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WEAK EVAPORATION OR CONDENSATION PROCESS ON A FLAT SURFACE WITH EXCITATION OF THE INNER DEGREES OF FREEDOM OF MOLECULES TAKEN INTO ACCOUNT

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The evaporation (condensation) rates and temperature jump are calculated in a vapor in contact with its intrinsic condensed phase. The contribution of the vapor molecule inner degrees of freedom is analyzed.

The solution of the problem of the Knudsen layer for a monatomic gas has been obtained in many papers. Investigation of the influence of the internal degrees of freedom of the molecules on the magnitude of the temperature jump, and if there is an evaporation (condensation) process, then on the magnitude of the evaporation rate is of interest. Expressions have been obtained in [1] for the density jumps, the tranlational—rotational and vibrational temperatures on a flat impermeable surface. Here the possible nonequilibrium of the molecule rotational degrees of freedom in the Knudsen layer is not taken into account. The temperature jump and temperature distribution near the wall in a monatomic gas are calculated in [2]. A model kinetic equation of Morse type [3] is used, in which the collision integral is replaced by two terms of relaxation type that model the elastic and inelastic collisions, respectively. The results of numerical computations are presented in the form of tables. In addition to the temperature jump in [4], a weak evaporation (condensation) process is considered with excitation of the molecule rotational and vibrational degrees of freedom taken into account. A numerical result is obtained for a diatomic gas with rotational degrees of freedom. Exactly as in [2], all the computations were performed on the basis of the model Morse equation [3]. This equation, which is one of the first for a gas with internal degrees of freedom, does not contain the necessary set of relaxation times and does not yield a correct description of all the distribution function moments of physical importance.

The purpose of this paper is to obtain analytical expressions for the evaporation rate and the temperature jump of a polyatomic gas with slow evaporation and condensation processes on a plane interphasal interface taken into account. Excitation of both the rotational and the vibrational degrees of freedom of the molecules are here taken into account. A model third-order kinetic equation [5] is used to solve the problem, which permits obtaining exact equations for all moments of the distribution function that have physical meaning, and as-

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sures accurate results for the passage to the hydrodynamic limit. The possibility of arbitrary accommodation of the translational, rotational, and vibrational energies of the molecules being reflected from the interphasal surface is taken into account in the boundary conditions for the distribution function.

Let the phase interface agree with the x = 0 plane, where the gas occupies the half space x > 0. A temperature tradient normal to the plane x = 0 is maintained in the vapor, and transport of the substance (evaporation and condensation), characterized by the mean mass rate U, holds. Evaporation (condensation) is assumed slow so that $(m/2\,kT_s)^{1/2}U \ll 1$. In this case the following problem linearization conditions are valid:

$$n = n_s(1+\nu_*),\ T = T_s(1+\tau_*),\ T^t = T_s(1+\tau_*^t),\ T^r = T_s(1+\tau_*^r),$$
$$T^v = T_s(1+\tau_*^v),\ \nu_*,\ \tau_*,\ \tau_*^t,\ \tau_*^r,\ \tau_*^v \ll 1. \tag{1}$$

Here T is understood to be the total temperature defined as $c_V T = \frac{3}{2}kT^t + c_V^r T^r + c_V^v T^v$.

It is assumed that the gas state on the upper boundary of the Knudsen layer is described by a Chapman—Enskog distribution function. It is hence assumed that far from the interphasal boundary the translational T^t, rotational T^r, and vibrational T^v temperatures are mutually equal; their distinction is taken into account only in the Knudsen layer, and is given a foundation by the different accommodations of each kind of energy. The total distribution function for molecules in the i-th rotational and j-th vibrational states is sought in the form of a perturbed Chapman—Enskog distribution

$$f_{ij} = P_i^r(T^r)\,P_j^v(T^v)\,f_0(x, V^2)\,[1 + \Phi_1 + h_{ij}(x, \mathbf{V})], \tag{2}$$

where

$$f_0(x, V^2) = n(x)\left[\frac{m}{2\pi kT^t(x)}\right]^{3/2}\exp\left[-\frac{mV^2}{2kT^t(x)}\right],$$
$$P_\beta^\alpha(T^\alpha) = \frac{\exp[-E_\beta^\alpha/kT^\alpha(x)]}{\sum\limits_\beta \exp[-E_\beta^\alpha/kT^\alpha(x)]},\quad \alpha = r,\ v;\ \beta = i,\ j.$$

The first-order correction to the Chapman—Enskog function is written in the form

$$\Phi_1 = -\frac{|\nabla T|}{p_s}\left(\frac{m}{2kT_s}\right)^{1/2} 2c_x\left[\frac{2}{5}\lambda^t(c^2 - 5/2) + \frac{k}{c_V^r}\lambda^r(\varepsilon_i^r - \langle\varepsilon^r\rangle) + \frac{k}{c_V^v}\lambda^v(\varepsilon_j^v - \langle\varepsilon^v\rangle)\right],$$
$$\mathbf{c} = \left(\frac{m}{2kT_s}\right)^{1/2}\mathbf{v},\ \varepsilon_i^r = E_i^r/kT_s,\ \langle\varepsilon^r\rangle = E_0^r/kT_s, \tag{3}$$

where the angular brackets denote taking the average over the internal states of the molecules.

Selection of the distribution function in the form (2) is convenient in that the desired perturbation function h_{ij} on the outer boundary of the Knudsen layer vanishes.

