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EFFECT OF VISCOUS TRANSFER OF MOMENTUM ON DIFFUSION IN A GAS MIXTURE

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The "13 momentum" approximation in Grad's method is used to derive a general set of equations of diffusion in a multicomponent gas mixture. The problem of diffusion in the presence of viscous transfer of momentum in a gas is studied in detail. An explicit expression is obtained for the barodiffusion constant α_p in a viscous flow of an arbitrary binary mixture. The magnitude of α_p depends significantly on the character of the interaction between the molecules and can have either sign. The nature of the difference between the derived value of α_p and the value of $(m_2 - m_1)/[m_1 y_1 + m_2(1 - y_1)]$, obtained by methods of irreversible thermodynamics, [5,6] is analyzed.

1. INTRODUCTION

THE present research is devoted to the investigation of the diffusion of an arbitrary multicomponent gas mixture in the presence of the viscous transfer of momentum in the gas. As is well known, in the consideration of the phenomenon of transfer in gases, use is made of two methods of solution of the kinetic equations: the method of Chapman-Enskog [1] and the "momentum method" recently developed by Grad.[2] Detailed analysis shows that the latter method has an unquestionable advantage every time that one is obliged to use higher approximations to the distribution function. Thus, for example, there is no interaction between diffusive and viscous momentum transfer in a gas within the framework of the most developed second approximation in the method of Chapman-Enskog. Such an interaction appears only in the third approximation, [1,3] even when all the macroscopic parameters of the mixture change relatively little within lengths of the order of the mean free path. It is not difficult to show that within the framework of Grad's "momentum method" the effect on diffusion of viscous momentum transfer appears directly in the use of the ordinary "13 momentum" approximation. Furthermore, the application of this method makes it possible to obtain the values of the kinetic coefficients in the equations of diffusion immediately in an approximation that is equivalent to the second approximation in the expansion in Sonine polynomials when the ordinary scheme of calculation of transfer coefficients is used.[1-4]

In the present work, a generalization of the Grad method to the case of a monatomic multicomponent gas is used. In the "13 momentum" approximation, a closed set of equations is obtained which makes it possible to consider all the transport phenomena in the gas mixture, and to compute the corresponding kinetic coefficients. In particular, a general set of equations is found which describes diffusion in the multicomponent mixture. The results obtained permit one to analyze completely the effect of viscous momentum transfer on diffusion. The value of the barodiffusion constant found for a two component mixture in purely viscous gas flow is shown to be related in significant fashion with the character of the mutual interaction of the molecules; this quantity differs essentially from the barodiffusion constant obtained both in the second approximation of the Chapman-Enskog method and in the framework of the thermodynamics of irreversible processes.[5,6]

The considerations given below assume the satisfaction of the conditions

$$\lambda / L \ll 1, \qquad \tau / T \ll 1, \tag{1.1}$$

where L and T are the characteristic linear and temporal scales of change of the macroscopic parameters of the mixture, and λ and τ are the effective length and time of free path of the molecules.

2. GENERAL SET OF EQUATIONS

We expand the distribution function of the component α of the gas mixture in a series of Hermite polynomials $H^{(s)}_{\alpha i_1 \ldots i_s}(\mathbf{c}_\alpha)$ defined in [2] (summation in the repeated Latin indices is carried out from 1 to 3):

$$f_\alpha(\mathbf{r}, \mathbf{v}_\alpha, t) = f_\alpha^{(0)} \sum_{s=0}^{\infty} \frac{1}{s!} \left(\frac{m_\alpha}{kT}\right)^s A^{(s)}_{\alpha i_1 \ldots i_s}(\mathbf{r}, t)\, H^{(s)}_{\alpha i_1 \ldots i_s}(\mathbf{c}_\alpha);$$

$$f_\alpha^{(0)} = \left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_\alpha c_\alpha^2}{2kT}\right), \qquad \mathbf{c}_\alpha = \mathbf{v}_\alpha - \mathbf{u}, \tag{2.1}$$

where m_α, $\mathbf{v}_\alpha$ are the mass and velocity of molecules of type α, $\mathbf{u}(\mathbf{r}, t)$ is the macroscopic velocity of the mixture as a whole, k is the Boltzman constant, T is the temperature.

The macroscopic parameters of the component α and of the mixture as a whole—the number densities n_α and n, the mass densities ρ_α and ρ, the mean velocities $\mathbf{u}_\alpha$ and $\mathbf{u}$, the diffusion current of the α component $\mathbf{j}_\alpha$ and the temperature T are defined by the usual expressions:

$$n_\alpha = \int f_\alpha \, d\mathbf{v}_\alpha, \qquad n = \sum_\alpha n_\alpha, \qquad \rho_\alpha = m_\alpha n_\alpha, \qquad \rho = \sum_\alpha \rho_\alpha,$$

$$\mathbf{u}_\alpha = \frac{1}{n_\alpha} \int \mathbf{v}_\alpha f_\alpha \, d\mathbf{v}_\alpha, \qquad \mathbf{u} = \frac{1}{\rho} \sum_\alpha \rho_\alpha \mathbf{u}_\alpha,$$

$$\mathbf{j}_\alpha = m_\alpha n_\alpha (\mathbf{u}_\alpha - \mathbf{u}) = m_\alpha \int \mathbf{c}_\alpha f_\alpha \, d\mathbf{v}_\alpha,$$

$$\tfrac{3}{2} n_\alpha kT = \tfrac{1}{2} \int (m_\alpha c_\alpha^2) f_\alpha \, d\mathbf{v}_\alpha, \qquad \tfrac{3}{2} nkT = \tfrac{1}{2} \sum_\alpha \int m_\alpha c_\alpha^2 f_\alpha \, d\mathbf{v}_\alpha. \tag{2.2}$$

