HEAT AND MASS TRANSFER OF A MULTIATOMIC GAS IN A CYLINDRICAL CAPILLARY WITH ARBITRARY KNUDSEN NUMBERS

I. V. Chermyaninov, V. G. Chernyak,
and A. N. Kulev

UDC 533.6.011.8

Processes of heat and mass transfer of a multiatomic gas in a cylindrical channel of circular cross section with arbitrary Knudsen numbers are considered on the basis of a model kinetic equation, taking account of the excitation of rotational and vibrational degrees of freedom of the molecules.

The motion of multiatomic gas in a cylindrical capillary under the action of pressure and temperature gradients was studied in [1]. The solution of the model Hanson–Morse equation, taking account of the excitation of a single form of internal energy, was obtained by a numerical method. It was shown that, within the limits of accuracy of the calculation, the thermal creep does not depend on the total Eucken factor f, while the total heat flux due to the temperature gradient does not depend on the translational Eucken factor f^{tr}. Hence, it was concluded that the thermal creep is independent of the internal degrees of freedom of the molecules. This conclusion of [1] is evidently incorrect, since, first, the Eucken factors f and f^{tr} are interrelated and, second, f^{tr} also depends on the internal degrees of freedom of the molecules [2].

In the present work, the heat and mass transfer of a multiatomic gas in a cylindrical capillary is described on the basis of the model equation of [3], which, in contrast to the Hanson–Morse equation, takes account of the possibility of excitation of two forms of internal energy: rotational and vibrational. The problem is solved by a variational method, which allows sufficiently accurate results to be obtained over the whole range of Knudsen numbers (Kn) and, in addition, leads to a simple analytical expressions for the fluxes in the two limiting cases: $\mathrm{Kn} \ll 1$ and $\mathrm{Kn} \gg 1$. This permits a clear analysis of the contribution of internal degrees of freedom of the molecules at different Kn to the thermal creep and to each of the components of the heat fluxes due to the pressure and temperature gradients. In addition, analytical expressions when $\mathrm{Kn} \ll 1$ are of independent interest for the experimental study of the characteristic parameters of multiatomic gases.

Consider the motion of a multiatomic single-component gas in a cylindrical capillary of radius R_0 due to longitudinal temperature and pressure gradients. (The capillary axis coincides with the coordinate axis OZ.) Rotational and vibrational degrees of freedom of the molecules are excited here. It is assumed that the translational, rotational, and vibrational temperatures in each cross section of the capillary are equal to each other, and to the temperature T, which varies along the channel. The state of the gas is assumed to be weakly perturbed, and the distribution function for the molecules in the i-th rotational and j-th vibrational states is written in the form of a small deviation from the Maxwell–Boltzmann equation

$$f_{ij} = P_i^{(r)} P_j^{(v)} f_0(z)(1 + h_{ij}),\ |h_{ij}| \ll 1, \tag{1}$$

$$f_0(z) = n(z)\left[\frac{m}{2\pi kT(z)}\right]^{3/2} \exp\left[-\frac{mv^2}{2kT(z)}\right],$$

$$P_\beta^{(\alpha)} = \frac{\exp[-E_\beta^{(\alpha)}/kT(z)}{\sum\limits_\beta \exp[-E_\beta^{(\alpha)}/kT(z)]},\ \alpha = r,\ v;\ \beta = i,\ j.$$

A. M. Gor'kii Ural State University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 47, No. 1, pp. 71-82, July, 1984. Original article submitted July 18, 1983.

0022-0841/84/4701-0797$08.50

Since intermolecular collisions accompanied by simultaneous transitions in both the rotational and the vibrational spectra are very rare [4], they will be neglected. Then, taking account of Eq. (1), the model kinetic equation [3] for the perturbation function h_{ij} is written in the following dimensionless form

$$\mathbf{c}_\perp \frac{\partial h_{ij}}{\partial \mathbf{r}} + c_z \nu + c_z \left[\left(c^2 - \frac{5}{2} \right) + \varepsilon_i^{(r)} - \langle \varepsilon^{(r)} \rangle + \varepsilon_j^{(v)} - \langle \varepsilon^{(v)} \rangle \right] \tau =$$

$$= R \left[2c_z u + \frac{4}{5} c_z \left(c^2 - \frac{5}{2} \right) (\varphi_1 Q^{(t)} + \varphi_2 Q^{(r)} + \varphi_3 Q^{(v)}) + \right.$$

$$\left. + \frac{2k}{c_V^r} c_z (\varepsilon_i^{(r)} - \langle \varepsilon^{(r)} \rangle)(\varphi_4 Q^{(r)} + \varphi_5 Q^{(t)}) + \frac{2k}{c_V^v} c_z (\varepsilon_j^{(v)} - \langle \varepsilon^{(v)} \rangle) \quad (\varphi_6 Q^{(v)} + \varphi_7 Q^{(t)}) - h_{ij} \right], \tag{2}$$

$$\nu = \frac{1}{P} \frac{dP}{dz}, \ \tau = \frac{1}{T} \frac{dT}{dz}, \ R = \frac{1}{\tau_\eta} \left(\frac{m}{2kT_0} \right)^{1/2} R_0,$$

