Available online at www.sciencedirect.com

ScienceDirect

Journal of Applied Mathematics and Mechanics 71 (2007) 718–736

Journal of APPLIED MATHEMATICS AND MECHANICS

www.elsevier.com/locate/jappmathmech

A phenomenological and kinetic description of diffusion and heat transport in multicomponent gas mixtures and plasma☆

V.M. Zhdanov, G.A. Tirskiy

Moscow, Russia

Received 19 June 2007

Abstract

Different forms of expressing diffusion and heat fluxes in multicomponent mixtures, obtained by methods of non-equilibrium thermodynamics and the kinetic theory of gas mixtures, are analysed and compared. It is shown that an alternative representation of the linear relations of non-equilibrium thermodynamics is possible, which enables them to be written in a form similar to that of the well-known Stefan–Maxwell equations. A relation between the phenomenological coefficients of non-equilibrium thermodynamics and the corresponding transport coefficients obtained in kinetic theory is established, with a confirmation that the Onsager reciprocity relations are satisfied. It is shown that there is an advantage in writing the transport relations on the basis of the "forces in terms of fluxes" representation, compared with the classical "fluxes in terms of forces" representation, used in standard schemes of phenomenological non-equilibrium thermodynamics and the Chapman–Enskog method, traditional for kinetic theory. A generalization of the Stefan-Maxwell equations and the equation for the heat flux is considered, which takes into account the contribution to these equations of the time and space derivatives of the fluxes. The relaxation form of the equations obtained enable one to approach the analysis of the propagation of small heat and concentration perturbations in gas mixtures to be justified, which, within the framework of classical transport relations, propagate with infinitely high velocity. The results presented in this review enable one to determine the areas of effective application of different methods of describing diffusion and heat transfer in multicomponent gas mixtures when solving specific gas-dynamic problems.

1. Introduction

The derivation of the closed systems of equations of gas dynamics for multicomponent media of necessity includes the derivation of the transport relations, which connect the fluxes of mass, momentum and energy in the mixture with gradients of the main gas-dynamic variables and external forces, acting on the particles of the medium. When electric and magnetic fields acting on charged particles are taken into account, these equations can also be used in the case of a plasma, if the latter is considered as a partially or fully ionised gas mixture, formed from electrons, ions and neutral atoms (molecules) of different kinds, and which satisfy the quasi-neutrality condition. The general equations of gas dynamics and plasma dynamics, obtained on the basis of a phenomenological as well as a kinetic approach, can be found in a number of well-known monographs.[1–10] Nevertheless, the choice of the appropriate expressions for the diffusion and heat fluxes occurring in these equations turns out to be non-unique. At present there is no single concept

---

☆ *Prikl. Mat. Mekh.* Vol. 71, No. 5, pp. 794–815, 2007.

E-mail addresses: vmzhdanov@mail.ru (V.M. Zhdanov), tirskiy@imec.msu.ru (G.A. Tirskiy).

doi:10.1016/j.jappmathmech.2007.11.005

in the literature regarding the effectiveness and advisability of using any particular transport relations in the case of multicomponent gas mixtures and plasma, obtained using various approaches.

In this review we analyse the present state of this problem. The complex structure of the expressions for the heat and diffusion fluxes in multicomponent gas mixtures leads to the need to establish a clear relation between the results of the phenomenological theory, based on the methods of non-equilibrium thermodynamics, and the results obtained in rigorous kinetic theory. One of the important criteria for finding such a correspondence is the satisfaction of the symmetry relations between the transport coefficients (the Onsager reciprocity relations[2,3]). The bilinear expression for the production of entropy,[3] obtained within the framework of non-equilibrium thermodynamics enables linear phenomenological relations between associated fluxes and generalized thermodynamic forces to be written down. These relations can be written most simply for the stress tensor components in the mixture, corresponding to shear and volume viscosity. When describing diffusion and heat transport the situation becomes more complicated, since the form of writing the production of entropy used may correspond to several versions of the representation of the linear phenomenological relations, connecting the diffusion and heat fluxes with the concentration gradients of the mixture components, the pressure and temperature gradients and also the external forces. In the kinetic theory of gas mixtures, different representations of the equations governing the transfer of the mass of components and heat transfer, obtained using different approximate methods of solving the Boltzmann kinetic equation (the Chapman–Enskog method,[5–8] Grad's moment method,[9–11] etc.) also correspond to this.

The representations of the transport equations usually considered both in non-equilibrium thermodynamics and in kinetic theory correspond to linear relations between the mass diffusion fluxes $\mathbf{J}_i$ and the reduced heat fluxes $\mathbf{J}'_q$ on the one hand and the relative temperature gradient $\nabla \ln T$ and the diffusion thermodynamic forces $\mathbf{d_k}$ on the other.[2–8] This classical method of describing the transport processes is sometimes called the "fluxes in terms of forces" representation.[12–14] Nevertheless, the structure of the expression for the production of entropy allows of another representation in which the associated "fluxes" and "forces" change places, so that it is possible to write the equations for the diffusion fluxes in the form of the so-called Stefan–Maxwell relations. One can also write the equation for heat transport in the mixture in the same representation, i.e. in the form permitted with respect to the temperature gradient in terms of the mass diffusion fluxes and the reduced heat flux. This method of description can be called the "forces in terms of fluxes" representation.[12–14]

The use of the rigorous kinetic theory of gases to derive the transport equations shows that the usual "fluxes in terms of forces" representation corresponds to the results of the standard Chapman–Enskog method,[5–8] which, in the case of mixtures of monatomic molecules, lead to formulae for the transport coefficients (multicomponent diffusion and thermal diffusion coefficients, and also the so-called "instantaneous" thermal conductivity λ') in the form of the ratio of determinants of the order of $N\xi+1$ to determinants of the order of $N\xi$. Here N is the number of components in the mixture and ξ corresponds to the order of the approximations (the number of retained terms in the expansion of the perturbed part of the distribution functions in orthgonal Sonin polynomials when calculating the transport coefficients[5–7]). The elements of the determinants in the solutions obtained are expressed in terms of so-called integral brackets of Sonine polynomials of different orders, which, in turn, are represented in the form of linear combinations $\Omega_{ij}^{ls}(T)$ – of integrals as functions of the temperature T, which also depend on the parameters of the interaction potentials of the i-th and j-th molecules. Here the total (true) thermal conductivity λ, which, unlike λ' has an actual practical meaning, and also the thermal diffusion ratios k_{Ti} are only obtained as a result of double matrix inversion. Additional terms and new polynomials, which depend on the internal state of the molecules, appear in the expansion of the distribution function when diatomic and polyatomic molecules occur in the composition of the mixture.[15–18] Then the order of the determinants in the expressions for the thermal conductivity and the thermal diffusion increases even more.