We also introduce the partial tensor of viscous stresses $p_{\alpha ik}$, the tensor of viscous stresses p_{ik}, the partial thermal flux $\mathbf{q}_\alpha$, and the thermal flux of the mixture $\mathbf{q}$, by the formulas

$$p_{\alpha ik} = m_\alpha \int \left(c_{\alpha i} c_{\alpha k} - \tfrac{1}{3} c_\alpha^2 \delta_{ik}\right) f_\alpha \, d\mathbf{v}_\alpha, \qquad p_{ik} = \sum_\alpha p_{\alpha ik};$$

$$\mathbf{q}_\alpha = \tfrac{1}{2} m_\alpha \int \mathbf{c}_\alpha c_\alpha^2 f_\alpha \, d\mathbf{v}_\alpha, \qquad \mathbf{q} = \sum_\alpha \mathbf{q}_\alpha. \tag{2.3}$$

The coefficients $A^{(s)}$ of the series (2.1), are tensors of rank s, equal to the mean values of the corresponding polynomials $H^{(s)}(\mathbf{c}_\alpha)$:

$$A^{(s)}_{\alpha i_1 \ldots i_s}(\mathbf{r}, t) = \int H^{(s)}_{\alpha i_1 \ldots i_s}(\mathbf{c}_\alpha) f_\alpha \, d\mathbf{v}_\alpha.$$

If we substitute (2.1) in the kinetic equation for the mixtures, and construct the transport equations for the Hermite polynomials, then we get an infinite set of nonlinear differential equations in $A^{(s)}$. (The corresponding set for the case of a single component gas is obtained in [2]—the generalization is trivial.) The transport equations for s = 0, 1, and 2 lead to equations of continuity for each component and for the mixture as a whole (s = 0), the equation of motion of the mixture (s = 1, summation over α) and to the equation for conservation of energy of the mixture (s = 2, tensor indices are contracted, summation is over α). However, these equations are not closed and contain the coefficients $A^{(1)}_{\alpha i}$, $A^{(1)}_{\alpha ik}$ and $A^{(3)}_{\alpha ikk}$. If we use the explicit expressions of the corresponding Hermite polynomials

$$H^{(0)} = 1; \qquad H^{(1)}_{\alpha i} = c_{\alpha i}, \qquad H^{(2)}_{\alpha ik} = c_{\alpha i} c_{\alpha k} - (kT/m_\alpha)\delta_{ik},$$

$$H^{(3)}_{\alpha ikk} = c_{\alpha i}(c_\alpha^2 - 5kT/m_\alpha), \tag{2.4}$$

then we can find the connection of these coefficients with the quantities (2.2), (2.3):

$$A^{(0)}_\alpha = n_\alpha, \qquad A^{(1)}_{\alpha i} = m_\alpha^{-1} j_{\alpha i}, \qquad A^{(2)}_{\alpha ik} = m_\alpha^{-1} p_{\alpha ik},$$

$$A^{(3)}_{\alpha ikk} = 2m_\alpha^{-1}(q_{\alpha i} - 5kTj_{\alpha i}/2m_\alpha) = 2m_\alpha^{-1} h_{\alpha i}. \tag{2.5}$$

The quantities (2.5) are determined by solution of the complete set of equations.

We consider the solution of the set of equations in an approximation which corresponds to the "13 momentum" approximation,[2] i.e., we set $A^{(s)}(\mathbf{r}, t) = 0$ for $s \geq 4$, and for s = 3 we keep only the components of the tensor or vector $A^{(3)}_{\alpha ikk}$ contracted over two indices. [It can be show that upon satisfaction of the conditions (1.1) in (2.1), only those coefficients in the velocity tensors are different from zero which are no higher than second rank. As a consequence of this, there is, in particular, an equivalence of the "20 momentum" approximation and the "13 momentum" approximation.]

In the approximation considered, the distribution function can be written in the form (see the similar expression in [7])

$$f_\alpha = f_\alpha^{(0)} \{n_\alpha + (1/kT) j_{\alpha i} c_{\alpha i} + (\rho_\alpha / 2kTp_\alpha) p_{\alpha ik} (c_{\alpha i} c_{\alpha k} - (kT/m_\alpha)\delta_{ik}) + \tfrac{1}{5} (\rho_\alpha / kTp_\alpha) h_{\alpha l} c_{\alpha l} [(m_\alpha c_\alpha^2 / kT) - 5]\}. \tag{2.6}$$

The corresponding closed system of equations has the form

$$\partial \rho_\alpha / \partial t + \operatorname{div}(\rho_\alpha \mathbf{u} + \mathbf{j}_\alpha) = 0, \tag{2.7}$$

$$dj_{\alpha i}/dt - j_{\alpha l}(\partial u_l / \partial x_i) + \tfrac{5}{3} j_{\alpha i}(\partial u_l / \partial x_l) + 2j_{\alpha l}\varepsilon_{il} + \rho_\alpha du_i/dt + \partial p_\alpha / \partial x_i - n_\alpha X_{\alpha i} + \partial p_{\alpha il} / \partial x_l = R_{\alpha i}; \tag{2.8}$$

$$\partial p_\alpha / \partial t + \partial (p_\alpha u_l) / \partial x_l + \tfrac{2}{3} \partial q_{\alpha l} / \partial x_l + \tfrac{2}{3} p_{\alpha il} (\partial u_i / \partial x_l) + \tfrac{2}{3} p_\alpha (\partial u_l / \partial x_l) - \tfrac{2}{3} F_{\alpha l} j_{\alpha l} = R_{\alpha ll}; \tag{2.9}$$

