

THERMODIFFUSION AND THE DIFFUSION THERMOEFFECT IN THE FLOW OF
LOW-TEMPERATURE PLASMAS

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An estimate is made of the contribution of the process of thermodiffusion and of the diffusion thermoeffect to the transport properties of low-temperature plasmas with reference to the example of the long-range trails appearing behind bodies during hypersonic re-entry into the atmosphere.

A very high accuracy of determining the transport properties of various gas mixtures is required in a number of applied problems, among which may be included those connected with the determination of the parameters of high-speed flows of low-temperature plasmas under rarefied-medium conditions. This is particularly important for hypersonic flows characterized by small Reynolds numbers, i.e., for cases when the conditions of the problem approach the limits of applicability of the hypothesis that the medium is continuous. In particular, the need arises to take into account certain cross-effects such as thermodiffusion and the diffusion thermoeffect.

In many cases thermodiffusion and the diffusion thermoeffect are effects of the second order compared to the diffusion and heat fluxes caused by the main driving forces (the gradients of the corresponding parameters). As a rule their effects are negligibly small [1-3]. Exceptions to this arise in the case of flows with large gradients of temperature and concentration $\nabla \ln T$, $\nabla \ln C_i$, which in combination with large differences in the masses or dimensions of the molecules of the individual components can lead to important contributions from these phenomena to the transport properties of the gas mixtures being considered. Such streams can include plasma flows [2-5]. Thus, for example, while in a neutral gas the value of the thermodiffusion ratio does not as a rule exceed $K_T \leq 0.1$, and for most mixtures is considerably smaller, in flows of strongly ionized plasmas it can reach $K_T \leq 0.4$ [3]. For the conditions of low-temperature plasmas this quantity takes on intermediate values. In spite of the large number of papers dealing with transport processes in feebly ionized plasmas [2-9], many of the problems connected with the phenomena of thermodiffusion and the diffusion thermoeffect have still been very little studied. This is explained by an insufficiency of information on the parameters of intermolecular interactions and by the large extent and complexity of the calculations, which are caused by the need to take into account higher approximations of the molecular-kinetic theory of gases when dealing with partially ionized gases. For example, in order to obtain acceptable accuracy in the calculation of the coefficients of thermal conductivity and thermodiffusion it is necessary to use at least the third approximation of the Chapman-Enskog method [6-9]. In particular, this is caused by the deterioration of the convergence of the Sonin polynomial series when there is a strong dependence of the electron-neutral particle collision cross-section on the energy of the electrons. In order to obtain accurate values of the transport coefficients it is then necessary to take into account several terms of the series [6]. It is for this reason that at present these coefficients have been calculated only for a limited number of the simplest mixtures and air [1-3, 9, 10].

The long-range trails arising behind bodies during hypersonic re-entry into the atmosphere can serve as an example of such flows. As a rule, such flows are far from a state of chemical equilibrium. It therefore does not appear to be possible to use for them coefficients calculated in advance even in the case of pure air trails, since these coefficients are determined for gases which are in a state of complete thermodynamic equilibrium [9, 10]. In addition, in the mathematical modeling of flows based, for example, on the Navier-Stokes, Prandtl, and other equations, difficulties arise which are often only inadequately dealt with in the current state of the development of numerical and computational

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methods. The present paper therefore gives not only an evaluation of the contribution of such cross-processes as thermodiffusion and the diffusion thermoeffect to the heat and mass fluxes in low-temperature plasmas of far hypersonic trails, but this is also carried out using the physical-mathematical model of references [6-8] which makes it possible to considerably reduce the amount of computation and permits the use of this procedure for the calculation of real gas-dynamic problems even when it is necessary to use higher approximations in the molecular-kinetic theory.

In defining the diffusion and heat fluxes we will follow references [6-8]. Here these fluxes can be calculated, making allowance for the various cross terms, without directly determining the transport coefficients. Together with the fact that terms of the order of $\varepsilon \ll 1$ are neglected, where $\varepsilon = (m_e/m_h)^{0.5}$ and m_e , m_h are the masses of the electrons and the "heavy" particles, this considerably reduces the amount of computation needed.