The complexity of the expressions and the complexity of the corresponding calculations of the kinetic properties of multicomponent mixtures to achieve the necessary accuracy becomes obvious and, for a number of transport coefficients (particularly in the case of a plasma) requires the use of values of $\xi = 2$–3.[19–21]

The scheme based on the "forces in terms of fluxes" representation turns out to be more convenient and effective in calculations. As was shown in Refs. 12,13, this form of writing corresponds to the results of the modified Chapman–Enskog method or the generalized Grad's method moment[22,9–10,14] in the rigorous kinetic theory. The corresponding transport coefficients for mixtures of monatomic molecules in this case can be written immediately in the form of the ratio of determinants of the order of $N(\xi\text{-}1)+1$ and $N(\xi\text{-}1)$. As a result one obtains much simpler expressions (without the need for double matrix inversion) for the true thermal conductivity of the mixture λ and thermal diffusion ratios k_{Ti} respectively in the expression for the heat flux and the equations for the diffusion fluxes in the Stefan–Maxwell form.

Below we analyse and compare the different forms of writing expressions for the diffusion and heat fluxes in multicomponent media, obtained at the phenomenological level, with the known results given by the kinetic theory of multicomponent gas mixtures. It is shown that an alternative representation of the linear relations of non-equilibrium thermodynamics is possible, which enables us to write them in a form similar to the representation of the Stefan–Maxwell equations. A relation is established between the phenomenological coefficients of non-equilibrium thermodynamics and the corresponding transport coefficients obtained in kinetic theory, with a confirmation that the Onsager reciprocity relations are satisfied.

We also discuss some new results which arise from the "extended non-equilibrium thermodynamics" developed in recent years.[23–30] We consider a generalization of the Stefan–Maxwell equations and the equations for the heat fluxes, which take into account the contribution to these equations of the time and space derivatives of the fluxes. The relaxation form of the equations obtained enables us, in this case, to provide a more valid approach to the analysis of the propagation of small thermal and concentration perturbations in gas mixtures. By taking into account more explicitly the processes that occur in a time of the order of the characteristic time between molecular collisions we can obtain a hyperbolic form of the equations for the concentrations of the components and the temperature of the mixture, thereby eliminating the paradox of an infinite velocity of propagation of small perturbations, which arise from the use of the usual linear relations of non-equilibrium thermodynamics for the corresponding fluxes.

2. General relations of non-equilibrium thermodynamics for multicomponent media

We will first recall the well-known relations of non-equilibrium thermodynamics,[3,4,6] which serve as a basis for considering alternative methods of representing the expressions for the fluxes of interest to us. For a phenomenological description of the processes of mass, momentum and energy transport in multicomponent media, within the framework of non-equilibrium thermodynamics, the initial expression, as is well known, is the expression for the production of entropy, which, ignoring chemical reactions, can be represented in the following form for an N-component mixture[3]

$$\sigma = -\frac{1}{T}\left(\mathbf{J}'_q \cdot \nabla \ln T + \sum_{i=1}^{N} \mathbf{J}_i \cdot [(\nabla \mu_i)_T - \mathbf{F}_i] + \pi_{rs}\varepsilon_{rs} + p_V \nabla \cdot \mathbf{v}\right) \tag{2.1}$$

Here $\mathbf{J}'_q$ is the reduced heat flux in the mixture, $\mathbf{J}_i$ is the mass diffusion flux of the i-th component, $(\nabla\mu_i)_T$ is the gradient of the chemical potential of the component with $T=\text{const}$, T is the temperature, π_{rs} are the components of the non-divergent part of the stress tensor (the components of the viscous-stress tensor) in Cartesian coordinates r, s, p_v is the scalar part of the stress tensor, corresponding to the volume viscosity, and $\mathbf{F}_i$ is the external force acting on a particle of the i-th species (per unit mass of the component). The components of the shear rates tensor have the form

$$\varepsilon_{rs} = \frac{1}{2}\left(\frac{\partial v_r}{\partial x_s} + \frac{\partial v_s}{\partial x_r}\right) - \frac{1}{3}\delta_{rs}\nabla \cdot \mathbf{v} \tag{2.2}$$

The corresponding vector fluxes are defined as

$$\mathbf{J}_i = \rho_i \mathbf{V}_i, \quad \mathbf{J}'_q = \mathbf{J}_q - \sum_{k=1}^{N} h_k \mathbf{J}_k \tag{2.3}$$

where $\rho_i = m_i n_i$ and $\mathbf{V}_i = \mathbf{v}_i - \mathbf{v}$ are the mass density and diffusion velocity of the i-th component respectively, $\mathbf{J}_q$ is the total heat flux in the mixture, h_i is the partial specific enthalpy,[31] n_i is the number density of the particles of the i-th species, and m_i is the mass of a particle. The diffusion velocity $\mathbf{V}_i$ is determined in a frame of reference which moves with the mean-mass velocity $\mathbf{v} = \rho^{-1}(\rho_1\mathbf{v}_1 + \ldots + \rho_N\mathbf{v}_N)$, where $\rho = \rho_1 + \ldots + \rho_N$ is the mass density of the mixture, and v_i ($i = 1, \ldots, N$) is the macroscopic velocity of particles of the i-th spices. The following obvious identity is then satisfied

$$\mathbf{J}_1 + \ldots + \mathbf{J}_N = 0 \tag{2.4}$$

The expression for σ (2.1) has a bilinear form, some of the factors of which are flux-type quantities (for example, $\mathbf{J}_i$, $\mathbf{J}'_q$, π_{rs}, p_V), while the others are quantities proportional to the gradient of a certain intensive variable of the state (for example, proportional to the temperature, velocity or specific chemical potential gradients), and also the external forces (or the potential gradients, if the forces are assumed to be conservative). The corresponding quantities are called generalized thermodynamic forces.