$$dp_{\alpha ik}/dt - 2\{(\partial u_l / \partial x_k) p_{\alpha il}\} + 4\{p_{\alpha il}\varepsilon_{lk}\} - 2\{F_{\alpha i} j_{\alpha k}\} + \tfrac{7}{3} p_{\alpha ik} (\partial u_l / \partial x_l) + \tfrac{4}{5}\{\partial q_{\alpha i} / \partial x_k\} + 2p_\alpha \varepsilon_{ik} = R_{\alpha ik}; \tag{2.10}$$

$$\begin{aligned} dh_{\alpha i}/dt &+ \tfrac{7}{5} h_{\alpha l} (\partial u_i / \partial x_l) + \tfrac{2}{5} h_{\alpha l} (\partial u_l / \partial x_i) + \tfrac{7}{5} h_{\alpha i} (\partial u_l / \partial x_l) + (7k/2m_\alpha) p_{\alpha il} (\partial T / \partial x_l) - F_{\alpha l} p_{\alpha il} \\ &+ (5k/3m_\alpha) j_{\alpha i} (\partial u_l / \partial x_l) + (2k/m_\alpha) j_{\alpha l} \varepsilon_{il} + (5k/2m_\alpha) j_{\alpha i} (dT/dt) + (kT/m_\alpha)(\partial p_{\alpha il} / \partial x_l) \\ &+ \tfrac{5}{2} (kp_\alpha / m_\alpha) \partial T / \partial x_i = R_{\alpha ikk}. \end{aligned} \tag{2.11}$$

The following notation is used here:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + u_l \frac{\partial}{\partial x_l}, \qquad F_{\alpha i} = \frac{X_{\alpha i}}{m_\alpha} - \frac{du_i}{dt},$$

$$\{A_{ik}\} = \tfrac{1}{2}(A_{ik} + A_{ki}) - \tfrac{1}{3} A_{ll}\delta_{ik}, \qquad \varepsilon_{ik} = \{\partial u_i / \partial x_k\}.$$

The "moments relative to the collision integral" appear on the right hand sides of Eqs. (2.8)—(2.11):

$$R_{\alpha i_1 \ldots i_s} = \sum_\beta \int [H^{(s)}_{\alpha i_1 \ldots i_s}(\mathbf{c}'_\alpha)$$

$$- H^{(s)}_{\alpha i_1 \ldots i_s}(\mathbf{c}_\alpha)]\, f_\alpha f_\beta g_{\alpha\beta}\, d\sigma_{\alpha\beta}\, d\mathbf{c}_\alpha\, d\mathbf{c}_\beta,$$

where $d\sigma_{\alpha\beta}$ is the differential scattering cross section; $g_{\alpha\beta} = |\mathbf{v}_\alpha - \mathbf{v}_\beta|$, the prime indicating the velocity after collision.

If conditions (1.1) are fulfilled, we can neglect the terms in them that are bilinear in j_α, $p_{\alpha ik}$ and h_α. (We note that if the molecules interact as $\sim r^{-5}$, then the coefficients in the bilinear terms generally vanish in the "13 momentum" approximation. In the real case, they are practically always small.) Then the general expressions for these quantities can be written in the form

$$R_{\alpha i} = \sum_\beta B^{(1)}_{\alpha\beta}(u_{\alpha i} - u_{\beta i}) + \sum_\beta B^{(2)}_{\alpha\beta}(h_{\alpha i} / m_\alpha p_\alpha - h_{\beta i} / m_\beta p_\beta); \tag{2.12}$$

$$R_{\alpha ik} = \sum_\beta [B^{(3)}_{\alpha\beta}(p_{\alpha ik} / p_\alpha) + B^{(4)}_{\alpha\beta}(p_{\beta ik} / p_\beta)], \tag{2.13}$$

$$R_{\alpha ikk} = \frac{kT}{m_\alpha} \sum_\beta \Big[\frac{5}{2m_\alpha} B^{(2)}_{\alpha\beta}(u_{\alpha i} - u_{\beta i}) + B^{(5)}_{\alpha\beta}(h_{\alpha i} / p_\alpha)$$

$$+ B^{(6)}_{\alpha\beta}(h_{\beta i} / p_\beta)\Big]. \tag{2.14}$$

The coefficients in (2.12)—(2.14) can be expressed as linear combinations of the known Chapman-Cowling integrals, $\Omega^{lr}_{\alpha\beta}$. Omitting the laborious but uncomplicated computations, we write down the final results:

$$B^{(1)}_{\alpha\beta} = -\tfrac{16}{3}\mu_{\alpha\beta} n_\alpha n_\beta \Omega^{11}_{\alpha\beta}, \tag{2.15}$$

$$B^{(2)}_{\alpha\beta} = -\tfrac{16}{3}\mu^2_{\alpha\beta} n_\alpha n_\beta \Big[\tfrac{2}{5}\Omega^{12}_{\alpha\beta} - \Omega^{11}_{\alpha\beta}\Big], \tag{2.16}$$

$$B^{(3)}_{\alpha\beta} = -\tfrac{16}{5} n_\alpha n_\beta (\mu^2_{\alpha\beta} / m_\alpha m_\beta)\Big[(m_\beta / m_\alpha)\Omega^{22}_{\alpha\beta} + \tfrac{10}{3}\Omega^{11}_{\alpha\beta}\Big], \tag{2.17}$$

$$B^{(4)}_{\alpha\beta} = -\tfrac{16}{5} n_\alpha n_\beta (\mu^2_{\alpha\beta} / m_\alpha m_\beta)\Big(\Omega^{22}_{\alpha\beta} - \tfrac{10}{3}\Omega^{11}_{\alpha\beta}\Big), \tag{2.18}$$

$$B^{(5)}_{\alpha\beta} = -\tfrac{64}{15} n_\alpha n_\beta (\mu^3_{\alpha\beta} / m_\alpha m_\beta)\Big[\Omega^{22}_{\alpha\beta} + \Big(\tfrac{15}{4} m_\alpha / m_\beta$$

