta' \cos \chi \rangle_{\alpha\beta}, \quad \Omega_{\alpha\beta}^{12} = \langle \zeta^2 (\zeta^2 - \zeta\zeta' \cos \chi) \rangle_{\alpha\beta}, \\ \Omega_{\alpha\beta}^{13} = \langle \zeta^2 (\zeta^4 - \zeta\zeta'^3 \cos \chi) \rangle_{\alpha\beta}, \quad \Omega_{\alpha\beta}^{22} = \langle \zeta^2 (\zeta^2 - \zeta\zeta' \cos \chi)^2 \rangle_{\alpha\beta},$$

where $\langle F \rangle_{\alpha\beta}$ corresponds to an abbreviation of the form

$$\langle F \rangle_{\alpha\beta} = (kT / 2\pi\mu_{\alpha\beta})^{1/2} Q_{\alpha}^{-1} Q_{\beta}^{-1} \sum_{ijkl} \int_0^{\infty} d\zeta \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \chi d\chi \\ \times [F \zeta^3 \exp(-\zeta^2 - \varepsilon_{\alpha i} - \varepsilon_{\beta j}) I_{\alpha\beta}(g, \chi, \varphi; i, j \rightarrow k, l)].$$

Here

$$\zeta = (\mu_{\alpha\beta} / 2kT)^{1/2} g, \quad \zeta'^2 = \zeta^2 - \Delta\varepsilon_{\alpha\beta}, \\ \Delta\varepsilon_{\alpha\beta} = \Delta\varepsilon_{\alpha} + \Delta\varepsilon_{\beta}, \quad \Delta\varepsilon_{\alpha} = \varepsilon_{\alpha k} - \varepsilon_{\alpha i}, \quad \Delta\varepsilon_{\beta} = \varepsilon_{\beta l} - \varepsilon_{\beta j},$$

and $I_{\alpha\beta}$ is the differential cross section for the scattering of the molecules of types α and β , accompanied by the transition of these molecules from the states i and j into the states k and l ; $g_{\alpha\beta} = |v_{\alpha} - v_{\beta}|$ —relative velocity of the colliding particles; χ and φ —polar and azimuthal angles describing the orientation of g' relative to g (the primes denote quantities after the collision; the index 1 is introduced to distinguish the colliding molecules when $\alpha = \beta$).

The still undetermined quantities in (2.11)–(2.13) are essentially connected with the contribution of the inelastic collisions. The expressions for them are

$$A_{\alpha\beta}^* Z_{\alpha\beta}^{-1} = \frac{5}{8} \frac{k}{c_{\alpha}^{\text{in}}} \frac{\langle \Delta\varepsilon_{\alpha\beta}^2 \rangle_{\alpha\beta}}{\Omega_{\alpha\beta}^{11}},$$

$$L_{\alpha\beta}^* = \langle \Delta\varepsilon_{\alpha} \rangle_{\alpha\beta} / \langle \Delta\varepsilon_{\alpha\beta}^2 \rangle_{\alpha\beta}, \quad M_{\alpha\beta}^* = \langle \Delta\varepsilon_{\alpha} \Delta\varepsilon_{\beta} \rangle_{\alpha\beta} / \langle \Delta\varepsilon_{\alpha\beta}^2 \rangle_{\alpha\beta},$$

$$E_{\alpha\beta}^* = \langle (\varepsilon_{\alpha i} - \langle \varepsilon_{\alpha} \rangle) (\zeta^2 - \zeta\zeta' \cos \chi) \rangle_{\alpha\beta} / \Omega_{\alpha\beta}^{11},$$

$$F_{\alpha\beta}^* = \langle (\varepsilon_{\alpha i} - \langle \varepsilon_{\alpha} \rangle) \left[\frac{2}{5} (\zeta^4 - \zeta\zeta'^3 \cos \chi) - (\zeta^2 - \zeta\zeta' \cos \chi) \right] \rangle_{\alpha\beta} / \Omega_{\alpha\beta}^{11},$$

$$G_{\alpha\beta}^* = \left\{ \langle (\varepsilon_{\alpha i} - \langle \varepsilon_{\alpha} \rangle) [\zeta^2 (\varepsilon_{\alpha i} - \langle \varepsilon_{\alpha} \rangle) - \zeta\zeta' (\varepsilon_{\alpha k} - \langle \varepsilon_{\alpha} \rangle) \cos \chi] \rangle_{\alpha\beta} - \frac{c_{\alpha}^{\text{in}}}{k} \langle \zeta^2 - \zeta\zeta' \cos \chi \rangle_{\alpha\beta} \right\} / \Omega_{\alpha\beta}^{11},$$

