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NONISOTHERMAL FLOW OF A POLYATOMIC GAS IN A CHANNEL
AND THE THERMOMOLECULAR PRESSURE DIFFERENCE EFFECT

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In [1] the nonisothermal flow of a rarefied polyatomic gas in a plane channel was considered, using the method of [2-4]. One of the results of [1] was an expression for the thermomolecular pressure difference (TPD) arising at the ends of the channel for a fixed temperature difference. It is known [5-13] that measurement of the TPD for polyatomic gases can serve as an independent source of information on the characteristics of the inelastic collisions between molecules, since the effect depends upon the translational part of the thermal conductivity (λ^t), which in turn depends explicitly on the rotational and vibrational collision numbers Z_r and Z_v . This was first discussed in [5, 14], where a theoretical expression for the TPD was obtained using the "dusty-gas" model. For small Knudsen numbers the dependence of the TPD effect on λ^t also follows from a rigorous kinetic analysis of viscous and thermal slipping in a polyatomic gas [15, 16]. The use of the dusty-gas model to interpret the experimental results involves, however, a whole set of parameters resulting from the model itself (empirical constants) and from the choice of an "average" temperature of the gas in the channel [6, 17]. This is evidently the reason for the rather large scatter in the results for Z_r for several polyatomic gases, as obtained by different authors [18]. A second cause of discrepancies between the results is the use in certain papers of nonrigorous expressions for the translational Eucken factor, in which the combined effect of the rotational and vibrational degrees of freedom of the molecules is not taken into account in a sufficiently correct way.

Since measurements of the TPD effect are usually done using packets of circular cylindrical capillaries, a more reliable method of interpreting the results should be based on

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expressions obtained from a rigorous solution of the kinetic equation for nonisothermal gas flow in a capillary. This problem was solved in [11, 19] on the basis of the linearized kinetic equation with an assumed collision integral (the third-order model) and the use of numerical or variational methods. In the present paper we consider the solution of this problem using the method of [2-4], which is extended to the case of flow of a polyatomic gas with two kinds of internal degrees of freedom. The resulting analytical expressions for the kinetic coefficients of the Onsager matrix, which describe mass and heat transport in the capillary, and the corresponding expressions for the TPD effect, are valid for intermediate Knudsen numbers close to the viscous flow regime with slip ($Kn \leq 0.25$). Comparison of the theoretical and experimental dependences of the effect in this region of Knudsen numbers gives the quantity Z_r for a series of molecular gases with known coefficients of accommodation at the wall. In the case of Z_r values determined by other methods, such as ultrasonic data, a comparison of this kind can give information on the coefficients of accommodation of the gas molecules at the wall of the channel.

Calculation of the Kinetic Coefficients. We consider the slow flow of a polyatomic gas in a circular cylindrical capillary of radius R under a small pressure gradient ($k = p_0^{-1} dp/dz$) and temperature gradient ($\tau = T_0^{-1} dT/dz$). We assume that both the rotational and vibrational degrees of freedom of the gas molecules are excited.

The solution for the distribution function of the molecules is assumed to have the form [1]

$$f_{ij}(v, r, z, \varepsilon_i^r, \varepsilon_j^v) = f_{ij0} \left[1 + kz + \tau z \left(\beta v^2 - \frac{5}{2} + \varepsilon_i^r - \bar{\varepsilon}^r + \varepsilon_j^v - \bar{\varepsilon}^v \right) + \Phi_{ij}(v, r, \varepsilon_i^r, \varepsilon_j^v) \right], \quad (1)$$

$$f_{ij0} = n_0 (\beta/\pi)^{3/2} Q_r^{-1} Q_v^{-1} \exp(-\beta v^2 - \varepsilon_i^r - \varepsilon_j^v), \quad \beta = m/2k_B T_0.$$

Here the subscript 0 corresponds to the parameters of an absolute Maxwell-Boltzmann distribution; $\varepsilon_i^r = E_i^r/k_B T_0$; $\varepsilon_j^v = E_j^v/k_B T_0$; E_i^r , E_j^v are the internal energies of molecules in the i -th rotational and j -th vibrational states:

$$\bar{\varepsilon}^r = Q_r^{-1} \sum_i \varepsilon_i^r \exp(-\varepsilon_i^r), \quad \bar{\varepsilon}^v = Q_v^{-1} \sum_j \varepsilon_j^v \exp(-\varepsilon_j^v),$$

$$Q_r = \sum_i \exp(-\varepsilon_i^r), \quad Q_v = \sum_j \exp(-\varepsilon_j^v).$$