$$c_i = \left(\frac{m}{2kT_0} \right)^{1/2} v_i, \ \varepsilon_i^{(r)} = \frac{E_i^{(r)}}{kT_0}, \ \varepsilon_j^{(v)} = \frac{E_j^{(v)}}{kT_0},$$

$$\varphi_1 = \frac{1}{3} - \frac{5}{9} \left(\frac{c_V^r}{k} \alpha + \frac{c_V^v}{k} \alpha' \right), \ \varphi_2 = \frac{5}{6} \alpha, \ \varphi_3 = \frac{5}{6} \alpha',$$

$$\varphi_4 = 1 - \frac{\alpha}{2} - \frac{1}{\beta}, \ \varphi_5 = \frac{1}{3} \frac{c_V^r}{k} \alpha, \ \varphi_6 = 1 - \frac{\alpha'}{2} - \frac{1}{\beta'},$$

$$\varphi_7 = \frac{1}{3} \frac{c_V^v}{k} \alpha',$$

$$\alpha = \frac{\tau_\eta}{\tau_{rr}}, \ \alpha' = \frac{\tau_\eta}{\tau_{vv}}, \ \beta = \frac{\tau_{Drr}}{\tau_\eta}, \ \beta' = \frac{\tau_{Dvv}}{\tau_\eta}, \ \tau_\eta = \frac{\eta}{P};$$

$$u = \left(\frac{m}{2kT_0} \right)^{1/2} U = \pi^{-3/2} \sum_{i,j} P_i^{(r)} P_j^{(v)} \int \exp(-c^2) c_z h_{ij} d\mathbf{c}, \tag{3}$$

$$Q^{(t)} = \left(\frac{m}{2kT_0} \right)^{1/2} \frac{q^{(t)}}{P_0} = \pi^{-3/2} \sum_{i,j} P_i^{(r)} P_j^{(v)} \int \exp(-c^2) c_z \left(c^2 - \frac{5}{2} \right) h_{ij} d\mathbf{c},$$

$$Q^{(\alpha)} = \left(\frac{m}{2kT_0} \right)^{1/2} \frac{q^{(\alpha)}}{P_0} = \pi^{-3/2} \sum_{i,j} P_i^{(r)} P_j^{(v)} \quad \int \exp(-c^2) c_z (\varepsilon_\beta^{(\alpha)} - \langle \varepsilon^{(\alpha)} \rangle) h_{ij} d\mathbf{c},$$

$$c_V^{(\alpha)} = k (\langle \varepsilon_\beta^{(\alpha)2} \rangle - \langle \varepsilon_\beta^{(\alpha)} \rangle^2), \ \alpha = r, \ v; \ \beta = i, \ j.$$

Here $\mathbf{r}$, $\mathbf{c}_\perp$ are two-dimensional vectors in the plane perpendicular to the OZ axis; the coordinates r, z are referred to R_0; the angle brackets denote averaging over the internal states of the molecules. The relaxation times τ_η, τ_{rr}, τ_{vv}, τ_{Drr}, τ_{Dvv} with a specified molecular-interaction potential may be calculated [4] or taken from experiment [5].

If the mean free path length of the molecule is determined in the form [4] $l = (\pi/4) \cdot \tau_\eta (8kT/\pi m)^{1/2}$, then the rarefaction parameter R of the gas is related to the Knudsen number as follows

$$R = \frac{\sqrt{\pi}}{2} \frac{R_0}{l} = \frac{\sqrt{\pi}}{2} \mathrm{Kn}^{-1}.$$

The boundary condition adopted is completely diffuse scattering of the gas molecules at the capillary surface

$$h_{ij}(|\mathbf{r}| = 1, \ \mathbf{c}) = 0, \ \mathbf{n} \cdot \mathbf{c}_\perp > 0, \tag{4}$$

where $\mathbf{n}$ is the normal to the channel surface directed toward the center.

Linearization of the problem allows the solution of Eq. (2) to be written in the form

$$h_{ij} = h_{ij}^P \nu + h_{ij}^T \tau. \tag{5}$$

Substituting Eq. (5) into Eqs. (2)-(4) and equating terms for the different gradients leads to a division of the overall problem into two: the first includes the equations describing heat and mass transfer under the action of the pressure gradient, while the second corresponds to the action of the temperature gradient.

If Eq. (2) is written in integral form [6], taking account of the boundary conditions in Eq. (4), and the resulting expression for the perturbation function is substituted into Eq. (3), two independent systems of integral-moment equations may be obtained for the macroscopic velocities u_P, u_T and the translational, rotational, and vibrational components of the dimensionless heat fluxes $Q_P^{(l)}$, $Q_T^{(l)}$ (l = t, r, v) due to the pressure and temperature gradients, respectively

$$u_{P,T}=\frac{R}{\pi}\int\limits_{(\Sigma)}\left[u_{P,T}J_0+\frac{2}{5}(\varphi_1Q_{P,T}^{(t)}+\varphi_2Q_{P,T}^{(r)}+\varphi_3Q_{P,T}^{(v)})(J_2-J_0)\right]\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}+K_{P,T}^{(1)};\tag{6}$$