$$H_{\alpha\beta}^* = \langle (\varepsilon_{\beta ij} - \langle \varepsilon_{\beta} \rangle) [\zeta^2 (\varepsilon_{\alpha i} - \langle \varepsilon_{\alpha} \rangle) - \zeta\zeta' (\varepsilon_{\alpha k} - \langle \varepsilon_{\alpha} \rangle) \cos \chi] \rangle_{\alpha\beta} / \Omega_{\alpha\beta}^{11}. \quad (2.15)$$

We note that by virtue of the condition $L_{\alpha\beta}^* + 2M_{\alpha\beta}^* + L_{\beta\alpha}^* = 1$ we get: $0 \leq L_{\alpha\beta}^* \leq 1$ and $0 \leq M_{\alpha\beta}^* \leq 1$. The coefficients $E_{\beta\alpha}^*$ and $F_{\beta\alpha}^*$ by replacing the indices α and β by αi and βj .

3. DIFFUSION, VISCOSITY, AND HEAT TRANSPORT IN A POLYATOMIC GAS MIXTURE

Equations (2.6)–(2.9) describe the diffusion, viscosity, and heat transport in a polyatomic mixture, and also the relations between them. They should be supplemented by equations for $n_{\alpha} \Delta E_{\alpha}^{\text{tr}}$ and $n_{\alpha} \Delta E_{\alpha}^{\text{in}}$, in which it is possible to neglect the nonlinear terms, in accord with the condition (2.5). In the general case, however, it is necessary to leave in these expressions the derivatives $d\Delta E_{\alpha}^{\text{tr}}/dt$ and $d\Delta E_{\alpha}^{\text{in}}/dt$, since the order of magnitude of the right sides of the equations is determined essentially by the values of $\tau_{E_{\alpha\beta}}^{-1} \sim Z_{\alpha\beta}^{-1} \tau_{\alpha\beta}^{-1}$ and when $Z_{\alpha\beta} \gg 1$ (hindered energy exchange) it may turn out to be that $\tau_{E_{\alpha\beta}} \sim \tau_L$. The energy relaxation equations, and the ensuing expressions for the volume viscosity, are discussed in the next section. We shall neglect here the contribution of the derivatives $\partial n_{\alpha} \Delta E_{\alpha}^{\text{tr}} / \partial x_r$ and $\partial n_{\alpha} \Delta E_{\alpha}^{\text{in}} / \partial x_r$, and also $\partial q_{\alpha r}^{\text{tr}} / \partial x_r$ and $\partial q_{\alpha r}^{\text{in}} / \partial x_r$ in the left sides of (2.6)–(2.9).

Solving (2.7)–(2.9) with respect to $\pi_{\alpha r s}$, h_{α}^{tr} , and h_{α}^{in} and substituting the obtained expressions in (2.6), we obtain a system of diffusion equations for a polyatomic mixture:

$$\sum_{\beta} \frac{n_{\alpha} n_{\beta} k T}{n [D_{\alpha\beta}]_1} (w_{\alpha r} - w_{\beta r}) = -p \frac{\partial y_{\alpha}}{\partial x_r} - \left(y_{\alpha} - \frac{\rho_{\alpha}}{\rho} \right) \frac{\partial p}{\partial x_r} \\ + 2 \left(\eta_{\alpha} - \frac{\rho_{\alpha}}{\rho} \eta \right) \frac{\partial \varepsilon_{rs}}{\partial x_s} - \sum_{\beta} \frac{n_{\alpha} n_{\beta} k T}{n [D_{\alpha\beta}]_1} \left(\frac{D_{\alpha}^T}{m_{\alpha} n_{\alpha}} - \frac{D_{\beta}^T}{m_{\beta} n_{\beta}} \right) \frac{\partial \ln T}{\partial x_r}. \quad (3.1)$$

For simplicity, we have left out of (3.1) the cumbersome terms that give the second-approximation corrections of the diffusion coefficient and the coefficient of the derivative $\partial \varepsilon_{rs} / \partial x_s$.