The nonequilibrium correction to the distribution function $\Phi_{ij}(v, r, \varepsilon_i^r, \varepsilon_j^v)$ satisfies the linearized kinetic equation, which for the cylindrical geometry of the problem is written as

$$v_r \frac{\partial \Phi_{ij}}{\partial r} + v_z k + v_z \tau \left(\beta v^2 - \frac{5}{2} + \varepsilon_i^r - \bar{\varepsilon}^r + \varepsilon_j^v - \bar{\varepsilon}^v \right) + \frac{v_\varphi^2}{r} \frac{\partial \Phi_{ij}}{\partial v_r} - \frac{v_r v_\varphi}{r} \frac{\partial \Phi_{ij}}{\partial v_\varphi} = \sum_{i_1 i_1'} \sum_{j_1 j_1'} \int f_{1i_1 j_1} (\Phi_{i_1' j_1'} + \Phi_{i_1 j_1'} - \Phi_{ij} - \Phi_{1i_1 j_1}) g \sigma(i_1 j_1 i_1' j_1', g, \chi, \varphi) d\Omega dv_1. \quad (2)$$

Below we use the system of moment equations following from (2), obtained in the same approximation as in [1-4], but extended to the case of two kinds of internal molecular motions (rotational and vibrational modes). Multiplication of (2) by the appropriate polynomials and then integration with respect to velocity and summation over the i and j quantum states gives

$$\frac{1}{r} \frac{\partial}{\partial r} r \pi_{rz} + p_0 k = 0; \quad (3)$$

$$\frac{\partial}{\partial r} \left(m s_{zrr} + \frac{2}{5} q_z^r + p_0 u_z \right) + \frac{m}{r} (s_{zrr} - s_{z\varphi\varphi}) = - \frac{p_0}{\eta} \pi_{rz}; \quad (4)$$

$$\frac{1}{r} \frac{\partial}{\partial r} r (M_{zrrr} + M_{zr\varphi\varphi} + M_{zrzz}) + \frac{5p_0}{m\rho_0} (k + \tau) = - \frac{4p_0}{3m\eta} \left[1 + \frac{10}{3\pi} \left(\frac{c^r}{k_B} A_r + \frac{c^v}{k_B} A_v \right) \right] q_z^r + \frac{20p_0}{3\pi m\eta} (A_r q_z^r + A_v q_z^v); \quad (5)$$

$$\frac{1}{r} \frac{\partial}{\partial r} r M_{rz}^r + p_0 \frac{c^r}{m k_B} \tau = \frac{4n_0}{3\pi\eta} \frac{c^r}{k_B} A_r q_z^t - \quad (6)$$

$$- \frac{n_0}{\eta} \left(\frac{\rho_0 D_r}{\eta} \right)^{-1} B_r q_z^r - \frac{n_0}{\eta} \frac{c^r}{k_B} \left(\frac{\rho_0 D_{rv}}{\eta} \right)^{-1} B_{rv} q_z^v;$$

$$\frac{1}{r} \frac{\partial}{\partial r} r M_{rz}^v + p_0 \frac{c^v}{k_B m} \tau = \frac{4n_0}{3\pi\eta} \frac{c^v}{k_B} A_v q_z^t - \quad (7)$$

$$- \frac{n_0}{\eta} \frac{c^v}{k_B} \left(\frac{\rho_0 D_{rv}}{\eta} \right)^{-1} B_{rv} q_z^r - \frac{n_0}{\eta} \left(\frac{\rho_0 D_v}{\eta} \right)^{-1} B_v q_z^v;$$

$$\frac{1}{r} \frac{\partial}{\partial r} r (4M_{zrrr} - M_{zr\varphi\varphi} - M_{zrzz}) - \frac{10}{r} M_{zr\varphi\varphi} = - \frac{15p_0}{2\eta} s_{zrr}; \quad (8)$$

