DEFINITION AND COMPUTATION OF EFFECTIVE TRANSPORT COEFFICIENTS FOR CHEMICAL-EQUILIBRIUM FLOWS OF PARTIALLY DISSOCIATED AND IONIZED GAS MIXTURES

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Exact transport equations have been derived previously [1, 2] in a new and computationally simpler form for a partially ionized multicomponent gas mixture; the corresponding expressions are given for all the transport coefficients in higher approximations of the expansion of the nonequilibrium component distribution functions in Sonin polynomials, and the behavior of these coefficients is subjected to a detailed numerical analysis in the example of partially ionized air. In the present article we discuss the derivation of transport equations for the special but important practical case of the flow of partially dissociated and partially ionized multicomponent gas mixtures under the condition of local chemical equilibrium at each point of the flow (this situation is common in practice, e.g., in continuum flow around bodies at large Mach and Reynolds numbers, in problems of chemical technology, etc.). A complete set of effective transport coefficients is introduced for the first time in application to this case, and they are analyzed numerically with the inclusion of higher approximations; practical recommendations are given on the basis of this analysis for the inclusion of higher approximations in the effective transport coefficients in connection with the solution of heat- and mass-transfer problems in a low-temperature plasma.

Transport phenomena in chemical-equilibrium gas mixtures are covered in an exhaustive literature. The first description of heat transfer with allowance for the additional diffusion transport of "chemical" energy was proposed by Nernst [3]. This approach was later elaborated (in [4-6], etc.) for binary gas mixtures in which one dissociation reaction takes place. The physical substantiation of this process reduces to the fact that the products of a reaction taking place in an elevated-temperature region diffuse into a lower-temperature region, where they enter into the reverse chemical reaction. An effective thermal conductivity has been introduced for multicomponent gas mixtures at rest ($\nabla p = 0$) with an arbitrary number of ongoing dissociation reactions [7, 8] and for partially ionized chemical-equilibrium mixtures [9, 10].

Several authors [3-10] have discussed the derivation of only the effective thermal conductivity in a rest medium, i.e., only molecular heat transfer, but not molecular mass transfer in the form of diffusion of the elements, which necessarily occurs in the presence of a temperature gradient in a multicomponent mixture with components having different diffusion properties, even when thermal diffusion is absent or when a pressure gradient exists [see Eq. (2.5) below]. Diffusion of the elements induces an additional heat-flux term, and the presence of a pressure gradient induces an additional term in the energy equation. The diffusion of the elements in chemical-equilibrium flows results in another whole series of crossover effective transport coefficients, so that the diffusion flux of a particular element depends on the gradients of all the elements. This fact was first brought to attention in [11, 12]. We note that the presence of reactions in a gas mixture tends to perturb the component distribution functions, in which case the transport coefficients, generally speaking, must be computed from the appropriate kinetic equations with collision integrals that include "chemical" collisions. Chemical reactions upset the equilibrium energy distribution. As a rule, however, the characteristic reaction time is large in comparison with the mean particle transit time, i.e., the reaction rate is small in comparison with, say, the relaxation rate of the Maxwell distribution. Under these conditions, the kinetic behavior of the reacting mixture is quantitatively similar to the behavior of a nonreacting gas in its principal features. This is because the elastic collision processes restoring the Maxwell distribution are far more intense that the collisions responsible for chemical reactions. Consequently, published estimates of the influence of reactions on the transport coefficients [13]

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show that their influence is slight, amounting to a few percent in the presence of dissociation reactions and yielding a somewhat more appreciable contribution [14, 15] in the presence of ionization reactions. As a rule, the increment to the thermal conductivity as a result of equilibrium chemical reactions and "diffusion of the heats of reaction" is considerably greater (by as much as two orders of magnitude) than its variation due to the influence of chemical reactions at the kinetic level. The duration of equilibrium chemical reactions is, by definition, much smaller than the characteristic hydrodynamic time and, on the other hand, much greater than the relaxation time of the Maxwell distribution. The present study therefore rests on the equations derived for mass transfer of the components and heat transfer without regard for the influence of "chemical" collisions on the transport coefficients in the form obtained in [1, 2].

1. STEFAN–MAXWELL RELATIONS AND HEAT FLUX FOR A QUASINEUTRAL GAS MIXTURE

We consider the system of equations for the diffusion fluxes of the components and the equation for the transfer of total heat flux due to gradients of the temperature, concentrations, and pressure and due to the electric fields present in the plasma under the conditions of local chemical equilibrium, proceeding from general representations of the total transport equations obtained by the methods of kinetic theory for partially ionized multicomponent gas mixtures.

For multicomponent mixtures of partially ionized and dissociated gases in the absence of external and induced magnetic fields, the component mass-transfer equations in the form of Stefan–Maxwell relations are written [1, 2]

$$\mathbf{d}_i = -\Delta_i \mathbf{J}'_i + x_i \sum_{k=1}^{N} \Delta_{ki} \mathbf{J}'_k, \quad \mathbf{J}'_k = \frac{\mathbf{J}_k}{m_k}, \quad i = 1, \ldots, N, \tag{1.1}$$

where $\mathbf{d}_i$ denotes the diffusion force vectors

$$\mathbf{d}_i = \nabla x_i + k_{pi} \nabla \ln p + k_{Ti}(\xi) \nabla \ln T - \frac{c_i}{p}\left(\rho e_i \mathbf{E} - \sum_{s=1}^{N} \rho_s e_s \mathbf{E}\right); \tag{1.2}$$

c_i, x_i, $\mathbf{J}_i$, k_{Ti}, k_{pi}, e_i, ρ_i, m_i are the mass concentration, mole concentration, diffusion flux, thermal-diffusion ratio, pressure-diffusion ratio, charge, density, and mass of the i-th component, respectively; p, T, and ρ are the pressure, temperature, and density of the mixture; Δ_{ij} are the resistance coefficients:

$$\Delta_{ij}^{-1} = n\mathscr{D}_{ij}(1) f_{ij}(\xi), \quad \Delta_i = \sum_{k=1}^{N} x_k \Delta_{ik};$$

$\mathscr{D}_{ij}(1)$ are the binary diffusion coefficients; $f_{ij}(\xi)$ are higher-harmonic approximations; and $\mathbf{E}$ is the electric field vector.