$$Q_{P,T}^{(t)}=\frac{R}{\pi}\int\limits_{(\Sigma)}\left[u_{P,T}(J_2-J_0)+\frac{2}{5}(\varphi_1Q_{P,T}^{(t)}+\varphi_2Q_{P,T}^{(r)}+\varphi_3Q_{P,T}^{(v)})\left(J_4-2J_2+\frac{5}{2}J_0\right)\right]\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}+K_{P,T}^{(2)};\tag{7}$$

$$Q_{P,T}^{(r)}=\frac{R}{\pi}\int\limits_{(\Sigma)}(\varphi_4Q_{P,T}^{(r)}+\varphi_5Q_{P,T}^{(t)})J_0\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}+K_{P,T}^{(3)};\tag{8}$$

$$Q_{P,T}^{(v)}=\frac{R}{\pi}\int\limits_{(\Sigma)}(\varphi_6Q_{P,T}^{(v)}+\varphi_7Q_{P,T}^{(t)})J_0\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}+K_{P,T}^{(4)},\tag{9}$$

$$K_P^{(1)}=-\frac{1}{2\pi}\int\limits_{(\Sigma)}\frac{J_0d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|},\ K_T^{(1)}=K_P^{(2)}=-\frac{1}{2\pi}\int\limits_{(\Sigma)}\frac{(J_2-J_0)\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|},$$

$$K_T^{(2)}=-\frac{1}{2\pi}\int\limits_{(\Sigma)}\frac{\left(J_4-2J_2+\frac{5}{2}J_0\right)d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|},\ K_P^{(3)}=K_P^{(4)}=0,$$

$$K_T^{(3)}=\frac{c_V^r}{k}K_P^{(1)},\ K_T^{(4)}=\frac{c_V^v}{k}K_P^{(1)},\ J_n(t)=\int\limits_0^\infty c^n\exp\left(-c^2-\frac{t}{c}\right)dc.$$

In Eqs. (6)-(9), the integration is taken over the cross-sectional area of the capillary Σ. The argument of the function $J_n(t)$ is $t = R|\mathbf{r}-\mathbf{r}'|$. Equations (6)-(9) define the local values of the macroscopic quantities. The quantities that are of practical interest, however, are the numerical I_n and heat I_q fluxes averaged over the channel cross section

$$\begin{gathered}I_n=\frac{n_0}{\Sigma}\int\limits_{(\Sigma)}U\,dr=2n_0\left(\frac{2kT_0}{m}\right)^{1/2}\int\limits_0^1u(r)\,r\,dr=L_{nn}X_n+L_{nq}X_q,\\ I_q=\frac{1}{\Sigma}\int\limits_{(\Sigma)}q\,dr=2\int\limits_0^1(q^{(t)}+q^{(r)}+q^{(v)})\,r\,dr=L_{qn}X_n+L_{qq}X_q,\end{gathered}\tag{10}$$

where the thermodynamic forces are chosen in the form [1]

$$X_n=-kv,\ X_q=-\frac{\tau}{T_0}.\tag{11}$$

According to the thermodynamics of nonequilibrium processes the cross terms should satisfy the Onsager reciprocity relation over the whole range of Kn in discontinuous systems [7]: $L_{nq} = L_{qn}$. For numerical calculations, it is expedient to use dimensionless quantities, related to the kinetic coefficients as follows

$$\begin{gathered}G_P=\left(\frac{m}{2kT_0}\right)^{1/2}\frac{k}{n_0}L_{nn},\ G_T=-\left(\frac{m}{2kT_0}\right)^{1/2}\frac{k}{P_0}L_{nq},\\ S_P^{(l)}=-\left(\frac{m}{2kT_0}\right)^{1/2}\frac{k}{P_0}L_{qn}^{(l)},\ S_T^{(l)}=\left(\frac{m}{2kT_0}\right)^{1/2}\frac{1}{P_0T_0}L_{qq}^{(l)},\ l=t,\ r,\ v,\\ L_{qn}=L_{qn}^{(t)}+L_{qn}^{(r)}+L_{qn}^{(v)},\ G_T=S_P^{(t)}+S_P^{(r)}+S_P^{(v)}.\end{gathered}\tag{12}$$

Important particular cases are the effect of thermomolecular pressure and the mechanocaloric effect. The first is a steady state in which the temperature gradient is maintained constant and the corresponding pressure gradient is established in the system. This state is characterized by the absence of a complete numerical flux averaged over the channel cross section, i.e., $I_n = 0$. Then it follows from Eqs. (10)-(12) that

$$\gamma = \frac{G_T}{G_P} = \frac{\nu}{\tau} = \frac{dP/P}{dT/T}. \tag{13}$$

The mechanocaloric effect is a second-order steady state [7] and is characterized by heat transfer along the channel with a constant pressure gradient, in the absence of a temperature gradient ($\tau = 0$). It follows from Eqs. (10), (12), and (13) that

$$I_q = \frac{L_{nq}}{L_{nn}} I_n = -\gamma k T_0 I_n. \tag{14}$$

Thus, the parameter γ also determines the magnitude of the mechanocaloric effect.