$$\frac{1}{r} \frac{\partial}{\partial r} r (4M_{zr\varphi\varphi} - M_{zrrr} - M_{zrzz}) + \frac{10}{r} M_{zr\varphi\varphi} = - \frac{15p_0}{2\eta} s_{z\varphi\varphi}; \quad (9)$$

$$s_{zrr} + s_{z\varphi\varphi} + s_{zzz} = 0. \quad (10)$$

The moments of the distribution function in these equations are defined as in [1], extended to the case of two modes. The right-hand sides of Eqs. (3)-(7) coincide with the expressions obtained in the 21-moment approximation of [20]. It is convenient to write them in a form where the coefficients of the appropriate moments depend explicitly on the coefficient of viscosity η and the dimensionless parameters $\rho_0 D_r/\eta$, $\rho_0 D_v/\eta$, $\rho_0 D_{rv}/\eta$, where D_r , D_v , and D_{rv} are the coefficients of diffusion of internal energy. Expressions for these quantities are given in [21]. The coefficients A and B are given by

$$A_r = \frac{1}{Z_r} + \frac{c^r}{2k_B Z_{rv}}, \quad A_v = \frac{1}{Z_v} + \frac{c^v}{2k_B Z_{rv}},$$

$$B_r = 1 + \frac{2}{\pi Z_r} \left(\frac{\rho_0 D_r}{\eta} \right), \quad B_v = 1 + \frac{2}{\pi Z_v} \left(\frac{\rho_0 D_v}{\eta} \right), \quad B_{rv} = 1 + \frac{1}{\pi Z_{rv}} \left(\frac{\rho_0 D_{rv}}{\eta} \right).$$

Here $Z_i = 4\tau_i/\pi\tau_\eta$ ($i = r, v, rv$); $\tau_\eta = \eta/p_0$; τ_r and τ_v correspond to the characteristic rotational and vibrational relaxation times, while τ_{rv} is the characteristic relaxation time for collisions accompanied by both rotational and vibrational transitions (see [20]).

A solution of (3)-(10) valid far from the wall of the capillary is found by assuming that the distribution function has the usual Grad form (but with the generalization of the internal degrees of freedom of the molecules taken into account [15, 20]). Hence

$$u_z^{\text{ac}}(r) = u_z^{\text{ac}}(R) - \frac{1}{4\eta} (R^2 - r^2) \frac{dp}{dz},$$

$$\pi_{rz}^{\text{ac}}(r) = - \frac{r}{2} \frac{dp}{dz}, \quad q_z^{\text{t ac}} = - \lambda^{\text{t}} \frac{dT}{dz} + \chi^{\text{t}} \frac{dp}{dz},$$

$$q_z^{\text{rac}} = - \lambda^{\text{r}} \frac{dT}{dz} + \chi^{\text{r}} \frac{dp}{dz}, \quad q_z^{\text{vac}} = - \lambda^{\text{v}} \frac{dT}{dz} + \chi^{\text{v}} \frac{dp}{dz},$$

$$s_{zrr}^{\text{ac}} = s_{z\varphi\varphi}^{\text{ac}} = \frac{2}{5} \frac{\eta}{\rho_0 m} \frac{dp}{dz}, \quad s_{zzz}^{\text{ac}} = - 2s_{zrr}^{\text{ac}}.$$

Here

$$\lambda^{\text{t}} = \frac{15k_B}{4m} \eta \left\{ 1 - \frac{1}{\Delta} \left[\frac{10}{3\pi} b_1 b_2 - \frac{4c^r}{3\pi k_B} \left(\frac{\rho_0 D_r}{\eta} \right) b_3 \left(1 + \frac{5}{\pi} A_r \right) - \frac{4c^v}{3\pi k_B} \left(\frac{\rho_0 D_v}{\eta} \right) b_4 \left(1 + \frac{5}{\pi} A_v \right) \right] \right\};$$

$$\chi^{\text{t}} = \frac{3\eta}{2\rho_0} \left\{ 1 - \frac{10}{3\pi\Delta} \left[b_1 b_2 - \frac{2c^r}{\pi k_B} A_r \left(\frac{\rho_0 D_r}{\eta} \right) b_3 - \frac{2c^v}{\pi k_B} A_v \left(\frac{\rho_0 D_v}{\eta} \right) b_4 \right] \right\};$$