It is important to note that, when choosing the fluxes and thermodynamic forces associated with them, a well-known arbitrariness is allowed: the unique requirement is that their product should constitute an appropriate bilinear form in the expression for σ. If we define the production of entropy by the expression

$$\sigma = \frac{1}{T}\sum_i \mathbf{Y}_i\mathbf{X}_i \tag{2.5}$$

the corresponding linear phenomenological relations between the fluxes $\mathbf{Y}_i$ and the generalized thermodynamic forces $\mathbf{X}_k$ are postulated in the form[3]

$$\mathbf{Y}_i = \sum_{k=1}^{n} L_{ik}\mathbf{X}_k \tag{2.6}$$

where L_{ik} are the phenomenological coefficients or the kinetic coefficients of the Onsager matrix. When choosing the fluxes and forces in accordance with condition (2.5) the coefficients of the matrix satisfy the symmetry principle, or the Onsager reciprocity relations

$$L_{ik} = L_{ki} \tag{2.7}$$

The linear phenomenological relations can be written most simply for the viscous-stress tensor and the scalar quantity corresponding to the contribution of the volume viscosity

$$\pi_{rs} = -2\eta\varepsilon_{rs}, \quad p_V = -\eta_V\nabla\cdot\mathbf{v} \tag{2.8}$$

where η and η_V are the coefficients of shear and volume viscosity respectively.

Different versions of the representation of the linear relations are possible for the vector fluxes $\mathbf{J}_i$ and $\mathbf{J}'_q$, and hence the problem of these are considered below in more detail. The expression for the production of entropy (2.1) will, for simplicity, be written solely for the corresponding vector quantities.

Eliminating the flux $\mathbf{J}_n$ in the second term of the expression for σ (2.1) using condition (2.4), we can represent the production of entropy in the form

$$\sigma = -\frac{1}{T}\mathbf{J}'_q\cdot\nabla\ln T - \frac{1}{T}\sum_{i=1}^{N-1}\mathbf{J}_i\cdot[(\nabla\mu_i)_T - (\nabla\mu_N)_T - \mathbf{F}_i + \mathbf{F}_N] \tag{2.9}$$

The linear phenomenological relations for the fluxes can then be written as

$$\mathbf{J}_i = -L_{iq}\nabla\ln T - \sum_{k=1}^{N-1} L_{ik}[(\nabla\mu_k)_T - (\nabla\mu_N)_T - \mathbf{F}_k + \mathbf{F}_N] \tag{2.10}$$

$$\mathbf{J}'_q = -L_{qq}\nabla\ln T - \sum_{k=1}^{N-1} L_{qk}[(\nabla\mu_k)_T - (\nabla\mu_N)_T - \mathbf{F}_k + \mathbf{F}_N] \tag{2.11}$$

while the symmetry relations have the form

$$L_{iq} = L_{qi}, \quad L_{ik} = L_{ki}; \quad i, k = 1, 2, \ldots, N-1 \tag{2.12}$$

As an example we will consider a binary mixture when there are no external forces acting on the molecules. It follows from condition (2.4) for this case that $\mathbf{J}_2 = -\mathbf{J}_1$, and hence it is sufficient to confine ourselves to the expression for the diffusion flux solely of the first component ($i = 1$), which, by relation (2.10), can be written as

$$\mathbf{J}_1 = -L_{11}[(\nabla\mu_1)_T - (\nabla\mu_2)_T] - L_{1q}\nabla\ln T \tag{2.13}$$

This expression can be easily represented in the more usual form[2]

$$\mathbf{J}_1 = -\rho D(\nabla c_1 + k_p \nabla \ln p + k_T \nabla \ln T) \tag{2.14}$$

Here $c_i = \rho_i/\rho$ is the mass concentration (mass fraction) of the i-th component, while the binary diffusion coefficient D, the barodiffusion ratio k_p and thermal ratio k_T are related to the phenomenological coefficients of the Onsager matrix by the relations

$$D = L_{11}\frac{1}{\rho_2}\left(\frac{\partial\mu_1}{\partial c_1}\right)_{p,T}, \quad \rho D k_p = L_{11} p\left[\frac{\partial(\mu_1 - \mu_2)}{\partial p}\right]_{c_1,T}, \quad \rho D k_T = L_{1q} \tag{2.15}$$

To write the expression for D we use the Gibbs–Duhem relation[3]

$$\sum_{k=1}^{N} \rho_k (\nabla\mu_k)_T = \nabla p \tag{2.16}$$

from which it follows, when $p = \text{const}$, that

$$(\partial\mu_2/\partial c_1)_{p,T} = -(\rho_1/\rho_2)(\partial\mu_1/\partial c_1)_{p,T}$$

For a mixture of perfect gases, using the well-known expression for the chemical potential of the i-th component of the mixture[31]

$$\mu_i = \frac{k_B T}{m_i}\left(\ln n_i - \frac{3}{2}\ln\frac{2\pi k_B T}{m_i}\right) + \text{const} \tag{2.17}$$

we obtain

$$D = \frac{k_B T}{n m_1 m_2 c_1 c_2} L_{11}, \quad k_p = \frac{m_2 - m_1}{\bar{m}} c_1 c_2, \quad k_T = \frac{1}{k_B T}\frac{m_1 m_2}{\bar{m}}\frac{L_{1q}}{L_{11}} c_1 c_2; \quad \bar{m} = \frac{\rho}{n} \tag{2.18}$$

where k_B is Boltzmann's constant.