We will confine our attention to the third approximation of the Chapman-Enskog method for electrons and to the second approximation for the "heavy" particles, which is quite acceptable for feebly ionized air. The corresponding systems of linear equations relative to the heat flux \mathbf{J}_i and diffusion flux \mathbf{I}_i will then have the following appearance [8].

1. For the heavy particles:

$$\frac{\nabla x_i}{x_i} = \sum_{j=1}^{NH} \frac{x_j}{D_{ij}} \left(\frac{\mathbf{I}_j}{\rho_j} - \frac{\mathbf{I}_i}{\rho_i} \right) + \frac{x_e}{D_{ei}} \frac{\mathbf{I}_e}{\rho_e} - \sum_{j=1}^{NH} \frac{x_j}{D_{ij}} \frac{m_{ij}}{m} a_{ij}^{01} (\mathbf{g}_j - \mathbf{g}_i) - \frac{x_e}{D_{ei}} a_{ei}^{01} \mathbf{g}_e + \frac{x_e}{D_{ei}} a_{ei}^{02} \mathbf{f}_e - \left(1 - \frac{m_i}{m} \right) \frac{P}{nkT} \nabla \ln P + z_i e \frac{\mathbf{E}}{kT}, \quad (1)$$

$$\sum_{j=1}^{NH} \left[\frac{C_i^2}{D_{ii}} a_{ii}^{11} (1 - C_i) \delta_{ij} - \frac{C_j^2}{D_{jj}} C_j a_{jj}^{11} (1 - \delta_{ij}) + \sum_{h=1}^{NH} \frac{x_j x_h}{D_{jh}} \times \right. \\ \left. \times \left(\frac{m_{hj}}{m} \right)^2 A_{jh}^i \right] \mathbf{g}_j = \sum_{j=1}^{NH} \frac{x_j x_i}{D_{ij}} \frac{m_{ij}}{m} a_{ij}^{10} \left(\frac{\mathbf{I}_i}{\rho_i} - \frac{\mathbf{I}_j}{\rho_j} \right). \quad (2)$$

Instead of one of the latter equations it is possible to use

$$\nabla \ln T = - \sum_{j=1}^{NH} \left[\frac{C_j^2}{D_{jj}} a_{jj}^{01} + \sum_{h=1}^{NH} \frac{x_j x_h}{D_{jh}} \left(\frac{m_{hj}}{m} \right)^2 A_{jh}^0 \right] \mathbf{g}_j. \quad (3)$$

2. For electrons:

$$\frac{\nabla x_e}{x_e} = - \sum_{j=1}^{NH} \frac{x_j}{D_{ej}} \frac{\mathbf{I}_e}{\rho_e} + \sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{01} \mathbf{g}_e - \sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{02} \mathbf{f}_e - \frac{P}{nkT} \nabla \ln P - e \frac{\mathbf{E}}{kT}, \quad (4)$$

$$\sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{01} \frac{\mathbf{I}_e}{\rho_e} = \left(\sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{11} + \frac{x_e}{D_{ee}} a_{ee}^{11} \right) \mathbf{g}_e - \left(\sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{12} + \frac{x_e}{D_{ee}} a_{ee}^{12} \right) \mathbf{f}_e, \quad (5)$$

$$\left(\sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{22} + \frac{x_e}{D_{ee}} a_{ee}^{22} \right) \mathbf{f}_e = - \sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{02} \frac{\mathbf{I}_e}{\rho_e} + \left(\sum_{j=1}^{NH} \frac{x_j}{D_{ej}} a_{ej}^{21} + \frac{x_e}{D_{ee}} a_{ee}^{21} \right) \mathbf{g}_e. \quad (6)$$

The following notation is used in these equations:

$$\mathbf{g}_i = \frac{m}{kT} \frac{\mathbf{J}_i}{\rho_i}; \quad \mathbf{g}_e = \frac{m_e}{kT} \frac{\mathbf{J}_e}{\rho_e}; \quad \mathbf{f}_e = \frac{35}{8} \mathbf{g}_{e2};$$

$$m = \sum_{j=1}^{NH} x_j m_j; \quad m_{ij} = \frac{m_i m_j}{m_i + m_j}; \quad \mathbf{v}_i = \frac{\mathbf{I}_i}{\rho_i};$$