$$+ \tfrac{25}{8} m_\beta / m_\alpha\Big)\Omega^{11}_{\alpha\beta} - {}^1/_2 (m_\beta / m_\alpha)(5\Omega^{12}_{\alpha\beta} - \Omega^{13}_{\alpha\beta})\Big], \tag{2.19}$$

$$B^{(6)}_{\alpha\beta} = -\tfrac{64}{15} n_\alpha n_\beta (\mu^3_{\alpha\beta} / m_\alpha m_\beta)\Big(\Omega^{22}_{\alpha\beta} - \tfrac{55}{8}\Omega^{11}_{\alpha\beta}$$

$$+ \tfrac{5}{2}\Omega^{12}_{\alpha\beta} - \tfrac{1}{2}\Omega^{13}_{\alpha\beta}\Big). \tag{2.20}$$

Here

$$\Omega^{lr}_{\alpha\beta} = \sqrt{\pi}\int_0^\infty\int_0^\infty \zeta^{2r+2} e^{-\zeta^2} g_{\alpha\beta}(1 - \cos^l \chi_{\alpha\beta})\, b\,db\, d\zeta,$$

where $\zeta = g_{\alpha\beta}(\mu_{\alpha\beta}/2kT)^{1/2}$, $\chi_{\alpha\beta}$ is the scattering angle in the center-of-mass system, $\mu_{\alpha\beta} = m_\alpha m_\beta/(m_\alpha + m_\beta)$ is the reduced mass of the colliding molecules.

The coefficients of (2.19), (2.20) can be simplified if we use the approximation of Kihara,[8]

$$B^{(5)}_{\alpha\beta} = -\tfrac{64}{15} n_\alpha n_\beta (\mu^3_{\alpha\beta} / m_\alpha m_\beta)\Big[\Omega^{22}_{\alpha\beta} + \tfrac{15}{4}(m_\alpha / m_\beta)$$

$$\times\Big(1 + \tfrac{1}{3} m^2_\beta / m^2_\alpha\Big)\Omega^{11}_{\alpha\beta}\Big], \tag{2.21}$$

$$B^{(6)}_{\alpha\beta} = -\tfrac{64}{15} n_\alpha n_\beta (\mu^3_{\alpha\beta} / m_\alpha m_\beta)(\Omega^{22}_{\alpha\beta} - 5\Omega^{11}_{\alpha\beta}). \tag{2.22}$$

3. DIFFUSION EQUATION IN A MULTICOMPONENT GAS MIXTURE

The set of equations (2.7)—(2.11) describes the phenomena of diffusion, thermal conductivity, and viscosity and their interrelations. The equations of hydrodynamics of the mixture also appear in this system. That is, in the summation of Eqs. (2.7) over α, we get the equation of continuity for the mixture

$$\partial\rho / \partial t + \operatorname{div}(\rho\mathbf{u}) = 0. \tag{3.1}$$

Summing (2.8) over α, we get the equation of motion for the mixture as a whole:

$$\rho\, du_i / dt = -\partial p / \partial x_i - \partial p_{ik} / \partial x_k + \sum_\alpha n_\alpha X_{\alpha i}. \tag{3.2}$$

(The summation of Eqs. (2.9) leads to the equation for the conservation of energy.)

For the determination of the quantities j_α, q and p_{ik}, it is necessary to make use of the remaining equations of the set (2.8)—(2.11). Analysis of these equations shows that in the maintenance of the condition (1.1) the derivatives dj_α/dt, dq_α/dt, $dp_{\alpha ik}/dt$ and the nonlinear terms in the left hand sides can be neglected. Taking this into account, and substituting du_i/dt in Eq. (2.8) from the equation of motion of the mixture (3.2) and the expression (2.12) for $R_{\alpha i}$, we find the set of diffusion equations in the multicomponent mixture:

$$\sum_\beta \frac{n_\alpha n_\beta kT}{n[D_{\alpha\beta}]_1}(u_{\alpha i} - u_{\beta i}) = -\left(\frac{\partial p_\alpha}{\partial x_i} - \frac{\rho_\alpha}{\rho}\frac{\partial p}{\partial x_i}\right)$$

$$+ [n_\alpha X_{\alpha i} - (\rho_\alpha / \rho)\sum_\beta n_\beta X_{\beta i}]$$

$$- [\partial p_{\alpha ik} / \partial x_k - (\rho_\alpha / \rho)(\partial p_{ik} / \partial x_k)]$$

$$+ \sum_\beta \xi_{\alpha\beta}\left(\frac{h_{\beta i}}{m_\beta n_\beta} - \frac{h_{\alpha i}}{m_\alpha n_\alpha}\right), \tag{3.3}$$

where $[D_{\alpha\beta}]_1$ is the first approximation (in the Chapman-Enskog method) to the coefficient of mutual diffusion of the binary mixture of α and β molecules:

$$[D_{\alpha\beta}]_1 = 3\,kT/16n\mu_{\alpha\beta}\Omega^{11}_{\alpha\beta},$$

$$\xi_{\alpha\beta} = (n_\alpha n_\beta / n[D_{\alpha\beta}]_1)\mu_{\alpha\beta}\big(\tfrac{6}{5} C^*_{\alpha\beta} - 1\big),$$

$$C^*_{\alpha\beta} = \Omega^{12}_{\alpha\beta}/3\,\Omega^{11}_{\alpha\beta}.$$

The values of $p_{\alpha ik}$ and $h_{\alpha i}$ [which figure in (3.3)] should in turn be determined from a solution of the system (2.10)—(2.11) which takes the following form in the approximation under consideration:

$$\tfrac{4}{5}\{\partial q_{\alpha i}/\partial x_k\} + 2p_\alpha \varepsilon_{ik} = R_{\alpha ik},$$

$$\partial p_{\alpha ik}/\partial x_k + \tfrac{5}{2}(p_\alpha/T)(\partial T/\partial x_i) = (m_\alpha/kT)R_{\alpha ikk}.$$