Since collisions accompanying transitions in both the rotational and vibrational spectra are simultaneously quite rare, we will therefore neglect them. Then taking into account (2), the model kinetic equation [5] for the perturbation function h_{ij} is written in dimensionless form:

$$c_x\frac{\partial h_{ij}}{\partial y} = \nu L + \nu_{ij}(1 - L) + \left(A_1\tau^t + \frac{2}{3}\alpha\frac{c_V^r}{k}\tau^r + \frac{2}{3}\alpha'\frac{c_V^v}{k}\tau^v\right)(c^2 - 3/2) +$$
$$+ [\tau^r(L - \alpha) + \alpha\tau^t](\varepsilon_i^r - \langle\varepsilon^r\rangle) + [\tau^v(L - \alpha') + \alpha'\tau^t](\varepsilon_j^v - \langle\varepsilon^v\rangle) +$$
$$+ \frac{4}{15}c_x(c^2 - 5/2)(\tau_0 R_1 + Z_1) + c_x(\varepsilon_i^r - \langle\varepsilon^r\rangle)(\tau_0 R_2 + Z_2) + c_x(\varepsilon_j^v - \langle\varepsilon^v\rangle)(\tau_0 R_3 + Z_3) - h_{ij}. \tag{4}$$

Here

$$R_1 = \left(1 + \frac{5}{6}\frac{c_V^r}{k}\alpha + \frac{5}{6}\frac{c_V^v}{k}\alpha'\right)\frac{m\lambda^t}{k\eta} - \frac{5}{4}\alpha\frac{m\lambda^r}{k\eta} - \frac{5}{4}\alpha'\frac{m\lambda^v}{k\eta} - \frac{15}{4},$$
$$R_2 = \frac{k}{c_V^r}\left(\frac{1}{\beta} + \frac{\alpha}{2}\right)\frac{m\lambda^r}{k\eta} - \frac{\alpha}{3}\frac{m\lambda^t}{k\eta} - 1,\quad R_3 = \frac{k}{c_V^v}\left(\frac{1}{\beta'} + \frac{\alpha'}{2}\right)\frac{m\lambda^v}{k\eta} - \frac{\alpha'}{3}\frac{m\lambda^t}{k\eta} - 1,$$

$$Z_1 = \left(1 - \frac{5}{3}\frac{c_V^r}{k}\alpha - \frac{5}{3}\frac{c_V^v}{k}\alpha'\right) S^t + 5/2\alpha S^r + 5/2\alpha' S^v,$$

$$Z_2 = 2\left[\frac{k}{c_V^r}\left(1 - \frac{1}{\beta} - \frac{\alpha}{2}\right) S^r + \frac{\alpha}{3} S^t\right],\ Z_3 = 2\left[\frac{k}{c_V^v}\left(1 - \frac{1}{\beta'} - \frac{\alpha'}{2}\right) S^v + \frac{\alpha'}{3} S^t\right],$$

$$A_1 = 1 - \frac{2}{3}\frac{c_V^r}{k}\alpha - \frac{2}{3}\frac{c_V^v}{k}\alpha',\ L = \frac{\pi}{4}(\alpha + \alpha'),\ \ y = x\frac{p_s}{\eta}\left(\frac{m}{2kT_s}\right)^{1/2},$$

$$\tau_0 = \frac{|\nabla T|}{T_s}\frac{\eta}{p_s}\left(\frac{2kT_s}{m}\right)^{1/2},\ \alpha = \frac{\tau_\eta}{\tau_{rr}},\ \alpha' = \frac{\tau_\eta}{\tau_{vv}},\ \beta = \frac{\tau_{Drr}}{\tau_\eta},$$

$$\beta' = \frac{\tau_{Dvv}}{\tau_\eta},\quad \tau_\eta = \frac{\eta}{p_s},$$

and the relaxation times τ_η, τ_{rr}, τ_{vv}, τ_{Drr}, τ_{Dvv} for a given intermolecular interaction potential can be calculated from formulas presented in [6], and their physical meaning and relationship to the transport coefficients are discussed in detail in this same paper.

The dimensionless quantities ν, ν_{ij}, τ^t, τ^r, τ^v, S^t, S^r, S^v in [4] that characterizes the relative deviation of the macroscopic parameters in the Knudsen layer from their values in the Navier–Stokes domain are determined as follows

$$\nu_* = -x\frac{|\nabla T|}{T_s} + \nu,\ \tau_*^l = x\frac{|\nabla T|}{T_s} + \tau^l, \tag{5}$$

$$Q^l = \left(\frac{m}{2kT_s}\right)^{1/2}\frac{q^l}{p_s} = -\left(\frac{m}{2kT_s}\right)^{1/2}\frac{|\nabla T|}{p_s}\lambda^l + S^l,\ l = t,\ r,\ v;$$

$$\mathbf{A} = \pi^{-3/2}\sum_{ij} P_i^r P_j^v \int \exp(-c^2)\,\mathbf{B} h_{ij} d\mathbf{c},\ \mathbf{A} = (A_n) = (\nu,\ \tau^t,\ \tau^r,\ \tau^v,\ S^t,\ S^r,\ S^v),$$

$$\mathbf{B} = (B_n) = [1,\ 2/3c^2 - 1,\ \varepsilon_i^r(\langle\varepsilon^r\rangle)^{-1} - 1,\ \ \varepsilon_j^v(\langle\varepsilon^v\rangle)^{-1} - 1,\ \ \mathbf{c}(c^2 - 5/2),$$
$$\mathbf{c}(\varepsilon_i^r - \langle\varepsilon^r\rangle),\ \mathbf{c}(\varepsilon_j^v - \langle\varepsilon^v\rangle)];$$

$\nu_{ij} = \pi^{-3/2}\int h_{ij}\exp(-c^2)d\mathbf{c}$ is the relative deviation of the numerical density of the molecules in the states i, j from the equilibrium value, q^t, q^r, q^v are the thermal flux density vector components due to the translational, rotational, and vibrational degrees of freedom of the molecules, respectively.