$$D_{ij} = \frac{3}{16 n m_{ij}} \frac{kT}{\Omega_{ij}^{11}}; \quad D_{ee} = \frac{3}{8 n m_e} \frac{kT}{\Omega_{ee}^{11}};$$

$$x_i = \frac{n_i}{n}; \quad C_i = \frac{\rho_i}{\rho}; \quad n = \sum_{i=1}^N n_i;$$

$$A_{jk}^0 = \frac{6}{5} \left(\frac{m_j^2}{m_k^2} - 1 \right) + \left(\frac{m_j}{m_k} + 1 \right) (1 - \delta_{jk}) a_{jk}^{22};$$

$$A_{jk}^i = \frac{6}{5} \left[\frac{m_j^2}{m_k^2} (\delta_{ij} - C_j) - (\delta_{ij} - C_i) \right] + (\delta_{ij} - \delta_{ik}) a_{jk}^{11} + (1 - \delta_{jk}) \left[\frac{m_j}{m_k} (\delta_{ij} - C_i) + (\delta_{ik} - C_i) \right] a_{jk}^{22}.$$

This system of equations is closed by using an expression derived from the condition of quasineutrality which makes it possible to eliminate the intensity of the induced electric field E :

$$\sum_{i=1}^N \frac{z_i I_i}{m_i} = 0. \quad (7)$$

These transport equations constitute a linear system of algebraic equations with respect to the diffusion and heat fluxes I_i , J_i , and to the auxiliary flux I_e .

The overall heat flux of the heavy particles is found by taking into account the flux caused by the transfer of energy of the internal degrees of freedom of the polyatomic molecules and the energy flux due to the transfer of mass [1]:

$$\begin{aligned} Q &= J_h + \sum_{i=1}^{NH} h_i I_i; \\ J_h &= \sum_{i=1}^{NH} (J_i - \lambda_B^i \nabla T_B^i - \lambda_K^i \nabla T_K^i); \\ \lambda_B^i &= \rho C_i b_i D_{ii} C_{vi}^B, \quad \lambda_K^i = \rho C_i b_i D_{ii} C_{vi}^K; \\ b_i &= \frac{1}{m} \left(\sum_j \frac{C_j}{m_j} \frac{D_{ii}}{D_{ij}} \right)^{-1}. \end{aligned} \quad (8)$$

In the equations given above, the terms α_{ijnm} represent linear functions of the collision integrals $\alpha_{ijkm} = F(\omega_{ij}^k s)$ where $\omega_{ij}^k s = \Omega_{ij}^k s / \Omega_{ij}^{11}$. Expressions for these can be found in [7, 8]. By specifying these by the interaction potentials between the particles, data for which can be taken from [8, 9, 11-13], it is possible to calculate in advance the quantities α_{ijkm} , which are represented by temperature functions.

For most flow conditions of low-temperature plasmas the system of equations given above is poorly conditioned, which is explained by the sharp differences (in order of magnitude) in the values of the concentrations of the components, and by the presence of components making up the gas mixture which differ markedly in the mass of the particles, etc. This is particularly characteristic of the feebly ionized plasmas of long-range trails. An iteration method of solution is therefore used for this linear system of algebraic equations $AX = B$ in which a trial solution $X(p)$ is first calculated by the method of Gauss, selecting the main elements. The precision of the solution is then improved by the iteration process $X(p+1) = X(p) + d(p)$, where $d(p)$ is the solution of the following system of equations: $Ad(p) = B - AX(p)$. If the system is not too poorly conditioned this process is convergent, and the number of iterations is selected based on a specified relative precision of the results obtained of $\delta \leq 3\%$.

As an example, let us investigate the flow of a low-temperature air plasma of a chemically non-equilibrium axisymmetric trail behind a body passing into the dense layers of the atmosphere at hypersonic velocity (using a cylindrical coordinate system X, Y, Φ with the X axis being the axis of symmetry). It is assumed that the flow consists of a gas mixture of the following composition: $O, O_2, N, N_2, NO, Ar, NO^+, e^-$. The transport properties of the stream are considered only in profiles along the Y axis. The initial profiles of all the parameters are shown in Fig. 1, where $\partial P / \partial y = 0$ and $C_{Ar} = \text{const}$. Such parameters arise, for instance, in the flow of a hypersonic axisymmetric trail behind a thin body flying in air with parameters $\rho_\infty = 0.21 \cdot 10^{-4} \text{ kg/m}^3$, $T_\infty = 185 \text{ K}$, at a velocity $V_\infty = 7.4 \cdot 10^3 \text{ m/sec}$ at a distance $x \approx 10d$ (where $d = 2R$ is the diameter of the body) from the object.