Instead of k_p and k_T it is often more convenient to use the so-called barodiffusion and thermal diffusion factors α_P and α_T, defined by the relations

$$k_p = \alpha_p c_1 c_2, \quad k_T = \alpha_T c_1 c_2 \tag{2.19}$$

Note that, unlike the diffusion and thermal diffusion coefficients, which are essentially kinetic quantities, the barodiffusion factor α_p is defined solely in terms of the thermodynamic parameters of the mixture.[2]

We will now turn our attention to the expressions for the heat fluxes. In the special case of a binary mixture considered here, the total heat flux is defined as

$$\mathbf{J}_q = \mathbf{J}'_q + (h_1 - h_2)\mathbf{J}_1 \tag{2.20}$$

where

$$\mathbf{J}'_q = -L_{qq}\nabla \ln T - L_{q1}[(\nabla\mu_1)_T - (\nabla\mu_2)_T] \tag{2.21}$$

Taking definitions (2.18) into account, the last expression can be represented as

$$\mathbf{J}'_q = -\lambda'\nabla T - \rho_1\left(\frac{\partial\mu_1}{\partial c_1}\right)_{p,T} \alpha_T D(\nabla c_1 + k_p \nabla p) \tag{2.22}$$

Instead of the "instantaneous" thermal conductivity λ' it is more convenient to use the thermal conductivity λ, which can be determined directly experimentally. This is due to the fact that the measurements are usually made under steady conditions, when there is no complete diffusion flux in the mixture. The presence of a temperature gradient leads to thermal diffusion and a steady state is only established after the thermal diffusion flux is compensated by the diffusion flux due to the concentration gradient.

Using the expression for $\mathbf{J}_1$ (2.14), we will represent $\mathbf{J}'_q$ in the form

$$\mathbf{J}'_q = -\lambda\nabla T + \alpha_T c_1\left(\frac{\partial\mu_1}{\partial c_1}\right)_{p,T}\mathbf{J}_1 \tag{2.23}$$

and the thermal conductivity is given by the expression

$$\lambda = \lambda' - \frac{\rho_1}{T}\left(\frac{\partial\mu_1}{\partial c_1}\right)_{p,T} D\alpha_T^2 c_1 c_2 \tag{2.24}$$

The total heat flux can then be written as

$$\mathbf{J}_q = -\lambda\nabla T + \left[(h_1 - h_2) + \alpha_T c_1\left(\frac{\partial\mu_1}{\partial c_1}\right)_{p,T}\right]\mathbf{J}_1 \tag{2.25}$$

The corresponding kinetic coefficients are connected with the phenomenological coefficients by the relations

$$\lambda' = \frac{1}{T^2}L_{qq}, \quad \rho D\alpha_T c_1 c_2 = L_{1q} = L_{q1} \tag{2.26}$$

In the special case of a mixture of perfect gases, using the definition of the specific enthalpy of a component $h_i = (5/2)k_B T/m_i$, we arrive at the following expression for the total heat flux in the mixture

$$\mathbf{J}_q = -\lambda\nabla T + \left(\frac{5}{2}k_B T\frac{m_2 - m_1}{m_1 m_2} + \alpha_T\frac{\bar{m}k_B T}{m_1 m_2}\right)\mathbf{J}_1; \quad \lambda = \lambda' - \frac{k_B\bar{m}}{m_1 m_2}\rho D\alpha_T^2 c_1 c_2 \tag{2.27}$$

Expressions (2.14) for the diffusion flux and (2.27) for the heat flux can be more convenient to use together with the equations of hydrodynamics of a binary mixture, when ρ, $\mathbf{v}$, T and c_1 are used as the fundamental macroscopic variables.

3. Linear relations for the vector fluxes using “thermodynamic diffusion forces”

The linear relations for the fluxes in the form (2.10) and (2.11) are the usual form of writing the results within a framework of non-equilibrium thermodynamics.[3,4,6] Nevertheless, alternative forms of representing of both the expression for the production of entropy and the corresponding linear relations are possible, which enable the relation between the results of non-equilibrium thermodynamics and the expressions of kinetic theory to be followed more clearly.[5–10,12–14]

We will use the fact that, since condition (2.4) is satisfied for the mass diffusion fluxes $\mathbf{J}_i$, we can add an arbitrary constant quantity to the thermodynamic force in the second term of the expression for the production of entropy (2.1). It is more convenient to introduce it in such a way as to satisfy the Gibbs–Duhem relation (2.16).

The production of entropy for the vector fluxes in this case can be written as

$$\sigma = -\frac{1}{T}\mathbf{J}'_q\cdot\nabla\ln T - \frac{1}{T}\sum_{i=1}^{N}\frac{\mathbf{J}_i}{\rho_i}\cdot p\mathbf{d}_i \tag{3.1}$$

The “thermodynamic diffusion force” $p\mathbf{d}_i$ is defined by the expression

$$p\mathbf{d}_i = \rho_i\left[(\nabla\mu_i)_T - \mathbf{F}_i - \frac{1}{\rho}\left(\nabla p - \sum_k \rho_k\mathbf{F}_k\right)\right] \tag{3.2}$$

and satisfies the condition

$$\sum_{i=1}^{N} p\mathbf{d}_i = 0 \tag{3.3}$$

The introduction of the quantity $p\mathbf{d}_i$ (3.2) leads to a form of writing the expressions which is more adequate to the results of the kinetic theory of gases. In the case of a mixture of perfect gases, for example, when using the expression for the chemical potential of the i-th component of the mixture (2.18), the expression for $\mathbf{d}_i$ takes the well-known form[5–8]

$$\mathbf{d}_i = \nabla\frac{n_i}{n} + \left(\frac{n_i}{n} - \frac{\rho_i}{\rho}\right)\nabla\ln p - \frac{1}{p}\left(\rho_i\mathbf{F}_i - \sum_{k=1}^{N}\rho_k\mathbf{F}_k\right) \tag{3.4}$$

The linear phenomenological relations for the fluxes, corresponding to representation (3.1), can be written as

$$\frac{\mathbf{J}_i}{\rho_i} = -\bar{L}_{iq}\nabla\ln T - \sum_{k=1}^{N}\bar{L}_{ik}p\mathbf{d}_k, \quad \mathbf{J}'_q = -\bar{L}_{qq}\nabla\ln T - \sum_{k=1}^{N}\bar{L}_{qk}p\mathbf{d}_k \tag{3.5}$$

while the Onsager reciprocity relations are similar to relations (2.12).