In the expression (1.2) for the vector of diffusion forces, the external force vectors $\mathbf{F}_i (\mathbf{F}_i = e_i \mathbf{E})$ are determined from the zero-magnetic-field conditions. Under the condition of quasineutrality (small deviations from electrical neutrality in an ionized gas produce very strong electric fields, which force the plasma rapidly back into the neutral state in a time $\tau = m_E / 4\pi n_E e^2$) we have

$$\sum_{k=1}^{N} x_k \frac{e_k}{e_E} = 0. \tag{1.3}$$

Condition (1.3) in conjunction with the condition of charge preservation in the reactions (1.6) $e_i = \nu_{iE} e_E$ (ν_{iE} denotes the stoichiometric coefficients of the ionization reaction, and the index E refers to the electron) can be used to eliminate the field $\mathbf{E}$ from the Stefan–Maxwell relations (1.1) and (1.2). For this purpose the expressions (1.2) for the diffusion force vector are substituted in Eqs. (1.1), and each equation (i = 1,...,N) is multiplied by e_i/e_E. Then summation is carried out from 1 to N, and condition (1.3) is invoked after transformation to differential form. This procedure makes it possible to derive an explicit expression for the field vector $\mathbf{E}$, which is then substituted in Eq. (1.2) and is thus eliminated from the Stefan–Maxwell relations. As a result [16],

$$\mathbf{d}_i = -\Delta_i \mathbf{J}'_i + x_i \sum_{k=1}^{N} \delta_{ik}^{(0)} \mathbf{J}'_k, \tag{1.4}$$

where

$$\mathbf{d}_i = \nabla x_i + k_{pi}^{(0)} \nabla \ln p + k_{\mathrm{T}i}^{(0)} \nabla \ln T. \tag{1.5}$$

Here

$$k_{\mathrm{T}i}^{(0)} = k_{\mathrm{T}i} - x_i \zeta_i \sum_{s=1}^{N} \zeta_s k_{\mathrm{T}s}; \quad \delta_{ij}^{(0)} = \Delta_{ij} + \zeta_i \sum_{k=1}^{N} x_k (\zeta_j - \zeta_k) \Delta_{kj}; \quad k_{pi}^{(0)} = k_{pi} - x_i \zeta_i \sum_{s=1}^{N} \zeta_s k_{ps}; \quad \zeta_i = e_i \left(\sum_{k=1}^{N} x_k e_k^2 \right)^{-1/2}.$$

The following relations are satisfied:

$$\sum_{i=1}^{N} k_{\mathrm{T}i}^{(0)} = 0, \quad \sum_{i=1}^{N} k_{pi}^{(0)} = 0, \quad \sum_{i=1}^{N} x_i \delta_{ij}^{(0)} = \Delta_j,$$

$$\sum_{i=1}^{N} e_i k_{\mathrm{T}i}^{(0)} = 0, \quad \sum_{i=1}^{N} e_i k_{pi}^{(0)} = 0, \quad \sum_{i=1}^{N} x_i e_i \delta_{ij}^{(0)} = e_j \Delta_j.$$

Equations (1.4) and (1.5) are of the same form as the corresponding equations for mixtures of neutral components, but the resulting expressions for the coefficients contain additional terms depending on the particle charges e_i. In the case of mixtures of neutral particles, for which all $e_i \equiv 0$, the additional terms in the expressions for the coefficients in relations (1.4) and (1.5) vanish, and the Stefan–Maxwell relations (1.4) and (1.5) go over to the ordinary relations for neutral mixtures in this case, i.e., they coincide with the system (1.1), (1.2) with $\mathbf{E} \equiv 0$.

For the subsequent analysis we transform from the mole concentrations x_i in relations (1.4) and (1.5) to the mass concentrations c_i, making use of the relations $[c_i = (m_i/m)x_i]$

$$\nabla c_i = \frac{m_i}{m^2} \left[\sum_{k=1}^{N} m_k (x_k \nabla x_i - x_i \nabla x_k) \right].$$

Moreover, to facilitate the solution of the hydrodynamic problems we set apart the component mass-transfer equations for the elements B_j ($j = 1,\ldots,L$), writing them separately from the transfer equations for the reaction products A_i ($i = L + 1,\ldots,N$); they are interrelated by the system of linearly independent reactions

$$A_i = \sum_{j=1}^{L} \nu_{ij} B_j, \quad i = L+1, \ldots, N, \tag{1.6}$$

where L is the number of elements, ν_{ij} are the stoichiometric coefficients of the reactions, and N is the number of components in the mixture.

As in [1], we define the element concentrations c_j^* and the element diffusion fluxes $\mathbf{J}_j^*$ as follows in accordance with the representation of the reactions in the form (1.6):

$$c_j^* = c_j + \sum_{k=L+1}^{N} \nu_{kj} \frac{m_j}{m_k} c_k, \quad \mathbf{J}_j^* = \mathbf{J}_j + \sum_{k=L+1}^{N} \nu_{kj} \frac{m_j}{m_k} \mathbf{J}_k. \tag{1.7}$$

As a result of simple transformations of the relations (1.4) and (1.5), we obtain for the elements $j = 1,\ldots,N$

$$\mathbf{d}_j^* = -\frac{\Delta_j}{m} \mathbf{J}_j^* + \frac{m_j}{m} \sum_{l=1}^{L} \Delta_{jl}^* \mathbf{J}_l^{*\prime} + \frac{m_j}{m} \sum_{k=L+1}^{N} \delta_{jk}^* \mathbf{J}_k', \tag{1.8}$$

where

$$\mathbf{d}_j^* = \nabla c_j^* + K_{pj}^* \nabla \ln p + K_{\mathrm{T}j}^* \nabla \ln T;$$

for the reaction products $i = L + 1,\ldots,N$

$$\mathbf{d}_i = -\frac{\Delta_i}{m} \mathbf{J}_i + c_i \sum_{l=1}^{L} \Delta_{il}^{(0)} \mathbf{J}_l^{*\prime} + c_i \sum_{k=L+1}^{N} \Delta_{ik}^{(1)} \mathbf{J}_k', \tag{1.9}$$

where

$$\mathbf{d}_i = \nabla c_i + K_{pi}^{(0)} \nabla \ln p + K_{\mathrm{T}i}^{(0)} \nabla \ln T.$$