For the viscous-stress tensor and the heat flux in the mixture we have

$$\pi_{rs} = -2\eta \varepsilon_{rs}, \quad (3.2) \\ \mathbf{q} = -\lambda \text{grad } T + \sum_{\alpha} \left(\frac{5}{2} + \langle \varepsilon_{\alpha} \rangle \right) p_{\alpha} \mathbf{w}_{\alpha} \\ + \sum_{\alpha} \sum_{\beta} \frac{n_{\beta} D_{\alpha}^T k T}{m_{\alpha} n [D_{\alpha\beta}]_1} (\mathbf{w}_{\alpha} - \mathbf{w}_{\beta}). \quad (3.3)$$

Here

$$\eta = \sum_{\alpha} \eta_{\alpha}, \quad \lambda = \sum_{\alpha} (\lambda_{\alpha}^{\text{tr}} + \lambda_{\alpha}^{\text{in}})$$

and D_{α}^T —coefficients of viscosity, thermal conductivity, and thermal diffusion of the mixture, defined by the expressions:

$$\eta = - \begin{vmatrix} a_{\alpha\beta} & y_{\alpha} \\ y_{\beta} & 0 \end{vmatrix} |a_{\alpha\beta}|^{-1},$$

$$\lambda = - \begin{vmatrix} b_{\alpha\beta} & b'_{\alpha\beta} & y_{\alpha} \\ g_{\alpha\beta} & g'_{\alpha\beta} & y_{\alpha} \frac{c_{\alpha}^{\text{in}}}{k} \\ y_{\beta} & y_{\beta} \frac{c_{\beta}^{\text{in}}}{k} & 0 \end{vmatrix} \begin{vmatrix} b_{\alpha\beta} & b'_{\alpha\beta} \\ g_{\alpha\beta} & g'_{\alpha\beta} \end{vmatrix}^{-1},$$

$$D_{\alpha}^T = - \frac{m_{\alpha}}{k} \left[\frac{m_{\beta}}{m_{\alpha} + m_{\beta}} \left(\frac{6}{5} C_{\alpha\beta}^* - 1 \right) \lambda_{\alpha}^{\text{tr}} + \frac{k}{c_{\alpha}^{\text{in}}} E_{\alpha\beta}^* \lambda_{\alpha}^{\text{in}} \right] \quad (3.4)$$

(D_{β}^T is obtained from D_{α}^T by interchanging the indices). To simplify the notation, and $a_{\alpha\beta}$, $b_{\alpha\beta}$, $b'_{\alpha\beta}$, $g_{\alpha\beta}$, and $g'_{\alpha\beta}$ in (3.4) stand for square “blocks” of order M , made up of the corresponding elements. The quantities y_{α} , $y_{\alpha}(c_{\alpha}^{\text{in}}/k)$ and y_{β} , $y_{\beta}(c_{\beta}^{\text{in}}/k)$ denote columns and rows containing N elements.

The partial kinetic coefficients η_{α} and $\lambda_{\alpha}^{\text{tr}}$ are obtained from (3.4) by replacing the determinants in the numerators of the expressions for η and λ by the products of the element common to the last row and the column number α by its co-factor. The expression for $\lambda_{\alpha}^{\text{in}}$ is obtained from λ by replacing the numerator of (3.4) by the product of the element common to the last row and column number $\alpha + N$ by its co-factor.

The expressions obtained above for η and λ agree with the corresponding results in^[3], obtained by the Chapman-Enskog method. The thermal-conductivity coefficient λ turns out to be equal to the value obtained by successively using the second approximation in the expansion in Sonine polynomials, in accordance with the scheme developed in^[9]. Monchick, Yun, and Mason^[3] state that the use of such a scheme for the calculation of the diffusion contribution to the influx (the last term on the right in (3.3)) leads only to a complication of the results compared with the rather cumbersome expression presented in their paper. This does not agree with the expression obtained here, which, just as in the case of monoatomic mixtures^[8], has a much simpler form³⁾ (the order of the determinants in the expression for D_{α}^T is lowered).