By virtue of condition (3.3), of the N thermodynamic diffusion forces $p\mathbf{d}_k$ only $N-1$ of the corresponding quantities turn out to be independent. Hence, instead of (3.1) it is more convenient to represent the production of entropy in the form

$$\sigma = -\frac{1}{T}\mathbf{J}'_q\cdot\nabla\ln T - \frac{1}{T}\sum_{i=1}^{N-1}\left(\frac{\mathbf{J}_i}{\rho_i} - \frac{\mathbf{J}_N}{\rho_N}\right)\cdot p\mathbf{d}_i \tag{3.6}$$

where the term with $i = N$ is eliminated from the summation over the index i. The corresponding linear phenomenological relations for the independent quantities are then written as

$$\frac{\mathbf{J}_i}{\rho_i} - \frac{\mathbf{J}_N}{\rho_N} = -\tilde{L}_{iq}\nabla\ln T - \sum_{k=1}^{N-1}\tilde{L}_{ik}p\mathbf{d}_k, \quad \mathbf{J}'_q = -\tilde{L}_{qq}\nabla\ln T - \sum_{k=1}^{N-1}\tilde{L}_{qk}p\mathbf{d}_k \tag{3.7}$$

Here

$$\tilde{L}_{iq} = \bar{L}_{iq} - \bar{L}_{Nq}, \quad \tilde{L}_{ik} = (\bar{L}_{ik} - \bar{L}_{Nk}) - (\bar{L}_{iN} - \bar{L}_{NN}) \tag{3.8}$$

It is easily noted that the new coefficients also satisfy symmetry relations of the form (2.12).

We will again consider the case of a binary mixture of gases. The quantity $\mathbf{d}_1 = -\mathbf{d}_2$ depends on the gradient of the molar, and not the mass, concentration of the component of the mixture. In this connection it is more convenient to use the definition of both the mass and molar diffusion flows of the components

$$\mathbf{J}_1 = \rho_1(\mathbf{v}_1 - \mathbf{v}), \quad \mathbf{J}_1^m = n_1(\mathbf{v}_1 - \mathbf{v}^m)$$

which can also be represented in the form

$$\mathbf{J}_1 = \frac{\rho_1\rho_2}{\rho}(\mathbf{v}_1 - \mathbf{v}_2) = \rho c_1 c_2(\mathbf{v}_1 - \mathbf{v}_2), \quad \mathbf{J}_1^m = \frac{n_1 n_2}{n}(\mathbf{v}_1 - \mathbf{v}_2) = n x_1 x_2(\mathbf{v}_1 - \mathbf{v}_2) \tag{3.9}$$

Here $\mathbf{v} = c_1\mathbf{v}_1 + c_2\mathbf{v}_2$ and $\mathbf{v}^m = x_1\mathbf{v}_1 + x_2\mathbf{v}_2$ are the mean-mass and mean-molar velocities of the mixture respectively, and $x_i = n_i/n$ is the molar concentration of the i-th component, where the concentration c_i and x_i are connected by the relation

$$c_1 c_2 = m_1 m_2\frac{n^2}{\rho^2}x_1 x_2 \tag{3.10}$$

The molar diffusion flux when there are no external forces, corresponding to the first relation of (3.7), is given by the expression

$$\mathbf{J}_1^m = -n x_1 x_2(\tilde{L}_{11}pd_1 + \tilde{L}_{1q}\nabla\ln T)$$

which, by analogy with (2.14), can be written in the form

$$\mathbf{J}_1^m = -n\mathcal{D}_{12}(\nabla x_1 + k_p^m \nabla \ln p + k_T^m \nabla \ln T) \tag{3.11}$$

The mass diffusion flux is then defined as

$$\mathbf{J}_1 = \frac{\rho c_1 c_2}{n x_1 x_2}\mathbf{J}_1^m = -\frac{m_1 m_2 n^2}{\rho}\mathcal{D}_{12}(\nabla x_1 + k_p^m \nabla \ln p + k_T^m \nabla \ln T) \tag{3.12}$$

while the corresponding kinetic coefficients have the form

$$\mathcal{D}_{12} = \rho_1 x_1 x_2 \tilde{L}_{11}\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p}, \quad \mathcal{D}_{12}k_P^m = p x_1 x_2 \tilde{L}_{11}\left[\rho_1\left(\frac{\partial \mu_1}{\partial p}\right)_{T,x_1} - \frac{\rho_1}{\rho}\right], \quad \mathcal{D}_{12}k_T^m = x_1 x_2 \tilde{L}_{1q} \tag{3.13}$$

For a mixture of perfect gases we obtain

$$\mathcal{D}_{12} = p x_1 x_2 \tilde{L}_{11}, \quad k_p^m = \frac{m_2 - m_1}{\bar{m}} x_1 x_2, \quad k_T^m = \frac{1}{p}\frac{\tilde{L}_{1q}}{\tilde{L}_{11}}; \quad \bar{m} = m_1 x_1 + m_2 x_2 \tag{3.14}$$

As in the previous version, instead of k_p^m and k_T^m it is more convenient to use the coefficients α_p^m and α_T^m, defined as

$$k_p^m = \alpha_p^m x_1 x_2, \quad k_T^m = \alpha_T^m x_1 x_2 \tag{3.15}$$

Note that for any method of description (in mass or molar variables) the following relations hold

$$\mathcal{D} = \mathcal{D}_{12}, \quad \alpha_p = \alpha_p^m, \quad \alpha_T = \alpha_T^m \tag{3.16}$$

We now return to the expression for the heat flux. In the case of a binary mixture considered taking expression (3.11) into account, the reduced heat flux can be represented in the form

$$\mathbf{J}_q' = -\tilde{L}_{qq}\nabla \ln T - \tilde{L}_{q1} p \mathbf{d}_1 = -\lambda' \nabla T - p\alpha_T \mathcal{D}_{12}\mathbf{d}_1 = -\lambda \nabla T + k_B T \alpha_T \mathbf{J}_1^m \tag{3.17}$$

The total heat flux can then be written as

$$\mathbf{J}_q = -\lambda \nabla T + \left[(h_1 - h_2)\frac{m_1 m_2}{\bar{m}} + k_B T \alpha_T\right]\mathbf{J}_1^m \tag{3.18}$$

The corresponding kinetic coefficients have the form

$$\lambda' = \frac{1}{T}\tilde{L}_{qq}, \quad \mathcal{D}_{12}\alpha_T = \tilde{L}_{1q} = \tilde{L}_{q1}, \quad \lambda = \lambda' - \frac{p}{T}\mathcal{D}_{12}\alpha_T^2 x_1 x_2 \tag{3.19}$$

For a mixture of perfect gases, bearing in mind the definition of the specific enthalpy of a component, we obtain

$$\mathbf{J}_q = -\lambda \nabla T + k_B T\left(\frac{5}{2}\frac{m_2 - m_1}{\bar{m}} + \alpha_T\right)\mathbf{J}_1^m \tag{3.20}$$

Note that, taking relation (3.12) between the mass and molar diffusion fluxes into account, the expressions for the total heat fluxes (3.20) and (2.27) turn out to be identical.

