Pergamon
www.elsevier.com/locate/jappmathmech

PII: S0021-8928(00)00003-4

J. Appl. Maths Mechs, Vol. 63, No. 6, pp. 841–861, 1999

0021-8928/99/$—see front matter

THE HYDRODYNAMIC EQUATIONS FOR CHEMICALLY EQUILIBRIUM FLOWS OF A MULTIELEMENT PLASMA WITH EXACT TRANSPORT COEFFICIENTS†

G. A. TIRSKII

Dolgoprudnyi

(*Received* 15 *July* 1999)

Explicit expressions for all of the effective transport coefficients are derived for thermochemically equilibrium flows using the exact mass and heat transfer equations, which are resolved with respect to the "forces" (the gradients of the hydrodynamic variables) via the flukes. It is shown that, in a mixture where the components have different diffusion properties, separation (diffusion) of the chemical elements occurs which leads to a state of affairs where the equilibrium concentrations, and together with them, the effective transport coefficients will be functions not only of the pressure and temperature but will also depend on the concentrations of the elements, determined when solving the problem (self-consistent concentrations of the elements). It is shown that the existence of an electric current and lack of quasineutrality (flow around electrically conducting walls—electrodes) does not change the structure of the expressions for the effective transport coefficients and does not add anything new. The approximate and incomplete treatment of thermochemically equilibrium flows of multicomponent gas mixtures and a plasma in previously published papers are especially noted. Numerical estimates of the effective transport coefficients are presented for an air plasma and the domains in the pressure–temperature plane with the required number of approximations in order to obtain results with an error of no worse than ~5% are indicated. © 2000 Elsevier Science Ltd. All rights reserved.

An extensive literature [1–8] exists on transport phenomena in thermochemically equilibrium multicomponent gas mixtures of electrically neutral and charged components when the temperature of all the components and the temperature of the internal degrees of freedom are identical (thermal equilibrium) and the time for the occurrence of the slowest process is much less than the characteristic hydrodynamic time, such as, for example, the time a fluid particle resides in the flow domain being considered. Heat transfer, taking account of the additional diffusion transport of "chemical" energy, was first considered by Nernst in the case of a single, very simple reaction [1]. Subsequently, a method for binary gas mixtures, in which a single fast dissociation reaction occurs, was developed in [2–4] and elsewhere. The effective thermal conductivity was derived in [5, 6] for the case of multicomponent mixtures at rest ($\nabla p = 0, p$ is the pressure in the mixture) with an arbitrary, finite number of chemical reactions taking place and the thermal conductivity for partially ionized, chemically equilibrium mixtures was derived in [7, 8].

The papers noted above do not completely and exactly solve the problem of the hydrodynamic description of thermochemically equilibrium flows of multicomponent gas mixtures and a plasma when the components have different diffusion properties, and the investigations were carried out outside the context of the complete system of diffusion and energy equations for equilibrium flows for the following reasons. First, in a number of papers, the energy equation for chemically equilibrium flows is described as for a homogeneous gas but with the conventional thermal conductivity replaced by an effective thermal conductivity. Second, these papers are limited solely to the calculation of the effective thermal conductivity and only in isobaric flows ($\nabla p = 0$). Taking account of the pressure gradient leads to an additional term in the energy equation for chemically equilibrium systems (see below: (8.11)). Third, the derivation of the expression for the thermal conductivity λ_r is based on the use of the mass transfer equations of the components in the Stefan–Maxwell form without making allowance for the effects of thermal and pressure diffusion. Fourth, quasineutrality is assumed in the case of a plasma (quasineutrality breaks down electrically conducting walls—electrodes) and it is assumed that there is no external force field [7]. Fifth, only molecular heat transfer with a specified element composition was considered, that is, no allowance was made for molecular mass transfer in the form of the diffusion of elements which, of necessity, manifests itself when there is a temperature gradient in a multicomponent mixture where the components have different diffusion properties even when the effects of thermal diffusion and pressure diffusion are neglected (see below: (8.16) and (8.17)).

---

†*Prikl. Mat. Mekh.* Vol. 63, No. 6, pp. 899–922, 1999.

Hence, in the general case, integrals with constant concentrations and zero diffusion fluxes of the elements $c_j^* = \text{const}, J_j^* = 0$ $(j = 1, \ldots, L)$, where L is the number of elements from which, as a result of the reaction, the N-component mixture is formed, do not exist in the case of chemically equilibrium flows of mixtures where the components have different diffusion properties. When account is taken of the diffusion of the elements in chemically equilibrium mixtures, this leads to the appearance of a further whole series of cross effective transport coefficients, as a result of which the diffusive flow of any given element depends on the concentration gradients of all the other elements. Attention was first drawn to this in [9, 10]. Finally, and this is the most important remark, the initial formulae for the transport coefficients were based on the use of the lowest approximations, that is, the first non-zero approximations when they were found in the form of a series of Sonin polynomials using the Chapman–Enskog method (CEM) for the solution of Boltzmann's equation [11].

It is necessary to take account of higher approximations when calculating the transport coefficients of a plasma in order to obtain quantitatively correct results. It has been repeatedly pointed out in the literature [12, 13] that the formulae which are conventionally used for the transport coefficients, obtained in the lower approximations of the Chapman–Enskog method [11] (the first approximation for the diffusion coefficients and the second approximation for the thermal conductivity and thermal diffusion coefficient), do not reduce to the exact formulae for the transport coefficients, obtained in [14, 15] by the method of statistical mechanics of charged particles, in the case of a completely ionized plasma. Calculations [16, 17] for certain single-element ionised gases such as argon and hydrogen, for example, show that, for the correct determination of the transport coefficients, it is necessary to take account of a minimum of three terms in the expansion of the perturbed distribution functions in series over Sonin polynomials (the third approximation). Confirmation of the need to take account of higher approximations in the case of ionized mixtures containing a light component can be found in [18].

For a low degree of ionization, the convergence of the approximations is slower, the more pronounced the change in the electron scattering cross-section for the atom as a function of the energy of the electron [19]. In particular, in the case of moderately ionized argon, it is necessary to take account of up to six approximations when calculating the electrical conductivity [17, 20, 21]. If, however, the scattering coefficient only changes slightly, it is sufficient to use the third degree of approximation for the electron heat conduction for any degree of ionization of a mixture [19].

The standard Chapman–Enskog procedure [11], which gives expressions for the molecular mass, momentum and energy fluxes of a mixture in terms of thermodynamic "forces" (in the terminology of the thermodynamics of irreversible processes, these "forces" are the concentration, temperature and pressure gradients, the components of the rate of deformation tensor and the external mass forces), leads to formulae for the transport of coefficients (the multicomponent diffusion coefficients and thermal diffusion coefficients, the instantaneous (not the true) thermal conductivity λ' and the thermal diffusion coefficient) in the form of the ratio of determinants of order $(N\xi + 1)$ to determinants of order $N\xi$, where N is the number of components in the mixture and ξ is the number of approximations [11, 22] (see formulae (2.4) and (2.5)).

Calculation of the true thermal conductivity and the diffusion coefficient, taking account of higher approximations using the method in [11], requires the calculation of Nth order determinants, the elements of which are determinants of the $(N\xi + 1)$th order. This procedure has only been carried out explicitly in the second approximation and only when calculating the thermal conductivity [23–25]. As before, the determination of the thermal diffusion coefficient requires, in these papers, the calculation of Nth order matrices with elements which are $(N\xi + 1)$th order determinants.

Transport coefficients have only been calculated using this classical scheme in the case of a single-element plasma [16, 17, 20, 21, 26–28]; it is not very suitable for solving gas dynamic problems.

Calculations of equilibrium transport coefficients [29, 30] based on the use of the classical transport equations [11] (the fluxes are in terms of "forces") should be mentioned. In this case, multicomponent diffusion and thermal diffusion coefficients are introduced which give rise to enormous computational difficulties and an enormous volume of results if the equilibrium transport coefficients for multicomponent mixtures are to be calculated in the higher approximations.

In addition to the difficulty which has been noted above, substitution of the expressions for the fluxes obtained in [11] into the equations of motion of the mixtures (the conservation equations) leads to a system of equations which cannot be solved with respect to higher derivatives of the required functions. At present, there are no general methods for the effective solution of such systems of equations even in the approximation of the various asymptotically simplified versions of the Navier–Stokes equations [31, 32]. For this purpose, it is necessary to have transport equations which are solved with respect to the "forces" via the fluxes. Such equations can be obtained without having to invert matrices if the Grade method [33] is used. However, the thirteenth moment Grade method for calculating transport coefficients is only equivalent in accuracy to the second Chapman–Enskog approximation [34].

In this paper, we introduce equations for the mass transfer of the elements and heat for thermochemically equilibrium flows and for all the effective transport coefficients in them in any approximation, which are free from any of the constraints in the papers cited above. These equations are based on simpler and more exact equations for the mass transfer of the components and energy obtained previously [35–37] in a form which is suitable for the numerical and analytic solution of problems and are solved with respect to the "forces" (the gradients of the hydrodynamic variables) via the fluxes.

1. CONSERVATION EQUATIONS FOR MIXTURES OF GASES AND A PLASMA

We shall consider the macroscopic (hydrodynamic) motion of a mixture of gases and a plasma (a partially ionized or completely ionized mixture of gases) under conditions of thermal equilibrium, that is, when the translational (kinetic or gas) temperature of all the components is the same and is equal to the temperature of the internal degrees of freedom of the particles. We consider a mixture consisting of N components. For the practical calculation of flows in which chemical reactions and ionization are occurring at an arbitrary rate, it is convenient to pick out L independent (basis) components for which it is possible, for example, to take the chemical elements and an electron component, and $R = N - L$ of the components (reaction products). The chemical symbols of the basis components are denoted by B_j ($j = 1, \dots, N$) and the reaction product symbols by A_i ($i = L + 1, \dots, N$). Then, without loss of generality, the linearly independent, stoichiometric equations of the reactions can be symbolically written in the form

$$A_i = \sum_{j=1}^{L} \nu_{ij} B_j - q_i(T), \quad i = L+1, \dots, N \tag{1.1}$$

where ν_{ij} are the stoichiometric coefficients for the reactions and q_i are the heats of the reactions. In accordance with representation (1.1), the laws of conservation of mass and charge in the reactions will have the form

$$m_i = \sum_{j=1}^{L} \nu_{ij} m_j, \quad e_i = \sum_{j=1}^{L} \nu_{ij} e_j \tag{1.2}$$

where m_i, e_i are the mass and charge of the ith particle. We now define the relative, or henceforth, simply the mass concentrations of the elements c_j^* ($j = 1, \dots, L$) and the mass diffusion fluxes of the elements $\mathbf{J}_j^*$ ($j = 1, \dots, L$) in accordance with the stoichiometric representation of the reactions (1.1) as follows:

$$c_j^* = c_j + \sum_{k=L+1}^{N} \nu_{kj} \frac{m_j}{m_k} c_k, \quad \mathbf{J}_j^* = \mathbf{J}_j + \sum_{k=L+1}^{N} \nu_{kj} \frac{m_j}{m_k} \mathbf{J}_k \tag{1.3}$$

Then, the system of Navier–Stokes equations, which expresses the laws of conservation of mass, momentum and energy in the mixture can be written in the form [38]

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0, \quad \rho \mathbf{v} = \sum_{k=1}^{N} \rho_k \mathbf{v}_k \tag{1.4}$$

$$\rho \frac{dc_j^*}{dt} + \operatorname{div} \mathbf{J}_j^* = 0, \quad \rho = \sum_{k=1}^{N} \rho_k, \quad j = 1, \dots, L \tag{1.5}$$

$$\rho \frac{dc_i}{dt} + \operatorname{div} \mathbf{J}_i = \dot{w}_i, \quad i = L+1, \dots, N \tag{1.6}$$

$$\rho \frac{d\mathbf{v}}{dt} = \sum_{k=1}^{N} \rho_k \mathbf{F}_k - \nabla p + \operatorname{div} \hat{\tau} \tag{1.7}$$

$$\rho \frac{d}{dt}\left(h + \frac{v^2}{2} \right) = \frac{\partial p}{\partial t} + \sum_{k=1}^{N} \rho_k \mathbf{F}_k \cdot \mathbf{v}_k + \operatorname{div}(\hat{\tau} \cdot \mathbf{v} - \mathbf{J}_q), \quad h = \sum_{k=1}^{N} c_k h_k \tag{1.8}$$

$$p = \frac{\rho}{m} kT, \quad \frac{1}{m} = \sum_{k=1}^{N} \frac{c_k}{m_k}, \quad \rho = \sum_{k=1}^{N} n_k m_k, \quad n = \sum_{k=1}^{N} n_k \tag{1.9}$$

Here, $\rho_i = n_i m_i$, n_i, $\mathbf{v}_i$, $c_i = \rho_i/\rho$, $x_i = n_i/n = (m/m_i)c_i$, $\mathbf{J}_i$, $\dot{w}_i$, $\mathbf{F}_i$, h_i are the mass density, the number of particles per unit volume, the mean statistical velocity, the mass relative or simply concentration, the relative molar concentration, the vector of the mass diffusion flow of the ith component, the rate of formation of mass of the ith component per unit volume due to reactions, the mass force acting on the ith component and the specific enthalpy of the ith component, respectively. Also ρ, $\mathbf{v}$, p, h, T, m, n, $\mathbf{J}_q$, $\hat{\tau}$ are the density, the mean statistical mass velocity of the mixture, the pressure, the specific enthalpy of the mixture, the temperature and average molecular mass of the mixture, the total number of particles, the vector of the total heat flux and the viscous stress tensor of the mixture as a whole, respectively, and k is Boltzmann's constant.