We take as boundary condition that the fraction α_m of molecules incident on the condensed phase surface is absorbed by it, while the fraction $(1 - \alpha_m)$ is reflected diffusely with a Maxwell velocity distribution and Boltzmann rotational and vibrational energy distributions with the temperatures T_r^t, T_r^r, T_r^v, respectively. The reflected molecules can here experience arbitrary accommodation of the translational, rotational, and vibrational energies.

We write the distribution function for the molecules leaving the surface in the following form

$$f_{ij}^+(x = 0,\ v_x > 0) = \alpha_m f_{ij}^s + (1 - \alpha_m) f_{ij}^r, \tag{6}$$

$$f_{ij}^s = P_i^r(T_s) P_j^v(T_s) n_s \left(\frac{m}{2\pi kT_s}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT_s}\right),$$

$$f_{ij}^r = P_i^r(T_r^r) P_j^v(T_r^v) n_r \left(\frac{m}{2\pi kT_r^t}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT_r^t}\right).$$

Under weak evaporation (condensation) conditions it is possible to set

$$n_r = n_s(1 + \nu_r),\ T_r^l = T_s(1 + \tau_r^l),\ l = t,\ r,\ v. \tag{7}$$

The unknown parameters ν_r, τ_r^t, τ_r^r, τ_r^v can be expressed in terms of the evaporation coefficient α_m, the accommodation coefficients of the translational α_E^t, rotational α_E^r, and vibrational α_E^v energies in conformity with the following relationship:

$$|N^+| = \alpha_m|N_s| + (1 - \alpha_m)|N^-|, \tag{8}$$

$$\alpha_E^l = \frac{(1-\alpha_m)\,|\mathbf{I}_{El}^-| - |\mathbf{I}_{El}^r|}{(1-\alpha_m)\,|\mathbf{I}_{El}^-| - |\mathbf{I}_{El}^w|}, \quad l = t,\ r,\ v. \tag{9}$$

Here $|N^{\mp}|$ is, respectively, the incident and the emitted vapor molecule flux from the interphasal surface, $|N_S|$ is the molecule flux from the surface in the case of thermal equilibrium between the vapor and its condensed phase, $|\mathbf{I}_{El}^-|$ is the energy flux of the translational, rotational, and vibrational degrees of freedom of molecules incident on the surface, $|\mathbf{I}_{El}^r|$ is the energy flux for molecules reflected by the surface, and $|\mathbf{I}_{El}^w|$ are the reflected molecules energy fluxes under the assumption that the translational, rotational, and vibrational temperatures equal to the surface temperature T_S.

Taking (7) into account after linearization, the boundary condition (6) for the perturbation function becomes

$$\begin{aligned} h_{ij}^+(0,\ c_x) = {} & (1-\alpha_m)\,[\nu_r + (c^2 - 3/2)\,\tau_r^t + (\varepsilon_i^r - \langle \varepsilon^r \rangle)\,\tau_r^r + (\varepsilon_j^v - \langle \varepsilon^v \rangle)\tau_r^v] + \\ & + \tau_0 c_x \left[\frac{2}{5}\frac{m\lambda^t}{k\eta}(c^2 - 5/2) + \frac{k}{c_V^r}\frac{m\lambda^r}{k\eta}(\varepsilon_i^r - \langle \varepsilon^r \rangle) + \frac{k}{c_V^v}\frac{m\lambda^v}{k\eta}(\varepsilon_j^v - \langle \varepsilon^v \rangle)\right]. \end{aligned} \tag{10}$$

Representing (4) in integral form with the boundary condition (10) taken into account, a system of integral-moment equations for the quantities $\nu(y)$, $\tau(y)$, $S^r(y)$, $S^v(y)$ can be obtained by means of the definitions (1) and (5):

$$\begin{aligned} \sqrt{\pi}\,\nu = {} & (1-\alpha_m)\,[\nu_r J_0 + \tau_r^t (J_2 - 1/2J_0)] - 2u_x J_1 + \frac{2}{5}\tau_0\left(\frac{m\lambda^t}{k\eta} - \frac{2}{3}R_1\right) \times \\ & \times (J_3 - 3/2J_1) + \int_0^\infty \left\{\nu J_{-1} + \left[\tau + \left(\frac{k}{c_V}\frac{1}{\alpha} - \frac{2}{3}\right)\frac{\partial S^r}{\partial y'} + \left(\frac{k}{c_V}\frac{1}{\alpha'} - \right.\right.\right. \\ & \left.\left.\left. - \frac{2}{3}\right)\frac{\partial S^v}{\partial y'}\right](J_1 - 1/2J_{-1}) + \frac{4}{15}Z_1 (J_2 - 3/2J_0)\,\mathrm{sgn}\,(y - y')\right\} dy'. \end{aligned} \tag{11}$$