Equations (3.1) differ from the ordinary diffusion equations^[3,5] in the presence of an additional term that takes into account the viscous momentum transfer in the mixture, and also in the presence of simpler expressions for the thermal diffusion coefficients D_{α}^T and D_{β}^T , the order of magnitude of the determinants in which is lowered from $3N + 1$ and $3N + 1$ and $2N$. As shown in^[8], for a stationary viscous flow of a gas mixture, allowance for the additional term leads to a different value of the barodiffusion constant in viscous flow than in the case of nonviscous flow. The diffusion equation (3.1) is transformed in this case into

$$\sum_{\beta} \frac{n_{\alpha} n_{\beta} k T}{n [D_{\alpha\beta}]_1} (w_{\alpha r} - w_{\beta r}) = -p \frac{\partial y_{\alpha}}{\partial x_r} - \left(y_{\alpha} - \frac{\eta_{\alpha}}{\eta} \right) \frac{\partial p}{\partial x_r} - \sum_{\beta} \frac{n_{\alpha} n_{\beta} k T}{n [D_{\alpha\beta}]_1} \left(\frac{D_{\alpha}^T}{m_{\alpha} n_{\alpha}} - \frac{D_{\beta}^T}{m_{\beta} n_{\beta}} \right) \frac{\partial \ln T}{\partial x_r}. \quad (3.5)$$

³⁾There is a misprint in [8]: the corresponding term should have a minus sign.

We note that for the calculation of η_{α} and η it is necessary to know, besides the quantities $[\eta_{\alpha\alpha}]_1$ and $[D_{\alpha\beta}]_1$, only $A_{\alpha\beta}^*$. An analysis shows that inelastic collisions have little influence on $A_{\alpha\beta}^*$ ^[3], so that it is possible to use the values calculated for this coefficient on the basis of the ordinary interaction potentials for monoatomic gases. Consequently, the barodiffusion constant $[\alpha_p]_1$, as well as the viscosity coefficient of the mixture $\eta = \sum_{\alpha} \eta_{\alpha}$, can be calculated with good approximation from the same expressions as in the case of monoatomic mixtures^[8] using the experimental values of the viscosity coefficient $\eta_{\alpha\alpha}$ and mutual diffusion $D_{\alpha\beta}$ for a real monoatomic gas. The calculation of the coefficients of thermal conductivity and thermal diffusion turns out to be more complicated therefore. For small values of $Z_{\alpha\beta}^{-1}$, the expressions for $\lambda_{\alpha}^{\text{tr}}$, $\lambda_{\alpha}^{\text{in}}$, and λ can be greatly simplified by linearization in terms of a small parameter. In^[10] are advanced certain considerations which make it possible to regard also the coefficients introduced above⁴⁾ $E_{\alpha\beta}^*$, $F_{\alpha\beta}^*$, $G_{\alpha\beta}^*$, and $H_{\alpha\beta}^*$ as small. At least their contribution decreases with decreasing role of the inelastic collisions, i.e., when $Z_{\alpha\beta} \gg 1$. In this case (“hindered” energy exchange), neglecting also terms proportional to $Z_{\alpha\beta}^{-1}$, we can put

$$b_{\alpha\alpha'} = b_{\alpha\beta'} = g_{\alpha\alpha} = g_{\beta\alpha} = g_{\alpha\beta'} = 0,$$

$$g_{\alpha\alpha'} = \frac{c_{\alpha}^{\text{in}}}{k} \left[\frac{y_{\alpha}^2}{kn [D_{\alpha\alpha}]_1} + \sum_{\gamma \neq \alpha} \frac{y_{\alpha} y_{\gamma}}{kn [D_{\alpha\gamma}]_1} \right],$$

where $[D_{\alpha\beta}]_1$ and all the quantities retained in $b_{\alpha\alpha}$ and $b_{\alpha\beta}$ coincide, accurate to negligibly small contributions of the inelastic collisions, with the values calculated on the basis of the theory of monoatomic gases. The correction to the thermal conductivity λ , connected with $g'_{\alpha\alpha}$, justifies the expression proposed by Hirschfelder for the generalized Eucken correction in the case of a polyatomic mixture^[12].

The possibility of lowering the order of the determinants in the expressions for D_{α}^T and D_{β}^T using the consecutive second approximation in the expansion in the Sonine polynomials was recently noted in^[13]. However, account is taken here of the contribution made to these coefficients only by the translational part of the thermal conductivity $\lambda_{\alpha}^{\text{tr}}$. Although the coefficients $E_{\alpha\beta}^*$ and $E_{\beta\alpha}^*$ are small and can vanish for certain particular models of the molecule interaction, neglect of the terms containing $\lambda_{\alpha}^{\text{in}}$ and $\lambda_{\beta}^{\text{in}}$ can lead to noticeable errors in the general case (particularly at values of the coefficient $(\frac{6}{5}) C_{\alpha\beta}^* - 1$ close to zero). On the other hand, if $C_{\alpha\beta}^*$ is determined from the experimental temperature dependence of $D_{\alpha\beta}$, then, in accordance with the relation