Equation (1.4) is the continuity equation for the mixture as a whole, Eqs (1.5) are the equations for the diffusion (mass balance) of the elements, Eqs (1.6) are the equations for the diffusion (mass balance) of the components, that is, of the reaction products, Eq. (1.7) is the momentum equation for the mixture as a whole, Eq. (1.8) is the energy equation for the mixture as a whole and Eq. (1.9) is the equation of state for a mixture of ideal (non-dense) gases.

As the elements, one can select any set of independent chemical components from which it is possible to obtain all the remaining components by writing out the independent reactions in the form of (1.1). If the gas is ionized the electron appears as a further element together with the others. However, any ion can also be chosen instead of the electron.

When solving actual problems it is convenient to use the $N - L$ equations for the diffusion of the reaction products (1.6) and the L equations for the diffusion of the elements (1.5) with zero right-hand sides (null sources) since no element is created or disappears in the reactions but only passes from one component to another.

2. MASS- AND HEAT-TRANSFER EQUATIONS SOLVED WITH RESPECT TO THE FLUXES (FLUXES VIA "FORCES")

In order to close the system of equations (1.4)–(1.9), it is necessary to have explicit expressions for the fluxes $\mathbf{J}_i (i = 1, \dots, N)$, $\mathbf{J}_q$ and $\hat{\tau}$, the so-called transport equations and, in addition, expressions for the source terms $\dot{w}_i$ $(i = 1, \dots, N)$. The transport equations for mixtures which only slightly deviate from the state of local thermodynamic equilibrium are represented in the form of linear relations which associate the "fluxes" with the corresponding thermodynamic "forces", that is, with the gradients of the hydrodynamic variables. The expression for the viscous stress tensor (the momentum transport equation) $\hat{\tau}$ in the Navier–Stokes (linear) approximation for the gas mixtures as a whole and the diffusion approximation has a well-known form which is identical to the equation for a homogeneous gas and is not given here. The expressions for $\dot{w}_i$ are also not presented here.

We will initially give the equations for the mass transfer of the components in a multicomponent, partially ionized mixture of gases in the well known classical form [11] (fluxes via "forces")

$$\mathbf{J}_i = \rho \sum_{j=1}^{N} \frac{m_i m_j}{m^2} D_{ij} \mathbf{d}_j - D_i^T \nabla \ln T, \quad i = 1, \dots, N \tag{2.1}$$

$$\mathbf{J}_q = -\lambda' \nabla T + \sum_{k=1}^{N} h_k \mathbf{J}_k - nkT \sum_{k=1}^{N} \frac{D_k^T}{\rho_k} \mathbf{d}_k \tag{2.2}$$

$$\mathbf{d}_i = \nabla x_i + (x_i - c_i) \nabla \ln p + \frac{c_i}{p} \left(\sum_{k=1}^{N} \rho_k \mathbf{F}_k - \rho \mathbf{F}_i \right), \quad i = 1, \dots, N \tag{2.3}$$

where $\mathbf{d}_i$ are the vectors of the diffusion "forces".

The multicomponent diffusion D_{ij} and thermal diffusion D_i^T coefficients are given by the following expressions in any approximation ξ for determining them in the form of series in Sonin polynomials [11]

$$D_{ij}(\xi) = \frac{3\rho x_i}{2m_j \det \mathbf{q}} \left(\frac{2\pi kT}{m_i} \right)^{1/2} \begin{vmatrix} 0 & \delta_{is} & 0 & \dots & 0 \\ \delta_{rj} - \delta_{ri} & \mathbf{q}_{rs}^{00} & \mathbf{q}_{rs}^{01} & \dots & \mathbf{q}_{rs}^{0,\xi-1} \\ 0 & \mathbf{q}_{rs}^{10} & \mathbf{q}_{rs}^{11} & \dots & \mathbf{q}_{rs}^{1,\xi-1} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \mathbf{q}_{rs}^{\xi-1,0} & \mathbf{q}_{rs}^{\xi-1,1} & \dots & \mathbf{q}_{rs}^{\xi-1,\xi-1} \end{vmatrix}, \ \xi \geqslant 1 \tag{2.4}$$

$$D_i^T(\xi)=\frac{15n_i(2\pi m_i kT)^{1/2}}{4\det \mathbf{q}}\begin{vmatrix} 0 & \delta_{is} & 0 & \cdots & 0 \\ 0 & \mathbf{q}_{rs}^{00} & \mathbf{q}_{rs}^{01} & \cdots & \mathbf{q}_{rs}^{0,\xi-1} \\ n_r & \mathbf{q}_{rs}^{10} & \mathbf{q}_{rs}^{11} & \cdots & \mathbf{q}_{rs}^{1,\xi-1} \\ 0 & \mathbf{q}_{rs}^{20} & \mathbf{q}_{rs}^{21} & \cdots & \mathbf{q}_{rs}^{2,\xi-1} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ & \mathbf{q}_{rs}^{\xi-1,0} & \mathbf{q}_{rs}^{\xi-1,1} & \cdots & \mathbf{q}_{rs}^{\xi-1,\xi-1} \end{vmatrix}, \quad \sum_{k=1}^{N} D_k^T=0 \qquad (2.5)$$

$\xi \geq 2, D_i^T(1) \equiv 0.$

where $\mathbf{q}_{rs}^{mp}$ is an $N \times N$ square matrix composed of the elements

$$q_{ij}^{mp}=\sqrt{\frac{2\pi m_i}{kT}}\left(Q_{ij}^{mp}-\frac{x_j}{x_i}\sqrt{\frac{m_j}{m_i}}Q_{ii}^{mp}\delta_{m0}\delta_{p0}\right), \quad i,j=1,\ \ldots,\ N;\ m,p=0,1,\ldots,\xi-1$$

and det $\mathbf{q}$ is a determinant of order $N\xi \times N\xi$ which is obtained by crossing out the first row and the first column from the numerator in (2.4) or (2.5).

The quantities Q_{ij}^{mp} are expressed in terms of complete integral brackets ("bracket" integrals) which, in turn, are expressed in the well known form in terms of collision integrals (Ω are integrals) which depend on the pairwise interaction potential [11, 41]. It is important to note that $D_i^T(1) \equiv 0$, that is, the thermal diffusion coefficient has a non-zero value, starting from the second approximation.

Hence, the equations for the mass transfer of the components in the standard Chapman–Enskog procedure are given by expressions (2.1) with coefficients (2.4) and (2.5), which represent the ratios of the $N\xi + 1$ order determinants to $N\xi$ order determinants. As a rule, Eqs (2.1) with the exact coefficients (2.4) and (2.5) are not used in this form when solving actual hydrodynamic problems because of their complexity, in particular, in the case of partially or fully ionized mixtures when it is necessary to take account of higher approximations.

The coefficient λ' in (2.2) is given by the expression [11, 16]

$$\lambda'(\xi)=-\frac{75k}{8}\frac{(2\pi kT)^{1/2}}{\det \mathbf{q}}\begin{vmatrix} 0 & 0 & n_j/m_j^{1/2} & 0 & \cdots & 0 \\ 0 & \mathbf{q}_{ij}^{00} & \mathbf{q}_{ij}^{01} & \mathbf{q}_{ij}^{02} & \cdots & \mathbf{q}_{ij}^{0,\xi-1} \\ n_i & \mathbf{q}_{ij}^{10} & \mathbf{q}_{ij}^{11} & \mathbf{q}_{ij}^{12} & \cdots & \mathbf{q}_{ij}^{1,\xi-1} \\ 0 & \mathbf{q}_{ij}^{20} & \mathbf{q}_{ij}^{21} & \mathbf{q}_{ij}^{22} & \cdots & \mathbf{q}_{ij}^{2,\xi-1} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \mathbf{q}_{ij}^{\xi-1,0} & \mathbf{q}_{ij}^{\xi-1,1} & \mathbf{q}_{ij}^{\xi-1,2} & \cdots & \mathbf{q}_{ij}^{\xi-1,\xi-1} \end{vmatrix} \qquad (2.6)$$

and has a non-zero value, starting from the second approximation, which is analogous to the result of the calculation of the thermal diffusion coefficient (2.5).

It is important that the following point be noted. The coefficient λ' is not equal to the conventionally defined thermal conductivity. According to expression (2.2), λ' can be interpreted as the thermal conductivity of a multicomponent mixture in which there are no diffusion "forces" $\mathbf{d}_i$ ($i = 1, \ldots, N$). If only a temperature gradient, which is constant throughout space, is created in an initially, spatially homogeneous gas mixture and the thermal conductivity is measured up to the instant of time when the diffusion thermal effect (the last term in (2.2)) manifests itself, then this measurement will give the coefficient λ'. However, concentration gradients appear with the passage of time and the diffusion forces will increase until the diffusion flows $\mathbf{J}_i$ disappear (until a steady state occurs). Measurement of the thermal conductivity in this steady state also gives the true thermal conductivity λ.

In order to obtain an expression for the true thermal conductivity λ in any approximation and, correspondingly, the heat flux, it is necessary to solve transport equation (2.1) with respect to the vectors $\mathbf{d}_i$ ($i = 1, \ldots, N$). The formal solution can be written in the form

$$\mathbf{d}_i=\frac{\rho}{n^2}\sum_{k=1}^{N}\frac{E_{ik}}{m_k}\mathbf{J}_k+\frac{\rho}{n^2}\sum_{k=1}^{N}\frac{E_{ik}D_k^T}{m_k}\nabla \ln T \qquad (2.7)$$

where E_{ik} are the elements of the matrix which is the inverse of the matrix with the elements $D_{ki}m_i$. Substituting solution (2.7) into (2.2), we obtain the required expression

$$\mathbf{J}_q = -\lambda\nabla T + \sum_{j=1}^{N}\left(h_j - \frac{\rho kT}{nm_j}\sum_{k=1}^{N}\frac{D_k^T E_{kj}}{\rho_k}\right)\mathbf{J}_j \tag{2.8}$$

with the true thermal conductivity, which is equal to

$$\lambda = \lambda' + \frac{\rho k}{n}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{E_{ij}D_i^T D_j^T}{\rho_i m_j} \tag{2.9}$$

The double summation (the last term) in (2.8) is the diffusion thermal effect and the coefficients in front of $\mathbf{J}_i$, like the double summation in (2.9), are complex expressions in which is the inverse of a matrix, since the coefficients E_{ik} are the elements of a matrix which is the inverse of a matrix in which, in turn, the elements are ratios of determinants of orders ($N\xi$ + 1) and $N\xi$. In the case of unionized mixtures, when the thermal diffusion coefficients are small, the contribution made by the double summation to the thermal conductivity is small (of the order of a few per cent [11]). However, in the case of a plasma, this leads to an appreciable error, since the presence of electrons in the mixture leads to the appearance of terms in (2.9) with small denominators, proportional to m_E and m_E^2, which greatly increases the contribution due to the effect of thermal diffusion [39]. Calculation of the dissipation function, as well as calculations using formula (2.9), show that the instantaneous value of the thermal conductivity is greater than the true thermal conductivity, that is, $\lambda' > \lambda$. For example, $\lambda' \approx 1.3\lambda$ [16] in the case of a completely ionized hydrogen plasma.

Hence, the classical Chapman–Enskog approach in [11] give extremely complex expressions for the true thermal conductivity and the thermal diffusion coefficient which are not very suitable for solving problems in gas dynamics.