In all real cases, $\partial q_{\alpha i}/\partial x_k$ is a quantity of second order of smallness (in λ/L). However, it is very significant that the derivative $\partial p_{\alpha ik}/\partial x_k$ in viscous flow is a quantity of first order of smallness, which follows directly from (3.2). Taking the foregoing into consideration and the explicit expressions (2.13) and (2.14) for $R_{\alpha i_1 \ldots i_s}$, we have

$$2p_\alpha \varepsilon_{ik} = -p^2 \sum_{\beta=1}^{N} a_{\alpha\beta}\frac{p_{\beta ik}}{p_\beta}, \tag{3.4}$$

$$\frac{p_\alpha}{T}\frac{\partial T}{\partial x_i} + \frac{2}{5}\frac{\partial p_{\alpha ik}}{\partial x_k} + \sum_{\beta=1}^{N}\frac{kT}{m_\alpha}\xi_{\alpha\beta}(u_{\alpha i} - u_{\beta i}) = -\frac{p^2}{T}\sum_{\beta=1}^{N} b_{\alpha\beta}\frac{h_{\beta i}}{p_\beta}, \tag{3.5}$$

where

$$a_{\alpha\alpha} = \frac{y_\alpha^2}{[\eta_{\alpha\alpha}]_1} + 2\sum_{\beta\neq\alpha}(y_\alpha y_\beta/(m_\alpha + m_\beta)n[D_{\alpha\beta}]_1) \times \left(1 + \frac{3}{5}\frac{m_\beta}{m_\alpha}A^*_{\alpha\beta}\right),$$

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

$$b_{\alpha\alpha} = \frac{y_\alpha^2}{[\lambda_{\alpha\alpha}]_1} + \frac{4}{25}\frac{T}{p}\sum_{\beta\neq\alpha}{}' \{y_\alpha y_\beta[\tfrac{15}{2}m_\alpha^2 + \tfrac{25}{4}m_\beta^2 - 3m_\beta^2 B^*_{\alpha\beta} + 4m_\alpha m_\beta A^*_{\alpha\beta}]/(m_\alpha + m_\beta)^2[D_{\alpha\beta}]_1\},$$

$$b_{\alpha\beta} = -\frac{4}{25}\frac{T}{p}[m_\alpha m_\beta/(m_\alpha + m_\beta)^2](y_\alpha y_\beta/[D_{\alpha\beta}]_1)\left(\tfrac{55}{4} - 3B^*_{\alpha\beta} - 4A^*_{\alpha\beta}\right), \quad \beta \neq \alpha.$$

Here $y_\alpha = n_\alpha/n$ is the molar concentration of the α component, the quantities

$$[\eta_{\alpha\alpha}]_1 = 5kT/8\Omega^{22}_{\alpha\alpha}, \quad [\lambda_{\alpha\alpha}]_1 = 75k^2T/32m_\alpha\Omega^{22}_{\alpha\alpha}$$

coincide with the values of the coefficients of viscosity and thermal conductivity of a simple gas consisting of α molecules (the first nonvanishing approximation in the expansion in Sonine polynomials[1]). The quantities

$$A^*_{\alpha\beta} = \Omega^{22}_{\alpha\beta}/2\Omega^{11}_{\alpha\beta}, \quad B^*_{\alpha\beta} = (5\Omega^{12}_{\alpha\beta} - \Omega^{13}_{\alpha\beta})/3\Omega^{11}_{\alpha\beta}$$

differ little from unity (for the model of molecules as solid elastic spheres $A^* = B^* = C^* = 1$; the Kihara approximation corresponds to $B^* = 5/4$ for all models).

Solving (3.4) we find

$$p_{\alpha ik} = -2\eta_\alpha \varepsilon_{ik}, \qquad \eta_\alpha = y_\alpha \sum_{\beta=1}^{N}\frac{y_\beta |a|_{\beta\alpha}}{|a|}. \tag{3.6}$$

For this case, $|a|$ and $|a|_{\beta\alpha}$ are respectively the determinant of the set of equations and the cofactor of the element $\beta\alpha$ of the determinant.

Substituting (3.6) in the left side of (3.5), and solving the resultant equation for $h_{\alpha i}$, we get

$$h_{\alpha i} = -\lambda_\alpha\frac{\partial T}{\partial x_i} + \frac{4}{5}\frac{T}{p}\sum_{\delta=1}^{N} y_\alpha \frac{|b|_{\delta\alpha}}{|b|}\frac{\partial}{\partial x_l}(\eta_\alpha \varepsilon_{il}) - \frac{T}{p}\sum_{\delta=1}^{N}\sum_{\nu=1}^{N}\frac{kT}{m_\delta}y_\alpha\frac{|b|_{\delta\alpha}}{|b|}\xi_{\delta\nu}(u_{\delta i} - u_{\nu i}), \tag{3.7}$$

$$\lambda_\alpha = y_\alpha \sum_{\delta=1}^{N} y_\delta \frac{|b|_{\delta\alpha}}{|b|}.$$