The expressions for the diffusion fluxes (3.11) and (3.12) and the expression for the heat flux (3.20) must be used together with the equations of the hydrodynamics of a binary mixture when n, $\mathbf{v}_m$, T and x_1 or ρ, $\mathbf{v}$, T and x_1 are used as the main macroscopic variables.

4. The “forces in terms of fluxes” representation. The Stefan–Maxwell equations

The relations of the previous section can be written in a form which is admitted in terms of the mass (or molar) diffusion fluxes of the components and the reduced heat flux in the mixture in terms of the gradients of the molar fractions (relative concentrations) of the components, the pressure and temperature gradients, and also the differences in the mass external forces acting on the different components of the mixture. This form of writing the transport equations is called the "fluxes in terms of forces" representation. A comparison with the results of the kinetic theory of gas mixtures shows that this representation corresponds in large measure to the well known expressions obtained using the classical Chapman–Enskog method.[5–8] Nevertheless, the bilinearity of the production of entropy enables us formally to choose any of the factors occurring in representation (2.1) or (3.6) as the fluxes and corresponding thermodynamic forces. Now this enables us, in addition to Eqs (3.5) or (3.7), to consider other forms of writing the linear relations for the diffusion and thermal fluxes, corresponding to the so-called "forces in terms of fluxes" representation.[12,13] As will be shown, the relations thus obtained also correspond to the well-known results of the kinetic theory of gases, obtained either using a certain modification of the Chapman–Enskog method,[12,13,32,33] or based on the Grad's moment.[9,10,14,22] Then, in a number of cases (particularly when using higher approximations), one obtains a considerable simplification of the expressions for the transport coefficients occurring in these relations, calculated by the methods of kinetic theory.

The version of the selection of these factors in the expression for the production of entropy (2.8) considered below corresponds to interchanging "fluxes" and "forces", so that the quantities $-p\mathbf{d}_i$, $-\nabla \ln T$ formally act as the "fluxes", and the quantities $\mathbf{J}_k/\rho_k - \mathbf{J}_N/\rho_N$, $\mathbf{J}'_q$ act as the "forces". The corresponding linear relations then take the form

$$-p\mathbf{d}_i = \Omega_{iq}\mathbf{J}'_q + \sum_{k=1}^{N-1}\Omega_{ik}\left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_N}{\rho_N}\right), \quad -\frac{1}{T}\nabla T = \Omega_{qq}\mathbf{J}'_q + \sum_{k=1}^{N-1}\Omega_{qk}\left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_N}{\rho_N}\right) \tag{4.1}$$

when the symmetry relations, analogous to relations (2.12), hold.

If we turn to the actual and not the formal definition of the fluxes and thermodynamic forces, the linear transport relations (4.1), unlike to relations (3.7), obviously correspond to the "forces in terms of fluxes" representation.

We will express the quantity $\mathbf{J}'_q$ from the last equation of (4.1) and substitute it into the first equality of (4.1). The linear relations obtained in this way can be written as

$$-p\mathbf{d}_i = \Lambda_{iq}\frac{1}{T}\nabla T + \sum_{k=1}^{N-1}\Lambda_{ik}\left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_N}{\rho_N}\right), \quad \mathbf{J}'_q = -\Lambda_{qq}\frac{1}{T}\nabla T + \sum_{k=1}^{N-1}\Lambda_{qk}\left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_N}{\rho_N}\right) \tag{4.2}$$

Here

$$\Lambda_{qq} = \frac{1}{\Omega_{qq}}, \quad \Lambda_{iq} = -\frac{\Omega_{iq}}{\Omega_{qq}}, \quad \Lambda_{ik} = \Omega_{ik} - \frac{\Omega_{iq}\Omega_{qk}}{\Omega_{qq}} \tag{4.3}$$

when symmetry relations, analogous to relations (2.12), are satisfied.

The first equality of (4.2) can be converted to a form when the relations for determining the mass diffusion fluxes take the form known as the "Stefan–Maxwell equations".[24,35] It follows from condition (3.3) that

$$\sum_{i=1}^{N}\sum_{k=1}^{N}\Lambda_{qk}\left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_N}{\rho_N}\right) = 0, \quad \sum_{i=1}^{N}\Lambda_{iq} = 0 \tag{4.4}$$

It is possible to satisfy the first of conditions (4.4) if

$$\sum_{i=1}^{N}\Lambda_{ik} = \sum_{k=1}^{N}\Lambda_{ki} = 0, \quad \text{или} \quad \Lambda_{ii} = -\sum_{k\neq i}\Lambda_{ki}$$

As a result, instead of the first equation of (4.2), we have the equations

$$-p\mathbf{d}_i = \Lambda_{iq}\frac{1}{T}\nabla T + \sum_{k\neq i}^{N}\Lambda_{ik}\left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_i}{\rho_i}\right) \tag{4.5}$$

To this we must add the last equation of (4.2), solved for the temperature gradient. This equation, together with Eq. (4.5), form a system of transport equations for the mass of the components and the heat in the form of "thermodynamic forces in terms of fluxes", where Eq. (4.5) are often called the Stefan–Maxwell relations. In principle these relations can also be obtained directly from Eq. (3.7) if we solve them for $\nabla \ln T$ and the thermodynamic diffusion forces $p\mathbf{d}_k$,[36] but this method turns out to be considerably more complicated than that considered above.

The diffusion relations in the form (4.5) were obtained by Stefan[34] and Maxwell[35] phenomenologically without taking thermal diffusion into account ($\Lambda_{iq} = 0$) with the fundamental assumption that the force acting on the i-th particle from the N-th particle is proportional to the difference of their diffusion velocities. The total resistance to the motion of the i-th particle in the mixture is then equal to the sum of the independent resistances from all the remaining particles of the other species.[37,38] Moreover, using the arguments of the theory of diffusion in binary mixtures, Stefan and Maxwell assumed that the matrix of the resistance coefficients Λ_{ik} for multicomponent mixtures is symmetrical.