$$\frac{6}{5} C_{\alpha\beta}^* - 1 = \frac{2}{5} [2 - (\partial \ln [D_{\alpha\beta}]_1 / \partial \ln T)_p - E_{\alpha\beta}^* - E_{\beta\alpha}^*],$$

knowledge of $E_{\alpha\beta}^*$ and $E_{\beta\alpha}^*$ turns out to be important also for the calculation of the “translational” part of the thermal diffusion coefficients. These two circumstances (besides the others mentioned in^[13]) possibly

⁴⁾The coefficients $E_{\alpha\beta}^*$, $F_{\alpha\beta}^*$, and $H_{\alpha\beta}^*$ vanish for the case when the relative velocity before and after the collisions do not depend on the initial states of the colliding particles (identical differential cross sections for all the scattering channels)^[10].

explain the noticeable discrepancies between the experimental and calculated values of the thermal diffusion coefficients for Ar-HCl and Ar-CO₂ mixtures, for which calculations by means of the formulas of the theory of monatomic gases give values close to zero.

4. ENERGY RELAXATION AND VOLUME VISCOSITY

The relaxation equation of the translational and internal energies of the mixture components are obtained from the kinetic equations by multiplying it by $m_{\alpha}c^2/2$ and $E_{\alpha i}$ with subsequent integration over the velocities and summation over i . The right sides of these equations, in accordance with the approximation (2.2) assumed for $f_{\alpha i}$, contain only terms that are proportional to small deviations of the translational and internal energies of the components from their equilibrium values. After eliminating from their left sides the derivatives dn_{α}/dt , du/dt , and dT/dt and neglecting the nonlinear terms (including the divergences of the diffusion and thermal fluxes), the relaxation equations can be represented in the form

$$\begin{aligned} n_{\alpha} \frac{d\Delta E_{\alpha}^{\text{tr}}}{dt} + \frac{c^{\text{in}}}{c_V} p_{\alpha} \frac{\partial u_i}{\partial x_i} &= -\frac{2}{3} \sum_{\beta} c_{\alpha\beta} \frac{n_{\beta} \Delta E_{\beta}^{\text{tr}}}{y_{\beta}} + \sum_{\beta} \frac{k}{c_{\beta}^{\text{in}}} c_{\alpha\beta} \frac{n_{\beta} \Delta E_{\beta}^{\text{in}}}{y_{\beta}}, \\ n_{\alpha} \frac{d\Delta E_{\alpha}^{\text{in}}}{dt} - \frac{c_{\alpha}^{\text{in}}}{c_V} p_{\alpha} \frac{\partial u_i}{\partial x_i} &= \frac{2}{3} \sum_{\beta} d_{\alpha\beta} \frac{n_{\beta} \Delta E_{\beta}^{\text{tr}}}{y_{\beta}} - \sum_{\beta} \frac{k}{c_{\beta}^{\text{in}}} d_{\alpha\beta} \frac{n_{\beta} \Delta E_{\beta}^{\text{in}}}{y_{\beta}}, \end{aligned} \quad (4.1)$$