$$\begin{aligned} \sqrt{\pi}\,\frac{c_V}{k}\,\tau = {} & (1-\alpha_m)\left[\nu_r (J_2 - 1/2J_0) + \tau_r^t\left(J_4 - J_2 + \frac{5}{4}J_0\right) + \left(\frac{c_V^r}{k}\tau_r^r + \right.\right. \\ & \left.\left. + \frac{c_V^v}{k}\tau_r^v\right) J_0\right] - 2u_x (J_3 - 1/2J_1) + \tau_0\left[\frac{2}{5}\left(\frac{m\lambda^t}{k\eta} - \frac{2}{3}R_1\right)\left(J_5 - 2J_3 + \right.\right. \\ & \left.\left. + \frac{7}{4}J_1\right) + \left(\frac{2}{5}R_1 + \frac{m\lambda^r}{k\eta} + \frac{m\lambda^v}{k\eta}\right) J_1\right] + \int_0^\infty \left\{\nu (J_1 - 1/2J_{-1}) + \right. \\ & + \tau\left[J_3 - J_1 + \left(\frac{c_V}{k} - \frac{1}{4}\right) J_{-1}\right] + \left[\left(\frac{k}{c_V}\frac{1}{\alpha} - \frac{2}{3}\right)\frac{\partial S^r}{\partial y'} + \left(\frac{k}{c_V}\frac{1}{\alpha'} - \right.\right. \\ & \left.\left. - \frac{2}{3}\right)\frac{\partial S^v}{\partial y'}\right]\left(J_3 - J_1 - \frac{1}{4}J_{-1}\right) + \frac{4}{15}Z_1\left(J_4 - 2J_2 + \frac{7}{4}J_0\right)\mathrm{sgn}\,(y - y') + \left.\left(\frac{c_V^r}{k}Z_2 + \frac{c_V^v}{k}Z_3\right) J_0\,\mathrm{sgn}\,(y - y')\right\} dy', \end{aligned} \tag{12}$$

$$\begin{aligned} \sqrt{\pi}\,S^r = {} & \frac{c_V^r}{k}\tau_r^r (1-\alpha_m) J_1 + \tau_0 \frac{m\lambda^r}{k\eta} J_2 + \frac{c_V^r}{k}\int_0^\infty \left\{\left[\tau + \frac{k}{c_V}\left(\frac{1}{\alpha}\frac{\partial S^r}{\partial y'} + \right.\right.\right. \\ & \left.\left.\left. + \frac{1}{\alpha'}\frac{\partial S^v}{\partial y'}\right) + \frac{k}{c_V^r}\frac{\partial S^r}{\partial y'}\left(1 - \frac{1}{\alpha}\right)\right] J_0\,\mathrm{sgn}\,(y - y') + (\tau_0 R_2 + Z_2) J_1\right\} dy', \end{aligned} \tag{13}$$

$$\begin{aligned} \sqrt{\pi}\,S^v = {} & \frac{c_V^v}{k}\tau_r^v (1-\alpha_m) J_1 + \tau_0 \frac{m\lambda^v}{k\eta} J_2 + \frac{c_V^v}{k}\int_0^\infty \left\{\left[\tau + \frac{k}{c_V}\left(\frac{1}{\alpha}\frac{\partial S^r}{\partial y'} + \right.\right.\right. \\ & \left.\left.\left. + \frac{1}{\alpha'}\frac{\partial S^v}{\partial y'}\right) + \frac{k}{c_V^v}\frac{\partial S^v}{\partial y'}\left(1 - \frac{1}{\alpha'}\right)\right] J_0\,\mathrm{sgn}\,(y - y') + (\tau_0 R_3 + Z_3) J_1\right\} dy', \end{aligned}$$

$$J_n(t) = \int_0^\infty c^n \exp\left(-c^2 - \frac{t}{c}\right) dc, \tag{14}$$

The argument of the functions J_n in the integrands is $t = |y - y'|$, while in the free terms $t = y$.

Relationships connecting the quantities τ^t, τ^r, τ^v and $\frac{\partial S^t}{\partial y}$, $\frac{\partial S^r}{\partial y}$, $\frac{\partial S^v}{\partial y}$ were used in (11)-(14). These relationships can be obtained by integrating (4) in velocity space with the weights

$$(c^2 - 5/2)\exp(-c^2), \quad (\varepsilon_i^r - \langle \varepsilon^r \rangle)\exp(-c^2), \quad (\varepsilon_j^v - \langle \varepsilon^v \rangle)\exp(-c^2):$$

$$\frac{\partial S^t}{\partial y} = \frac{c_V^r}{k}\alpha\tau^r + \frac{c_V^v}{k}\alpha'\tau^v - \left(\frac{c_V^r}{k}\alpha + \frac{c_V^v}{k}\alpha'\right)\tau^t, \quad \frac{\partial S^r}{\partial y} = \frac{c_V^r}{k}\alpha(\tau^t - \tau^r),$$

$$\frac{\partial S^v}{\partial y} = \frac{c_V^v}{k}\alpha'(\tau^t - \tau^v). \tag{15}$$

To close the system of equations (11)-(14), four integral relationships are used that can easily be obtained from (8) and (9). For a further analysis it is convenient to introduce the functions

$$\nu(y) = \varphi(y) + \mu_1, \quad \tau(y) = \psi(y) + \mu_2, \tag{16}$$

where $\mu_1 = \lim_{y\to\infty} \nu$, $\mu_2 = \lim_{y\to\infty} \tau$ define the density and vapor temperature jumps, respectively, on the interphasal boundary.