Making use of (3.6) and (3.7), we get the final set of equations of diffusion in the multicomponent mixture (we write $\eta = \Sigma\eta_\alpha$):

$$\begin{aligned}\sum_\beta \frac{n_\alpha n_\beta kT}{n[D_{\alpha\beta}]_1}(u_{\alpha i} - u_{\beta i}) = &-\left[\frac{\partial p_\alpha}{\partial x_i} - \frac{\rho_\alpha}{\rho}\frac{\partial p}{\partial x_i}\right] + \left[n_\alpha X_{\alpha i} - \frac{\rho_\alpha}{\rho}\sum_\beta n_\beta X_{\beta i}\right] + \sum_\beta \xi_{\alpha\beta}\left(\frac{\lambda_\alpha}{m_\alpha n_\alpha} - \frac{\lambda_\beta}{m_\beta n_\beta}\right)\frac{\partial T}{\partial x_i}\\ &+ 2\left[\eta_\alpha - \frac{\rho_\alpha}{\rho}\eta\right]\frac{\partial \varepsilon_{ik}}{\partial x_k} + \frac{4}{5}k\left(\frac{T}{p}\right)^2\sum_{\beta=1}^{N}\sum_{\delta=1}^{N}\xi_{\alpha\beta}\eta_\delta\left[\frac{|b|_{\delta\beta}}{m_\beta|b|} - \frac{|b|_{\delta\alpha}}{m_\alpha|b|}\right]\frac{\partial \varepsilon_{ik}}{\partial x_k}\\ &- k\left(\frac{T}{p}\right)^2\sum_{\beta=1}^{N}\sum_{\delta=1}^{N}\sum_{\nu=1}^{N}\frac{kT}{m_\delta}\xi_{\alpha\beta}\xi_{\delta\nu}\left(\frac{|b|_{\delta\beta}}{m_\beta|b|} - \frac{|b|_{\delta\alpha}}{m_\alpha|b|}\right)(u_{\delta i} - u_{\nu i}),\end{aligned} \tag{3.8}$$

The resultant equations differ from the usual set of diffusion equations [4-9] by the presence of the last three terms. Two of them are as a whole related to the effect of viscous momentum transfer by the relative motion of the components. The appearance of the last term is connected with the fact that, in contrast with [9], the "13 momentum" approximation used corresponds in this case to the complete second approximation of the method which uses the expansion in Sonine polynomials. It should be noted that even for the thermodiffusion term [third term on the right in (3.8)] a much simpler expression is obtained.

Let us consider the case of a purely viscous steady-state flow of gas when the pressure gradient and the external forces are counterbalanced by the forces of "viscous friction" (inertial terms in the equation of motion (3.2) are negligibly small). Then, in place of (3.8), we have

$$\begin{aligned}\sum_\beta \frac{n_\alpha n_\beta kT}{n[D_{\alpha\beta}]_1}(\mathbf{u}_\alpha - \mathbf{u}_\beta) &+ k\left(\frac{T}{p}\right)^2\sum_{\beta=1}^{N}\sum_{\delta=1}^{N}\sum_{\nu=1}^{N}\frac{kT}{m_\delta}\xi_{\alpha\beta}\xi_{\delta\nu}\left[\frac{|b|_{\delta\beta}}{m_\beta|b|} - \frac{|b|_{\delta\alpha}}{m_\alpha|b|}\right](\mathbf{u}_\delta - \mathbf{u}_\nu) = -[\nabla p_\alpha - \nabla p(\eta_\alpha + \omega_\alpha)/\eta]\\ &+ \left\{n_\alpha \mathbf{X}_\alpha - \frac{\eta_\alpha + \omega_\alpha}{\eta}\sum_\beta n_\beta \mathbf{X}_\beta + T\sum_\beta \xi_{\alpha\beta}\left(\frac{\lambda_\alpha}{m_\alpha n_\alpha} - \frac{\lambda_\beta}{m_\beta n_\beta}\right)\nabla \ln T\right\},\end{aligned} \tag{3.9}$$

where

$$\omega_\alpha = \frac{2}{5}k\left(\frac{T}{p}\right)^2\sum_{\beta=1}^{N}\sum_{\delta=1}^{N}\xi_{\alpha\beta}\eta_\delta\left[\frac{|b|_{\delta\beta}}{m_\beta|b|} - \frac{|b|_{\delta\alpha}}{m_\alpha|b|}\right].$$

In conclusion of this section, we note the following. If we sum (3.6) over all components, then we get the usual expression for the viscous stress tensor with the coefficient of viscosity of the mixture $\eta = \sum_{\alpha} \eta_{\alpha}$, which coincides with the well-known value found in[4]. The expression for the total thermal flux, which is obtained as the result of summation of (3.7), recalls in its form the expression given in[9]:

$$\mathbf{q} = -\lambda \nabla T + \tfrac{5}{2} kT \sum_{\alpha} \frac{\mathbf{j}_{\alpha}}{m_{\alpha}} + T \sum_{\alpha} \sum_{\beta} \frac{\lambda_{\alpha}}{n_{\alpha} m_{\alpha}} \xi_{\alpha\beta} (\mathbf{u}_{\alpha} - \mathbf{u}_{\beta}). \tag{3.10}$$

(For simplicity, we omit the terms connected with the second derivative of the velocity.) However, in this case, the expression for $\lambda = \sum_{\alpha} \lambda_{\alpha}$ differs from the complicated expression in[9], and coincides with the coefficient of thermal conductivity of the mixture obtained in direct application of the second approximation in the expansion in Sonine polynomials.[10] Also, the last term in (3.10) has a simpler form than in[9].

4. DIFFUSION OF A TWO-COMPONENT MIXTURE FLOW

We analyze in detail the results obtained in the previous section for the case of a two-component mixture. For diffusive flow of component 1 in a system of coordinates where there is no molar transfer of the gas as a whole, we get from (3.9)

$$\begin{aligned} \mathbf{G}_1 &= ny_1(1-y_1)(\mathbf{u}_1 - \mathbf{u}_2) \\ &= -nD_{12}[\nabla y_1 + \alpha_p y_1(1-y_1)\nabla \ln p \\ &+ [\alpha_T]_1 y_1(1-y_1)\nabla \ln T]. \end{aligned} \tag{4.1}$$

Here $D_{12} = [D_{12}]_1/(1 - \Delta_{12})$ is the coefficient of mutual diffusion, which corresponds to the second approximation in the expansion in Sonine polynomials, $|\alpha_T|$, is the thermal diffusion constant, α_p is the barodiffusion constant in viscous flow.