Here

$$\Delta_{jl}^{*}=x_j\Delta_{jl}+\sum_{k=L+1}^{N}x_k\nu_{kj}\Delta_{kl}+x_j^{*}\sum_{r=1}^{N}x_r\left(\frac{m_l}{m}-\frac{m_r}{m}\right)\Delta_{rl}+\left(x_j\zeta_j^{*}+\sum_{k=L+1}^{N}x_k\nu_{kj}\zeta_k^{*}\right)\sum_{r=1}^{N}x_r(\zeta_l-\zeta_r)\,\Delta_{rl},$$

$$\delta_{jk}^{*}=\nu_{kj}(\Delta_j-\Delta_k)+\Delta_{jk}^{*}-\sum_{l=1}^{L}\nu_{kl}\Delta_{jl}^{*},$$

$$\Delta_{ij}^{(0)}=\Delta_{ij}-\sum_{s=1}^{N}x_s\left(\frac{m_s}{m}-\frac{m_j}{m}\right)\Delta_{sj}-\zeta_j^{*}\sum_{s=1}^{N}x_s(\zeta_s-\zeta_j)\,\Delta_{sj},$$

$$\Delta_{jk}^{(1)}=\Delta_{jk}^{(0)}-\sum_{l=1}^{L}\nu_{kl}\Delta_{jl}^{(0)},\quad \zeta_i^{*}=\zeta_i-\sum_{k=1}^{N}c_k\zeta_k,\quad x_j^{*}=x_j+\sum_{l=L+1}^{N}\nu_{lj}x_l,$$

$$K_{\mathrm{T}j}^{*}=K_{\mathrm{T}j}^{(0)}+\sum_{k=L+1}^{N}\nu_{kj}(m_j/m_k)\,K_{\mathrm{T}k}^{(0)},$$

$$K_{\mathrm{T}i}^{(0)}=\frac{m_i}{m}k_{\mathrm{T}i}-c_i\sum_{s=1}^{N}\frac{m_s}{m}k_{\mathrm{T}s}-c_i\zeta_i^{*}\sum_{s=1}^{N}\zeta_s k_{\mathrm{T}s},$$

$$K_{pj}^{*}=K_{pj}^{(0)}+\sum_{k=L+1}^{N}\nu_{kj}(m_j/m_k)\,K_{pk}^{(0)},$$

$$K_{pi}^{(0)}=\frac{m_i}{m}k_{pi}-c_i\sum_{s=1}^{N}\frac{m_s}{m}k_{ps}-c_i\zeta_i^{*}\sum_{s=1}^{N}\zeta_s k_{ps}.$$

By virtue of the conditions

$$\sum_{j=1}^{L}\mathbf{d}_j^{*}=0\,\text{and}\,c_E^{*}=\frac{m_E}{m}\sum_{k=1}^{N}x_k\frac{e_k}{e_E}=0$$

the number of independent relations (1.8), (1.9) will be N — 1 for a mixture of electrically neutral components and N — 2 for a quasineutral mixture containing charged particles. In conclusion, we represent the system of equations (1.8), (1.9) in a more complete form, introducing the dimensionless Schmidt numbers used in hydrodynamic problems. Denoting $S_i = (\mu(\xi)/m)\Delta_i$, we obtain for the elements j = 1,...,L

$$\mathbf{d}_j^{*}=-\frac{S_j}{\mu(\xi)}\mathbf{J}_j^{*}+\frac{m_jS_j}{\mu(\xi)}\left(\sum_{l=1}^{L}\alpha_{jl}^{*}\mathbf{J}_l^{*\prime}+\sum_{k=L+1}^{N}\beta_{jk}^{*}\mathbf{J}_k^{\prime}\right); \tag{1.10}$$

for the reaction products i = L + 1,...,N

$$\mathbf{d}_i=-\frac{S_i}{\mu(\xi)}\mathbf{J}_i+x_i\frac{m_iS_i}{\mu(\xi)}\left(\sum_{l=1}^{L}\alpha_{il}\mathbf{J}_l^{*\prime}+\sum_{k=L+1}^{N}\beta_{ik}\mathbf{J}_k^{\prime}\right),$$

where

$$\alpha_{jl}^{*}=\frac{\Delta_{jl}^{*}}{\Delta_j};\quad \alpha_{il}=\frac{\Delta_{il}^{(0)}}{\Delta_i};\quad \beta_{jl}^{*}=\frac{\delta_{jl}^{*}}{\Delta_j};\quad \beta_{ik}=\frac{\Delta_{ik}^{(1)}}{\Delta_i}.$$

We also transform the total heat-flux equation [1]

$$\mathbf{J}_q=-\lambda(\xi)\nabla T+kT\sum_{k=1}^{N}\alpha_{\mathrm{T}k}(\xi)\,\mathbf{J}_k^{\prime}+\sum_{k=1}^{N}h_k\mathbf{J}_k$$

[$\lambda(\xi)$ is the "true" thermal conductivity, k is the Boltzmann constant, $\alpha_{\mathrm{T}k}(\xi)$ is the thermal diffusion coefficient, and h_k is the specific enthalpy of the k-th component], introducing the element diffusion fluxes $\mathbf{J}_j^{*}$ in place of the component diffusion fluxes $\mathbf{J}_j$ and making use of the relations (1.7) between them. Relations for the enthalpies of the reaction products can be deduced from the energy conservation law:

$$h_i=\sum_{l=1}^{L}\nu_{il}\frac{m_l}{m_i}h_l-q_i(T),\quad i=L+1,\ \ldots,\ N,$$

which we incorporate into the reactions (1.6) to obtain

$$\mathbf{J}_q=-\lambda(\xi)\nabla T+\sum_{j=1}^{L}h_j^{T}\mathbf{J}_j^{*}-\sum_{k=L+1}^{N}q_k^{T}\mathbf{J}_k, \tag{1.11}$$

where

$$h_j^T = h_j + kT\alpha'_{Tj};\quad \beta_{Ti} = \alpha_{Ti} - \sum_{j=1}^{L} \nu_{ij}\alpha_{Tj};\quad q_i^T = q_i - kT\beta'_{Ti};$$

$$\beta'_{Ti} = \frac{\beta_{Ti}}{m_i};\quad \alpha_{Ti} = \frac{k_{Ti}(\xi)}{x_i};\quad \alpha'_{Ti} = \frac{\alpha_{Ti}}{m_i}.$$

Here $q_i(T)$ denotes the specific heats of the reactions (1.6), and $h_i(T)$ are the specific enthalpies. Transforming to the total enthalpy gradient ($H = h + v^2/2$) in (1.11):

$$\nabla H = \nabla\left(\sum_{k=1}^{N} c_k h_k + \frac{v^2}{2}\right) = c_p \nabla T + \sum_{j=1}^{L} h_j \nabla c_j^* - \sum_{k=L+1}^{N} q_k \nabla c_k + \nabla\left(\frac{v^2}{2}\right),$$

we have

$$\mathbf{J}_q = -\frac{\mu}{\sigma}\left[\nabla H - \nabla\left(\frac{v^2}{2}\right) - \sum_{j=1}^{L}\left(h_j \nabla c_j^* + \frac{\sigma}{\mu} h_j^T \mathbf{J}_j^*\right) + \sum_{k=L+1}^{N}\left(q_k \nabla c_k + \frac{\sigma}{\mu} q_k^T \mathbf{J}_k\right)\right],$$

where $\sigma = (\mu(\xi)c_p)/\lambda(\xi)$ is the Prandtl number and c_p is the specific heat of the mixture at constant pressure. The transport equations (1.8), (1.9), and (1.12) are valid for an arbitrary course of the chemical reactions.