Substitution of the relationships (16) into (11) and (12), and the subsequent double-integration of the expressions obtained with respect to y in the range (y, ∞) results in equations which take the following form when (16) is taken into account at y = 0:

$$\begin{aligned}
\frac{\sqrt{\pi}}{2}\left(\frac{c_V}{k}+1\right)\mu_1 = {} & \frac{\sqrt{\pi}}{4}(1-\alpha_m)\left[\nu_r\left(\frac{c_V}{k}+1\right) + \tau_r^t\left(\frac{c_V}{k}-3/2\right) - \right. \\
& \left. - \frac{c_V^r}{k}\tau_r^r - \frac{c_V^v}{k}\tau_r^v\right] - u_x\left(\frac{c_V}{k}+1/2\right) + \frac{\tau_0}{2}\left[\left(\frac{c_V}{k}-5/2\right)\frac{1}{5}\left(\frac{m\lambda^t}{k\eta} - \right.\right. \\
& \left.\left. \frac{2}{3}R_1\right) - \frac{3}{5}\frac{m\lambda^t}{k\eta} - \frac{m\lambda^r}{k\eta} - \frac{m\lambda^v}{k\eta}\right] - \int_0^\infty \left\{\nu\left[J_3 - \left(\frac{c_V}{k}+5/2\right)J_1\right] + \right. \\
& + \tau\left[J_5 - J_3\left(\frac{c_V}{k}+3\right) + 3/2\left(\frac{c_V}{k}+1/2\right)J_1\right] + \left[\left(\frac{k}{c_V}\frac{1}{\alpha}-\frac{2}{3}\right)\frac{\partial S^r}{\partial y'} + \right. \\
& \left. + \left(\frac{k}{c_V}\frac{1}{\alpha'}-\frac{2}{3}\right)\frac{\partial S^v}{\partial y'}\right]\left[J_5 - J_3\left(\frac{c_V}{k}+3\right) + 1/2\left(\frac{c_V}{k}+3/2\right)J_1\right] - \\
& \left. - \frac{4}{15}Z_1\left[J_6 - J_4\left(\frac{c_V}{k}+4\right) + 3/2\left(\frac{c_V}{k}+\frac{19}{6}\right)J_2 - \frac{5}{4}\sqrt{\pi}\right] - \left(\frac{c_V^r}{k}Z_2 + \frac{c_V^v}{k}Z_3\right)\left(J_2 - \frac{\sqrt{\pi}}{2}\right)\right\}dy';
\end{aligned} \tag{17}$$

$$\begin{aligned}
\frac{\sqrt{\pi}}{2}\left(\frac{c_V}{k}+1\right)\mu_2 = {} & \frac{\sqrt{\pi}}{4}(1-\alpha_m)\left(5/2\tau_r^t + \frac{c_V^r}{k}\tau_r^r + \frac{c_V^v}{k}\tau_r^v\right) - \frac{u_x}{2} + \\
& + \frac{\tau_0}{2}\left(\frac{13}{10}\frac{m\lambda^t}{k\eta} + \frac{m\lambda^r}{k\eta} + \frac{m\lambda^v}{k\eta} - \frac{7}{15}R_1\right) + \int_0^\infty \left\{\nu(J_3 - 3/2J_1) + \tau\left[J_5 - \right.\right. \\
& \left. - 2J_3 + \left(\frac{c_V}{k}+\frac{1}{4}\right)J_1\right] + \left[\left(\frac{k}{c_V}\frac{1}{\alpha}-\frac{2}{3}\right)\frac{\partial S^r}{\partial y'} + \left(\frac{k}{c_V}\frac{1}{\alpha'}-\frac{2}{3}\right) \times \right. \\
& \left. \times \frac{\partial S^v}{\partial y'}\right]\left(J_5 - 2J_3 + \frac{1}{4}J_1\right) - \frac{4}{15}Z_1\left(J_6 - 3J_4 + \frac{13}{4}J_2 - \frac{5}{4}\sqrt{\pi}\right) - \left.\left(\frac{c_V^r}{k}Z_2 + \frac{c_V^v}{k}Z_3\right)\left(J_2 - \frac{\sqrt{\pi}}{2}\right)\right\}dy'.
\end{aligned} \tag{18}$$

The argument of the functions J_n in (17) and (18) is $t = y'$.

Therefore, to calculate the density μ_1 and temperature μ_2 jumps, the functions $\nu(y)$, $\tau(y)$, $S^r(y)$, $S^v(y)$, $\nu_r(y)$, $\tau_r^t(y)$, $\tau_r^r(y)$, $\tau_r^v(y)$ must be determined from (8), (9), (11)-(14).

These equations are linear integral equations of Fredholm type, hence, the Galerkin method [7] can be used for their solution. Here the selection of the kind of trial functions for the macroscopic quantities is important. It should here be kept in mind that the profiles of the macroscopic quantities in direct proximity to the interphasal surface are described exactly by free terms of the integral-moment equations (11)-(14). Hence, the form of the trial functions should be selected by starting from the behavior of the macroscopic quantities far from the surface in the Navier–Stokes region. According to (16), the functions $\nu(y)$ and $\tau(y)$ for $y \to \infty$ tend to certain constant values. As regards the functions $S^l(y)$, where l = t, r, v, which are corrections to the translational, rotational, and vibrational components of the heat flux in the Knudsen layer, then they vanish as $y \to \infty$. Therefore, in a first approximation certain constants can be selected as trial functions for ν and τ while S^l is set equal to zero. As the solution of an analogous problem showed for a monatomic gas [8], such an approximation induces no more than a 1.5% error. The same accuracy should apparently be expected even in the case of a polyatomic gas.