3. MASS AND HEAT TRANSFER EQUATIONS, SOLVED WITH RESPECT TO THE GRADIENTS OF THE HYDRODYNAMIC VARIABLES ("FORCES" VIA FLUXES)

We will now derive simple and accurate transport equations in any approximation which are equivalent to (2.1) and (2.2). The idea behind the derivation of these transport equations was put forward in [32, 40] and finally implemented in [35].

In any approximation, the equations for the transfer of mass of the components (the Stefan–Maxwell relations) take the form [35]

$$\mathbf{d}_i = \sum_{j=1}^{N}\frac{x_i x_j f_{ij}(\xi)}{\mathcal{D}_{ij}(1)}\left(\frac{\mathbf{J}_j}{\rho_j} - \frac{\mathbf{J}_i}{\rho_i}\right) - k_{Ti}(\xi)\nabla\ln T, \quad i = 1,\ldots,N \tag{3.1}$$

where $f_{ij} = f_{ji} = (1 - \varphi_{ij})$, the correction coefficients for the higher approximation, are equal to

$$\varphi_{ij}(\xi) = \frac{2}{3}\frac{\mathcal{D}_{ij}(1)}{x_i x_j \det\mathbf{g}}\begin{vmatrix} 0 & \mathbf{g}_{js}^{01} & \cdots & \mathbf{g}_{js}^{0,\xi-1} \\ \mathbf{g}_{ri}^{10} & \mathbf{g}_{rs}^{11} & \cdots & \mathbf{g}_{rs}^{1,\xi-1} \\ \vdots & \vdots & & \vdots \\ \mathbf{g}_{ri}^{\xi-1,0} & \mathbf{g}_{rs}^{\xi-1,1} & \cdots & \mathbf{g}_{rs}^{\xi-1,\xi-1} \end{vmatrix}, \quad \xi \geqslant 2, \quad \varphi_{ij}(1) \equiv 0 \tag{3.2}$$

$$\varphi_{ij}(\xi) = \varphi_{ji}(\xi), \quad \sum_{j=1}^{N}\frac{x_i x_j}{\mathcal{D}_{ij}(1)}\varphi_{ij}(\xi) = 0, \quad g_{rs}^{mp} = \frac{1}{n}\sqrt{\frac{m_s}{2\pi kT}}q_{rs}^{mp}$$

$$i, j\ r, s = 1, \ldots, N;\ m, p = 0, 1, \ldots, \xi - 1$$

where $\mathbf{g}_{rs}^{mp}$ are $N \times N$ square matrices composed of the elements g_{rs}^{mp} and det $\mathbf{g}$ is the determinant obtained from the determinant in the numerator of (3.2) by crossing out the first column and the first row.

In any approximation, the thermal diffusion relations k_{Ti} have the form [35]

$$k_{Ti}(\xi) = -\frac{5}{2\det \mathbf{g}} \begin{vmatrix} 0 & x_s & 0 & \dots & 0 \\ \mathbf{g}_{ri}^{10} & \mathbf{g}_{rs}^{11} & \mathbf{g}_{rs}^{12} & \dots & \mathbf{g}_{rs}^{1,\xi-1} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathbf{g}_{ri}^{\xi-1,0} & \mathbf{g}_{rs}^{\xi-1,1} & \mathbf{g}_{rs}^{\xi-1,2} & \dots & \mathbf{g}_{rs}^{\xi-1,\xi-1} \end{vmatrix}, \quad i = 1,\dots,N$$

$$\sum_{j=1}^{N} k_{Tj}(\xi) = 0, \quad \xi \geqslant 2, \quad k_{Ti}(1) \equiv 0 \tag{3.3}$$

and are expressed in terms of the thermal diffusion coefficients $D_i^T(\xi)$ as follows:

$$k_{Ti}(\xi) = -\sum_{j=1}^{N} \frac{x_i x_j f_{ij}(\xi)}{\mathscr{D}_{ij}(1)} \left[\frac{D_j^T(\xi)}{\rho_j} - \frac{D_i^T(\xi)}{\rho_i} \right] \tag{3.4}$$

The approximate Stefan–Maxwell relations, given in [11] are obtained from the exact relations (3.1) if we put $\xi = 2$ and $f_{ij} = 1$ in them, which corresponds to taking account, non-consecutively, of the diffusion coefficients in the first approximation and the thermal diffusion coefficients in the second approximation. In order to obtain the correct Stefan–Maxwell relations k_{Ti} in the second approximation, we must put $\xi = 2$ and $f_{ij}(2) = 1 - \varphi_{ij}(2)$ in (3.1), where

$$\varphi_{ij}(2) = \frac{2}{3} \frac{\mathscr{D}_{ij}(1)}{x_i x_j \det \mathbf{g}} \begin{vmatrix} 0 & \mathbf{g}_{js}^{01} \\ \mathbf{g}_{ri}^{10} & \mathbf{g}_{rs}^{11} \end{vmatrix}$$

It is important to note that the coefficients $k_{Ti}(\xi)$ are expressed more simply by formula (3.3) than the thermal diffusion coefficients (2.5) (the determinants are N orders less!).

According to the theory in [35], in the total heat flux in any approximation has the form

$$\mathbf{J}_q = -\lambda(\xi)\nabla T + \sum_{j=1}^{N} h_j \mathbf{J}_j + nkT \sum_{j=1}^{N} \frac{k_{Tj}}{\rho_j} \mathbf{J}_j \tag{3.5}$$

where the true thermal conductivity, in any approximation, is given by the expression (compare with (2.9))

$$\lambda(\xi) = -\frac{75}{8} \frac{nk}{\det \mathbf{g}} \begin{vmatrix} 0 & x_s & 0 & \dots & 0 \\ x_r & \mathbf{g}_{rs}^{11} & \mathbf{g}_{rs}^{12} & \dots & \mathbf{g}_{rs}^{1,\xi-1} \\ 0 & \mathbf{g}_{rs}^{21} & \mathbf{g}_{rs}^{22} & \dots & \mathbf{g}_{rs}^{2,\xi-1} \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & \mathbf{g}_{rs}^{\xi-1,1} & \mathbf{g}_{rs}^{\xi-1,2} & \dots & \mathbf{g}_{rs}^{\xi-1,\xi-1} \end{vmatrix}, \quad \xi \geqslant 2, \quad \lambda(1) \equiv 0 \tag{3.6}$$

If we confine ourselves to the second approximation ($\xi = 2$), then an expression is obtained from general formula (3.6) which is identical to the expression from [23] if account is taken of the fact that

$$g_{rs}^{mp} = \frac{1}{n} \sqrt{\frac{m_s}{2\pi kT}} q_{rs}^{mp}$$

This expression from [23] has been considered previously [11] as an approximate formula. If we put $\xi = 2$ in expressions (3.3), these expressions are found to be identical to the coefficients $k_{Ti}(\xi)$ ($i = 1, \dots, N$) presented solely in the second approximation in [41]. It is interesting to note that the thermal conductivity $\lambda(4)$ has earlier been postulated [17] as an approximated expression for the thermal conductivity in the fourth approximation. Actually, it follows from the derivation of formula (3.6) that this will be the exact fourth approximation.

Hence, the transport equations with the exact and simpler transport coefficients are obtained without the double inversion of matrices and serve as a basis for solving hydrodynamic problems associated with investigations of the flows of a multicomponent plasma and, in particular, as if they are specially represented in a form which is convenient for converting the equations of motion of multicomponent mixtures of thermochemically equilibrium flows to canonical form with a complete set of all the effective transport coefficients, which will be done later.

4. EQUATIONS FOR THE MASS TRANSFER OF THE COMPONENTS IN A QUASINEUTRAL PLASMA

The practical absence of space charge outside a sphere of radius λ_D ($\lambda_D = [kT/(4\pi n_E e^2)]^{1/2}$, that is, the Debye radius, where n_E is the number density of electrons and e is the electron charge), is a characteristic feature of an ionized gas, which is called the ambipolar or, more precisely, the quasineutral region. The transport equations (3.1) are substantially simplified in this case. The mass forces $\mathbf{F}_i$ ($i = 1, \ldots, N$) that appear in (2.3) (the magnetic field induced by internal currents will be small as a relativistic effect), will be determined by the electric field $\mathbf{E}(\mathbf{F}_i = \mathbf{E}e_i/m_i)$ which is induced by charge separation: when there are concentration, pressure or temperature gradients, the electrons, due to their relatively low mass, will diffuse at a far greater rate, dragging ions behind them.

The small induction of the space charges will generate exceedingly strong electric fields which will force the plasma to make a rapid return, after a time $\tau = (m_E 4\pi n_E e^2)^{1/2}$ which is much less than the time between collisions of the particles, to a state of electrical neutrality, which is expressed by the condition

$$\sum_{k=1}^{N} x_k e_k = 0 \text{ or } \sum_{k=1}^{N} e_k \nabla x_k = 0 \tag{4.1}$$

Substituting ∇x_i from relations (3.1) into (4.1) and taking account of (2.3), where the mass forces are equal to $\mathbf{F}_i = \mathbf{E}e_i/m_i$, we obtain an expression for the electric field vector

$$\mathbf{E} = -\frac{kT}{e_i}\zeta_i\left[\sum_{i=1}^{N}\sum_{k=1}^{N} x_k \Delta_{ik}(\zeta_k - \zeta_i)J_i' + \sum_{k=1}^{N} z_k c_k \nabla \ln p - \sum_{k=1}^{N} z_k k_{Tk} \nabla \ln T\right] \tag{4.2}$$

$$\frac{\zeta_i}{e_i} = \left(\sum_{k=1}^{N} x_k e_k^2\right)^{-1/2}, \quad \Delta_{ij}^{-1} = n\mathfrak{D}_{ij}(1) f_{ij}^{-1}(\xi), \quad n = \sum_{k=1}^{N} n_k \tag{4.3}$$

Here, the resistance coefficients $\Delta_{ij} = \Delta_{ji}$ have been introduced for convenience.

Substituting $\mathbf{E}$ into the expressions for the mass forces $\mathbf{F}_i$, occurring in the equalities (2.3), we obtain from (3.1) the Stefan–Maxwell relations for a quasineutral mixture of gases

$$\mathbf{d}_i \equiv \nabla x_i + k_{pi}^{(0)} \ln p + k_{Ti}^{(0)} \nabla \ln T = -\Delta_i \mathbf{J}_i' + x_i \sum_{k=1}^{N} \delta_{ik}^{(0)} \mathbf{J}_k', \quad i = 1, \ldots, N \tag{4.4}$$

where

$$k_{pi}^{(0)} = k_{pi} - x_i \zeta_i \sum_{k=1}^{N} c_k \zeta_k, \quad k_{Ti}^{(0)} = k_{Ti} - x_i \zeta_i \sum_{s=1}^{N} \zeta_s k_{Ts}$$

$$\delta_{ik}^{(0)} = \Delta_{ik} + \zeta_i \sum_{r=1}^{N} x_r (\zeta_k - \zeta_r)\Delta_{rk}, \quad \Delta_i = \sum_{k=1}^{N} x_k \Delta_{ik}, \quad \mathbf{J}_i' = \frac{1}{m_i}\mathbf{J}_i$$

By virtue of condition (4.1) and the definition $k_{pi} = x_i - c_i$, the coefficients in (4.4) satisfy the following relations

$$\begin{gathered}\sum_{i=1}^{N} k_{pi}^{(0)} = \sum_{i=1}^{N} k_{Ti}^{(0)} = 0, \quad \sum_{i=1}^{N} x_i \delta_{ik}^{(0)} = \Delta_k, \quad \sum_{i=1}^{N} x_k \zeta_k^2 = 1 \\ \sum_{i=1}^{N} z_i k_{pi}^{(0)} = \sum_{i=1}^{N} z_i k_{Ti}^{(0)} = 0, \quad \sum_{i=1}^{N} x_i z_i \delta_{ik}^{(0)} = z_k \Delta_k\end{gathered} \tag{4.5}$$

Hence, in the case of a partially ionized gas mixture, there will be $N - 2$ independent relations (4.4) and, for a mixture of neutral components, there will be $N - 1$ such relations.

A Debye region exists close to the surface past which the flow occurs in which the asymptotic solution (4.1), (4.2) does not hold. For zero charged particle densities on the surface, solution (4.2) for $\mathbf{E}$ has a singularity. In order to obtain the solution for $\mathbf{E}$ in this Debye layer ($\lambda_D \ll L$), it is necessary to construct an internal solution using a scheme which has previously been described in [42].