If we write α_p in the form

$$\alpha_p = [\alpha_p]_1 [1 - \Delta_p] - \tfrac{2}{5} [\alpha_T]_1, \tag{4.2}$$

then

$$[\alpha_p]_1 = \frac{{}^3\!/_5 A^*_{12} [(m_1+m_2)^2/2m_1m_2] \{(m_2-m_1)/(m_2+m_1) + [\nu_1 y_1 - \nu_2(1-y_1)]\}}{1 + {}^3\!/_5 A^*_{12} [(m_1/m_2)\, y_1 + (m_2/m_1)(1-y_1) + \{(m_1+m_2)^2/2m_1m_2\}\, y_1(1-y_1)(\nu_1+\nu_2)]}, \tag{4.3}$$

$$\nu_1 = (\Omega^{22}_{11}/\Omega^{22}_{12} - 1), \quad \nu_2 = (\Omega^{22}_{22}/\Omega^{22}_{12} - 1), \tag{4.4}$$

and the quantity Δ_p is written in terms of the value of the thermal diffusion constant $[\alpha_T]_1$ and the corrections of the second approximation to the diffusion coefficient Δ_{12}, the expressions for which can be found in[1, 9]:

$$\Delta_p = \frac{2}{5}\left\{(m_2-m_1)\, y_1(1-y_1)[\alpha_T]_1 + \frac{(m_1+m_2)\Delta_{12}}{{}^6\!/_5 C^*_{12} - 1}\right\} \Big/ [m_1 y_1 + m_2(1-y_1)] \tag{4.5}$$

(as a rule, Δ_p is much less than unity).

The expression for the barodiffusion constant (4.2) differs significantly from the corresponding value of α_p for the case of nonviscous flow. The latter is easily obtained from consideration of the general diffusion equation (3.8) if we set $\partial \epsilon_{ik}/\partial x_k = 0$ in it; as a result, we get the following well-known expression for the two-component mixture:

$$\alpha_p = (m_2 - m_1)/[m_1 y_1 + m_2(1-y_1)]. \tag{4.6}$$

The most important difference between (4.2) and (4.6) is that the barodiffusion constant in viscous flow depends on the character of the mutual interaction of the molecules. Furthermore, in contrast with (4.6), the barodiffusion constant can have an arbitrary sign in the general case. This is made especially clear if one considers the case of small relative mass difference and effective scattering cross section of the molecules of the mixture. Introducing, by analogy with Chapman[1], the effective molecular diameters s_{11}, s_{22}, s_{12}, determined by the expressions

$$\begin{aligned} s^2_{11} &= \tfrac{1}{2}(m_1/\pi kT)^{1/2}\,\Omega^{22}_{11}, \\ s^2_{22} &= \tfrac{1}{2}(m_2/\pi kT)^{1/2}\,\Omega^{22}_{22}, \\ s^2_{12} &= \tfrac{1}{2}[2m_1m_2/(m_1+m_2)\pi kT]^{1/2}\,\Omega^{22}_{12}, \end{aligned} \tag{4.7}$$

and expanding (4.3) in a series in small quantities, we get an approximate form for $[\alpha_p]_1$:

$$\begin{aligned} [\alpha_p]_1 = [6A^*/(5+3A^*)]\{&\tfrac{3}{2}(m_2-m_1)/(m_2+m_1) \\ &+ [(s^2_{11}/s^2_{12} - 1)\, y_1 - (s^2_{22}/s^2_{12} - 1)(1-y_1)]\}. \end{aligned} \tag{4.8}$$

The term in the square brackets in (4.8) depends only on the nature of the forces of interaction of the molecules, and for $m_2 = m_1$ the sign of $[\alpha_p]_1$ is uniquely determined by the ratio of the effective scattering diameters. For molecules considered as rigid elastic spheres, s_{11} and s_{22} coincide simply with the diameters of the molecule σ_1 and σ_2, and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$. Applying this approximation to other interaction models, we find

$$\begin{aligned} [\alpha_p]_1 &= [9A^*/(5+3A^*)](m_2-m_1)/(m_2+m_1) \\ &- [6A^*/(5+3A^*)](\sigma_2-\sigma_1)/\sigma_{12}. \end{aligned} \tag{4.9}$$

We also write out the corresponding complete expression for α_p in the Kihara approximation:

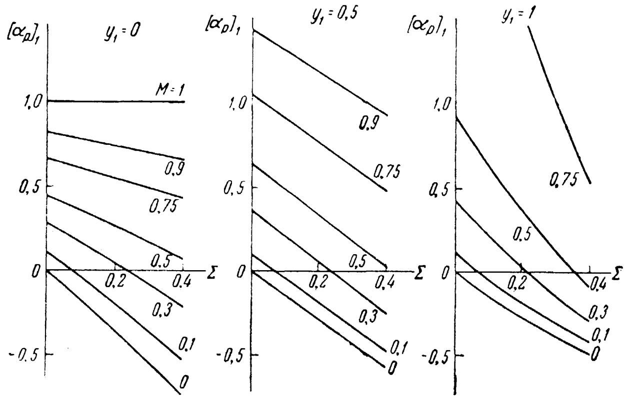
$$\alpha_p = \frac{9A^*}{5+3A^*}\left[1 + \frac{(6C^*-5)(25+25A^*-18A^{*2})}{24A^{*2}(5+2A^*)}\right]\frac{m_2-m_1}{m_2+m_1} - \frac{6A^*}{5+3A^*}\left[1 - \frac{5(6C^*-5)(1+3A^*)}{12A^*(5+2A^*)}\right]\frac{\sigma_2-\sigma_1}{\sigma_{12}}. \quad (4.10)$$