$$\lambda^{\text{r}} = \eta \frac{c^r}{m} \left(\frac{\rho_0 D_r}{\eta} \right) \left\{ 1 + \frac{1}{\Delta} \left[\frac{5}{\pi} b_3 + \left(1 + \frac{10}{3\pi} b_1 \right) (b_5 - b_2) + \frac{20c^r}{3\pi^2 k_B} \left(\frac{\rho_0 D_r}{\eta} \right) A_r b_3 + \frac{20c^v}{3\pi^2 k_B} \left(\frac{\rho_0 D_v}{\eta} \right) A_v (b_6 + b_4) \right] \right\};$$

$$\chi^{\text{r}} = \frac{2}{\pi\Delta} \frac{\eta}{\rho_0} \frac{c^r}{k_B} \left(\frac{\rho_0 D_r}{\eta} \right) b_3;$$

$$\lambda^{\text{v}} = \eta \frac{c^v}{m\Delta} \left(\frac{\rho_0 D_v}{\eta} \right) \left[\left(1 + \frac{10}{3\pi} b_1 \right) b_7 - \frac{20c^r}{3\pi^2 k_B} \left(\frac{\rho_0 D_r}{\eta} \right) A_r b_6 + \frac{5}{\pi} b_4 \right];$$

$$\begin{aligned}\chi^v &= \frac{2}{\pi\Delta} \frac{\eta}{\rho_0} \frac{c^v}{k_B} \left(\frac{\rho_0 D_v}{\eta} \right) b_4; \quad \Delta = \left(1 + \frac{10}{3\pi} b_1 \right) b_2 - \frac{20}{3\pi^2} \frac{c^r}{k_B} A_r \left(\frac{\rho_0 D_r}{\eta} \right) b_3 - \\ &\quad - \frac{20}{3\pi^2} \frac{c^v}{k_B} A_v \left(\frac{\rho_0 D_v}{\eta} \right) b_4; \quad b_1 = \frac{c^r}{k_B} A_r + \frac{c^v}{k_B} A_v; \\ b_2 &= B_r B_v - a_r a_v B_{rv}^2; \quad b_3 = A_r B_v - a_v A_v B_{rv}; \quad b_4 = B_r A_v - a_r A_r B_{rv}; \\ b_5 &= B_v - a_v B_{rv}; \quad b_6 = A_r - A_v; \quad b_7 = B_r - a_v B_{rv}; \\ a_r &= \frac{c^r}{k_B} \frac{D_r}{D_{rv}}; \quad a_v = \frac{c^v}{k_B} \frac{D_v}{D_{rv}}.\end{aligned}$$

We next calculate expressions for the heat flux and hydrodynamic velocity averaged over the cross section of the channel. It follows from the solution of (3) that the relation $\pi_{rz}(r) = -\frac{r}{2} \frac{dp}{dz}$ is valid over the entire flow region. Substitution of this expression into (4), integration of the resulting expression with respect to r , and calculation of the average over the cross section of the capillary gives

$$\frac{m}{2} (\langle s_{zrr} \rangle + \langle s_{z\varphi\varphi} \rangle) + \frac{2}{5} \langle q_z^r \rangle + p_0 \langle u_z \rangle = L_1, \quad (11)$$

$$L_1 = m s_{zrr}(R) + \frac{2}{5} q_z^r(R) + p_0 u_z(R) - \frac{p_0 R^2}{8\eta} \frac{dp}{dz}, \quad \langle Q \rangle = \frac{2}{R^2} \int_0^R Q(r) r dr.$$