5. STEFAN-MAXWELL RELATIONS FOR THE MASS DESCRIPTION OF DIFFUSION

When solving hydrodynamic problems, it is more convenient to have the Stefan–Maxwell relations (3.1) written in terms of ∇c_i instead of ∇x_i, due to the fact that the diffusion equations (1.5) and (1.6) are written in terms of the mass concentrations c_i and the mass diffusion fluxes $\mathbf{J}_i$. Since, $c_i = x_i m_i/m$ we obtain

$$\nabla c_i = \sum_{k=1}^{N} \frac{m_i m_k}{m^2}(x_k \nabla x_i - x_i \nabla x_k), \quad i = 1,\dots,N$$

Substituting ∇x_i from (4.4) into this, we find the mass transfer equations in a quasineutral plasma, written in terms of the mass concentration gradients

$$\nabla c_i + K_{pi}^{(0)} \nabla \ln p + K_{Ti}^{(0)} \nabla \ln T = -\frac{\Delta_i}{m}\mathbf{J}_i + c_i \sum_{k=1}^{N} \Delta_{ik}^{(0)} \mathbf{J}_k' \tag{5.1}$$

where

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

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

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

$$\zeta_i^* = \zeta_i - \sum_{k=1}^{N} c_k \zeta_k, \quad i,j = 1,\dots,N$$

The coefficients obtained above satisfy the conditions

$$\sum_{k=1}^{N} K_{pk}^{(0)} = \sum_{k=1}^{N} K_{Tk}^{(0)} = 0, \quad \sum_{k=1}^{N} c_k \Delta_{ki}^{(0)} = \frac{m_i}{m} \Delta_i, \quad \sum_{k=1}^{N} c_k \frac{e_k}{m_k} \Delta_{ki}^{(0)} = \frac{e_i}{m} \Delta_i \tag{5.2}$$

$$i = 1, \dots, N$$

$$\sum_{k=1}^{N} K_{pk}^{(0)} \frac{e_k}{m_k} = \sum_{k=1}^{N} K_{Tk}^{(0)} \frac{e_k}{m_k} = 0$$

For a plasma, in the general case, there will therefore be $N - 2$ independent relations (5.1) and, for mixtures of uncharged components ($e_i = 0, i = 1, \dots, N$), there will be $N - 1$ such relations.

6. THE STEFAN-MAXWELL RELATIONS FOR THE DIFFUSION OF ELEMENTS

In accordance with the definition of the concentrations and the diffusion fluxes of the elements (1.3), $\mathbf{J}_j$ ($j = 1, \dots, L$) can be eliminated from Eqs (5.1) and the equations for the mass transfer of the elements c_j^* ($j = 1, \dots, L$) and the equations for the transfer of the concentrations of the reaction products c_i ($i = L + 1, \dots, N$) can be obtained separately

$$\nabla c_j^* + K_{pj}^* \nabla \ln p + K_{Tj}^* \nabla \ln T = -\frac{\Delta_j}{m}\mathbf{J}_j^* + \frac{m_j}{m} \sum_{l=1}^{L} \Delta_{jl}^* \mathbf{J}_l^{*\prime} + \frac{m_j}{m} \sum_{k=L+1}^{N} \delta_{jk}^* \mathbf{J}_k', \quad j = 1,\dots,L \tag{6.1}$$

$$\nabla c_i + K_{pi}^{(0)} \nabla \ln p + K_{Tj}^{(0)} \nabla \ln T = -\frac{\Delta_i}{m}\mathbf{J}_i + c_i \sum_{l=1}^{L} \Delta_{il}^{(0)} \mathbf{J}_l^{*\prime} + c_i \sum_{k=L+1}^{N} \Delta_{ik}^{(1)} \mathbf{J}_k', \quad i = L+1,\dots,N \tag{6.2}$$

where

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

$$\Delta_{jl}^{*} = x_j \Delta_{jl} + \sum_{k=L+1}^{N} x_k \nu_{kj} \Delta_{kl} + x_j^{*} \sum_{s=1}^{N} x_s \left(\frac{m_l}{m} - \frac{m_s}{m} \right) \Delta_{sl} +$$

$$+ \left(x_j \zeta_j^{*} + \sum_{k=L+1}^{N} x_k \nu_{kj} \zeta_k^{*} \right) \sum_{s=1}^{N} x_s (\zeta_l - \zeta_s) \Delta_{ls}$$

$$\delta_{jk}^{*} = \nu_{kj} (\Delta_j - \Delta_k) + \Delta_{jk}^{*} - \sum_{l=1}^{L} \nu_{kl} \Delta_{jl}^{*}, \quad \Delta_{ik}^{(1)} = \Delta_{ik}^{(0)} - \sum_{l=1}^{L} \nu_{kl} \Delta_{il}^{(0)}$$

$$i, j, k, l = 1, \ldots, N$$

$$\mathbf{J}_j^{*\prime} = \frac{1}{m_j} \mathbf{J}_j^{*}, \quad c_j^{*} = \frac{m_j x_j^{*}}{m}, \quad x_j^{*} = x_j + \sum_{k=L+1}^{N} \nu_{kj} x_k; \quad j = 1, \ldots, L$$

The relations for the coefficients

$$\sum_{j=1}^{L} K_{pj}^{*} = \sum_{j=1}^{L} K_{Tj}^{*} = 0, \quad \sum_{j=1}^{L} m_j \Delta_{jl}^{*} = m_l \Delta_l, \quad \sum_{j=1}^{L} m_j \delta_{jk}^{*} = 0 \tag{6.3}$$

$$k = 1, \ldots, N$$

hold by virtue of the conservation of mass (1.2) in reactions (1.1) and conditions (5.2).

Relations ($x_E^{*} = 0$)

$$\Delta_{El}^{*} = 0, \quad l = 1, \ldots, L, \quad l \neq E; \quad \Delta_{EE}^{*} = \Delta_E \tag{6.4}$$

$$\Delta_{Ei}^{*} = \nu_{iE} \Delta_i, \quad \delta_{Ei}^{*} = 0, \quad i = L+1, \ldots, N; \quad K_{pE}^{*} = K_{TE}^{*} = 0$$

also hold by virtue of charge conservation (1.2) in reactions (1.1).

The subscript E refers to the electron.

Hence, in the case of the diffusion of elements in a plasma, there will be $L - 2$ independent Stefan–Maxwell relations (6.1) and, for a mixture of electrically neutral gases, there will be $L - 1$ such relations. Relations (6.2) represent a system of $R = N - L$ independent equations which, together with the $R = N - L$ equations for the diffusion of the reaction products (1.6), form a closed system for determining the concentrations c_i and the diffusion fluxes $\mathbf{J}_i$ ($i = L + 1, \ldots, N$) of the reaction products. Equations (1.5) and (6.1) determine the concentrations c_j^{*} and the diffusion fluxes $\mathbf{J}_j^{*}$ of the elements.

In conclusion, we will now represent the system of mass transfer equations (6.1) and (6.2) in an improved form by introducing generalized, dimensionless Schmidt numbers $S_i = (\mu/m)\Delta_i$ (μ is the coefficient of viscosity of the mixture), which are accepted in problems of hydrodynamics. We then obtain the mass transfer equations for the elements

$$\mathbf{d}_j^{*} = -\frac{S_j}{\mu} \mathbf{J}_j^{*} + \frac{m_j S_j}{\mu} \left(\sum_{l=1}^{L} \alpha_{jl}^{*} \mathbf{J}_l^{*\prime} + \sum_{k=L+1}^{N} \beta_{jk}^{*} \mathbf{J}_k^{\prime} \right), \quad j = 1, \ldots, L \tag{6.5}$$

and for the reaction products

$$\mathbf{d}_i = -\frac{S_j}{\mu} \mathbf{J}_i + x_i \frac{m_i S_i}{\mu} \left(\sum_{l=1}^{L} \alpha_{il} \mathbf{J}_l^{*\prime} + \sum_{k=L+1}^{N} \beta_{ik} \mathbf{J}_k^{\prime} \right), \quad i = L+1, \ldots N \tag{6.6}$$

where

$$\alpha_{jl}^{*} = \frac{\Delta_{jl}^{*}}{\Delta_j}, \quad \alpha_{il} = \frac{\Delta_{il}^{(0)}}{\Delta_i}, \quad \beta_{jk}^{*} = \frac{\delta_{jk}^{*}}{\Delta_j}, \quad \beta_{ik} = \frac{\Delta_{ik}^{(1)}}{\Delta_i} \tag{6.7}$$

In (6.5) and (6.6), the vectors d_j^{*} and $\mathbf{d}_i$ are the left-hand sides of Eqs (6.1) and (6.2), respectively.

7. DIFFERENT FORMS OF THE ENERGY AND HEAT INFLUX EQUATIONS FOR A MIXTURE

To obtain the complete system of effective transport coefficients for thermochemically equilibrium flows, it is necessary to start from the exact energy equation (1.8). We introduce into express (3.5) for the total thermal flux the specific enthalpy of the mixture

$$h = e + \frac{p}{\rho} = \sum_{k=1}^{N} c_k h_k; \quad \frac{dh_i}{dT} = c_{pi}, \quad i = 1,\dots,N$$

where c_{pi} are the specific (per unit mass) heat capacities of the components and h_i are the specific enthalpies of the components, defined apart from their additive constants by the expression $h_i = \int c_{pi} dT + h_{i0}$. Then

$$dh = c_p dT + \sum_{k=1}^{N} h_k dc_k, \quad c_p = \sum_{k=1}^{N} c_{pk} c_k \tag{7.1}$$

whence

$$\lambda \nabla T = \frac{\mu}{\sigma} dh - \frac{\mu}{\sigma} \sum_{k=1}^{N} h_k dc_k, \quad \sigma = \frac{\mu c_p}{\lambda} \tag{7.2}$$

The total heat flux (3.5), expressed in terms of the temperature and the specific enthalpy of the mixture, will then be

$$\mathbf{J}_q = -\frac{\mu}{\sigma}\left[c_p \nabla T - \frac{\sigma}{\mu} \sum_{k=1}^{N} h_k^T \mathbf{J}_k\right] = -\frac{\mu}{\sigma}\left[\nabla h - \sum_{k=1}^{N}\left(h_k \nabla c_k + \frac{\sigma}{\mu} h_k^T \mathbf{J}_k\right)\right] \tag{7.3}$$

where σ is the Prandtl number, defined in terms of the coefficient of viscosity of the mixture μ, the thermal conductivity of the mixture λ and the heat capacity of the mixture c_p; h_i^T is the specific enthalpy of the ith component written taking account of thermal diffusion (see (7.11)).

Substituting expression (7.3) into Eq. (1.8), we obtain the energy equation, written in terms of h in the substantial form

$$\rho \frac{d}{dt}\left(h + \frac{v^2}{2}\right) = \frac{\partial p}{\partial t} + \operatorname{div}\left\{\frac{\mu}{\sigma}\left[\nabla h + \frac{\sigma}{\mu}\hat{\tau} \cdot \mathbf{v} - \sum_{k=1}^{N}\left(h_k \nabla c_k + \frac{\sigma}{\mu} h_k^T \mathbf{J}_k\right)\right]\right\} + \sum_{k=1}^{N} \rho_k \mathbf{F}_k \cdot \mathbf{v}_k \tag{7.4}$$

Subtracting the kinetic energy equation (the scalar product of the momentum equation (1.7) and v) from Eq. (7.4), we obtain the heat influx equation, written in terms of the enthalpy of the mixture

$$\rho \frac{dh}{dt} = \frac{\partial p}{\partial t} + \operatorname{div}\left\{\frac{\mu}{\sigma}\left[\nabla h - \sum_{k=1}^{N}\left(h_k \nabla c_k + \frac{\sigma}{\mu} h_k^T \mathbf{J}_k\right)\right]\right\} + \hat{\tau} : \hat{e} + \sum_{k=1}^{N} \rho_k \mathbf{F}_k \cdot \mathbf{J}_k \tag{7.5}$$

It is now natural to introduce into Eq. (7.4) the total enthalpy of the mixture $H = h + \upsilon^2/2$ in terms of which this equation is written in the most compact form

$$\rho \frac{dH}{dt} = \frac{\partial p}{\partial t} - \operatorname{div} \mathbf{J}_H + \sum_{k=1}^{N} \rho_k \mathbf{F}_k \cdot \mathbf{v}_k \tag{7.6}$$

$$\mathbf{J}_H = -\frac{\mu}{\sigma}\left[\nabla H + \frac{\sigma}{\mu}\hat{\tau} \cdot \mathbf{v} - \nabla\left(\frac{v^2}{2}\right) - \sum_{k=1}^{N}\left(h_k \nabla c_k + \frac{\sigma}{\mu} h_k^T \mathbf{J}_k\right)\right] \tag{7.7}$$

Note that the energy and heat influx equations, which have been described above in different forms, retain their form regardless of the fact of whether reactions occur at a finite rate in the flow or in an equilibrium manner or are frozen. In the account of the energy (or heat influx) equation which has been presented, the heats of chemical reactions appear in the internal energy and enthalpy of the mixture.