To determine the fluxes in Eq. (10), the system in Eqs. (6)-(9) must be solved. These are Fredholm-type equations of the second kind, the Bubnov–Galerkin method may be used for their solution [8]. Choice of the type of trial functions for the macroparameters is important here. Note that the profiles of the macroscopic quantities in almost free-molecular conditions is accurately described by the free terms of the integral Eqs. (6)-(9). Therefore, if the solution is to describe the whole range of Kn, the form of the trial functions must be chosen on the basis of the macroparameters in almost continuum conditions. Taking account of the problem symmetry, the desired functions u_P, $_T$, $Q^{(l)}_{P,T}$ (l = t, r, v) may be written as series expansions in the four basis functions $\{r^{2k}\}$ (k = 0, 1, ...). In particular, in the first approximation, the following expressions may be written

$$\begin{gathered} u_k(r) = a_k + b_k r^2, \\ Q_k^{(l)}(r) = c_k^{(l)},\ l = t,\ r,\ v,\ k = P,\ T. \end{gathered} \tag{15}$$

The trial functions in Eq. (15) correspond in form with the solutions of the Navier–Stokes and heat-conduction equations. As shown by the solution of the analogous problem for a monoatomic gas [9], this approximation has an error of no more than 1.5% over the whole range of Kn. The same accuracy should also evidently be expected in the case of a multiatomic gas.

To determine the constants a_k, b_k, $c_k^{(l)}$, the trial functions in Eq. (15) must be substituted into Eqs. (6)-(9) and orthogonality of the discrepancy obtained to the chosen basis functions is required. The orthogonality condition takes the form

$$(f, g) \equiv 2\pi \int_0^1 f(r) g(r) r dr = 0.$$

Thus, the quantities a_k, b_k, $c_k^{(l)}$ are found from the solution of a system of five linear algebraic equations. Once they are known, it is not difficult to obtain expressions for the fluxes I_n, I_q and the parameter γ. The final expressions are unwieldy in form, and therefore are not given here.

The asymptotic expansions of these expressions are of interest for two limiting cases: almost free-molecular conditions ($R \ll 1$)

$$\begin{gathered} G_P = 0{,}72225 + 0{,}5R \ln R - 0{,}1921\, R - 0{,}4012 R^2, \\ G_T = 0{,}37613 + 0{,}5R \ln R + 0{,}0579 R - 0{,}6018 R^2, \\ S_P^{(t)} = G_T,\ S_P^{(r)} = S_P^{(v)} = 0, \\ S_T^{(t)} = 1{,}6926 + 1{,}25 R \ln R - 0.23025 R - 1{,}3039 R^2, \\ S_T^{(r)} = \frac{c_V^r}{k} G_P,\ S_T^{(v)} = \frac{c_V^v}{k} G_P; \end{gathered} \tag{16}$$

almost-continuum conditions ($R \gg 1$)

$$G_P = \frac{R}{8} + \frac{1}{2\sqrt{\pi}} \left(\frac{\pi}{4} + 1 \right) + \dots; \tag{17}$$

$$G_T = \frac{3}{20}\frac{m\lambda^t}{k\eta}\frac{1}{R} - \frac{1}{20\sqrt{\pi}}\frac{m\lambda^t}{k\eta}\left[\pi - \frac{8}{5} + \frac{\frac{27}{5}\left(1+\frac{\alpha\beta}{2}\right)\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0} + \right.$$

$$\left. + \frac{\alpha\beta\left(1+\frac{\alpha'\beta'}{2}\right)\frac{m\lambda^r}{k\eta} + \alpha'\beta'\left(1+\frac{\alpha\beta}{2}\right)\frac{m\lambda^v}{k\eta}}{\Delta_1}\right]\frac{1}{R^2} + \cdots; \tag{18}$$

$$S_P^{(t)} = \frac{\frac{9}{16}\left(1+\frac{\alpha\beta}{2}\right)\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0}\frac{1}{R} - \frac{\frac{3}{16\sqrt{\pi}}\left(1+\frac{\alpha\beta}{2}\right)\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0}\left[\pi - \frac{8}{5} + \right.$$

$$\left. + \frac{\frac{27}{5}\left(1+\frac{\alpha\beta}{2}\right)\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0} + \frac{\frac{5}{4}\frac{c_V^r}{k}(\alpha\beta)^2\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0\left(1+\frac{\alpha\beta}{2}\right)} + \frac{\frac{5}{4}\frac{c_V^v}{k}(\alpha'\beta')^2\left(1+\frac{\alpha\beta}{2}\right)}{\Delta_0\left(1+\frac{\alpha'\beta'}{2}\right)}\right]\frac{1}{R^2} + \cdots; \tag{19}$$

$$S_P^{(r)} = \frac{\frac{3}{16}\frac{c_V^r}{k}\alpha\beta\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0}\frac{1}{R} - \frac{\frac{1}{16\sqrt{\pi}}\frac{c_V^r}{k}\alpha\beta\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0} \times$$

$$\times\left\{\pi - \frac{8}{5} + \frac{3\left(1+\frac{\alpha'\beta'}{2}\right)\left[\frac{9}{5}\left(1+\frac{\alpha\beta}{2}\right) + \beta\left(1 + \frac{5}{6}\frac{c_V^r}{k}\alpha + \frac{5}{6}\frac{c_V^v}{k}\alpha'\right)\right]}{\Delta_0} + \right.$$