Averaging (5)-(9) over the cross section of the capillary, we have

$$\begin{aligned}-\frac{4p_0}{3m\eta} \left(1 + \frac{10}{3\pi} b_1 \right) \langle q_z^r \rangle + \frac{20p_0}{3\pi m\eta} A_r \langle q_z^r \rangle + \frac{20p_0}{3\pi m\eta} A_v \langle q_z^v \rangle &= L_2, \\ \frac{4n_0}{3\pi\eta} \frac{c^r}{k_B} A_r \langle q_z^r \rangle - \frac{n_0}{\eta} \left(\frac{\rho_0 D_r}{\eta} \right)^{-1} B_r \langle q_z^r \rangle - \frac{n_0}{\eta} \frac{c^r}{k_B} \left(\frac{\rho_0 D_{rv}}{\eta} \right)^{-1} B_{rv} \langle q_z^v \rangle &= L_3, \\ \frac{4n_0}{3\pi\eta} \frac{c^v}{k_B} A_v \langle q_z^r \rangle - \frac{n_0}{\eta} \frac{c^v}{k_B} \left(\frac{\rho_0 D_{rv}}{\eta} \right)^{-1} B_{rv} \langle q_z^r \rangle - \frac{n_0}{\eta} \left(\frac{\rho_0 D_v}{\eta} \right)^{-1} B_v \langle q_z^v \rangle &= L_4, \\ -\frac{15p_0}{2\eta} (\langle s_{zrr} \rangle + \langle s_{z\varphi\varphi} \rangle) &= L_5,\end{aligned} \quad (12)$$

where

$$\begin{aligned}L_2 &= \frac{2}{R} [M_{zrrr}(R) + M_{zr\varphi\varphi}(R) + M_{zrzz}(R)] + \frac{5p_0^2}{m\rho_0} (k + \tau); \\ L_3 &= \frac{2}{R} M_{rz}^r(R) + p_0 \frac{c^r}{mk_B} \tau; \quad L_4 = \frac{2}{R} M_{rz}^v(R) + p_0 \frac{c^v}{mk_B} \tau; \\ L_5 &= \frac{2}{R} [3M_{zrrr}(R) + 3M_{zr\varphi\varphi}(R) - 2M_{zrzz}(R)].\end{aligned}$$

The solution (11) and (12) reduces to the results

$$\begin{aligned}\langle u_z \rangle &= \frac{1}{p_0} L_1 + \frac{m\rho_0}{5p_0^2} \chi^r L_2 + \frac{m}{p_0} \frac{k_B}{c^r} \chi^r L_3 + \frac{m}{p_0} \frac{k_B}{c^v} \chi^v L_4 + \frac{m\eta}{15p_0^2} L_5, \\ \langle q_z \rangle &= \langle q_z^r \rangle + \langle q_z^r \rangle + \langle q_z^v \rangle = -\frac{m^2 \chi^r}{5k_B p_0} L_2 - \frac{m \chi^r}{n_0 c^r} L_3 - \frac{m \chi^v}{n_0 c^v} L_4.\end{aligned} \quad (13)$$

The unknown quantities L_i on the wall of the channel are found with the help of the approximate method of Loyalka [1-4].

We introduce the dimensionless quantities $J_m^* = J_m/mJ_0 = 2\beta^{1/2} \langle u_z \rangle$, $J_q^* = J_q/k_B T_0 J_0 = 2\beta^{1/2} p_0^{-1} \langle q_z \rangle$, where J_m and J_q are the averaged mass and heat fluxes per unit cross-sectional area of the capillary, and $J_0 = n_0/2\beta^{1/2}$. Then, according to the principles of irreversible thermodynamics [22], $J_m^* = -L_{mm} kR - L_{mq} \tau R$, $J_q^* = -L_{qm} kR - L_{qq} \tau R$. General expressions for the coefficients L_{ij} follow from (13) using the explicit expressions for L_n ($n = 1-5$) and have the form

$$L_{mm} = \frac{\delta}{4} + (2 - \kappa) \left[\frac{1}{\sqrt{\pi}} + \frac{\sqrt{\pi}}{4} \frac{(2 - \kappa)}{\kappa} \right] + \frac{\kappa}{5} \left(1 + \frac{\rho_0}{\eta} \chi^r \right) \frac{1}{\delta} -$$