2. MASS-TRANSFER AND HEAT-FLUX EQUATIONS FOR CHEMICAL-EQUILIBRIUM FLOWS

We consider the component mass-transfer equations (1.8), (1.9) and the heat-flux equation (1.12) under the condition of chemical equilibrium. In this case the mass source terms $\dot{W}_i$ in the complete Navier—Stokes equation [1] degenerate into finite relations, which are called the chemical equilibrium conditions and are replaced by the mass conservation equations for the components, i.e., the reaction products. Of all the differential equations expressing the conservation of mass of the components, only the equations for the conservation of mass of the chemical elements c_j^* ($j = 1,\ldots,L$) are left, and they are closed by (1.8). For a given element composition c_j^*, the component concentrations x_i ($i = 1,\ldots,N$) are determined from the system of algebraic equations [17]

$$\begin{gathered}\frac{\prod_{j=1}^{L} x_j^{\nu_{ij}}}{x_i} = \frac{K_{pi}(T)}{p^{\nu_i}},\quad i = L+1,\ldots,N;\\ x_j \frac{m_j}{m} + \sum_{i=L+1}^{N} \nu_{ij} \frac{m_j}{m} x_i = c_j^*,\quad j = 1,\ldots,L,\quad \sum_{k=1}^{N} x_k = 1,\end{gathered}\tag{2.1}$$

where $K_{pi}(T)$ is the equilibrium constant and $\nu_i = \sum_{j=1}^{L} \nu_{ij} - 1$. The first group of equations (2.1) represents the Gulberg and Waage (mass action) chemical equilibrium condition for the chemical reactions and Saha's ionization equation; the second group represents the material balance equations. For ionized gas mixtures the system (2.1) is augmented with the quasineutrality condition $c_E^* = 0$.

The system (2.1) establishes the implicit dependence of the reaction-product concentrations x_i ($i = L + 1,\ldots,N$) in terms of the concentrations of the chemical elements c_j^* ($j = 1,\ldots,L$), p, and T, making it possible to eliminate the reaction-product concentration gradients ∇c_i ($i = L + 1,\ldots,N$) and the reaction-product fluxes $\mathbf{J}_i$ ($i = L + 1,\ldots,N$) in Eqs. (1.8) and (1.12) by expressing them in terms of the respective element quantities ∇c_j^* and $\mathbf{J}_j^*$ and also in terms of ∇p and ∇T.

Accordingly, we transform to the mass concentrations c_i in the system (2.1), apply the operation ∇ to the logarithm of each chemical-equilibrium equation, express ∇c_j ($j = 1,\ldots,L$) in terms of ∇c_j^* ($j = 1,\ldots,L$) and ∇c_i ($i = L + 1,\ldots,N$) by means of (1.7), and invoke the van't Hoff isochore [3]:

$$\frac{d \ln K_{pi}(T)}{dT} = \frac{m_i q_i}{kT^2},\quad i = L+1,\ldots,N.\tag{2.2}$$

Then to determine $\nabla c_i' = \nabla(e_i/m_i)$ ($i = L + 1,\ldots,N$) we have the system of equations

$$\sum_{k=L+1}^{N} a_{ik}\nabla c_k' = -\frac{m_i q_i}{mkT}\nabla \ln T + \frac{\nu_i}{m}\nabla \ln p + \sum_{j=1}^{L}\nu_{ij}^{*}\nabla c_j^{*\prime}, \tag{2.3}$$

where

$$a_{ik} = a_{ki} = \sum_{j=1}^{L}\frac{\nu_{ij}\nu_{kj}}{x_j} - \nu_i\nu_j + \frac{\delta_{ik}}{x_i}; \quad \nu_{ij}^{*} = \frac{\nu_{ij}}{x_j} - \nu_i.$$

To determine the diffusion fluxes of the reaction products $\mathbf{J}_i$ ($i = L + 1,\ldots,N$) we use Eqs. (1.1), (2.1), and (2.2). Eliminating the component—element diffusion fluxes from them by means of (1.7) and expressing $\mathbf{J}_j$ in terms of $\mathbf{J}_j^{*}$, we arrive at the system of equations [16]

$$\sum_{k=L+1}^{N} b_{ik}\mathbf{J}_k' = \frac{m_i q_i^T}{kT}\nabla \ln T + \sum_{j=1}^{L} d_{ij}\mathbf{J}_j^{*\prime}, \tag{2.4}$$

where

$$b_{ik} = b_{ki} = \sum_{j=1}^{L}\frac{\nu_{ij}\nu_{kj}}{x_j}\Delta_j - \sum_{j=1}^{L}\sum_{l=1}^{L}\nu_{ij}\nu_{kl}\Delta_{jl} + \sum_{j=1}^{L}(\nu_{ij}\Delta_{jk} + \nu_{kj}\Delta_{ji}) - \Delta_{ik} + \frac{\delta_{ik}}{x_i}\Delta_i;$$

$$d_{ij} = \Delta_{ij} + \nu_{ij}\Delta_j/x_j - \sum_{l=1}^{L}\nu_{il}\Delta_{lj}, \quad j = 1, \ldots, L; \quad k, i = L + 1, \ldots, N.$$

It must be noted that the system (2.4) is obtained in the same form even without the assumption of quasineutrality of the mixture, but the electric field **E** does not occur explicitly in (2.4), by virtue of the equations for the conservation of mass and charge in the reactions [16]. Moreover, the retention of the term characterizing the pressure diffusion in (1.1) does not introduce a term with $\nabla \ln p$ on the right-hand side of (2.4).