where

$$\begin{aligned} c_{\alpha\beta} &= y_{\alpha} \left\{ \delta_{\alpha\beta} \sum_{\gamma} \frac{2m_{\gamma}^2}{(m_{\alpha} + m_{\gamma})^2} \left[\frac{c_{\alpha}^{\text{in}}}{k} \tau_{E\alpha\gamma}^{-1} (1 + \delta_{\alpha\gamma}) \right. \right. \\ &\left. \left. + \frac{3}{2} \frac{m_{\alpha}}{m_{\gamma}} \tau_{\alpha\gamma}^{-1} (1 - \delta_{\alpha\gamma}) \right] + (1 - \delta_{\alpha\beta}) \frac{2m_{\alpha}m_{\beta}}{(m_{\alpha} + m_{\beta})^2} \left(\frac{c_{\alpha}^{\text{in}}}{k} \tau_{E\alpha\beta}^{-1} - \frac{3}{2} \tau_{\alpha\beta}^{-1} \right) \right\}, \\ c_{\alpha\beta}' &= y_{\alpha} \frac{c_{\alpha}^{\text{in}}}{k} \left[\delta_{\alpha\beta} \sum_{\gamma} \frac{2m_{\gamma}}{m_{\alpha} + m_{\gamma}} (L_{\alpha\gamma}^* + M_{\alpha\gamma}^*) \tau_{E\alpha\gamma}^{-1} (1 + \delta_{\alpha\gamma}) \right. \\ &\left. + (1 - \delta_{\alpha\beta}) \frac{2m_{\beta}}{m_{\alpha} + m_{\beta}} (L_{\beta\alpha}^* + M_{\beta\alpha}^*) \tau_{E\alpha\beta}^{-1} \right], \\ d_{\alpha\beta} &= y_{\alpha} \frac{c_{\alpha}^{\text{in}}}{k} \left[\delta_{\alpha\beta} \sum_{\gamma} \frac{2m_{\gamma}}{m_{\alpha} + m_{\gamma}} (L_{\alpha\gamma}^* + M_{\alpha\gamma}^*) \tau_{E\alpha\gamma}^{-1} (1 + \delta_{\alpha\gamma}) \right. \\ &\left. + (1 - \delta_{\alpha\beta}) \frac{2m_{\alpha}}{m_{\alpha} + m_{\beta}} (L_{\alpha\beta}^* + M_{\alpha\beta}^*) \tau_{E\alpha\beta}^{-1} \right], \\ d_{\alpha\beta}' &= y_{\alpha} \frac{c_{\alpha}^{\text{in}}}{k} \left[\delta_{\alpha\beta} \left(\tau_{E\alpha\beta}^{-1} + \sum_{\gamma} 2L_{\alpha\gamma}^* \tau_{E\alpha\gamma}^{-1} \right) \right. \\ &\left. + (1 - \delta_{\alpha\beta}) 2M_{\alpha\beta}^* \tau_{E\alpha\beta}^{-1} \right]. \end{aligned} \quad (4.2)$$

Here

$$\tau_{E\alpha\beta}^{-1} = 2n_{\beta} (k/c_{\alpha}^{\text{in}}) \langle \Delta E_{\alpha\beta}^2 \rangle_{\alpha\beta}$$

is the characteristic frequency of collisions with exchange of energy between the translational and internal degrees of freedom. If the energy exchange is easily effected ($\tau_{E\alpha\beta} \sim \tau_{\alpha\beta}$), then, in accordance with (2.5), it is possible to neglect the derivatives $d\Delta E_{\alpha}^{\text{tr}}/dt$ and $d\Delta E_{\alpha}^{\text{in}}/dt$ in the left sides of (4.1). As a result, we arrive at a system of linear algebraic equations, from which we determine $n_{\alpha} \Delta E_{\alpha}^{\text{tr}}$ and $n_{\alpha} \Delta E_{\alpha}^{\text{in}}$. By definition, the total stress tensor of the mixture equals

$$P_{rs} = (nkT + 2/3 n \Delta E^{\text{tr}}) \delta_{rs} + \pi_{rs},$$

and in our case

$$2/3 n \Delta E^{\text{tr}} = 2/3 \sum_{\alpha} n_{\alpha} \Delta E_{\alpha}^{\text{tr}} = -\zeta \operatorname{div} \mathbf{u}, \quad (4.3)$$

where ζ - coefficient of volume viscosity of the mixture, defined by the expression

$$\zeta = -\frac{p}{c_V} \begin{vmatrix} c_{\alpha\beta}^{00} & c_{\alpha\beta}^{01} & y_{\alpha} c_{\alpha}^{\text{in}} \\ c_{\alpha\beta}^{10} & c_{\alpha\beta}^{11} & y_{\alpha} c_{\alpha}^{\text{in}} \\ y_{\beta} & 0 & 0 \end{vmatrix} \begin{vmatrix} c_{\alpha\beta}^{00} & c_{\alpha\beta}^{01} \\ c_{\alpha\beta}^{10} & c_{\alpha\beta}^{11} \end{vmatrix}^{-1}. \quad (4.4)$$

Here, as before, $c_{\alpha\beta}^{\text{rs}}$ are used to denote the square "blocks" of order N , made up of the corresponding elements, while $y_{\alpha} c_{\alpha}^{\text{in}}$, $y_{\alpha} c_{\alpha}^{\text{in}}$, and y_{β} denote the columns and rows containing N elements.