$$\begin{aligned}
& -\frac{\kappa}{\sqrt{\pi}} \left[\frac{4}{25} \left(\frac{\rho_0}{\eta} \chi^t + \frac{13}{6} \right) + \frac{12}{25} \left(\frac{\rho_0}{\eta} \chi^t \right)^2 + \frac{k_B}{c^r} \left(\frac{\rho_0}{\eta} \chi^r \right)^2 + \frac{k_B}{c^v} \left(\frac{\rho_0}{\eta} \chi^v \right)^2 \right] \frac{1}{\delta^2}, \\
L_{mq} = L_{qm} = & -\frac{(2+\kappa)m\lambda^t}{10k_B\eta\delta} + \frac{\kappa m \rho_0}{\sqrt{\pi} \eta^2 k_B} \left[\frac{12}{25} \lambda^t \frac{\eta}{\rho_0} \left(\frac{\rho_0}{\eta} \chi^t + \frac{1}{6} \right) + \right. \\
& \left. + \frac{k_B}{c^r} \lambda^r \chi^r + \frac{k_B}{c^v} \lambda^v \chi^v \right] \frac{1}{\delta^2}, \\
L_{qq} = & \frac{\lambda m}{\eta k_B \delta} - \frac{\kappa m^2}{\sqrt{\pi} k_B^2 \eta^2} \left[\frac{12}{25} (\lambda^t)^2 + \frac{k_B}{c^r} (\lambda^r)^2 + \frac{k_B}{c^v} (\lambda^v)^2 \right] \frac{1}{\delta^2}.
\end{aligned}$$

Here $\delta = \beta^{1/2} p_0 R / \eta$ is the reciprocal of the Knudsen number; $\lambda = \lambda^t + \lambda^r + \lambda^v$. We note that the cross coefficients L_{iV} satisfy the Onsager reciprocity relations ($L_{mq} = L_{qm}$).

The TPD Effect. The relative magnitude of the thermomolecular pressure difference Δp arising at the ends of the capillary at a fixed value of the temperature difference ΔT is given by $\gamma = (\Delta p / p_0) / (\Delta T / T_0) = -(L_{mq} / L_{mm})$.

In order to compare directly the theoretical and experimental results, it is desirable to simplify the above expressions for L_{mm} and L_{mq} by taking into account the difference in the orders of magnitude of the characteristic relaxation times for the rotational and vibrational degrees of freedom.

First of all we note that the contribution of the vibrational degrees of freedom in γ for most diatomic molecules (N_2 , O_2 , CO , and so on) at room temperature can be neglected because the vibrational heat capacity is small ($c^v/k_B \ll 1$). In addition, the condition $1 \leq Z_r \ll Z_v$ is satisfied for most diatomic and polyatomic gases over a wide temperature region. Together with Z_v^{-1} , the quantities Z_{rv}^{-1} , D_r/D_{rv} , and D_v/D_{rv} are also small, since they are determined by the rare collisions that involve simultaneous rotational and vibrational transitions [20]. In this case, even if $c^v/k_B \sim 1$, one can omit in the expressions for L_{mm} and L_{mq} terms containing χ^v and terms proportional to these small parameters, and for the same reason one can simplify the expressions for λ^t , λ^r , χ^t , χ^r which then coincide with the expressions (14) and (15) of [1], where only a single type of internal degree of freedom was considered.

Therefore, over a wide temperature region the dependence of the TPD effect on the internal state of the molecules is characterized by its dependence on the parameters c^v/k_B , Z_r , $\rho_0 D_r / \eta$, which are determined solely by the rotational degrees of freedom of the molecules.

The theoretical and experimental values of γ as a function of the reciprocal of the Knudsen number are compared in Figs. 1-5 for $\delta \geq 3$ ($Kn \leq 0.33$). Experimental results* were used on the TPD effect for the flow of a gas in circular cylindrical capillaries for small temperature differences inside the sample ($\Delta T = 20$ K at $T_1 = 273.2$ K) [23].

It is evident from Fig. 1 that the experimental data for monatomic gases is closely reproduced by the theoretical dependence for $Kn \leq 0.2$ with $\kappa = 1$ (curve 1) for Xe and $\kappa = 0.9$ (curve 2) for He. The same values of the coefficient of accommodation of tangential momentum follow from measurements of Poiseuille flow in the viscous flow regime with slip

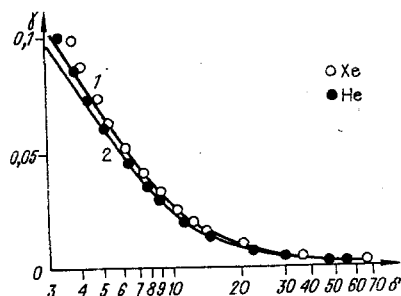


Fig. 1

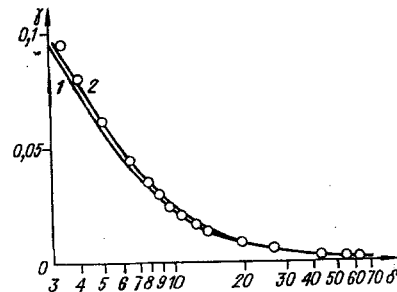


Fig. 2

*The authors thank A. N. Kulev for giving us data from the measurement of the TPD effect for a series of gases.