Only the element mass-transfer equations are needed in order to close the system of Navier—Stokes equations for chemical-equilibrium flows. We therefore eliminate the sums $\sum_{k=L+1}^{N}\beta_{jk}^{*}\mathbf{J}_k'$ from (1.10), using the solution of the system (2.4) to do so. As a result, we have

$$\mathbf{d}_j = -\frac{S_j}{\mu}\mathbf{J}_j^{*} + \frac{m_j S_j}{\mu}\sum_{l=1}^{L}\alpha_{jl}^{(e)}\mathbf{J}_l^{*\prime}, \tag{2.5}$$

where

$$\mathbf{d}_j = \nabla c_j^{*} + \left(K_{\mathrm{T}j}^{*} - \frac{m_j}{m}\delta_j^{(e)}\right)\nabla \ln T + K_{pj}^{*}\nabla \ln p.$$

Here

$$\alpha_{jl}^{(e)} = \alpha_{jl}^{*} + \alpha_{jl}^{**};$$

$$\alpha_{jl}^{**} = -\frac{1}{\Delta_j \det\|b_{ik}\|}\begin{vmatrix} 0 & d_{L+1,l} & \ldots & d_{N,l} \\ \delta_{j,L+1}^{*} & b_{L+1,L+1} & \ldots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \delta_{j,N}^{*} & b_{N,L+1} & \ldots & b_{N,N} \end{vmatrix}; \tag{2.6}$$

$$\delta_j^{(e)} = -\frac{1}{kT \det\|b_{ik}\|}\begin{vmatrix} 0 & Q_{L+1}^{T} & \ldots & Q_N^{T} \\ \delta_{j,L+1}^{*} & b_{L+1,L+1} & \ldots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \delta_{j,N}^{*} & b_{N,L+1} & \ldots & b_{N,N} \end{vmatrix}. \tag{2.7}$$

Equation (1.12) is transformed for chemical-equilibrium flows. The sums $\sum_{k=L+1}^{N} q_k\nabla c_k$ and $\sum_{k=L+1}^{N} q_k^T\mathbf{J}_k$ involved in (1.12) can be written as follows with the aid of the solution of Eqs. (2.3) and (2.4):

$$\sum_{k=L+1}^{N} q_k\nabla c_k = -c_{pr}\nabla T + a(\nu, Q)\frac{\nabla p}{\rho} + \sum_{j=1}^{L} a(\nu^{*}, Q)\nabla c_j^{*}; \tag{2.8}$$

$$\sum_{k=L+1}^{N} q_k^T \mathbf{J}_k = \lambda_r \nabla T + \sum_{j=1}^{L} b_j(d, Q^T)\,\mathbf{J}_j^*, \tag{2.9}$$

where

$$c_{pr} = -\frac{1}{mkT^2 \det\|a_{ik}\|}\begin{vmatrix} 0 & Q_{L+1} & \dots & Q_N \\ Q_{L+1} & a_{L+1,L+1} & \dots & a_{L+1,N} \\ \vdots & \vdots & & \vdots \\ Q_N & a_{N,L+1} & \dots & a_{N,N} \end{vmatrix}; \tag{2.10}$$

$$\lambda_r = -\frac{1}{kT^2 \det\|b_{ik}\|}\begin{vmatrix} 0 & Q_{L+1}^T & \dots & Q_N^T \\ Q_{L+1}^T & b_{L+1,L+1} & \dots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ Q_N^T & b_{N,L+1} & \dots & b_{N,N} \end{vmatrix}; \tag{2.11}$$

$$a_j(\nu^*, Q) = -\frac{1}{m_j \det\|a_{ik}\|}\begin{vmatrix} 0 & Q_{L+1} & \dots & Q_N \\ \overset{*}{\nu}_{L+1,j} & a_{L+1,L+1} & \dots & a_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \overset{*}{\nu}_{N,j} & a_{N,L+1} & \dots & a_{N,N} \end{vmatrix}; \tag{2.12}$$

$$b_j(d, Q^T) = -\frac{1}{m_j \det\|b_{ik}\|}\begin{vmatrix} 0 & Q_{L+1}^T & \dots & Q_N^T \\ d_{L+1,j} & b_{L+1,L+1} & \dots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ d_{N,j} & b_{N,L+1} & \dots & b_{N,N} \end{vmatrix};$$

$$a(\nu, Q) = -\frac{1}{kT \det\|a_{ik}\|}\begin{vmatrix} 0 & Q_{L+1} & \dots & Q_N \\ \nu_{L+1} & a_{L+1;L+1} & \dots & a_{L+i,N} \\ \vdots & & & \\ \nu_N & a_{N,L+1} & \dots & a_{N,N} \end{vmatrix}, \tag{2.13}$$

$$Q_i = m_i q_i; \quad Q_i^T = m_i q_i^T.$$

Then the expression obtained for (1.12) with the use of (2.8) and (2.9) acquires the compact form

$$\mathbf{J}_q = -\lambda_{\text{eff}} \nabla T - \sum_{j=1}^{L} b_j^* \mathbf{J}_j^*, \tag{2.14}$$

where

$$\lambda_{\text{eff}} = \lambda + \lambda_r; \quad b_j^* = b_j(d_j, Q^T) - h_j^T;$$

λ_{eff} is an effective thermal conductivity equal to the sum of the molecular thermal conductivity, which characterizes heat transfer through translational degrees of freedom, plus the heat-transfer coefficient λ_r associated with diffusion of the reacting components. Equation (1.12), written in terms of the total enthalpy, is transformed to

$$\mathbf{J}_q = -\frac{\mu}{\sigma_{\text{eff}}}\left[\nabla\left(H - \frac{v^2}{2}\right) + a(\nu, Q)\frac{\nabla p}{\rho} + \sum_{j=1}^{L}\left(a_j^* \nabla c_j^* + \frac{\sigma_{\text{eff}}}{\mu} b_j^* \mathbf{J}_j^*\right)\right], \tag{2.15}$$

where

$$\sigma_{\text{eff}} = \frac{\mu c_{p\text{eff}}}{\lambda_{\text{eff}}} = \frac{\mu(c_{pr} + c_p)}{\lambda + \lambda_r}; \quad a_j^* = a_j(\nu^*, Q) - h_j \tag{2.16}$$

(σ_{eff} is the effective Prandtl number).