Substituting the trial functions in (11) and (12) and requiring orthogonality of the expressions obtained to the corresponding basis functions, we obtain a system of algebraic equations which, together with (8) and (9), determine the functions ν and τ uniquely. Substituting them into (17) and (18) we obtain expressions for the quantities μ_1 and μ_2. The method used here is elucidated in greater detail in [8]. Consequently, the formulas for the evaporation rate U and temperature jump δT on the flat interphase boundary have the form

$$U = \left(\frac{2kT_s}{m}\right)^{1/2}\left[\varepsilon_1 \frac{\delta n}{n_s} + \delta_1 \frac{l}{T_s}\,\frac{dT(0)}{dx}\right],$$

$$\delta T = T_s\mu_2 = T_s\left[\varepsilon_2\left(\frac{m}{2kT_s}\right)^{1/2} U + \delta_2 \frac{l}{T_s}\,\frac{dT(0)}{dx}\right], \quad \varepsilon_1 = -(\varepsilon_1')^{-1}, \quad \delta_1 = \delta_1'\varepsilon_1. \tag{19}$$

The coefficients ε_1', δ_1' and ε_2, δ_2 have the form

$$\varepsilon_1' = \frac{(1-\alpha_m)}{\alpha_m} 2\sqrt{\pi} - \frac{\sqrt{\pi}}{2}\left[1 + \frac{K_1 + (1-\alpha_m)(1-\alpha_E^t)K_4 + \frac{16}{\pi}\left(\frac{c_V}{k} + 1/2\right)}{4\left(\frac{c_V}{k} + 1\right)}\right], \tag{20}$$

$$\begin{aligned}
4\left(\frac{c_V}{k} + 1\right)\delta_1' = {} & \left\{K_1\left(1 - \frac{4}{15}R\right) + \frac{8}{5\pi}\left[\left(\frac{c_V}{k} - 5/2\right)\left(1 - \frac{2}{3}R\right) - 3\right] + \right. \\
& \left. + (1-\alpha_m)\left[(1-\alpha_E^t)\left(1 - \frac{2}{3}R\right)K_4 + \frac{1}{3}(K_1 - 2)K_5\right]\right\}\frac{m\lambda^t}{k\eta} + \frac{m\lambda^r}{k\eta} \times \\
& \times \left\{K_1\left(1 + \frac{\alpha}{3}\right) + \frac{4}{\pi}\left[\frac{\alpha}{3}\left(\frac{c_V}{k} - 5/2\right) - 2\right] + (1-\alpha_m)\left[\frac{5}{6}\alpha(1-\alpha_E^t)K_4 + \right.\right. \\
& \left.\left. + (1-\alpha_E^r)(K_1 - 2)\left(1 - \frac{1}{\beta} - \frac{\alpha}{2}\right)\right]\right\} + \frac{m\lambda^v}{k\eta}\left\{K_1\left(1 + \frac{\alpha'}{3}\right) + \right. \\
& + \frac{4}{\pi}\left[\frac{\alpha'}{3}\left(\frac{c_V}{k} - 5/2\right) - 2\right] + (1-\alpha_m)\left[\frac{5}{6}\alpha'(1-\alpha_E^t)K_4 + (1-\alpha_E^v) \times \right. \\
& \left.\left. (K_1 - 2)\left(1 - \frac{1}{\beta'} - \frac{\alpha'}{2}\right)\right]\right\} + K_1 + \frac{4}{\pi}\left(\frac{c_V}{k} - 5/2\right) + \\
& + (1-\alpha_m)\left\{5/2(1-\alpha_E^t)K_4 + (K_1 - 2)\left[\frac{c_V^r}{k}(1-\alpha_E^r) + \frac{c_V^v}{k}(1-\alpha_E^v)\right]\right\},
\end{aligned} \tag{21}$$

$$\varepsilon_2 = -\frac{\sqrt{\pi}}{4\left(\frac{c_V}{k} + 1\right)}\left[(K_2 + 5/4)(1-\alpha_m)(1-\alpha_E^t) + K_2 + \frac{4}{\pi}\right], \tag{22}$$

$$\begin{aligned}
2\left(\frac{c_V}{k} + 1\right)\delta_2 = {} & \left\{K_2\left(1 - \frac{4}{15}R\right) + \frac{26}{5\pi}\left(1 - \frac{14}{39}R\right) + (1-\alpha_m) \times \right. \\
& \left. \times\left[\left(K_2 + \frac{5}{4}\right)(1-\alpha_E^t)\left(1 - \frac{2}{3}R\right) + \frac{1}{3}(K_2 + 1)K_5\right]\right\}\frac{m\lambda^t}{k\eta} + \frac{m\lambda^r}{k\eta} \times \\
& \times\left\{K_2\left(1 + \frac{\alpha}{3}\right) + \frac{4}{\pi}\left(1 + \frac{7}{12}\alpha\right) + (1-\alpha_m)\left[(K_2 + 1)(1-\alpha_E^r) \times \right.\right.
\end{aligned}$$

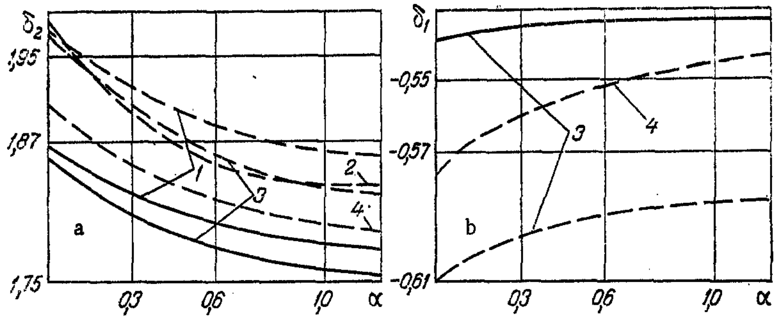

Fig. 1. Dependence of the parameters δ_2 (a) and δ_1 (b) on the quantity α for $\alpha_E^t = \alpha_E^r = \alpha_E^v = 1$: 1) [2]; 2) [1]; 3) our results; 4) [4].