$$\left. + \frac{\frac{5}{4}\frac{c_V^v}{k}\alpha'\alpha'\beta'\left[\beta'\left(1+\frac{\alpha\beta}{2}\right) - \beta\left(1+\frac{\alpha'\beta'}{2}\right)\right]}{\Delta_0\left(1+\frac{\alpha'\beta'}{2}\right)}\right\}\frac{1}{R^2} + \cdots; \tag{20}$$

$$S_T^{(t)} = \frac{1}{2}\frac{m\lambda^t}{k\eta}\frac{1}{R} - \frac{1}{2\sqrt{\pi}}\frac{m\lambda^t}{k\eta}\left[\frac{\frac{9}{5}\left(1+\frac{\alpha\beta}{2}\right)\left(1+\frac{\alpha'\beta'}{2}\right)}{\Delta_0} + \right.$$

$$\left. + \frac{\frac{\alpha\beta}{3}\left(1+\frac{\alpha'\beta'}{2}\right)\frac{m\lambda^r}{k\eta} + \frac{\alpha'\beta'}{3}\left(1+\frac{\alpha\beta}{2}\right)\frac{m\lambda^v}{k\eta}}{\Delta_1}\right]\frac{1}{R^2} + \cdots; \tag{21}$$

$$S_T^{(r)} = \frac{1}{2}\frac{m\lambda^r}{k\eta}\frac{1}{R} - \frac{1}{2\sqrt{\pi}}\frac{m\lambda^r}{k\eta}\left\{\frac{\left[\left(1+\frac{5}{6}\frac{c_V^r}{k}\alpha\right)\left(1+\frac{\alpha'\beta'}{2}\right) + \frac{5}{6}\frac{c_V^v}{k}\alpha'\right]\beta}{\Delta_0} + \right.$$

$$\left. + \frac{\alpha\left[\frac{5}{12}\alpha'\beta'\frac{m\lambda^v}{k\eta} + \frac{3}{5}\left(1+\frac{\alpha'\beta'}{2}\right)\frac{m\lambda^t}{k\eta}\right]}{\Delta_2}\right\}\frac{1}{R^2} + \cdots, \tag{22}$$

where

$$\Delta_0 = 1 + \frac{\alpha}{2}\left(\frac{5}{3}\frac{c_V^r}{k} + \beta\right)\left(1+\frac{\alpha'\beta'}{2}\right) + \frac{\alpha'}{2}\left(\frac{5}{3}\frac{c_V^v}{k} + \beta'\right)\left(1+\frac{\alpha\beta}{2}\right) - \frac{1}{4}\alpha\alpha'\beta\beta';$$

$$\Delta_1 = 1 + \frac{\alpha\beta}{2}\left(1+\frac{2}{3}\frac{c_V^r}{k}\right)\left(1+\frac{\alpha'\beta'}{2}\right) + \frac{\alpha'\beta'}{2}\left(1+\frac{2}{3}\frac{c_V^v}{k}\right)\left(1+\frac{\alpha\beta}{2}\right) - \frac{1}{4}\alpha\alpha'\beta\beta';$$

$$\Delta_2 = 1 + \frac{5}{4}\alpha\left(1+\frac{2}{3}\frac{c_V^r}{k}\right)\left(1+\frac{\alpha'\beta'}{2}\right) + \frac{5}{6}\frac{c_V^v}{k}\alpha'\left(1+\frac{\alpha\beta'}{2}\right) + \frac{\alpha'\beta'}{2}.$$

The asymptotic expressions for $S_P^{(v)}$ and $S_T^{(v)}$ are obtained, respectively, from the expressions for $S_P^{(r)}$ and $S_T^{(r)}$ by replacing the index r by v and the parameters α and β by α' and β'.

In conditions close to the free-molecular case, Eq. (16) for the fluxes G_P, G_T, $S_P^{(t)}$, $S_P^{(t)}$ corresponds to the case of a monoatomic gas [9]. The internal components $S_P^{(r)}$, $S_P^{(v)}$

of the heat flux due to the pressure gradient are zero in this case, as a result of the absence of the only factor which causes them: inelastic collision between molecules.

Equations (17)-(22), which, with the exception of Eq. (17), are obtained here for the first time, describe the heat and mass transfer of a multiatomic gas in a capillary when $R \gg 1$, in the case where the basis role is played by intermolecular collisions. If the vibrational degrees of freedom of the molecule are not excited, the first terms for G_P, G_T, and S_T coincide with those given in [1]; the second terms in the expansions ($\sim R^{-2}$) in Eqs. (18), (21), and (22) show that the thermal creep and the total heat flux due to the temperature gradient have a complex dependence both on f and on f^{tr}. This result does not agree with the conclusions of [1].