The elements of the determinants $c_{\alpha\beta}^{\text{rs}}$ are expressed in terms of $c_{\alpha\beta}$, $c'_{\alpha\beta}$, $d_{\alpha\beta}$, and $d'_{\alpha\beta}$ (4.2), apart from arbitrary terms that vanish when the determinants are calculated:

$$\begin{aligned} c_{\alpha\beta}^{00} &= c_{\alpha\beta} - y_{\beta} K_{\alpha}^{(0)}, & c_{\alpha\beta}^{01} &= c_{\alpha\beta}' + \frac{2}{3} y_{\beta} \frac{c_{\beta}^{\text{in}}}{k} K_{\alpha}^{(0)}, \\ c_{\alpha\beta}^{10} &= d_{\alpha\beta} + y_{\beta} K_{\alpha}^{(1)}, & c_{\alpha\beta}^{11} &= d_{\alpha\beta}' - \frac{2}{3} y_{\beta} \frac{c_{\beta}^{\text{in}}}{k} K_{\alpha}^{(1)}. \end{aligned}$$

The form of these relations follows from the fact that the system of equations for $n_{\beta} \Delta E_{\beta}^{\text{tr}}$ and $n_{\beta} \Delta E_{\beta}^{\text{in}}$ should be supplemented by the condition (2.4). In particular, the results given in [3] correspond to the choice of the following expressions for $K_{\alpha}^{(0)}$ and $K_{\alpha}^{(1)}$

$$K_{\alpha}^{(0)} = \sum_{\gamma} \frac{2m_{\gamma}^2}{(m_{\alpha} + m_{\gamma})^2} \left[\frac{c_{\alpha}^{\text{in}}}{k} \tau_{E\alpha\gamma}^{-1} (1 + \delta_{\alpha\gamma}) + \frac{3}{2} \frac{m_{\alpha}}{m_{\gamma}} \tau_{\alpha\gamma}^{-1} (1 - \delta_{\alpha\gamma}) \right],$$

$$K_{\alpha}^{(1)} = 3/2 \tau_{E\alpha\alpha}^{-1} + \sum_{\gamma} L_{\alpha\gamma}^* \tau_{E\alpha\gamma}^{-1}.$$

It must be emphasized that a linear relation between $n\Delta E^{\text{tr}}$ and $\operatorname{div} \mathbf{u}$ obtains only in the case of "easy" exchange of energy. More accurately, when the condition $\tau_{\alpha\beta} \lesssim \tau_{E\alpha\beta} \ll \tau_L$ is satisfied. When $Z_{\alpha\beta} \gg 1$, this condition can be violated, and it is necessary to retain the time derivatives in Eqs. (4.1). We note that the coefficients $c'_{\alpha\beta}$, $d_{\alpha\beta}$, and $d'_{\alpha\beta}$ in the right sides of the equations are of the order of $Z_{\alpha\beta}^{-1} \tau_{\alpha\beta}^{-1}$, whereas $c_{\alpha\beta} = c_{\alpha\beta}^{\text{D}} + c_{\alpha\beta}^{\text{E}}$, where $c_{\alpha\beta}^{\text{D}}$ no longer contains $Z_{\alpha\beta}^{-1}$, corresponding to an intense exchange of energy between the translational degrees of freedom of the individual components. Since, however, $\sum_{\alpha} c_{\alpha\beta}^{\text{D}} = 0$, only the terms $\sim Z_{\alpha\beta}^{-1} \tau_{\alpha\beta}^{-1}$ remain in the right side of the equation for $\Delta E^{\text{tr}} = \sum_{\alpha} y_{\alpha} \Delta E_{\alpha}^{\text{tr}}$, and ensure in the case when $Z_{\alpha\beta}^{-1} \ll 1$ a very slow exchange of energy between the translational degrees of freedom of the mixture as a whole and the internal degrees of freedom of the individual components. Therefore, by combining with the equation for ΔE^{tr} and neglecting terms $\sim Z_{\alpha\beta}^{-1}$, the equations for $\Delta E_{\alpha}^{\text{tr}}$ are conveniently written in the form

$$n_{\alpha} \frac{d}{dt} (E_{\alpha}^{\text{tr}} - E^{\text{tr}}) = -\frac{2}{3} \sum_{\beta} n c_{\alpha\beta}^{\text{D}} (E_{\beta}^{\text{tr}} - E^{\text{tr}}). \quad (4.5)$$