Four different methods are considered for the determination of the transport properties of the gaseous air mixture in order to determine the contribution of thermodiffusion and the diffusion thermoeffect to the magnitudes of the corresponding fluxes of the parameters.

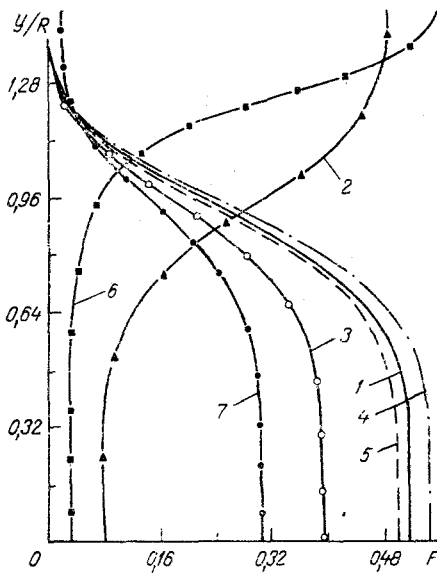


Fig. 1

Fig. 1. Initial profiles of the relative mass concentrations C_i^* and of the temperature $T^* = T/T_\infty$ and density $\rho^* = \rho/\rho_\infty$: 1) $C_O = C^*_O \cdot 10^{-1}$; 2) $CO_2 = 0.136 + 2C^*_O_2$; 3) $C_N = C^*_N \cdot 0.5 \cdot 10^{-3}$; 4) $CNO = C^*_NO \cdot 10^{-1}$; 5) $C_e = 2 \cdot 10^{-10} C^*_e$; 6) $\rho^* = \rho/\rho_\infty$; 7) $T^* = T/T_\infty \times 300$.

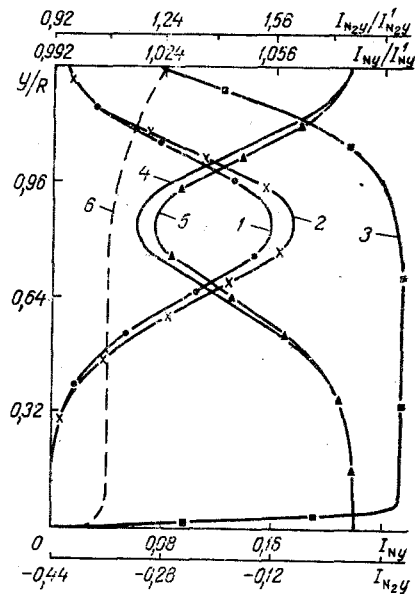


Fig. 2

Fig. 2. Profiles of the diffusion fluxes for atomic nitrogen N and of molecular nitrogen N_2 for the variants j : $IN_y(j) \cdot 10^6 \text{ kg}/(\text{m}^2 \cdot \text{sec})$, $IN_{2y}(j) \cdot 10^4 \text{ kg}/(\text{m}^2 \cdot \text{sec})$; 1) $IN_y(1)$; 2) $IN_y(4)$; 3) $IN_y(4)/IN_y(1)$; 4) $IN_{2y}(1)$; 5) $IN_{2y}(4)$; 6) $IN_{2y}(4)/IN_{2y}(1)$.

Model 1. General case of determining the diffusion and heat fluxes using the system of equations (1)-(7).

Model 2. The transport properties are determined analogously to model 1 with the condition $\alpha_{ee}^{12} = \alpha_{ee}^{21} = 0$, i.e., the mutual effects of the fluxes g_e and f_e on each other are excluded.

Model 3. As in model 2, $\alpha_{ee}^{12} = \alpha_{ee}^{21} = 0$ here also. However, it is assumed additionally that $\alpha_{ej}^{20} = \alpha_{ej}^{02} = 0$, i.e., the thermodiffusion of components under the influence of the auxiliary heat flux f_e and the reciprocal effect of the diffusion of electrons on this flux f_e are excluded from consideration.