We next explicitly introduce the heats of reaction and thereby reveal the possibility of writing the energy and heat influx equations in terms of the temperature. We transform the energy and heat influx equations, explicitly separating out the terms which contain the heats of chemical reactions, including ionization reactions.

Note that the actual occurrence of reactions does not, as a rule, correspond to the notation of (1.1) and, furthermore, the actual number of reactions is, as a rule, greater than $N - L$. The elucidation of the actual mechanism of the reactions which are taking place and the number of such reactions is a separate problem, the results of the solution of which have no effect on the conclusions of this section. However, using the independent reactions (1.1), we introduce all the independent heats of reactions in terms of which the heats of all the remaining reactions which are actually occurring are expressed (Hess' law). According to the first law of thermodynamics, the heat of reaction, required to form unit mass of the product A_i $(i = L + 1, \dots, N)$ at a pressure p and a temperature T, is determined by the specific enthalpies of the components h_i $(i = 1, \dots, N)$ in accordance with the form of reactions (1.1)

$$-q_i(T) = h_i - \sum_{j=1}^{L} \nu_{ij} \frac{m_j}{m_i} h_j, \quad i = L+1,\dots,N \tag{7.8}$$

From (7.8), we obtain

$$-q_i(T) = -q_i(0) + \int_0^T c_{pi} dT - \sum_{j=1}^{L} \nu_{ij} \frac{m_j}{m_i} \int_0^T c_{pi} dT, \quad i = L+1,\dots,N \tag{7.9}$$

where $q_i(0)$ are the heats of reaction at absolute zero and are specified parameters of the problem. Formulae (7.9) serve for converting heats of reaction, specified at one temperature, to another temperature.

Hence, in order to define the model it is necessary to specify the heat capacities of all of the components c_{pi} $(i = 1, \dots, N)$ and $N - L$ independent heats of reaction q_i at some fixed temperature T, for example, $T = 0$. The enthalpies of all the components will be determined to L arbitrary additive constants h_{j0} $(j = 1, \dots, L)$, which do not have values by virtues of the invariance of the energy (and the heat influx) equation with respect to the values of these constants [38].

We will now write all the expressions (sums), containing the concentrations and their derivatives, and the diffusion fluxes, having eliminated the concentrations c_j $(j = 1, \dots, L)$ and the diffusion fluxes of the components, that is, the elements of $\mathbf{J}_i$ $(j = 1, \dots, L)$ from them, in terms of the concentrations c_j^* $(j = 1, \dots, L)$ and the diffusion fluxes of the elements $\mathbf{J}_j^*$ $(j = 1, \dots, L)$ and, using formulae (1.3), we obtain

$$h = \sum_{k=1}^{N} c_k h_k = \sum_{j=1}^{L} c_j^* h_j - \sum_{k=L+1}^{N} q_k c_k, \quad dh = c_p dT + \sum_{j=1}^{N} h_j dc_j^* - \sum_{k=L+1}^{N} q_k dc_k$$

$$\sum_{k=1}^{N} \left(h_k \nabla c_k + \frac{\sigma}{\mu} h_k^T \mathbf{J}_k \right) = \mathbf{D} - \mathbf{Q} \tag{7.10}$$

where

$$\mathbf{D} = \sum_{j=1}^{L} \left(h_j \nabla c_j^* + \frac{\sigma}{\mu} h_j^T \mathbf{J}_j^* \right), \quad \mathbf{Q} = \sum_{k=L+1}^{N} q_k \nabla c_k + \frac{\sigma}{\mu} q_k^T \mathbf{J}_k$$

$$h_j^T = h_j + \frac{\alpha_{Tj}}{m_j} kT, \quad \alpha_{Tj} = \frac{k_{Tj}}{x_j}; \quad j = 1,\dots,L \tag{7.11}$$

$$q_i^T = q_i - \frac{\beta_{Ti}}{m_i}, \quad \beta_{Ti} = \alpha_{Ti} - \sum_{j=1}^{L} \nu_{ij} \alpha_{Tj}; \quad i = L+1,\dots,N$$

The total heat flux (7.3) will then be equal to

$$\mathbf{J}_q = -\frac{\mu}{\sigma} \left[\nabla h - \sum_{j=1}^{L} \left(h_j \nabla c_j^* + \frac{\sigma}{\mu} h_j^T \mathbf{J}_j^* \right) + \sum_{k=L+1}^{N} \left(q_k \nabla c_k + \frac{\sigma}{\mu} q_k^T \mathbf{J}_k \right) \right] \tag{7.12}$$

It follows from this last expression that, if, when there is a thermal diffusion effect, one introduces the concept of generalized heats of reaction $q_i^T = q_i - \beta_{Ti}/m_i$, instead of q_i and the concept of generalized specific enthalpies of the basis components $h_j^T = h_j + (\alpha_{Tj}/m_j)kT$, instead of h_j, the structure of the expression for the total heat flux $\mathbf{J}_q$ (7.12) will be identical to the expression for $\mathbf{J}_q$ when there is no thermal diffusion effect.

We will now write the heat influx equation in terms of the enthalpy of the mixture h. From (7.5), we obtain, using (7.12)

$$\rho\frac{dh}{dt} = \frac{dp}{dt} + \operatorname{div}\left[\frac{\mu}{\sigma}(\nabla h - \mathbf{D} + \mathbf{Q})\right] + \hat{\tau} : \hat{e} + \sum_{k=1}^{N} \mathbf{F}_k \cdot \mathbf{J}_k \tag{7.13}$$

The energy equation, written in terms of the total enthalpy, will be

$$\rho\frac{dH}{dt} = \frac{dp}{\partial t} + \operatorname{div}\left\{\frac{\mu}{\sigma}\left[\nabla H + \frac{\sigma}{\mu}\hat{\tau}\cdot\mathbf{v} - \nabla\left(\frac{v^2}{2}\right) - \mathbf{D} + \mathbf{Q}\right]\right\} + \sum_{k=1}^{N} \rho_k \mathbf{F}_k \cdot \mathbf{v}_k \tag{7.14}$$

Finally, we write the heat influx equation in terms of the temperature. Substituting the expression for dh from (7.11) into Eq. (7.5), we shall have

$$\rho\left(c_p\frac{dT}{dt} + \sum_{j=1}^{L} h_j \frac{dc_j^*}{dt} - \sum_{k=L+1}^{N} q_k \frac{dc_k}{dt}\right) =$$

$$= \frac{dp}{dt} + \operatorname{div}\left[\frac{\mu}{\sigma}\left(c_p\nabla T - \frac{\sigma}{\mu}\sum_{j=1}^{L} h_j^T \mathbf{J}_j^* + \frac{\sigma}{\mu}\sum_{k=L+1}^{N} q_k^T \mathbf{J}_k\right)\right] + \hat{\tau} : \hat{e} + \sum_{k=1}^{N} \rho_k \mathbf{F}_k \cdot \mathbf{v}_k$$

or, when account is taken of the diffusion equations of the elements (1.5) and the reaction products (1.6), as well as equalities (7.8) and (7.10), we finally obtain the heat influx equation, written in terms of the temperature, in the form

$$\rho c_p \frac{dT}{dt} = \frac{dp}{dt} + \operatorname{div}\left(\lambda\nabla T - kT\sum_{k=1}^{N}\frac{\alpha_{Tk}}{m_k}\mathbf{J}_k\right) + \sum_{k=L+1}^{N} q_k \dot{w}_k - \sum_{k=1}^{N} \nabla h_k \mathbf{J}_k + \hat{\tau} : \hat{e} + \sum_{k=1}^{N} \rho_k \mathbf{F}_k \cdot \mathbf{v}_k \tag{7.15}$$

8. THE NAVIER–STOKES EQUATIONS FOR FLOWS OF MIXTURES OF GASES AND PLASMA IN THERMOCHEMICAL AND IONIZATION EQUILIBRIUM. THE EFFECTIVE TRANSPORT COEFFICIENTS

A chemically equilibrium flow occurs when the time taken for the slowest reaction to occur in the flow t_{ch} is much less than the characteristic hydrodynamic time t_{fl}, for example, the time a liquid particle resides in the flow, which is equal to L/v (L is the characteristic length of the flow domain considered and v is the characteristic of the flow velocity). In this case, if the temperatures of all the degrees of freedom of the particles are the same, then a thermochemically equilibrium flow occurs. In this case, considerable simplification of the system of diffusion equations (1.5), (1.6) and (3.1) and the energy equations (1.8) and (3.5) is possible, that is, part of the overall system of Navier–Stokes equations (1.4)–(1.9), if the conditions of chemical equilibrium are used as the first integrals of the system of equations.

In the case of local thermodynamic equilibrium in the flow, the diffusion equations for the reaction products (1.6) in the asymptotic limit as $t_{\text{fl}}/t_{\text{ch}} \to \infty$ are replaced by the conditions of chemical equilibrium, which, when the reactions are expressed in the form (1.1), will be written as

$$\prod_{j=1}^{L}\frac{x_j^{\nu_{ij}}}{x_i} = \frac{K_{pi}(T)}{p^{\nu_i}}, \quad \nu_i = \sum_{j=1}^{L}\nu_{ij} - 1, \quad i = L+1,\dots,N \tag{8.1}$$

These equations are a consequence of the Guldberg–Waage law of mass action for chemical reactions and Saha's equilibrium ionization conditions. Equations (8.1) can be written in terms of the partial pressures in the form

$$\prod_{j=1}^{L}\frac{p_j^{\nu_{ij}}}{p_i} = K_{pi}(T), \quad i = L+1,\dots,N \tag{8.2}$$

where p_i are the partial pressures of the components and $K_{pi}(T)$ are the equilibrium constants (functions) which depend solely on the temperature and are calculated in statistical physics.

We next assume that $K_{pi}(T)$ are known. These conditions can be considered as first integrals of the equations of motion of a multicomponent mixture, which hold at any point in the flow and replace the diffusion equations for the reaction products (1.6). These integrals can be used to simplify the energy equations (7.13) and (7.14).

We now express the vectors ∇c_i and $\mathbf{J}_i$ $(i = L + 1, \ldots, N)$, which occur in Eq. (7.14), in terms of ∇T, ∇p, ∇c_j^* and $\mathbf{J}_i$ $(i = L + 1, \ldots, N)$ and, in conditions (8.1), we change to the mass concentrations

$$\prod_{j=1}^{L} \frac{c_j'^{\nu_{ij}}}{c_i'} = \frac{K_{pi}(T)}{(pm)^{\nu_i}}, \quad c_i' = \frac{c_i}{m_i}, \quad i = 1, \ldots, N \tag{8.3}$$

and take the logarithmic differential of these equalities. In the resulting equations, we next replace dc_j^* $(j = 1, \ldots, L)$ in terms of $dc_j^{*\prime}$ $(j = 1, \ldots, L)$ and dc_i' $(i = L + 1, \ldots, N)$ using (1.3). We then obtain a system of simultaneous algebraic equations for determining $dc_i' = dc_i/m_i$

$$\sum_{k=L+1}^{N} a_{ik} dc_k' = -\frac{m_i q_i}{mkT} d \ln T + \frac{\nu_i}{m} d \ln p + \sum_{j=1}^{L} \nu_{ij}^* dc_j^{*\prime}, \quad i = L+1, \ldots, N \tag{8.4}$$

where

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

$$j = 1, \ldots, L; \quad i, k = L + 1, \ldots, N$$

Here, the van't Hoff isochore equations

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

have been used.

It is clear from (8.4) that the chemically equilibrium concentrations of the reaction products c_i $(i = L + 1, \ldots, N)$ and, later, the concentrations of the basis components

$$c_j = c_j^* - \sum_{k=L+1}^{N} \nu_{kj} \frac{m_j}{m_k} c_k; \quad j = 1, \ldots, L$$

depend on $T, p, c_1^*, \ldots, c_L^*$.