Consequently, after a time on the order of the mean-free-path time τ_0 the translational energies of the components E_{α}^{tr} relax to a common E^{tr} . Therefore for states satisfying the condition (2.5) we can assume that $E_{\alpha}^{\text{tr}} = E^{\text{tr}}$ for all α , whereas the relaxation of E^{tr} to $E_0^{\text{tr}} = 3kT/2$ and the relaxation of all the internal energies of the components E_{α}^{in} to $E_{\alpha_0}^{\text{in}}$ is described by a system of equations in the form

$$\frac{d\Delta E_{\alpha}^{\text{in}}}{dt} - kT \frac{c_{\alpha}^{\text{in}}}{c_V} \frac{\partial u_l}{\partial x_l} = -\tau_{E\alpha}^{-1} \left(\Delta E_{\alpha}^{\text{in}} - \frac{2}{3} \frac{c_{\alpha}^{\text{in}}}{k} \Delta E^{\text{tr}} \right),$$

$$\frac{d\Delta E^{\text{tr}}}{dt} + kT \frac{c^{\text{in}}}{c_V} \frac{\partial u_l}{\partial x_l} = \sum_{\beta} y_{\beta} \tau_{E\beta}^{-1} \left(\Delta E_{\beta}^{\text{in}} - \frac{2}{3} \frac{c_{\beta}^{\text{in}}}{k} \Delta E^{\text{tr}} \right), \quad (4.6)$$

where

$$\tau_{E\alpha}^{-1} = \sum_{\gamma} 2L_{\alpha\gamma} \tau_{E\alpha\gamma}^{-1}$$

and we used the additional assumption, according to which the "complicated" collisions accompanied by the transitions of both colliding particles are much less frequent than collisions with transition of one particle ($M_{\alpha\beta}^* \ll 1$). We note that there are no grounds whatever for splitting the system (4.6), as was done in ^[10] as a result of the vanishing of ΔE^{tr} , and consequently the $\tau_{E\alpha}$ cannot be regarded exactly as the partial relaxation times. This casts doubts on the method proposed in ^[10] for determining $\tau_{E\alpha\beta}^{-1}$ from experiments on the absorption of ultrasound developed on the basis of the customarily employed phenomenological relaxation equations for a polyatomic mixture^[14].

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¹C. S. Wang Chang and G. E. Ulenbeck, Report CM-681 University of Michigan Publication, (1951); see also: Studies in Statistical Mechanics, ed. J. de Boer and G. E. Uhlenbeck, II, John Wiley & Sons, Inc. N. Y. (1964).

²L. Waldmann and E. Trubenbacher, Z. Naturforsch. **17a**, 364 (1962).

³L. Monchick, K. S. Yun, and E. A. Mason, J. Chem. Phys. **39**, 654 (1963).

⁴S. Chapman and T. G. Cowling, Mathematical Theory of Nonuniform Gases Cambridge, 1952.

⁵J. O. Hirschfelder, C. Curtiss, and R. Bird, Molecular Theory of Gases and Liquids, Wiley.

⁶V. M. Zhdanov, Zh. Eksp. Teor. Fiz. **53**, 2099 (1967) [Sov. Phys.-JETP **26**, 1187 (1968)].

⁷H. Grad, Comm. Pure and Appl. Math. **2**, 331 (1949); **4**, 71 (1952); **5**, 61 (1952).

⁸V. Zhdanov, Yu. Kagan, and A. Sazykin, Zh. Eksp. Teor. Fiz. **42**, 857 (1962) [Sov. Phys.-JETP **15**, 596 (1962)].

⁹C. Muckenfuss and C. Curtiss, J. Chem. Phys. **29**, 1273 (1958).

¹⁰L. Monchick, A. N. G. Pereira, and E. A. Mason, J. Chem. Phys. **42**, 3241 (1965).

¹¹E. V. Stupochenko, S. A. Losev, and A. I. Osipov, Relaksatsionnye protsessy v udarnykh volnakh (Relaxation Processes in Shock Waves), Nauka, 1965.

¹²J. O. Hirschfelder, J. Chem. Phys. **26**, 282 (1957); 6 Symp. Combust. Yale Univ. (1957), p. 351.

¹³L. Monchick, R. J. Munn, and E. A. Mason, J. Chem. Phys. **45**, 3051 (1966).

¹⁴K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves, Acad. Press (1959).

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