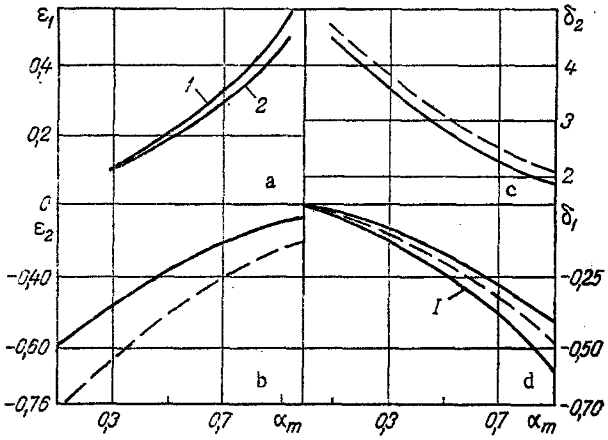

Fig. 2. Dependence of the parameters ε_1 (a) for $\alpha_E^t = \alpha_E^r = \alpha_E^v = 1$, ε_2 (b) for $\alpha_E^t = \alpha_E^r = \alpha_E^v = 0.5$, δ_2 (c) for $\alpha_E^t = \alpha_E^r = \alpha_E^v = 0.5$, $\alpha = 0.3$, δ_1 (d) for $\alpha_E^t = \alpha_E^r = \alpha_E^v = 1$, $\alpha = 0.3$ on the evaporation coefficient (I — monatomic gas).

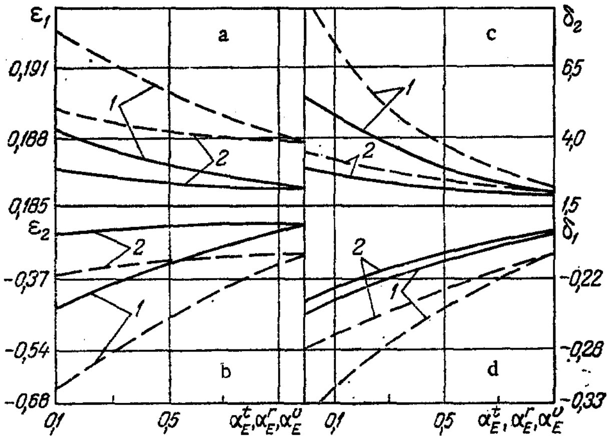

Fig. 3. Dependence of the parameters ε_1 (a) for $\alpha_m = 0.5$, ε_2 (b) for $\alpha_m = 0.5$, δ_2 (c) for $\alpha_m = 0$, $\alpha = 0.3$, δ_1 (d) for $\alpha_m = 0.5$, $\alpha = 0.3$ on the accommodation coefficients of translational, rotational, and vibrational energies.

$$\times\left(1-\frac{1}{\beta}-\frac{\alpha}{2}\right)+\frac{5}{6}\alpha\left(K_2+5/4\right)\left(1-\alpha_E^t\right)\Bigg]\Bigg\}+\frac{m\lambda^v}{k\eta}\Bigg\{K_2\left(1+\frac{\alpha'}{3}\right)+$$
$$+\frac{4}{\pi}\left(1+\frac{7}{12}\alpha'\right)+(1-\alpha_m)\Bigg[(K_2+1)(1-\alpha_E^v)\left(1-\frac{1}{\beta'}-\frac{\alpha'}{2}\right)+$$
$$+\frac{5}{6}\alpha'\left(K_2+\frac{5}{4}\right)(1-\alpha_E^t)\Bigg]\Bigg\}+K_2+\frac{7}{\pi}+(1-\alpha_m)\Bigg\{5/2\left(K_2+\frac{5}{4}\right)\times \tag{23}$$
$$(1-\alpha_E^t)+(K_2+1)\left[\frac{c_V^r}{k}(1-\alpha_E^r)+\frac{c_V^v}{k}(1-\alpha_E^v)\right]\Bigg\}.$$

Here

$$K_1=\left\{(1-\alpha_m)\left[\left(\frac{c_V}{k}-4\right)(1-\alpha_E^t)-2\frac{c_V^r}{k}(1-\alpha_E^r)-2\frac{c_V^v}{k}(1-\alpha_E^v)\right]-\left(\frac{c_V}{k}+1\right)\right\}\Big/K_3,$$
$$K_2=\left\{(1-\alpha_m)\left[5/2\,(1-\alpha_E^t)+\frac{c_V^r}{k}(1-\alpha_E^r)+\frac{c_V^v}{k}(1-\alpha_E^v)\right]+\frac{c_V}{k}+1\right\}\Big/K_3,$$
$$K_3=\frac{c_V}{k}+\frac{1}{2}-(1-\alpha_m)\left[2\,(1-\alpha_E^t)+\frac{c_V^r}{k}(1-\alpha_E^r)+\frac{c_V^v}{k}(1-\alpha_E^v)\right],$$
$$K_4=K_1+1/2\,\frac{c_V}{k}-2,$$
$$K_5=\frac{c_V^r}{k}\alpha(1-\alpha_E^r)+\frac{c_V^v}{k}\alpha'(1-\alpha_E^v),\ R=1+5/6\,\frac{c_V^r}{k}\alpha+5/6\,\frac{c_V^v}{k}\alpha'.$$