The solution of system (8.4) can immediately be written in terms of the ratio of determinants (Cramer's rule). Using this solution, we find the sum which is subsequently needed

$$\sum_{k=L+1}^{N} m_k q_k dc_k' = -c_{pr} dT + a(\nu, \overline{Q}) \frac{dp}{\rho} + \sum_{j=1}^{L} a_j(\nu^*, Q) dc_j^* \tag{8.5}$$

where

$$c_{pr} = -\frac{k}{m\Delta(a)} \begin{vmatrix} 0 & \overline{Q}_{L+1} & \cdots & \overline{Q}_N \\ \overline{Q}_{L+1} & a_{L+1,L+1} & \cdots & a_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \overline{Q}_N & a_{N,L+1} & \cdots & a_{N,N} \end{vmatrix}$$

$$a(\nu, \overline{Q}) = -\frac{l}{\Delta(a)} \begin{vmatrix} 0 & \overline{Q}_{L+1} & \cdots & \overline{Q}_N \\ \nu_{L+1} & a_{L+1,L+1} & \cdots & a_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \nu_N & a_{N,L+1} & \cdots & a_{N,N} \end{vmatrix}$$

$$a_j(\nu^*, Q) = -\frac{1}{m_j \Delta(a)} \begin{vmatrix} 0 & Q_{L+1} & \cdots & Q_N \\ \nu^*_{L+1,j} & a_{L+1,L+1} & \cdots & a_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \nu^*_{N,j} & a_{N,L+1} & \cdots & a_{N,N} \end{vmatrix}, \quad j = 1, \ldots, L$$

$$\Delta(a) = \det \| a_{ik} \| = \begin{vmatrix} a_{L+1,L+1} & \cdots & a_{L+1,N} \\ \vdots & & \vdots \\ a_{N,L+1} & \cdots & a_{N,N} \end{vmatrix}$$

$$Q = m_i q_i, \quad \overline{Q}_i = \frac{m_i q_i}{kT} = \frac{Q_i}{kT}$$

We now return to the calculation of the diffusion fluxes of the reaction products $\mathbf{J}_i$ ($i = L + 1, \ldots, N$). We take the logarithmic gradient of the equilibrium conditions (8.1), having used the van't Hoff isochore equations here

$$\sum_{j=1}^{L} \nu_{ij} \frac{\nabla x_j}{x_j} - \frac{\nabla x_i}{x_i} = \frac{m_i q_i}{kT} \nabla \ln T - \nu_i \nabla \ln p, \quad i = L+1, \ldots, N$$

and, into these equalities, we substitute ∇x_i ($i = 1, \ldots, N$) from the Stefan–Maxwell relations (3.1) which we rewrite in the form

$$\nabla x_i = -\mathbf{J}'_i \sum_{k=1}^{N} x_k \Delta_{ik} + x_i \sum_{k=1}^{N} \Delta_{ik} \mathbf{J}'_k - (x_i - c_i) \nabla \ln p - \frac{c_i}{p} \left(\sum_{k=1}^{N} \rho_k \mathbf{F}_k - \rho \mathbf{F}_i \right) - k_{Ti} \nabla \ln T$$

Next, if the diffusion fluxes of the components of the elements $\mathbf{J}_i$ ($j = 1, \ldots, L$) are eliminated using (1.3) and we use the conditions for the conservation of mass and charge in reactions (1.2), we obtain a system of linear vector equations for the diffusion fluxes of the reaction products of the following form

$$\sum_{k=L+1}^{N} b_{ik} \mathbf{J}'_k = \frac{m_i q_i^T}{kT} \nabla \ln T + \sum_{j=1}^{L} d_{ij} \mathbf{J}^{*\prime}_j, \quad i = L+1, \ldots, N \tag{8.6}$$

where

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

$$i, k = L + 1, \ldots, N$$

$$\Delta_i = \sum_{k=1}^{N} x_k \Delta_{ik}, \quad i = 1, \ldots, N$$

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

It is important to note that the electric field has not occurred in the defining parameters of the diffusion fluxes $\mathbf{J}_j$ in (8.6) by virtue of the quasineutrality conditions (1.2), and it has also not occurred in the term with ∇p. We shall again write the solution of system (8.6) in terms of determinants (Cramer's rule) and immediately present the expression for the sum

$$\sum_{k=L+1}^{N} q_k^T \mathbf{J}_k = \sum_{k=L+1}^{N} m_k q_k^T \mathbf{J}'_k = \lambda_r \nabla T + \sum_{j=1}^{L} b_j(d, Q^T) \mathbf{J}_j \tag{8.7}$$

which will be required later, where the following notation for the reaction thermal conductivity λ_r and the coefficients b_j are introduced

$$\lambda_r = -\frac{k}{\Delta(b)}\begin{vmatrix} 0 & \overline{Q}^T_{L+1} & \cdots & \overline{Q}^T_N \\ \overline{Q}^T_{L+1} & b_{L+1,L+1} & \cdots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \overline{Q}^T_N & b_{N,L+1} & \cdots & b_{N,N} \end{vmatrix}, \quad Q^T_i = m_i q^T_i, \quad \overline{Q}^T_i = \frac{m_i q^T_i}{kT}$$

$$b_j(d,Q^T) = -\frac{1}{m_j\Delta(b)}\begin{vmatrix} 0 & \overline{Q}^T_{L+1} & \cdots & Q^T_N \\ d_{L+1,j} & b_{L+1,L+1} & \cdots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ d_{N,j} & b_{N,L+1} & \cdots & b_{N,N} \end{vmatrix}$$

$$\Delta(b) = \det \| b_{ik} \| = \begin{vmatrix} b_{L+1,L+1} & \cdots & b_{L+1,N} \\ \vdots & & \vdots \\ b_{N,L+1} & \cdots & b_{N,N} \end{vmatrix}$$

Expressions (8.4) and (8.6) are central in the case of equilibrium chemical reactions. Substituting expression (8.5) for *dh* into (7.10) and expression (8.7) into (7.12), we find

$$dh = c_{p\,\mathrm{eff}}dT - \sum_{j=1}^{L} a^*_j dc^*_j - \frac{a(\mathrm{v},\overline{Q})}{\rho}dp, \quad c_{p\,\mathrm{eff}} = c_p + c_{pr} \tag{8.8}$$

$$\mathbf{J}_q = -\lambda_{\mathrm{eff}}\nabla T - \sum_{j=1}^{L} b^*_j \mathbf{J}^*_j = -\frac{\mu}{\sigma_{\mathrm{eff}}}\left[\nabla h + \sum_{j=1}^{L}\left(a^*_j\nabla c^*_j + \frac{\sigma_{\mathrm{eff}}}{\mu}b^*_j\mathbf{J}^*_j\right) + a(\mathrm{v},\overline{Q})\frac{\nabla p}{\rho}\right] \tag{8.9}$$

$$\lambda_{\mathrm{eff}} = \lambda + \lambda_r, \quad \sigma_{\mathrm{eff}} = \frac{\mu c_{p\,\mathrm{eff}}}{\lambda_{\mathrm{eff}}} = \frac{\mu(c_p + c_{pr})}{\lambda + \lambda_r}$$

where the concept of an effective heat capacity of the mixture, $c_{p\,\mathrm{eff}}$, and effective thermal conductivity of the mixture, λ_{eff} and an effective Prandtl number, σ_{eff}, constructed using the effective heat capacity and the effective thermal conductivity, has been introduced. In addition, the notation

$$a^*_j = a_j(\mathrm{v}^*,Q) - h_j, \quad b^*_j = b_j(d,Q^T) - h^T_j, \quad j = 1,\ldots,L$$

has been introduced.

It is now possible to derive the energy and heat influx equations for thermochemically equilibrium flows. Substituting expressions (8.8) and (8.9) into Eq. (7.13), taking account of relations (7.12), we obtain the heat influx equation for the case of thermochemically equilibrium flows, written in terms of the temperature

$$\begin{aligned}\rho c_{p\,\mathrm{eff}}\frac{dT}{dt} &= [1 + a(\mathrm{v},\overline{Q})]\frac{dp}{dt} + \mathrm{div}\left[\lambda_{\mathrm{eff}}\nabla T + \sum_{j=1}^{L}(b^*_j - a^*_j)\mathbf{J}^*_j\right] + \\ &+ \sum_{j=1}^{L}\mathbf{J}^*_j\nabla a^*_j(\mathrm{v}^*,Q) + \hat{\tau}:\hat{e} + \sum_{k=1}^{N}\mathbf{F}_k\cdot\mathbf{J}_k\end{aligned} \tag{8.10}$$

and, respectively, the heat influx equation, written in terms of the enthalpy

$$\rho\frac{dh}{dt} = \frac{dp}{dt} + \mathrm{div}\left\{\frac{\mu}{\sigma_{\mathrm{eff}}}\left[\nabla h + \sum_{j=1}^{L}\left(a^*_j\nabla c^*_j + \frac{\sigma_{\mathrm{eff}}}{\mu}b^*_j\mathbf{J}^*_j\right) + \frac{a(\mathrm{v},\overline{Q})}{\rho}\nabla p\right]\right\} + \hat{\tau}:\hat{e} + \sum_{k=1}^{N}\mathbf{F}_k\cdot\mathbf{J}_k \tag{8.11}$$

The energy equation, written in terms of the total enthalpy *H*, for locally thermodynamic equilibrium flows will be

$$\rho\frac{dH}{dt} = \frac{\partial p}{\partial t} - \mathrm{div}\,\mathbf{J}^{(e)}_H + \sum_{k=1}^{N}\rho_k\mathbf{F}_k\cdot\mathbf{v}_k \tag{8.12}$$

where

$$\mathbf{J}_H^{(e)} = -\frac{\mu}{\sigma_{\text{eff}}}\left[\nabla H + \frac{\sigma_{\text{eff}}}{\mu}\hat{\tau}\cdot\mathbf{v} - \nabla\left(\frac{v^2}{2}\right) + a(\mathrm{v},\bar{Q})\frac{\nabla p}{\rho} + \sum_{j=1}^{L}\left(a_j^*\nabla c_j^* + \frac{\sigma_{\text{eff}}}{\mu}b_j^*\mathbf{J}_j^*\right)\right] \tag{8.13}$$

Hence, it is now possible, using equilibrium conditions (8.3), to eliminate the concentration gradients and the diffusion fluxes of the reaction products by using the solution of algebraic equations ((8.4) and (8.7), respectively).

Unlike the case of a homogeneous reacting gas, additional terms, proportional to ∇p, ∇c_j^* and $\mathbf{J}_j^*$ are omitted in the paper cited above, have appeared in Eq. (8.12) when there are equilibrium reactions. The concentrations of the elements c_j^* and the diffusion fluxes of the elements $\mathbf{J}_j^*$ ($j = 1, \ldots, L$) will be found from the diffusion equations (1.5) of the elements, supplemented by the corresponding transport equations (6.5) of the elements in which it is necessary to eliminate the diffusion fluxes of the reaction products $\mathbf{J}_k$ ($k = L + 1, \ldots, N$) and thereby obtain the Stefan–Maxwell relations for chemically equilibrium flows.