Consequently, under the chemical-equilibrium condition the transport equation for the total heat flux (2.14) contains not only the additional so-called "chemical" contribution to the thermal conductivity λ_{eff}, but also an additional term involving the diffusion fluxes of the elements $\sum_{j=1}^{L} b_j^* \mathbf{J}_j^*$, and (2.15) contains an additional contribution from the chemical reactions, which is manifested in the advent of terms involving ∇p, ∇c_j^*, and $\mathbf{J}_j^*$, which have not been discussed previously in the literature.

The transport coefficients in the mass-transfer equations (2.5) and in the equation for the total heat flux (2.15) associated with chemical reactions depend only on the local composition of the plasma, p, T, the element concentrations c_j^* ($j = 1,\dots,L$), which must be

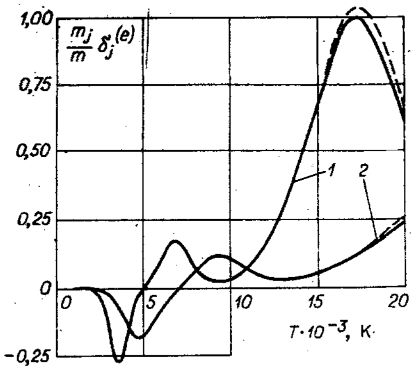

Fig. 1

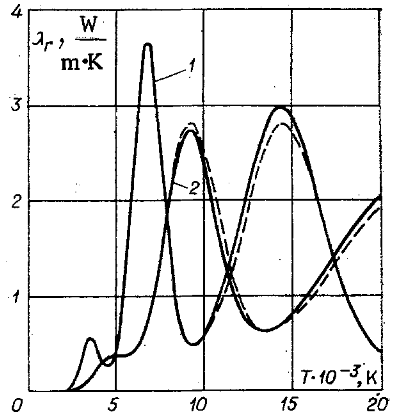

Fig. 2

determined from the solution of the specific problem, and also on the particle collision integrals $Q_{ij}^{l,s}(T)$.

3. NUMERICAL COMPUTATION OF THE EFFECTIVE TRANSPORT COEFFICIENTS OF IONIZED AIR IN CHEMICAL-EQUILIBRIUM FLOWS

We have computed all the effective transport coefficients involved in (2.5) and (2.15) on the basis of the transport coefficients obtained in higher approximations for a partially ionized mixture of oxygen and nitrogen [1], and we have investigated the influence of the transport properties of the mixture and the thermal effects of equilibrium chemical reactions on the computed coefficients. Here we give the most interesting results.

Figure 1 shows the values of $\delta_j^{(e)}m_j/m$ [Eq. (2.5)] for O (oxygen) with values of the pressure $p = 1.013\cdot 10^5$ Pa (curve 1) and $p = 1.013\cdot 10^7$ Pa (curve 2). The quantity $\delta_j^{(e)}m_j/m$ attains a value of 0.2-0.3 in the region of dissociation of air. This means that even when we neglect thermal diffusion ($k_{Ti} = 0$) and pressure diffusion ($k_{pi} = 0$), the diffusion fluxes of the elements $\mathbf{J}_j^*$ ($j = 1,\ldots,L$) have nonzero values in the presence of a temperature gradient, owing to the difference in the diffusion properties of the components ($\delta_j^{(e)} \equiv 0$ for identical diffusion properties of the components). Consequently, an appreciable separation of the elements occurs in the flow in the presence of dissociation chemical reactions (this result has been obtained previously in the numerical analysis of specific flows of dissociating gases [18]). In the ionization region, $\delta_j^{(e)}m_j/m$ increases even more, and the element separation effect becomes more pronounced. For identical diffusion properties of the components in the mixture $\Delta_{ik} = \Delta$ ($i, k = 1,\ldots,N$), the coefficient $\delta_j^{(e)}$ is identically zero, and separation of the elements does not occur for $k_{Ti} = k_{pi} = 0$ ($i = 1,\ldots,N$).

The coefficients λ_r (2.11) and c_{pr} (2.10) occurring in the equation for the total heat flux (2.14) [or (2.15)] in equilibrium chemical reactions enter into the equation in the form of the combination σ_{eff} (2.16). In the event of strong reactions (dissociation of N_2, O_2, NO or ionization of N, O), the values of λ_r and c_{pr} can be several times the corresponding values of λ and c_p for chemically frozen flows. Figure 2 shows the values of λ_r, W/m·K, at $p = 1.03\cdot 10^5$ and $1.013\cdot 10^7$ Pa (curves 1 and 2). However, the variation of the effective Prandtl number, which is shown in Fig. 3, exerts a weaker influence than the separate variations of λ_r and c_{pr}; thus, the variation of σ_{eff} is $\sim$10% in the region of dissociation reactions and $\sim$40% in the region of ionization reactions (twofold ionization has been disregarded in the given computations, and the Prandtl number σ_{eff} turned out to be small at high temperatures and low pressures). Curves 1-3 in Fig. 3 correspond to $p = 1.013\cdot 10^3$, $1.013\cdot 10^5$, and $1.013\cdot 10^7$ Pa.

For the analysis of the influence of terms containing the gradients ∇H, ∇p, ∇c_j^*, and $\mathbf{J}_j^*$ on the heat flux (2.15), it is instructive to trace the variation of the coefficients of these terms in the equation. Figures 4-6 show the values of the coefficients $A = a(\nu, Q)(p/\rho h)$ (2.13), a_j^*/h (2.16), and b_j^*/h (2.14), respectively, after transformation to dimensionless form in accordance with Eq. (2.15). The results of the numerical computations illustrate the behavior of A in dissociation and ionization, but the actual value of this coefficient varies from 0 to 0.20 over the entire region of T and p. The ranges of variation of a_j^*/h and b_j^*/h are approximately identical: from 0 to 2.5.