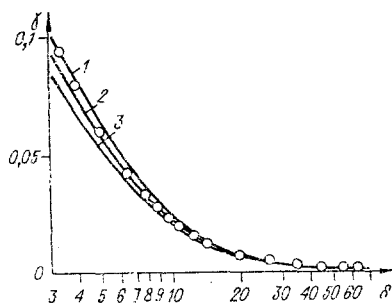


Fig. 3

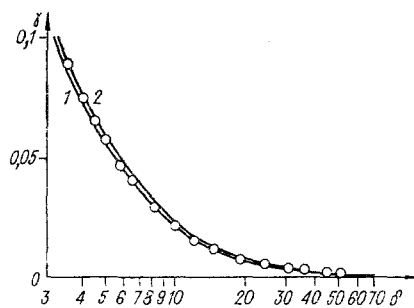


Fig. 4

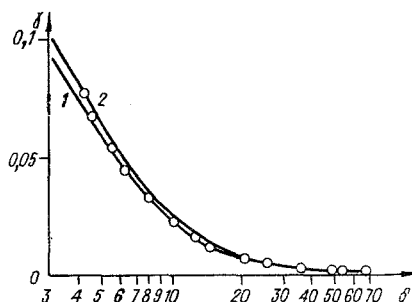


Fig. 5

($\kappa = 0.895 \pm 0.004$ for He and $\kappa = 1.010 \pm 0.040$ for Xe [24]). The deviation between the theoretical curves and the experimental values for $\text{Kn} \geq 0.2$ is obviously connected with the region of applicability of the solution obtained here.

The experimental values of γ as a function of δ are shown in Fig. 2 for molecular nitrogen. Also, theoretical curves calculated from the formulas given here are plotted for $Z_r = 3$ and 6 (curves 1 and 2) and $D_r = D_{11}$ [D_{11} is the coefficient of self-diffusion ($\rho_0 D_{11}/\eta = 1.32$)]. The value $\kappa = 0.92$ for N_2 was taken from [24]. We note the satisfactory agreement of the results in the region $Z_r = 3-6$. These values correspond closely to the data from ultrasonic measurements ($Z_r = 4.3$ [25, 26], 5.8 [27]). Taking into account the experimental error ($\sim 1.5\%$ [23]), the observed resolution of the theoretical curves for $Z_r \geq 3$ does not allow one to determine Z_r with high accuracy.

Figure 3 illustrates the possibility of using the TPD effect to determine κ for a known value of Z_r ($Z_r = 4.3$) for the case of nitrogen. It is evident that the resolution of the curves in the dependence on κ is more noticeable in this case (curves 1-3 correspond to $\kappa = 1, 0.9, 0.8$).

Figure 4 shows the results of a comparison for carbon dioxide. According to the ultrasonic data [28], the value of Z_r for CO_2 lies between about 1.3 and 2. The theoretical curves shown in Fig. 4 were constructed for $Z_r = 1.5$ and 2 (curves 1 and 2, respectively). As follows from [29], when $Z_r \leq 2.5$ it is necessary to take into account that $D_r \neq D_{11}$ and, therefore, in the calculation of γ the ratio D_r/D_{11} was calculated with the help of the approximate equation [29]: $D_r/D_{11} = 1 + 0.27Z_r^{-1} - 0.44Z_r^{-2} - 0.90Z_r^{-3}$.

Satisfactory agreement between the theoretical and experimental values takes place for $\kappa = 1.0$ in the case $Z_v = 1.5$ [24].

The results for methane are shown in Fig. 5. The ultrasonic measurements give $Z_r = 10.0$ [27]. The theoretical curves were constructed for $\kappa = 0.9$ (curve 1) and 1 (curve 2) for $Z_r = 10$. The comparison shows that there is satisfactory agreement between the experimental data and the theoretical curve for $\kappa = 0.9$.

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