Model 4. The conditions of model 3 are used, namely, $\alpha_{ee}^{12} = \alpha_{ee}^{21} = \alpha_{ej}^{02} = \alpha_{ej}^{20} = 0$, but it is assumed in addition that $\alpha_{ij}^{01} = \alpha_{ij}^{10} = 0$. Thus the main terms in the equations which have been given which describe the phenomena of thermodiffusion and the diffusion thermoeffect are eliminated. Model 4 is therefore a model in which these processes are completely absent, i.e., the interactions of the heat fluxes g_i , f_e and the diffusion fluxes I_i are excluded.

The thermodiffusion ratio is a complex function of the temperature, concentration, molecular weights depending parametrically on the nature of the intermolecular interactions, being unique for all functions of the transport coefficients, changing sign at specified values of the parameters of the gas mixture, and tending to zero in the absence of a dependence between the frequency of collision of the particles (the collision cross section) and their velocities.

Figure 2 shows the profiles of the diffusion fluxes of atomic nitrogen N and molecular nitrogen N_2 , $IN_y(j)$ and $IN_{2y}(j)$, respectively, calculated using the models $j = 1, 4$. The thermodiffusional flux of the lightest of the "heavy" particles (the N molecules) is directed along the gradient of the temperature T in the zone of the hot flow near the axis, i.e., its direction is opposed to that of the main diffusion flux of atomic nitrogen caused by the gradient of the concentration x_N . Therefore IN_y is reduced when the Soret effect is taken into account, and the condition $IN_y(1) > IN_y(4)$ is satisfied for the corresponding fluxes.

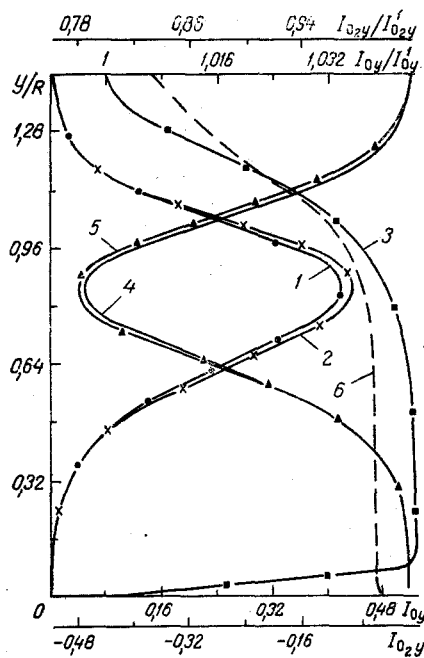


Fig. 3

Fig. 3. Profiles of the diffusion fluxes of atomic oxygen O and molecular oxygen O₂ for the variants j: I_{Oy}(j)·10⁴ kg (m²·sec), I_{O_{2y}}(j)·10⁴ kg(m²·sec): 1) I_{Oy}(1); 2) I_{Oy}(4); 3) I_{Oy}(4)/I_{Oy}(1); 4) I_{O_{2y}}(1); 5) I_{O_{2y}}(4); 6) I_{O_{2y}}(4)/I_{O_{2y}}(1).

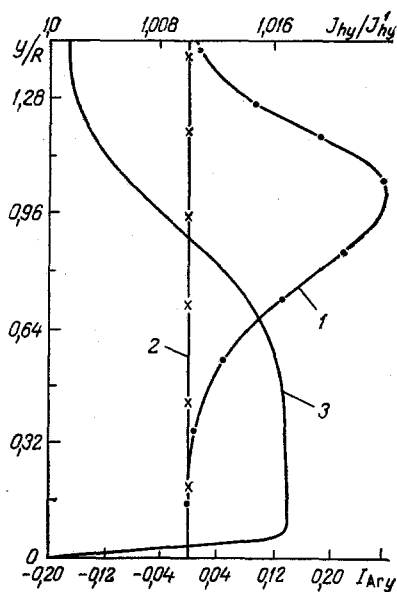


Fig. 4

Fig. 4. Profiles of the diffusion fluxes of argon Ar and of the heat flux of the heavy particles for the variants j; I_{Ary}(j)·10⁶ kg (m²·sec), J_{hy}(j)·10⁻¹ J/(m²·sec); 1) I_{Ary}(1); 2) I_{Ary}(4); 3) J_{hy}(4)/J_{hy}(1).