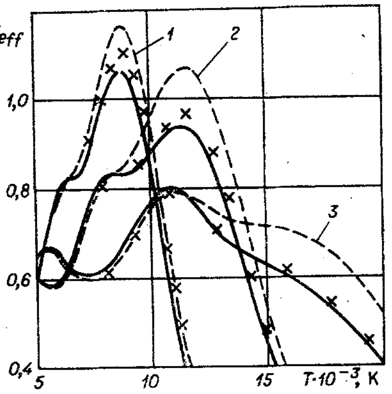

Fig. 3

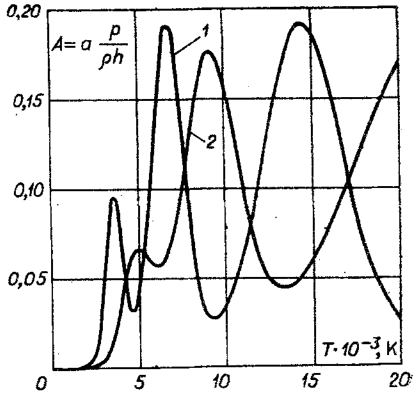

Fig. 4

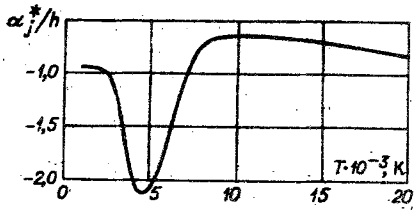

Fig. 5

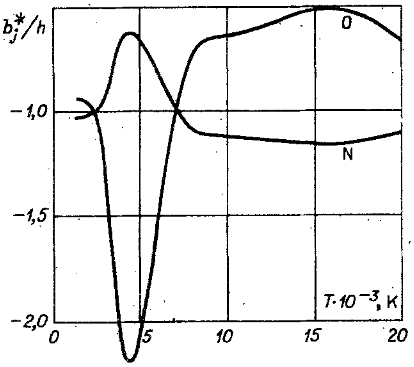

Fig. 6

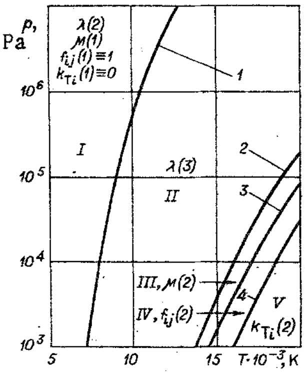

Fig. 7

The influence of thermal and pressure diffusion on the fluxes can be estimated according to the values of K^*_{Tj} and K^*_{pj}. We shall not give the detailed results of the numerical computations of these coefficients; we merely point out that K^*_{Tj} does not exceed ~ 0.01 in dissociation or ~ 0.025 in ionization, while K^*_{pj} does not exceed ~ 0.08 in dissociation or 0.06 in ionization [19]. Curves 1 and 2 in Fig. 4 correspond to $p = 1.013 \cdot 10^5$ and $1.013 \cdot 10^7$ Pa, and the pressure $p = 1.013 \cdot 10^5$ in Figs. 5 and 6.

4. INFLUENCE OF HIGHER APPROXIMATIONS ON THE EFFECTIVE TRANSPORT COEFFICIENTS

The convergence of the higher approximations in the computation of the effective coefficients in the transport equations has not been systematically investigated before. The expression for λ_r [8, 9] used extensively in the computation of the effective thermal conductivity of an ionized gas was obtained without inclusion of the higher approximations. Calculations of the coefficient λ_r in the higher approximations have not been carried out to date. The same is true of $\delta_j^{(e)} m_j/m$, which has been neglected previously in the calculation of chemical-equilibrium flows, so that the influence of higher approximations on these coefficients is unknown.

It has been shown [2] that different numbers (orders) ξ of approximations must be used, generally speaking, for different coefficients in order to compute the transport coefficients with a prescribed accuracy. The effective transport coefficients are functions of some or all of the transport coefficients, and so the analysis of their convergence with respect to ξ must be carried out completely with allowance for the different orders of convergence of the molecular coefficients. Numerical computations of the effective transport coefficients with allowance for different approximations in the original transport coefficients have indicated good convergence of all the effective coefficients for dissociated and ionized air.

The influence of inclusion of the higher harmonics in the calculation of $\delta_j^{(e)}$ (2.7) is shown in Fig. 1, in which the solid curves represent the exact values of $\delta_j^{(e)} m_j/m$, i.e., the fourth approximation $\xi = 4$ is used in this case for the calculation of the quantities $k_{Ti}(\xi)$ and $\varphi_{ij}(\xi)$ used in the computation of $\delta_j^{(e)}$; the dashed curves represent the values of $\delta_j^{(e)} m_j/m$

computed without regard for thermal diffusion, i.e., for $k_{Ti} = 0$, and without regard for the correction factors to the resistance coefficients Δ_{ij} [2] (for $\varphi_{ij} = 0$). It is seen that neglect of the thermal-diffusion ratios k_{Ti} and the correction factors φ_{ij} in the calculation of $\delta_j^{(e)}$ induces appreciable error (∿2-5%) only in the region of partial ionization.

Figure 2 shows the results of the computation of λ_r (2.11) with the use of different orders of approximation ξ in the calculation of the quantities k_{Ti}, φ_{ij} required for the computation of λ_r. It is found that the contribution of the thermal-diffusion ratios k_{Ti} to λ_r does not exceed ∿5% over the entire investigated range, and the correction factors φ_{ij} introduce a 2% contribution to λ_r. Thus, in the computation of $\delta_j^{(e)}$ and λ_r it is not required to calculate the values of $k_{Ti}(\xi)$ and $\varphi_{ij}(\xi)$ in the higher approximations, and k_{Ti} and φ_{ij} can be neglected altogether within ∿5% error limits.

The Prandtl number σ_{eff} (2.16) is shown in Fig. 3. Since higher approximations are inconsequential in the computation of λ_r, the number of approximations required for the computation of σ_{eff} is determined by the accuracy of computation of the ratio $\mu(\xi)/\lambda(\xi)$. It is sufficient to compute the coefficient $\lambda(\xi)$ within 2% error limits in the third approximation ξ, and to compute $u(\xi)$ in the second approximation [2]. The solid curves in Fig. 3 represent the exact values of σ_{eff}, i.e., the computations of all the original transport coefficients are carried out in the highest approximations ξ, and the dashed curves represent the values of σ_{eff} obtained with the computation of $\lambda(\xi)$ in the second approximation ($\xi = 2$) and of the coefficient $\mu(\xi)$ in the first approximation. The x's in Fig. 3 indicate the values of σ_{eff} computed without the correction coefficients to Δ_{ij} and without the thermal-diffusion ratios ($\varphi_{ij} = 0$, $k_{Ti} = 0$). It is therefore evident that the role of k_{Ti} and φ_{ij} in the computation of σ_{eff} is small, and their influence on σ_{eff} is ∿5%. However, the viscosity and thermal conductivity coefficients must be computed in the second and third approximations ξ, respectively. The incorrect choice of the approximation order ξ in the computation of σ_{eff} can produce $\gtrsim$60% error in the region of strong ionization.