Numerical calculations of the macroscopic quantities are performed with an accuracy of no less than 0.1% for any value of R ($0.01 \leqslant R \leqslant 30$). The values of α, α', β, β' are chosen on the basis of experiment. The value of α varies from zero (slow energy transfer between the translational and rotational degrees of freedom of the molecules, $\tau_\eta \ll \tau_{rr}$) to 1.2 (easy energy transfer, $\tau_\eta \sim \tau_{rr}$) [4]. Since in the scale of the mean free path of the molecules the vibrational relaxation is a very slow process (the vibrational collisional numbers are of the order of 10^3-10^7 [10]), the parameter α' is chosen in the interval [0; 0.001]. The choice made for $\beta = \rho D_{rr}/\eta$ and $\beta' = \rho D_{vv}/\eta$ ($\rho = mn$) is $\beta \approx \beta' \approx 1.32$, which is valid for a wide temperature range for nonpolar molecules [4, 10, 11].

In the absence of inelastic collisions with $\alpha = \alpha' = 0$ (the Eucken approximation), the thermal creep G_T and translational components of the heat fluxes $S_P^{(t)}$, $S_T^{(t)}$ are no different from the results for a monoatomic gas [9], while the internal components $S_P^{(r)}$, $S_P^{(v)}$ of the heat flux are zero. Hence, the internal degrees of freedom of the molecules only make a contribution to these fluxes in the presence of inelastic collisions. The internal components $S_T^{(r)}$, $S_T^{(v)}$ of the heat flux due to the temperature gradient are the result both of inelastic collisions and of diffusional transfer of rotationally and vibrationally excited molecules, respectively.

Numerical estimates of the contribution of internal degrees of freedom of the molecules at various values of R may be given here. The Poiseuille flux G_P depends very weakly on the internal degrees of freedom of the molecules: their greatest contribution is 1.5% when $R = 1$, $\alpha = 1.2$ for a diatomic gas with rotational degrees of freedom ($c_V^r/k = 1$). The Poiseuille flux is reduced here.

The relative contribution of rotational degrees of freedom of diatomic molecules to the thermal creep G_T at various values of R is shown in Fig. 1a. With increases in R, the thermal creep decreases, and is zero in the hydrodynamic limit. The relative contribution of internal degrees of freedom increases with increase in R. Thus, in viscous conditions with slip ($R = 30$), the decrease in G_T in comparison with the results for a monoatomic gas $G_T^{(0)}$ reaches 16.5% with increase in α from 0 to 1.2. Decrease in the thermal creep is due to the conversion of some of the translational energy of the molecules to internal energy in inelastic collisions.

In Figs. 1b and 2a, the translational $S_P^{(t)}$, rotational $S_P^{(r)}$, and vibrational $S_P^{(v)}$ components of the heat flux due to the pressure gradient are shown as a function of the rarefaction parameter R and the parameter α for a diatomic gas. It follows from Fig. 1b that, when $R \gg 1$, the decrease in the translational component of the isothermal heat flux in comparison with the results for a monoatomic gas $S_P^{(0)}$ amounts to 35% when $\alpha = 1.2$.

The isothermal heat fluxes $S_P^{(t)}$, $S_P^{(r)}$, $S_P^{(v)}$ are purely kinetic phenomena occurring only in a rarefied gas. In the limit of a continuous medium, they do not exist (Fig. 2a). In almost free-molecular conditions, as in Eq. (16), the heat transfer is due solely to translational motion of the molecules. This means that, in intermediate conditions, the fluxes $S_P^{(r)}$, $S_P^{(v)}$ should have a maximum (Fig. 2a). It is evident that, with increase in α at fixed R, $S_P^{(v)}$ decreases; this indicates a dependence of the vibrational component of the isothermal heat flux on the proportion of translational—rotational transitions in intermolecular collisions.

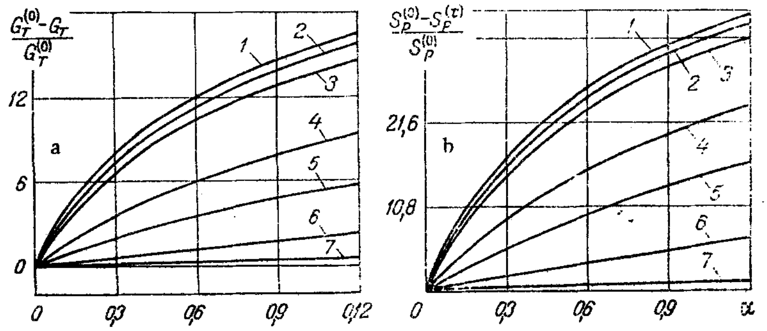

Fig. 1. Relative contribution of inelastic intermolecular collisions to the thermal creep G_T, % (a), and translational components of the heat flux $S_P^{(t)}$, % (b), for a diatomic gas ($c_V^r/k = 1$) when R = 30 (1), 10 (2), 5 (3), 1 (4), 0.4 (5), 0.1 (6), 0.01 (7).