As can be seen from the graphs which are provided the effect of thermodiffusion on I_{Ny} appears to fall within the limits $\delta \leq 9\%$.

Under the conditions being considered molecular nitrogen can still be regarded as a "light" component even though it has twice the molecular weight. As in the case of the atomic nitrogen, the thermodiffusional flux of N₂ is directed along the temperature gradient. However, here it coincides in direction with the main concentrational flux and increases the latter $|I_{N_2y}(1)| > |I_{N_2y}(4)|$ by an amount in the range $\delta \leq 8\%$ (in the zone of the greatest values of I_{N_{2y}}).

Figure 3 gives the analogous graphs for atomic oxygen O and molecular oxygen O₂. As in the case of the atomic nitrogen N, thermodiffusion decreases the diffusion flux of atomic oxygen O, but only in the range $\delta < 5\%$. However, the thermodiffusional flux of O₂, which refers to particles of greater mass, is directed against the temperature gradient towards the periphery of the trail. Hence, in contrast to the case of N₂, the diffusional flux of the molecules of O₂ arising as a result of Fick's law is decreased $|I_{O_2y}(1)| < |I_{O_2y}(4)|$ by an amount in the range $\delta < 6\%$ (in the zone of the greatest values of I_{O_{2y}}).

The most marked Soret effect occurs in the case of the diffusion of argon molecules Ar. Since the initial relative mass concentration of Ar is specified as being constant over the cross section, C_{Ar}(y) = const., the diffusion flux given by Fick's law is I_{Ary} = 0. Since the pressure gradient is assumed to be equal to zero, $\partial P/\partial y = 0$, i.e., there is no barodiffusion, the only cause producing a diffusion flux of argon is thermodiffusion. In fact, as can be seen from Fig. 4, I_{Ary}(4) = 0, but I_{Ary}(1) ≠ 0, i.e., it causes a flux of the mass of argon, though this is not large. Since Ar possesses the largest molecular weight of all the particles being considered, its thermodiffusion flux is directed against the temperature gradient towards the boundaries of the trail, as can be clearly seen from Fig. 4.

This same figure also gives a curve characterizing the ratio of the heat fluxes of the heavy particles J_{hy}(j) [8] calculated using models j = 1 and j = 4, i.e., taking into account and not taking into account, respectively, the diffusion thermoeffect. It is clear that the Dufour effect occurs extremely feebly for the heavy particles, being of the order of $\delta < 2\%$.

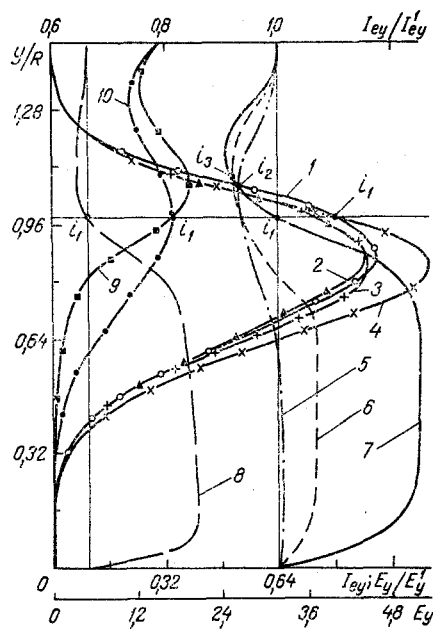


Fig. 5. Profiles of the diffusion fluxes of electrons e^- and of NO^+ ions, and profiles of the strength of the internal electrical field for the variants j : $I_{ey}(j) \cdot 10^{13}$ kg $(m^2 \cdot sec)$, $I_{NO+y}(j) = m_{NO} + I_{ey}(j) / m_e$, $E_y(j)$ volts; 1) $I_{ey}(1)$; 2) $I_{ey}(2)$; 3) $I_{ey}(3)$; 4) $I_{ey}(4)$; 5) $I_{ey}(2)/I_{ey}(1)$; 6) $I_{ey}(3)/I_{ey}(1)$; 7) $I_{ey}(4)/I_{ey}(1)$; 8) $[E_y(4)/E_y(1)] \cdot 10^{-1}$; 9) $E_y(1)$; 10) $E_y(4)$.