The influence of the accuracy of computation of $k_{Ti}(\xi)$ and $\varphi_{ij}(\xi)$ on α_{jl}^{**} in the element transport equation (2.5) and on a_j^* (2.16) and b_j^* (2.14) in the total heat-flux equation (2.15) is found to be the same as in the computation of $\delta_j^{(e)}$. The influence of the higher approximations on the computation of K_{Tj}^* in (2.5) is determined entirely by the accuracy of computation of $k_{Ti}(\xi)$, but the coefficients K_{Tj}^* themselves are rather small, and it is not essential to include higher approximations in the computation of $k_{Ti}(\xi)$. The coefficients K_{pj}^* in (2.5) and $a(\nu, Q)$ (2.13) in (2.15) are of a purely thermodynamic nature and do not depend on the higher approximations. Nor does the coefficient $S_j/\mu = \Delta_j/m$ depend on the higher approximations; by virtue of the conditions [1] $x_j/\mathscr{D}_{ij}(1)]\,\varphi_{ij}(\xi) = 0$ the coefficient Δ_j does not depend on the correction factors $\varphi_{ij}(\xi)$.

Thus, the thermal-diffusion ratios $k_{Ti}(\xi)$ and the correction factors $\varphi_{ij}(\xi)$ must be computed in the second approximation ξ (the first nonzero approximation) in the computation of the element diffusion fluxes $\mathbf{J}_j^*$ and the total heat flux $\mathbf{J}_q$ for partially ionized air. In the region of partial ionization $k_{Ti}(\xi)$ can be neglected within ∿5% error limits in the computation of all the investigated coefficients, and $\varphi_{ij}(\xi)$ can be neglected in the computation of all the effective coefficients in the total heat-flux equation. For the computation of the coefficients in the total heat-flux equation the transport coefficients $\mu(\xi)$ (viscosity) and $\lambda(\xi)$ (thermal conductivity) must be computed in the second and third approximations, respectively. The orders of the determinants in the expressions for $\mu(2)$ and $\lambda(3)$ are identical and equal to 2N in this case.

The situation described here is illustrated in Fig. 7, where the regions I-V in the T–p plane are separated by curves 1-4, which indicate the rightmost boundary to which the transport coefficients $\lambda(\xi)$, $\mu(\xi)$, $k_{Ti}(\xi)$, $\varphi_{ij}(\xi)$ must be calculated in specified approximations ξ in order to ensure the calculation of the effective coefficients in the transport equations within at most ∿5% error limits [the arguments (in parentheses) of the coefficients indicate the order of approximation ξ]. It is evident from the monogram that all the transport coefficients without exception must be computed in the higher approximations only beginning with region V in the case of partially ionized air.

LITERATURE CITED

1. A. F. Kolesnikov and G. A. Tirskii, "Hydrodynamic equations for partially ionized multicomponent gas mixtures with transport coefficients in higher approximations," in: Molecular Gas Dynamics [in Russian], Nauka, Moscow (1982).
2. S. A. Vasil'evskii, I. A. Sokolova, and G. A. Tirskii, "Exact transport equations and coefficients for a multicomponent gas mixture and a partially ionized plasma," Zh. Prikl. Mekh. Tekh. Fiz., No. 4 (1984).
3. R. Haase, Thermodynamics of Irreversible Processes, Addison-Wesley, Reading, Mass. (1968).
4. R. Haase, "Zur Thermodynamik der irreversibler Prozess III," Z. Naturforsch., Teil A, 8, No. 11, 729 (1953).
5. J. Meixner, "Zur Theorie der Wärmeleitfähigkeit reagierender fluider Mischungen," Z. Naturforsch., Teil A, 7 (1952).
6. J. O. Hirschfelder, "Heat transfer in chemical reaction mixtures," J. Chem. Phys., 26, No. 2 (1957).
7. R. S. Brokaw, "Thermal conductivity of gas mixtures in chemical equilibrium. 2," J. Chem. Phys., 32, No. 4 (1960).
8. J. N. Butler and R. S. Brokaw, "Thermal conductivity of gas mixtures in chemical equilibrium," J. Chem. Phys., 26, No. 6 (1957).
9. I. A. Krinberg, "Influence of ionization reactions on the thermal conductivity of a plasma," Teplofiz. Vys. Temp., 3, No. 6 (1965).
10. A. A. Luchina, "Influence of chemical reactions on the thermal conductivity and diffusion fluxes in a plasma," Inzh.-Fiz. Zh., 29, No. 4 (1975).
11. G. A. Tirskii, Method of Successive Approximations for the Integration of a Laminar Boundary Layer with Chemical Reactions, Including Ionization Reactions, Report No. 1016 of the Institute of Mechanics, Moscow State University [in Russian], Inst. Mekh. Mosk. Gos. Univ., Moscow (1969).
12. O. N. Suslov, G. A. Tirskii, and V. V. Shchennikov, "Description of chemical-equilibrium flows of multicomponent ionized mixtures within the framework of the Navier-Stokes and Prandtl equations," Zh. Prikl. Mekh. Tekh. Fiz., No. 1 (1971).
13. G. Ya. Gerasimov, "Transport phenomena in a dissociating gas," Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 4 (1981).
14. G. Ya. Gerasimov, "Transport phenomena in a partially ionized gas with allowance for the ionization reaction," Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 3 (1974).
15. G. Ludwig and M. Hale, "Boundary-layer theory with dissociation and ionization," in: Problems of Mechanics [collection of articles translated into Russian], No. 4, IL, Moscow (1963).
16. G. A. Tirskii, "Hydrodynamic description of chemical-equilibrium flows of partially ionized nonideal gas mixtures," in: Selected Problems of Continuum Mechanics [in Russian], Izd. Mosk. Gos. Univ., Moscow (1978).
17. S. N. Kazeikin, Computation of the Thermodynamic and Transport Properties of High-Temperature Air, Preprint No. 108 of the Institute of Applied Mechanics [in Russian], Inst. Prikl. Mekh. Akad. Nauk SSSR (1978).
18. O. M. Suslov, "Multicomponent diffusion and heat transfer in the flow of a chemical-equilibrium ionized gas around a body," Zh. Prikl. Mekh. Tekh. Fiz., No. 3 (1972).
19. S. A. Vasil'evskii, L. G. Efimova, et al., Computation of the Transport Coefficients in a Multicomponent Plasma in Higher Approximations: Element Separation Effect in a Plasma in Chemical and Ionization Equilibrium, Report No. 2427 of the Institute of Mechanics, Moscow State University [in Russian], Inst. Mekh. Mosk. Gos. Univ., Moscow (1980).