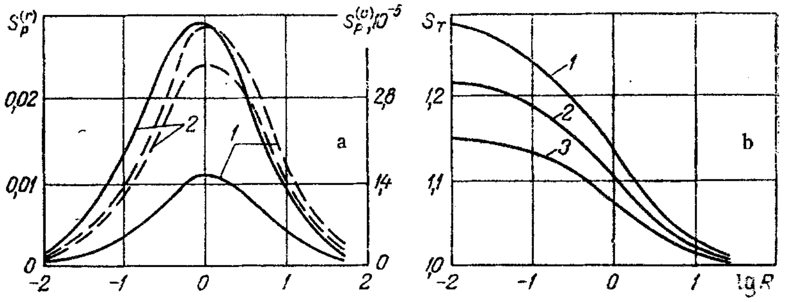

Fig. 2. Internal components of the heat fluxes $S_P^{(r)}$ and $S_P^{(v)}$ (a) with $\alpha = 0.3$ (1) and 1.2 (2) and the total heat flux due to the temperature gradient (b) for a diatomic gas ($c_V^r/k = c_V^v/k = 1$) as a function of the rarefaction parameter R.

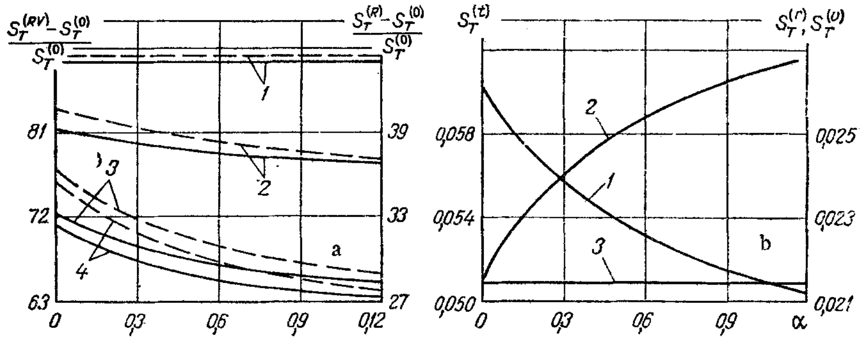

Fig. 3. The contribution of inelastic intermolecular collisions to the total heat flux due to the temperature gradient (a) for a diatomic gas with rotational-vibrational degrees of freedom of the molecules $S_T^{(RV)}$, %, $c_V^r/k = c_V^v/k = 1$ (continuous curves), with purely rotational degrees of freedom $S_T^{(R)}$, %, $c_V^r/k = 1$ (dashed curves) when R = 0.01 (a), 1 (2), 10 (3), and 30 (4), and to each of the components of the heat flux (b): 1) $S_T^{(t)}$; 2) $S_T^{(r)}$; 3) $S_T^{(v)}$ (R = 30).

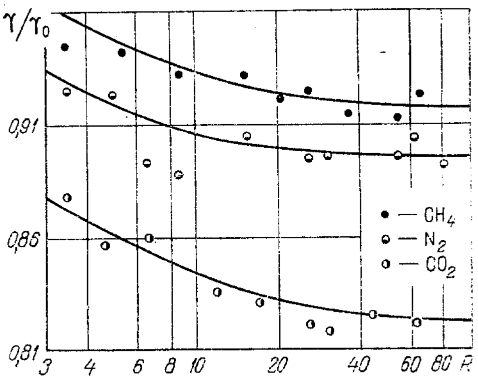

Fig. 4. Ratio of γ for the sample gas to γ_0 for a monoatomic gas as a function of the rarefaction parameter R.

TABLE 1. Experimental Values of the Translational Eucken Factor f^{tr}, the Proportion of Inelastic Collisions α, and the Rotational Collisional Number Z_r

Gas	f^{tr}	α	Z_r
N_2	2,24±0,01	0,437±0,028	2,91±0,19
CO_2	2,05±0,02	0,547±0,054	2,33±0,23
CH_4	2,29±0,02	0,172±0,023	7,39±0,96
Kr	2,53±0,01	0	∞

The total heat fluxes for a diatomic gas with vibrational—rotational (curve 1) and purely rotational (curve 2) degrees of freedom and a monoatomic gas (curve 3) are shown in Fig. 2b as a function of R. For each component of the flux $S_T^{(t)}$, $S_T^{(r)}$, and $S_T^{(v)}$, when $R \gg 1$, the Fourier heat-conduction law holds. In almost free-molecular conditions, the fluxes $S_T^{(r)}$ and $S_T^{(v)}$ are also nonzero in Eq. (16), since they are due to the diffusion of rotationally and vibrationally excited molecules.

The relative contribution of the internal degrees of freedom of the molecules to the total heat flux due to the temperature gradient is shown in Fig. 3 as a function of the proportion of inelastic collisions α with various values of R. It is evident that the total heat flux due to the temperature gradient depends strongly on the internal degrees of freedom of the molecules for all values of R. For a gas with rotational—vibrational degrees of freedom of the molecules, their relative contribution is 63-89%; for a gas with purely rotational degrees of freedom, the corresponding figure is 27-44%. The deviation from the result for a monoatomic gas $S_T^{(o)}$ is greatest in the limit close to free-molecular conditions ($R = 0.01$), which is explained by the great contribution of the diffusional mechanism of heat transfer in these conditions. With increase in the proportion of inelastic collisions, the total heat flux decreases (Fig. 3a). This is because the decrease in the translational component $S_T^{(t)}$ with increase in α is larger than the increase in the internal component of the heat flux $S_T^{(r)}$ (Fig. 3b).