Let us consider the dependence of the evaporation rate and the temperature jump on the molecule internal degrees of freedom, on the evaporation coefficient α_m, and the accommodation coefficients of the translational α_E^t, rotational α_E^r, and vibrational α_E^v energies.

For total accommodations ($\alpha_E^t = \alpha_E^r = \alpha_E^v = 1$) the parameters $\varepsilon_{1,2}$ depend on the internal degrees of freedom only in terms of the internal specific heats. The contribution of the internal degrees of freedom to these parameters is not identical in comparison to the result for a monatomic gas [8]. Thus, if ε_1 diminishes by ∿9 and ∿6%, respectively, for a gas with rotational—vibrational and only rotational degrees of freedom, then ε_2 increases by ∿47 and ∿31%, respectively. (The magnitude of the change in the coefficients ε_1 and ε_2 in [4] is 3% and 28%, respectively in [4].) As regards the quantities $\delta_{1,2}$, then for $\alpha_E^t = \alpha_E^r = \alpha_E^v = 1$ their dependence on the internal degrees of freedom is more complex than for $\varepsilon_{1,2}$. Besides the internal specific heats, this dependence appears even in terms of the ratio of the relaxation times α, α', β, β'. The dependence of the parameters δ_1 and δ_2 on α is represented in Fig. 1. It is known [9] that for nonpolar molecules $\beta = \beta' = 1.32$; the quantity α' is selected, for simplicity, equal to zero. (The gas with rotational degrees of freedom is described by the dashed curve in the figures, and with rotational—vibrational degrees of freedom by the solid curve.) It is seen in Fig. 1b that the coefficient δ_1 increases very slightly (∿2%) as α grows. But the distinction from the result for a monatomic gas ($\delta_1 = -0.73$) reaches ∿20% for a gas with rotational and ∿27% with rotational—vibrational degrees of freedom. The dependence of δ_1 on α in [4] is rather steeper and the discrepancy for $\alpha \approx 1.2$ is ∿7%.

The parameter δ_2 is reduced as α grows, which is explained by the passage of part of the translational energy into internal for intermolecular collisions. This diminution in δ_2 for a gas with rotational degrees of freedom reaches 16% and 20% for rotational—vibrational degrees of freedom as compared to the result for a monatomic gas ($\delta_2 = 2.17$). Let us note that the results presented for δ_2 in this paper differ by not more than 3.5% from the majority of data available in the literature.

The dependence of the parameters $\varepsilon_{1,2}$ and $\delta_{1,2}$ on the evaporation coefficient α_m is represented in Fig. 2. As α_m increases, the quantities $\varepsilon_{1,2}$ grow, where the difference between the monatomic gas (curve 1) and the gas with rotational and rotational—vibrational degrees of freedom (curve 2) is insignificant for ε_1. On the other hand, the coefficients $\delta_{1,2}$ diminish as α_m grows, here the values of δ_1 are very close for small α_m both for the monatomic and polyatomic gases and are different just for $\alpha_m \approx 1$.

The accommodation dependence of the parameters $\varepsilon_{1,2}$ and $\delta_{1,2}$ is presented in Fig. 3. Curves 1 describe the dependence of these parameters on the coefficient α_E^t for $\alpha_E^r = \alpha_E^v = 1$, and curves 2 on α_E^r for $\alpha_E^t = \alpha_E^v = 1$. This same curve describes the dependence of $\varepsilon_{1,2}$ and $\delta_{1,2}$ on the accommodation coefficient of the translational energy is seen in all the graphs, while it is considerably weaker for the internal energy accommodation coefficients.

NOTATION

m, molecule mass; k, Boltzmann constant; T_s, condensed phase surface temperature; n_s, p_s, number density and pressure of the saturated vapor for T_s; T^t, T^r, T^v, T, respectively, the translational, rotational, vibrational, and total temperatures; c_V^v, c_V^r, c_V, specific heats corresponding to the vibrational and rotational degrees of molecule freedom, and the total specific heat for constant volume; n(x), number vapor density; U, evaporation rate; E_i^r, E_j^v, respectively, the energies of the i-th rotational, and the j-th vibrational levels; E_0^r, E_0^v, equilibrium values of the rotational and vibrational energies; λ^t, λ^r, λ^v, respectively, the heat conduction coefficients due to the translational rotational, and vibrational degrees of freedom; v_i, i-th component of the molecule velocity; P_i^r, P_j^v, respectively, the probability of the rotational E_i^r and E_j^v states; η, coefficient of dynamic viscosity of the gas; n_r, T_r^t, T_r^r, T_r^v, respectively, the density and the translational, rotational, and vibrational temperatures of the reflected molecules; α_m, α_E^t, α_E^r, α_E^v, respectively, the evaporation coefficient energies; δn, δT, respectively, the vapor density and temperature jumps on the interphasal boundary; l, length of the molecule mean free path.

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