In the case of thermochemically equilibrium flows, only the mass transfer equations for the elements are required for the closure of the diffusion part of the system of Navier–Stokes equations. We therefore eliminate the sum $\Sigma_{k=L+1}^{N}\beta_{jk}^*\mathbf{J}'_k$ from Eq. (6.5) using system (8.6) for this solution. As a result, we find

$$\sum_{k=L+1}^{N}\beta_{jk}^*\mathbf{J}'_k = \sum_{k=L+1}^{N}\frac{\delta_{jk}^*}{\Delta_j}\mathbf{J}'_k = \frac{\delta_j^{(e)}}{\Delta_j}\nabla\ln T + \sum_{l=1}^{L}\Theta_{jl}^{(e)}\mathbf{J}_l^{*\prime}, \quad j = 1, \ldots, L \tag{8.14}$$

where

$$\begin{aligned}
\delta_j^{(e)} &= -\frac{1}{\det\|b_{ik}\|}\begin{vmatrix} 0 & \bar{q}'_{L+1} & \cdots & \bar{q}'_N \\ \Delta^*_{j,N+1} & b_{L+1,L+1} & \cdots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \Delta^*_{j,N} & b_{N,L+1} & \cdots & b_{N,N} \end{vmatrix} \\
\Theta_{jl}^{(e)} &= -\frac{1}{\det\|b_{ik}\|}\begin{vmatrix} 0 & d_{L+1,l} & \cdots & d_{N,l} \\ \delta^*_{j,L+1} & b_{L+1,L+1} & \cdots & b_{L+1,N} \\ \vdots & \vdots & & \vdots \\ \delta^*_{j,N} & b_{N,L+1} & \cdots & b_{N,N} \end{vmatrix} \\
& j,\, l = 1, \ldots, L \\
& \bar{q}'_i = \frac{q_i}{kT} - \frac{\beta_{Ti}}{m_i}, \quad i = L+1, \ldots, N
\end{aligned} \tag{8.15}$$

Substituting expression (8.14) into Eq. (6.5), we obtain the required Stefan–Maxwell relations for the diffusion of the elements in the case of thermochemically equilibrium flows

$$\mathbf{d}_j^{(e)} = -\frac{S_j}{\mu}\mathbf{J}_j^* + \frac{m_j S_j}{\mu}\sum_{l=1}^{L}\alpha_{jl}^{(e)}\mathbf{J}_l^{*\prime}, \quad \alpha_{jl}^{(e)} = (\alpha_{jl}^* + \Theta_{jl}^{(e)}), \quad j = 1, \ldots, L \tag{8.16}$$

where the diffusion force vectors $\mathbf{d}_j^{(e)}$ for chemically equilibrium flows will be

$$\mathbf{d}_j^{(e)} = \nabla c_j^* + \left(K_{Tj}^* - \frac{m_j}{m}\delta_j^{(e)}\right)\nabla\ln T + K_{pj}^*\nabla\ln p, \quad j = 1, \ldots, L \tag{8.17}$$

By virtue of relations (6.3) and the expressions for $\delta_j^{(e)}$ and $\Theta_{jl}^{(e)}$, the coefficients in Eqs (8.16) satisfy the relations

$$\sum_{j=1}^{L}K_{Tj}^* = \sum_{j=1}^{L}K_{pj}^* = 0, \quad \sum_{j=1}^{L}m_j S_j\alpha_{jk}^{(e)} = m_k S_k, \quad k = 1, \ldots, N; \quad \sum_{j=1}^{L}m_j S_j\Theta_j^{(e)} = 0, \quad \sum_{j=1}^{L}m_j\delta_j^{(e)} = 0$$

Furthermore, in the case of a quasineutral plasma, but, generally speaking, when there is a current in it, by virtue of relations (6.4), the following further additional conditions for the coefficients of Eqs (8.16) hold

$$K^*_{TE} = K^*_{pE} = 0, \quad \delta^{(e)}_E = 0, \quad \Theta^{(e)}_{El} = 0, \quad \alpha^{(e)}_{El} = 0, \quad l = 1, \ldots, L; \quad l \neq E, \quad \Theta^{(e)}_{EE} = 1$$

It is important to note that, if all of the binary coefficients are equal to one another, then $\delta^{(e)}_j \equiv 0$.

In the case of chemically equilibrium flows, there will therefore be $L - 2$ independent Stefan–Maxwell relations (8.16) for a plasma and $L - 1$ such relations in the case of electrically neutral gases. Equations (8.16) together with equations (1.5) for the diffusion of the elements will also constitute the diffusion part of the general problem of the flow of thermochemically equilibrium, partially ionized, quasineutral mixtures of gases and plasma. In this case also, only the diffusion fluxes of the elements and the concentration gradients of the elements, which are related by Eqs (8.16), remain in the energy equation (8.12). The mass transfer equations for the reaction products (6.2) or (6.6) turn into identities when account is taken of relations (8.6). After solving the problem, the distribution in the flow of the sources of the masses of reactions $\dot{w}_i$ ($i = L + 1, \ldots, N$) can be found from the equations for the diffusion of the reaction products (1.6).

9. NUMERICAL CALCULATION OF THE EFFECTIVE TRANSPORT COEFFICIENTS FOR IONIZED AIR

The equilibrium transport coefficients were calculated using the final expressions derived. We will now present some very interesting results. The detailed numerical data are presented in [43].

The values of the coefficient $(m_j/m)\delta_j^{(e)}$ for oxygen (a recalculation is possible for nitrogen) at pressures $p = 1.013 \times 10^5$; 1.013×10^7 Pa are depicted by the solid curves in Fig. 1 (curves 1 and 2). Over the range where air dissociates (4000–7000 K), the coefficient $(m_j/m)\delta_j^{(e)}$ reaches a value of 0.2 to 0.3. This means that, even in the case when thermal diffusion and barodiffusion are neglected ($k_{Ti} = k_{pi} = K^*_{Tj} = K^*_{pj} = 0$), the diffusion fluxes of the elements $\mathbf{J}^*_j$ ($j = O, N, E$) due to the differences in the diffusion properties of the components ($\delta_j^{(e)} \equiv 0$ when the binary diffusion coefficients of all the components are the same) are non-zero when a temperature gradient exists. A significant separation of the elements therefore occurs (a result which has previously been obtained in a numerical calculation of actual flows of dissociated air [44]). In the ionization region ($T \approx 16000$–17000 K), the effect of the separation of the elements becomes even more substantial ($(m_j/m)\ \delta_j^{(e)} \approx 1$. The dashed curves in Figs 1–3 will be explained later.

The reactive thermal conductivity λ_r (in formula (8.7)) is shown in Fig. 2 (the solid curves are for the same two pressures) and this coefficient can exceed the thermal conductivity for frozen flows several-fold.

The change in the effective Prandtl number σ_{eff} (Fig. 3) with temperature turns out to be smaller than the individual changes in λ_r and c_{pr} (c_{pr} is not given here). Over the range where dissociation reactions occur, the change in $\sigma_{\text{eff}} \sim 20\%$ while, over the range where ionization occurs, it is $\sim 40\%$ (double ionization has been neglected in the calculation presented here and, in the high-temperature domain at low values of the Prandtl number, σ_{eff} is found to be of the order of 0.1). The solid and dashed curves 1, 2, and 3 in Fig. 3 correspond to $p = 1.013 \times 10^3$, 1.013×10^5, 1.013×10^7 Pa.

The values of the dimensionless coefficient $A = a(\nu, \tilde{Q})(p/\rho h)$, which appear in the heat influx equation (8.11) are shown in Fig. 4 for the two pressures $p = 1.013 \times 10^5$, 1.013×10^7 (curves 1 and 2 correspond to these values).

The coefficients from the same equation a^*_j/h, b^*_j/h are shown in Fig. 5 for the elements O and N, which show the appreciable effect of the separation of the elements on the heat flux (see the additional terms in the expression for the heat flux (8.9) appearing after ∇h). Here, $p = 1.013 \times 10^5$ Pa.

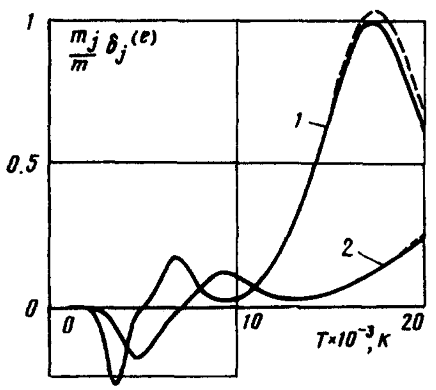

Fig. 1.

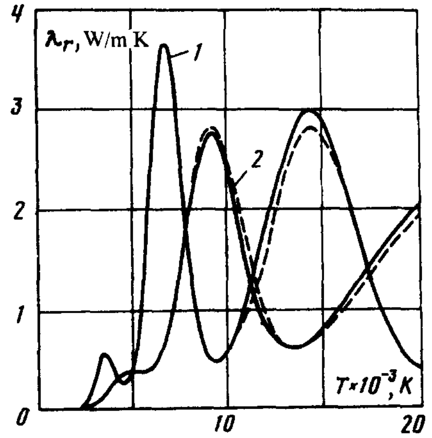

Fig. 2.

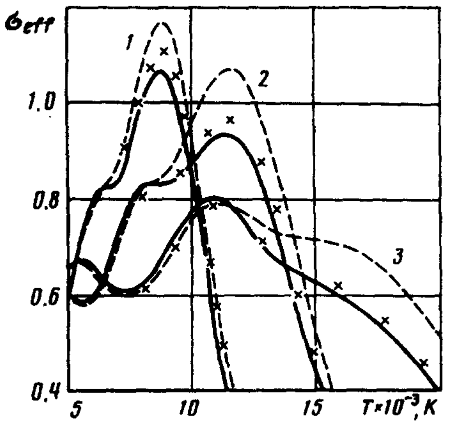

Fig. 3.

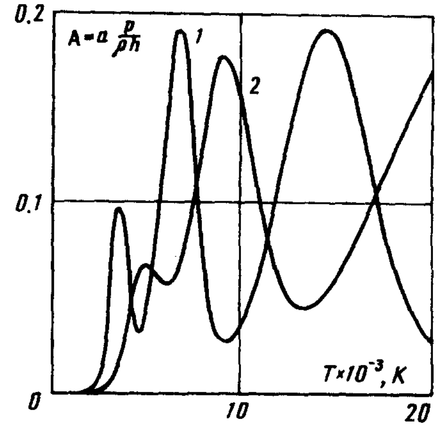

Fig. 4.

Numerical calculations of the effective transport coefficients taking account of the higher approximations showed good convergence over the temperature ranges where there is dissociation and ionization. Values of $(m_j/m)\delta_j^{(e)}$ for the fourth approximation ($\xi = 4$, the solid curves) are presented in Fig. 4. The dashed lines are the values $(m_j/m)\delta_j^{(e)}$, calculated ignoring thermal diffusion ($k_{Ti} \equiv 0$) and without taking account of the correction factors to the resistance coefficients Δ_{ij} (formula (4.3) when $f_{ij} = 1$). A difference of 2–5% is only observed in the region of partial ionization. The contribution to λ_r from the effect of thermal diffusion ($k_{Ti} \neq 0$) does not exceed 5% and the correction factors φ_{ij} make a contribution of $\sim$ 2% to λ_r (the dashed curves in Fig. 2 when $k_{Ti} = 0$ and $\varphi_{ij} = 0$).

Since the higher approximations are not very important in the calculation of λ_r, the number of approximation necessary to calculate σ_{eff} is determined by the accuracy of the calculation of the ratio $\mu(\xi)/\lambda(\xi)$. It suffices to calculate $\lambda(\xi)$ with an accuracy of 2% in the third approximation and $\mu(\xi)$ in the second approximation. The values of σ_{eff}, calculated taking account of higher approximations, are represented by the solid curve in Fig. 3, the values of σ_{eff}, obtained when $\lambda(\xi)$ is calculated in the second approximation ($\xi = 2$) and the coefficient $\mu(\xi)$ is calculated in the first approximation, is shown by the dashed curve in this figure). The values of σ_{eff}, calculated without taking account of the correction coefficients to Δ_{ij} ($\varphi_{ij} = 0, f_{ij} = 1$) and without taking account of the thermal diffusion relations ($k_{Ti} \equiv 0$), are denoted by the small crosses in Fig. 3. Hence, in the case of an air plasma up to temperatures of less than 2×10^4 K, the contribution of k_{Ti} and φ_{ij} in the calculation of σ_{eff} is less than 5%. However, it is necessary to calculate the coefficient of viscosity and the thermal conductivity in the second and third approximations respectively. An incorrect choice of the number of approximations (up to the point where convergence of the coefficients is obtained as ξ increases) in the calculation of σ_{eff} can lead to an error of up to 60% in the region where intense ionization occurs.

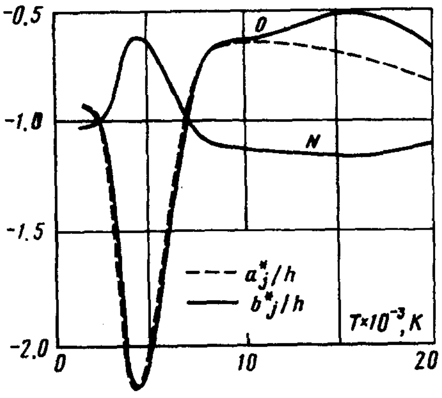

Fig. 5.

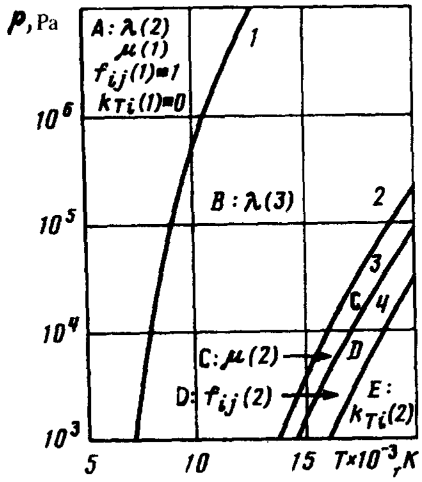

Fig. 6.

The effect of the accuracy of the calculation of $k_{Ti}(\xi)$ and $\varphi_{ij}(\xi)$ $\Theta_{jl}^{(e)}$(the second formula of (8.15)) in the equation for the transport of the elements and of a_j^* and b_j^* in the equation for the total heat flux (8.13) is found to be the same as in the calculation of $\delta_j^{(e)}$.