5. Comparison with the results of the kinetic theory of gas mixtures

It is useful to establish a relation between the expressions obtained above and the results that are known from the kinetic theory of multicomponent gas mixtures.[5–10,12–14] The expressions for the mass diffusion flux of the i-th component $\mathbf{J}_i$ and the reduced heat flux $\mathbf{J}'_q$, following from the results of the kinetic theory of monatomic gaseous mixtures, obtained by the Chapman–Enskog method, are usually written as follows[7,8]:

$$\mathbf{J}_i = -\rho_i\left(\sum_k D_{ik}\mathbf{d}_k + D_{Ti}\frac{1}{T}\nabla T\right) = -\rho_i\sum_k D_{ik}\left(\mathbf{d}_k + k_{Tk}\frac{1}{T}\nabla T\right) \tag{5.1}$$

$$\mathbf{J}'_q = -\lambda'\nabla T - p\sum_k D_{Tk}\mathbf{d}_k \tag{5.2}$$

Here D_{ik} and D_{Ti} are the multlicomponent diffusion and thermal diffusion coefficients, k_{Ti} are the thermal diffusion ratios and λ' is the "instantaneous" thermal conductivity of the mixture. The quantity $\mathbf{d}_k$ is then defined by relation (3.4).

The diffusion coefficients D_{ik} satisfy the conditions

$$D_{ik} = D_{ki}, \quad D_{ii} > 0 \tag{5.3}$$

while the thermal diffusion ratios are introduced as the solution of the equations[5]

$$\sum_k D_{ik}k_{Tk} = D_{Ti}, \quad i, k = 1, \ldots, N \tag{5.4}$$

Moreover, it follows from condition (2.4) and definition (5.4) that

$$\sum_i \frac{\rho_i}{\rho}D_{ik} = 0, \quad \sum_i \frac{\rho_i}{\rho}D_{Ti} = 0, \quad \sum_i k_{Ti} = 0 \tag{5.5}$$

Hence, for an N-component mixture we have $N(N-1)/2$ independent diffusion coefficients and N independent thermal diffusion coefficients.

Note that the expression for the reduced heat flux $\mathbf{J}'_q$ can be represented in a somewhat different form if we eliminate the vectors $\mathbf{d}_k$ from expression (5.2) using Eq. (5.1). As a result we obtain

$$\mathbf{J}'_q = -\lambda\nabla T + p\sum_k k_{Tk}\frac{\mathbf{J}_k}{\rho_k}; \quad \lambda = \lambda' - \frac{p}{T}\sum_k k_{Tk}D_{Tk} \tag{5.6}$$

The total heat flux in a mixture of perfect gases is defined in the form

$$\mathbf{J}_q = \mathbf{J}'_q + \sum_{k=1}^{N} h_k\mathbf{J}_k; \quad h_k = \frac{5}{2}\frac{k_B T}{m_k} \tag{5.7}$$

Taking equality (5.6) into account, we arrive at the expression

$$\mathbf{J}_q = -\lambda\nabla T + p\sum_k\left(\frac{5}{2}\frac{n_k}{n} + k_{Tk}\right)\frac{\mathbf{J}_k}{\rho_k} \tag{5.8}$$

The expression for $\mathbf{J}'_q$ (5.6) (or for $\mathbf{J}_q$ in the form (5.8)) is preferable for specific use compared with the expression for $\mathbf{J}'_q$ in the form (5.2), since, unlike the "instantaneous" thermal conductivity λ' the "true" thermal conductivity λ, as already discussed above, can be measured directly experimentally. Under actual experimental conditions, the diffusion fluxes vanish, and the total heat flux is given by expression (5.8), in which we must put $\mathbf{J}_k = 0$. We then arrive at the usual Fourier law for the heat flux with a true thermal conductivity λ.

Note that the last of conditions (5.5) also enable us to represent expression (5.6) in the form

$$\mathbf{J}'_q = -\lambda\nabla T + p\sum_{k=1}^{N} k_{Tk}\left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_N}{\rho_N}\right) \tag{5.9}$$

A comparison of relations (5.1), (5.2) and (5.9) with the phenomenological expressions (3.5) and the last expression of (4.2) gives the following relation between the phenomenological and kinetic transport coefficients

$$\bar{L}_{ik} = \frac{1}{p}D_{ik}, \quad \bar{L}_{iq} = \bar{L}_{qi} = D_{Ti}, \quad \bar{L}_{qq} = T\lambda' \tag{5.10}$$

$$\Lambda_{qk} = \Lambda_{kq} = pk_{Tk}, \quad \Lambda_{qq} = T\lambda \tag{5.11}$$

The symmetry of the corresponding transport coefficients, obtained within the framework of kinetic theory,[7,8] is then found to correspond completely with the Onsager reciprocity relations of the type (2.12), postulated by non-equilibrium thermodynamics.

We must draw attention to the fact that, in the first version of the kinetic theory of multicomponent gas mixtures, developed by Curtiss and Hirschfelder, and described in detail in the well-known monograph,[6] the expressions for $\mathbf{J}_i$ and $\mathbf{J}'_q$ were written in the form

$$\mathbf{J}_i = \frac{n^2}{\rho}\sum_j m_i m_j \tilde{D}_{ij}\mathbf{d}_j - \tilde{D}_{Ti}\frac{1}{T}\nabla T, \quad \mathbf{J}'_q = -\lambda'\nabla T - p\sum_j\frac{\tilde{D}_{Tj}}{\rho_j}\mathbf{d}_j \tag{5.12}$$

It follows from these expressions and the condition $d_1 + \ldots + d_N = 0$ that the multicomponent diffusion coefficients $\tilde{D}_{ij}$ in this form of notation are not defined uniquely. This drawback of the theory was eliminated in Ref. 6 using the arbitrary assumption that all the diagonal diffusion coefficients are equal to zero, which leads to a loss of symmetry of the non-diagonal coefficients in the first expression of (5.12). The expressions given there for the diffusion fluxes in the form (5.1), which are more suitable than the relations of non-equilibrium thermodynamics, were proposed for the first time by Waldmann[8] (see also Ref. 3) and are used in the well-known monograph.[7] They can be obtained if the search for a solution of the integral equations for the non-equilibrium correction to the distribution function, which are considered in the Chapman–Enskog method, is somewhat modified. The non-diagonal coefficients D_{ij}, as was shown in Ref. 39, then satisfy the symmetry conditions (5.3).