It follows from (4.10) that the coefficients for $(m_2 - m_1)/(m_2 + m_1)$ and $(\sigma_1 - \sigma_2)/\sigma_{12}$ for different models of intermolecular interaction take on values from 1.31 and 0.873 (the Maxwell model; $F \sim r^{-5}$) up to $^{75}/_{56}$ and $^{4}/_{7}$ (solid spheres), respectively. In the latter case, the first coefficient increases by 19 per cent, in the second, it decreases 24 per cent in comparison with the first approximation for $[\alpha_p]_1$, (4.9).

As an illustration of the barodiffusion constant for arbitrary relations of the masses and scattering cross sections of the molecules, curves are given in the figure for the dependence $[\alpha_p) = f(\Sigma)$, where $\Sigma = (\sigma_2 - \sigma_1)/\sigma_{12}$ at different values of $M = (m_2 - m_1)/(m_2 + m_1)$ for the model of rigid elastic spheres.

Now, proceeding to the general analysis of the problem, we note that, within the framework of thermodynamics of irreversible processes, the barodiffusion constant depends only on thermodynamic quantities and is rigorously equal to the value (4.6).[5,6] At first glance, we come to a contradiction, inasmuch as in this case, as in the present research, only the smallness of the gradients of macroscopic quantities is assumed (i.e., $\lambda/L \ll 1$). On the other hand, in the framework of the development of the hydrodynamics of irreversible processes, the transfer of momentum to viscous flow, which is characterized by a tensor of second rank, need not generally affect the diffusive flow, which is a vector. However, it is possible to form a vector quantity of the form $\partial\epsilon_{ik}/\partial x_k$, from the tensor ϵ_{ik}. Although this quantity corresponds to the second derivative of macroscopic quantities, it has the first order of smallness in the case of purely viscous flow, as follows directly from (3.2); this fact is actually determined by the value of the pressure gradient. Thus, at this point, the canonical methods of the thermodynamics of irreversible processes, which assume an expansion in thermodynamic forces (which figure in the expression for the time derivative of the entropy), should be appreciably expanded, so as to include also the "force" of the type described.

The considerations given by us were developed in general form by one of the authors (Yu. Kagan). It was shown that in the application of the thermodynamics of irreversible processes to spatially inhomogeneous problems including a number of independent thermodynamic forces (among which is the decomposition of the currents) it is necessary to introduce the values of the corresponding tensor, which is obtained by differentiation of the thermodynamic forces with respect to the coordinates. In a number of cases, especially in multidimensional problems (different characteristic lengths for the change of macroscopic quantities in different directions), new terms in kinetic fluxes can be shown to be of the same order as the terms usually considered, which, in particular, also appears in the case of barodiffusion in viscous flow.



In correspondence with what has been pointed out above, the general expression for diffusive flow of a two component mixture in an arbitrary liquid is seen to be equal to

$$G_{1i} = -a\frac{\partial\mu}{\partial x_i} - b\frac{\partial T}{\partial x_i} - c\frac{\partial\varepsilon_{ik}}{\partial x_k} - d\frac{\partial\varepsilon_0}{\partial x_i},$$

where a, b, c, d are independent kinetic coefficients; $\epsilon_0 = \operatorname{div} \mathbf{u}$; μ is the chemical potential of the mixture (it is associated with the chemical potential of the components μ_i by the relation $\mu = \mu_1/m_1 - \mu_2/m_2$[5]). For purely viscous flow of an incompressible (in the hydrodynamic sense) liquid, the barodiffusion constant is equal to

$$\alpha_p = p\left(\frac{\partial\mu}{\partial p}\right)_{y_1,T} \Big/ \left(\frac{\partial\mu}{\partial y_1}\right)_{p,T} y_1(1-y_1) + kTc \Big/ 2\eta D_{12}y_1(1-y_1).$$

Thus α_p is established doubly as a kinetic quantity (compare the opposite confirmation in[5]).

In the case of a monatomic case in the approximation considered in the research

$$c = \left(\alpha_p - \frac{m_2-m_1}{m_1y_1 + m_2(1-y_1)}\right)\frac{2\eta D_{12}y_1(1-y_1)}{kT},$$

where α_p is determined in correspondence with (4.2)–(4.5).

The situation, which is analogous to that described above, arises also in the application of the second approximation to the distribution function in the Chapman-Enskog method. As is well known, the neglect of terms which contain both the squares of the first derivatives and also the second derivatives of the macroscopic quantities correspond to this approximation. As a result, diffusion and viscous momentum transfer are shown to be independent in this approximation, and we actually arrive at expressions which describe diffusion in nonviscous flow. The terms which take into account the interaction between viscous momentum transfer and diffusion are only in the third approximation of the method.

Making use of this approximation, Chapman and Cowling[3] found the value of the barodiffusion constant in the case of a mixture with a small relative difference in molecular weights of the components and the same law of interaction of the molecules. This result coincides with the expression for $[\alpha_p]_1$ obtained in our work for the special case of an isotropic mixture if we set $\sigma_1 = \sigma_2$ in (4.9).

In conclusion, we note that the concrete values of the barodiffusion constant in the case of arbitrary mixtures can be computed from (4.2) if we use a definite model of interaction of the molecules (for example, the Lennard-Jones potential). Corresponding tables for the collision integrals used, and for the quantities A*, B*, C* which are necessary for calculations of α_p, can be found in[9].

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