Using Eqs. (17) and (18), the proportion of inelastic collisions α (or the rotational number Z_r [2, 4]) may be determined from a comparison of theory and experimental results for the thermomolecular pressure. These formulas have been used in the analysis of experimental data for several multiatomic gases [12] obtained for long glass capillaries with a mean temperature $T_0 \sim 283°K$ and a temperature difference $\Delta T \sim 20°K$. To eliminate an accommodational dependence of the thermal creep [12], the ratio of γ for the sample gas to γ_0 for a monoatomic gas is determined from experiment for $R \gg 1$. Krypton is chosen as the monoatomic gas, since the accommodation coefficient in krypton is close to the accommodation coefficients of the gases under investigation. As a result, values of f^{tr}, α, and the rotational number Z_r are obtained (Table 1). The results obtained for Z_r agree with existing data [13].

A comparison of theory with experiment is shown in Fig. 4. The theoretical results (continuous curves) are obtained with the values of α in Table 1. The discrepancy between the theoretical and experimental results is no more than 2% over the whole range of R investigated.

NOTATION

Kn, Knudsen number; f, f^{tr}, total and translational Eucken factors; R_0, capillary radius; m, molecular mass; k, Boltzmann's constant; n, T, numerical density and temperature of gas; v_i, i-th component of the molecular velocity; h_{ij}, perturbation function; $E_i^{(r)}$, $E_j^{(v)}$, energy of the i-th rotational and j-th vibrational levels; $E_0^{(r)}$, $E_0^{(v)}$, equilibrium values of the rotational and vibrational energy; $P_i^{(r)}$, $P_i^{(v)}$, probability of rotational and vibrational states of energy E_i^r and E_j^v; ν, τ, logarithmic pressure and temperature gradients; T_0, mean gas temperature; R, rarefaction parameter of gas; C_V^r, C_V^v, contributions of rotational and vibrational degrees of freedom of the molecule to the specific heat at constant volume; U, macroscopic gas velocity; $q^{(t)}$, $q^{(r)}$, $q^{(v)}$, components of the heat flux density due to translational, rotational, and vibrational degrees of freedom of the molecules; P, η, pressure and dynamic viscosity of the gas; l, free path length of molecules; u_P, velocity of Poiseuille flow; u_T, rate of thermal creep; Σ, cross-sectional area of capillary; I_n, I_q, numerical and heat fluxes averaged over the channel cross section; γ, universal index characterizing the thermomolecular pressure difference; λ^t, λ^r, λ^v, thermal conductivities due to translational, rotational, and vibrational degrees of freedom of the molecules; ρ, mass density of the gas; D_{rr}, D_{vv}, diffusion coefficients of rotationally and vibrationally excited molecules among the unexcited molecules; Z_r, rotational collisional number.

LITERATURE CITED

1. S. K. Loyalka, T. S. Storvick, and S. S. Lo, "Thermal transpiration and mechanocaloric effect. 4. Flow of a polyatomic gas in a cylindrical tube," J. Chem. Phys., 76, No. 8, 4157-4170 (1982).
2. G. Ganzi and S. I. Sandler, "Determination of thermal transport properties from thermal transpiration measurements," J. Chem. Phys., 55, No. 1, 132-140 (1971).
3. P. E. Suetin, I. V. Chermyaninov, and V. G. Chernyak, "Approximating kinetic equation for weakly nonequilibrium states of polyatomic gases," Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 2, 183-187 (1982).
4. M. Ya. Alievskii, "Relaxation, sound propagation, and transfer processes in molecular gases," Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 5, 53-67 (1970).
5. B. F. Gordiets, A. I. Osipov, and K. A. Shelepin, Kinetic Processes in Gases and Molecular Lasers [in Russian], Nauka, Moscow (1980).
6. V. G. Chernyak, B. T. Porodnov, and P. E. Suetin, "Motion of a rarefied gas in long tubes with accommodating walls at arbitrary Knudsen numbers," Zh. Tekh. Fiz., 43, No. 11, 2420-2426 (1973).
7. S. R. De Groot and P. Mazur, Non-Equilibrium Thermodynamics, Elsevier (1962).
8. S. G. Mikhlin, Variational Methods in Mathematical Physics [in Russian], Nauka, Moscow (1970).
9. V. G. Chernyak, V. V. Kalinin, and P. E. Suetin, "Theory of thermomolecular pressure and the mechanocaloric effect in a cylindrical channel," Inzh.-Fiz. Zh., 37, No. 1, 91-98 (1979).
10. E. A. Mason and L. Monchick, "Heat conductivity of polyatomic and polar gases," J. Chem. Phys., 36, No. 6, 1622-1639 (1962).
11. R. C. Reed, D. M. Prausnits, and T. K. Sherwood, Properties of Gases and Liquids [Russian translation], Khimiya, Leningrad (1982).
12. B. T. Porodnov, A. N. Kulev, and F. T. Tuchvetov, "Thermal transporation in a circular capillary with a small temperature difference," J. Fluid Mech., 88, Part 4, 609-622 (1978).
13. V. M. Sudnik, "Review of theoretical and experimental work on determining the relaxation time of rotational energy in some multiatomic gases," in: Investigating Processes of Heat and Mass Transfer in Materials in Various Aggregate States [in Russian], Minsk (1977), pp. 54-65.