The concluding Fig. 6 reflects the situation which has been described, where the domains A, B, C and D, separated by curves 1–4 which indicate the boundaries, reflect the situation which has been described. It is in these domains that the transport coefficients $\lambda(\xi)$, $\mu(\xi)$, $k_{Ti}(\xi)$, $\varphi_{ij}(\xi)$ have to be calculated in the required approximations ξ in order to ensure an error for the effective transport coefficients to be no worse than ~5% in the case of an air plasma.

10. CONCLUSIONS

Finally, we draw a number of fundamental conclusions.

1. The effect of barodiffusion in relations (2.3) and the dependence of the right-hand side of the equilibrium conditions (8.3) on the pressure mutually compensate one another by virtue of the law of conservation of mass (1.2) in reactions (1.1) and, therefore, the diffusion fluxes of the reaction products $\mathbf{J}_i$ $(i = L + 1, \ldots, N)$, as follows from system of equations (8.6) and unlike the concentrations of the reaction products which are determined from (8.5), do not depend explicitly on the pressure gradient.

2. When account is taken of thermal diffusion in the energy equation, this leads to the replacement of the specific enthalpies h_j of the basis components by the effective enthalpies: $h_j^T = h_j + kT\alpha'_{Tj}$ $(j = 1, \ldots, L)$ (7.11) and the heats of reaction $\bar{q}_i$ by the "effective heats": $q_i^T = q_i - \beta'_{Ti}$ $(i = L + 1, \ldots, N)$ (7.11).

3. Equations (8.4) and (8.6) and their solutions (8.5) and (8.7) are obtained without any assumptions regarding the quasineutrality of the mixture and the absence of an electric current in it. If such assumptions are introduced, it does not change the form of the solutions of (8.5) and (8.7) nor consequently, the form of all the effective coefficients and the equations of the diffusion–thermal part (1.5) and (8.16), (8.12) and (8.13) of the overall system of Navier–Stokes equations.

4. If a partially ionized, chemically equilibrium mixture of gases is formed by the heating of an initially two-element mixture of gases, then the diffusion flux of the jth element will depend solely on the single gradient of its own (jth) concentration and the gradients of the remaining hydrodynamic parameters, that is, the cross-effects of barodiffusion and thermal diffusion.

5. The existence of components in a moving gas mixture with unequal binary diffusion coefficients or taking account of thermal and barodiffusion leads to a state of affairs where the concentrations of the elements c_j^* $(j = 1, \ldots, L)$ do not retain a constant value in the flow, even when there is no delivery (blowing) of the substance from the walls around which the flow occurs. For this reason, the diffusion fluxes of the elements $\mathbf{J}_j^* \neq 0$. In other words, Eqs (1.5), together with relations (8.16), do not, in general, admit of the trivial solution $\mathbf{J}^*_j = 0, c_j^* = c_{jw}^* = \text{const}$ $(j = 1, \ldots, L)$ due to the existence of the effects of multicomponent diffusion of components with different binary diffusion coefficients. This leads to a state of affairs where the chemically equilibrium composition of the mixture at the point being considered will not only depend on the pressure and temperature but also on the concentrations of the chemical elements, which change in the flow in accordance with (1.5) and (8.6). This has not been taken into account in any of the papers cited above. This is the main difference between an exact calculation of the equilibrium composition of the mixture in the flow and the numerous approximate calculations for a fixed or moving mixture or an inviscid, non-heat conducting and diffusion-free gas mixture, when the element chemical composition is specified and is constant in each flow field and the concentrations of the components and the thermodynamic properties of the mixture depend solely on two variables: the pressure and temperature.

I wish to thank S. S. Vasil'evskii for carrying out the calculation.

This research was supported financially by the Russian Foundation for Basic Research (97-01-00940) and the International Association for the Promotion of Cooperation with Scientists from the Independent States of the Former Soviet Union (95-IN-RU-1329).

REFERENCES

1. VON HAASE, R., *Thermodynamik der irreversible Prozess*. Dr. Dietrisch Steinkopff Verlag, Darmstadt, 1963.
2. VON MEIXNER, J., Zur Theorie der Wärmeleitfähigkeit reagierender fluider Mischungen. *Z. Naturforsch*. 1952, **7a**, 8, 553–559.
3. VON HAAS, R., Zur Thermodynamik der irreversible Prozess. III. *Z. Naturforsch*. **8a**, 11, 729–740.
4. HIRSCHFELDER, J. O., Heat transfer in chemical reaction mixtures. *J. Chem. Phys*., 1957, **26**, 2, 274–281.
5. BUTLER, J. N. and BROKAW, R. S., Thermal conductivity of gas mixtures in chemical equilibrium. *J. Chem. Phys*., 1957, **26**, 6, 1636–1643.

6. BROKAW, R. S., Thermal conductivity of gas mixtures in chemical equilibrium. *J. Chem. Phys.*, 1960, **32**, 4, 1005–1006.
7. KRINBERG, I. A., The effect of ionization reactions on the thermal conductivity of a plasma. *Teplogiz. Vys. Temp.*, 1965, **3**, 6, 838–844.
8. LUCHINA, A. A., The effect of chemical reactions on the thermal conductivity and diffusion fluxes in a plasma. *Inzh.-Fiz. Zh.*, 1975, **29**, 4, 706–715.
9. TIRSKII, G. A., The method of successive approximations for integrating the equations of a laminar, multicomponent, boundary layer with chemical reactions, including ionization. *Otchet Inst. Mekh. Mosk. Gos. Univ.*, 1016, 1969.
10. SUSLOV, O. N., TIRSKII, G. A. and SHCHENNIKOV, V. V., A description of the chemical equilibrium flows of multicomponent, ionized mixtures within the framework of the Navier–Stokes and Prandtl equations. *Zh. Prikl. Mekh. Tekh. Fiz.*, 1971, **1**, 73–89.
11. HIRSCHFELDER, J. O., CURTISS, C. F. and BIRD, R. B., *Molecular Theory of Gases and Liquids.*Wiley, New York; Chapman & Hall, London, 1954.
12. KANEKO, S., Transport coefficients of plasmas in a magnetic field. *J. Phys. Soc. Japan*, 1960, **15**, 9, 1685–1696.
13. AHTYE, W. F., Total thermal conductivity of plasmas in a magnetic field. *J. Phys. Soc.* Japan, 1960, **15**, 9, 1685–1696.
14. SPITZER, L. Jr., HÄRM, R., Transport phenomena in a completely ionized gas. *Phys. Rev.*, 1953, **89**, 5, 977–981.
15. SPITZER, L. Jr., *Physics of Fully Ionized Gases.* N.Y.: Wiley, 1962.
16. DEVOTO, R. S., Transport properties of ionized monoatomic gases. *Phys. Fluids*. 1966, **9**, 6, 1230–1240.
17. DEVOTO, R. S., Transport coefficients of partially ionized argon. *Phys. Fluids*. 1967, **10**, 2, 354–364.
18. YAROSHENKO, T. I., The use of the third approximation of the Chapman–Enskog theory to calculate the thermal conductivity of binary mixtures of monatomic gases and estimation of the influence of the thermal diffusion effect. *Inzh.-Fiz. Zh.*, 1978, **35**, 6, 987–993.
19. KRUGER, C. H., MITCHNER, M. and DAYBELGE, U., Transport properties of MHD-generator plasmas. *AIAA Journal*. 1968, **6**, 9, 1712–1723.
20. LI, C. P. and DEVOTO, R. S., Fifth and sixth approximations to the electron transport coefficients. *Phys. Fluids*, 1968, **11**, 2, 448–450.
21. DEVOTO, R. S., Transport coefficients of ionized argon. *Phys. Fluids*. 1973, **16**, 5, 616–623.
22. CURTISS, C. F. and HIRSCHFELDER, J. O., Transport properties of multicomponent gas mixtures. *J. Chem. Phys.*, 1949, **17**, 6, 550–555.
23. MUCKENFUSS, C. and CURTISS, C. F., Thermal conductivity of multicomponent gas mixtures. *J. Chem. Phys.*, 1958, **29**, 6, 1273–1277.
24. MONCHIK, L., MUNN, R. J. and MASON, E. A., Thermal diffusion in polyatomic gases: a generalized Stefan–Maxwell diffusion equation. *J. Chem. Phys.*, 1966, **45**, 8, 3051–3058.
25. MONCHIK, L., Estimates of error bounds of gas transport properties. *J. Chem. Phys.*, 1970, **53**, 11, 4367–4371.
26. CAPITELLI, M., Simplified expressions for the calculation of the contribution of the heavy components to the transport coefficients of partially ionized gases. *Z. Naturforsch.*, 1972, **27**, 5, 809–812.
27. CAPITELLI, M. and DEVOTO, R. S., Transport coefficients of high-temperature nitrogen. *Phys. Fluids*. 1973, **16**, 11, 1835–1841.
28. CAPITELLI, M., Transport properties of partially ionized gases. *J. de Phys. Suppl.*, 1977, **38**, 8, 227–237.
29. SOKOLOVA, I. A., Transport coefficients and collision integrals of air and its components. In *Aerophysical Investigations, Issue 4. Inst. Teor. Prikl. Mekh. Sib. Otd. Akad. Nauk SSSR*, Novisibirsk, 1974, 39–104.
30. PAVLOV, G. A., *Transport Processes in a Plasma with strong Coulomb Interaction.* Energoizdat, Moscow, 1995.
31. TIRSKII, G. A., Continuous models in problems of hypersonic flow of a rarefied gas past blunt bodies. *Prikl. Mat. Mekh.*, 1997, **61**, 6, 903–930.
32. TIRSKII, G. A., Equations of motion of partially ionized, multicomponent gas mixture in the normal Cauchy form with exact transport coefficients. *Nauch. Trudy Inst. Mekh. Mosk. Gos. Univ.*, 1974, 32, 6–22.
33. ZHDANOV, V. M., *Transport Phenomena in a Multicomponent Plasma*. Energoizdat, Moscow, 1982.
34. KOGAN, M. N., *Rarefied Gas Dynamics*. Nauka, Moscow, 1967.
35. KOLESNIKOV, A. F. and TIRSKII, G. A., Hydrodynamic equations for partially ionized multicomponent gas mixtures with transport coefficients in higher approximations. In *Molecular Gas Dynamics*, Nauka, Moscow, 1982, 20-44.
36. VASIL'EVSKII, S. A., SOKOLOVA, I. A. and TIRSKII, G. A., Exact equations and transport coefficients for a multicomponent mixture of gases and a partially ionized plasma. *Zh. Prikl. Mekh. Tekh. Fiz.*, 1984, 4, 15–24.
37. KOLESNICHENKO, A. V. and TIRSKII, G. A., The Stefan–Maxwell relations and heat flux for non-ideal multicomponent continua. In *Numerical Methods in Continuum Mechanics*, Vychisl. Tsentr Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1976, 7, 4, 106–121.
38. PILYUGIN, N. N. and TIRSKII, G. A., Dynamics of an Ionized Radiating Gas. *Izd. Mosk. Gos. Univ.*, Moscow, 1989.
39. CHAPMAN, S., Thermal diffusion in ionized gases. *Proc. Phys. Soc.* London, 1958, **72**, 3, 465, 353–362.
40. GENS, A. V. and TIRSKII, G. A., The hydrodynamic equations for multicomponent mixtures with transport coefficients in higher approximations. *Izv. Akad. Nauk SSSR. MZhG*, 1972, 6, 153–157.
41. FERZIGER, J. H. and KAPER, H. G., *Mathematical Theory of Transport Processes in Gases.* North-Holland, Amsterdam, 1972.
42. BENILOV, M. S. and TIRSKII, G. A., Calculation of electrical effects in an ionized multicomponent gas around electrically conducting bodies. The splitting method. *Prikl. Mat. Mekh.*, 1979, **43**, 2, 288–304.
43. VASIL'EVSKII, S. A., YEFIMOVA, L. G., KOLESNIKOV, A. F., SOKOLOVA, I. A. and TIRSKII, G. A., Calculation of transport coefficients in a multicomponent plasma in higher approximations. Effect of the separation of elements in a plasma in chemical and ionization equilibrium. *Otchet Inst. Mekh. Mosk. Gos. Univ.*, 2427, 1980.
44. SUSLOV, O. N., Multicomponent diffusion and heat exchange in the flow of a chemically equilibrium ionized gas past a body. *Zh. Prikl. Mekh. Tekh. Fiz.*, 1972, 3, 53–59.

Translated by E.L.S.