Figure 5 shows the profiles of the diffusion fluxes of electrons $I_{ey}(j)$ calculated using models $j = 1, 2, 3, 4$. The mass flux of electrons arises as a result of a complex interaction between the main concentration diffusion, thermodiffusion, and the internal electric field, which leads to the ambipolar nature of the process. In the cold zone of the flow the main concentration fluxes of electrons I_{ey}^K and of NO^+ ions I_{NO+y}^K are directed towards the boundaries of the trail. The thermodiffusion flux of e^- , I_{ey}^T , (which for electrons has quite a large value as a result of their small mass m_e) is directed along the temperature gradient in the hot zone near the axis. In the zone near the axis the analogous flux for NO^+ , I_{NO+y}^T , has the opposite direction, while in the cold zone near the boundary it is directed along the temperature gradient, and hence there is a point of inversion. It therefore correspondingly increases or decreases the main concentration flux I_{NO+y} . The assumption of an ambipolar nature of the diffusion leads to the appearance of an internal electric field (within the limits of a sphere of the Debye radius) of strength E (E_x, E_y) as shown in Fig. 5, which ensures the simultaneous diffusion of NO^+ and e^- . The difference in the nature of the thermodiffusion of the electrons and the NO^+ ions leads to a change in E_y (see curves for $E_y(1)$ and $E_y(4)$ in Fig. 5). The decrease in I_{ey} and the increase in I_{NO+y} in the hot zone near the axis lead to some weakening of the induced electric field which is larger the greater is the magnitude of the Soret effect. The actual differences $\delta(j)$ of the fluxes $I_{ey}(j)$ from the corresponding flux $I_{ey}(1)$ in this zone amount to: $\delta(2) < 0.1\%$; $\delta(3) < 7\%$; $\delta(4) < 30\%$, while the value of the field strength $E_y(1)$ is less than $E_y(4)$ by more than three times. The simultaneous effects of these factors lead to the appearance both for the electrons and for the NO^+ ions of points of inversion whose positions shift into the zone near the axis as the effect of thermodiffusion increases. The coordinates of the inversion points $y(i_j)$ for the models j are: $y(i_3) \approx 1.1R$; $y(i_2) \approx 1.06R$; $y(i_1) \approx 0.98R$. The points i are shown in Fig. 5. For comparison it can be noted that the inversion point for NO molecules has the coordinate $y(i_1) \approx 1.35R$.

The results which have been obtained make it possible to estimate the contributions of thermodiffusion and the diffusion thermoeffect to the transport properties of feebly ionized plasmas of long-range hypersonic trails which develop under the conditions of rarefied air media. They show that these processes, which have relatively little effect on the fluxes of the heavy particles, can lead to definite discrepancies in calculating the transport properties of the charged components (up to 30% in the diffusion fluxes, up to 300% in the strength of the internal electric field). This in turn can influence the distribution

of the parameters of the trail as a whole (which are primarily related to the concentrations of the charged components).

NOTATION

I_i, J_i , diffusion and heat fluxes of the i -th component; P_e, P_h, P, T , pressures of the electrons, heavy particles, and mixture; temperature; n, n_i , number of particles per unit volume of the mixture and of the i -th component; ρ, ρ_i , density of the mixture and of the i -th component; D_{ij}, E , binary diffusion coefficients to a first approximation, and strength of the internal electric field; $e, e \cdot z_i, m_i$, charge of the electron, charge and mass of the i -th component; $N, N_H = N - 1$, quantity of the component and of the heavy particles; v_i , diffusion velocity of the i -th component; Ω_{ij}^{mn} collision integrals for particles of species i and j ; $g_{e2}(f_e)$, auxiliary flux of the electron component for the third approximation (higher moment of the electron distribution function); $\lambda_B^i, \lambda_K^i, C_{viB}, C_{viK}, T_B^i, T_K^i$, thermal conductivities, heat capacities, temperatures of the rotational and vibrational degrees of freedom, respectively; h_i , enthalpy of molecule of the i -th species; f_e , auxiliary flux; Q , overall heat flux of heavy particles.

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