Within the framework of the usual Chapman–Enskog Scheme[7,8] the coefficients D_{ij}, D_{Ti} and λ' in expressions (5.1) and (5.2), are written as the result of the solution of the systems of algebraic equations for the coefficients of the expansion of the non-equilibrium part of the distribution function 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 corresponds to the order of the approximations (the number of terms retained in the expansion of the distribution function in Sonine orthogonal polynomials when calculating the transfer coefficients in the Chapman–Cowling method[5–8]). The elements of the determinants are expressed in terms of the so-called integral brackets of Sonine polynomials of different orders, which, in turn, are represented in the form of linear combinations of set of so-called $\Omega_{ij}^{(l,r)}$ (T)-integrals as a functions of the temperature, which also depend on the parameters of the interaction potentials of the particles of the i-th and j-th species. Here it can be seen that the true thermal conductivity λ (5.6), and also the thermal diffusion ratios k_{Ti}

when higher approximations are taken into account are only obtained as a result of calculating N-th order determinants (the solution of Eq. (5.4)), the elements of which are, in turn, determinants of the $(N\xi+1)$-th order. Obtaining them therefore requires double matrix inversion.

In practical gas-dynamic problems the number N can be fairly large, for example, for air plasma $N=11$, and to obtain integral accuracy it is necessary to take $\xi=2$ or $\xi=3$.[40] Calculations of the transport coefficients in this case are extremely time consuming and are complicated by the fact that, in the case of thermochemically equilibrium flows, they will be functions not only of the temperature and pressure, but also of the chemical element composition, which changes in the flow. Hence, this classical scheme for calculating the transport coefficients is not very suitable for solving gas-dynamic problems and so far has not been used when solving any interesting specific problems. In addition to the above difficulty in evaluating determinants, the number of which is of the order of several tens, for practical multicomponent mixtures the formulation of expressions for the diffusion fluxes in the form (5.1) in the conservation equation leads to a system of equations that are unsolvable for higher derivatives of the required concentrations. At present there are no general methods available for the effective solution of such systems of equations even in the approximation of different asymptotically simplified versions of the Navier–Stokes equations.

Note that, in the terminology employed in Ref. 7, the first non-zero approximation serves as the first approximation for each kinetic coefficient. Then, for the multicomponent diffusion coefficients D_{ij}, defined in the first approximation, it is sufficient to take into account only one term in the expansion in Sonine polynomials $(\xi=1)$, while to determine D_{Ti} two terms $(\xi=2)$ are necessary, and hence thermal diffusion is sometimes called a second-order transport phenomenon. It was shown in Ref. 41 that, using the so-called complete second approximation, when both coefficients are determined taking two terms of the expansion into account, using a definite procedure one can considerably simplify the expressions for the true thermal conductivity λ and the thermal diffusion ratios k_{Ti}. In this case these coefficients can be written in the form of ratios of determinants of order $N+1$ to determinants of order N instead of the ratio of determinants of order $2N+1$ and $2N$. Expressions for these coefficients and for the elements of the determinants corresponding to them in the form of linear combinations of Ω-integrals are known.[6,7] Note, however, that for higher approximations $(\xi\geq 3)$ it has not been proved that it is possible to simply the expressions for the transport coefficients within the framework of the usual scheme of the Chapman–Enskog method.

As was pointed out in Refs. 22,12,13, in many cases it is preferable to represent the equations for the diffusion velocities (or mass diffusion fluxes) in the form of Stefan–Maxwell equations. A similar representation, which also takes into account the contribution of thermal diffusion, was considered previously in Ref.6, but the result obtained turned out to be not completely consistent, since the diffusion coefficients in this case were determined in the first approximation $(\xi=1)$, while the thermal diffusion coefficients were determined in the second approximation $(\xi=2)$, which led to an unjustified complication of the expressions for these coefficients.

It was shown in Refs. 22,9,10,14 that the Stefan–Maxwell equations and the expressions for the heat flux, the form of which corresponds to representation (3.7) considered above within the framework of non-equilibrium thermodynamics, can be obtained using Grad's method moment,[11] extended to the case of a multicomponent gas mixture. Similar results were obtained for the first time in Refs. 12,13 within the framework of the Chapman–Enskog method in any approximation with respect to ξ using some modifications of the method of solving the system of algebraic equations for the coefficients, which involves an expansion of the non-equilibrium part of the distribution. The Stefan–Maxwell equations were derived in Refs. 32,33 as a result of a certain modification of the solution of the first approximation of the Chapman–Enskog method. All these results turn out to be completely equivalent to one another. The corresponding equations of multicomponent diffusion and the expression for the total heat flux can be represented as [12–14]

$$\begin{aligned} -p\mathbf{d}_i &= \sum_{k\neq i}^{N}\frac{n_i n_k kT}{n[\mathcal{D}_{ik}]_1}[1-\Delta_{ik}(\xi)]\left(\frac{\mathbf{J}_i}{\rho_i}-\frac{\mathbf{J}_k}{\rho_k}\right)+pk_{Ti}(\xi)\frac{1}{T}\nabla T \\ \mathbf{J}_q &= -\lambda(\xi)\nabla T+p\sum_k\left(\frac{5}{2}\frac{n_k}{n}+k_{Tk}(\xi)\right)\frac{\mathbf{J}_k}{\rho_k} \end{aligned} \qquad (5.13)$$

In Eq. (5.13) $[D_{ik}]_1$ corresponds to the usual binary diffusion coefficient for the i-th and k-th components, determined, in the first approximation of the Chapman–Cowling method,[3]

$$[\mathcal{D}_{ik}]_1 = \frac{3k_BT}{16n\mu_{ik}\Omega_{ik}^{(1,1)}(T)} \tag{5.14}$$

where μ_{ik} is the reduced mass of molecules of the i-th and k-th components. In this case $\Delta_{ik}(\xi)$ is the correction to the binary diffusion coefficient in an arbitrary approximation with respect to ξ. The coefficients λ and Δ_{ik} and the thermal diffusion ratios k_{Ti}, obtained by the above methods, are defined by expressions which represent the ratio of determinants of order $N(\xi-1)+1$ to determinants of order $N(\xi-1)$, i.e. by much simpler expressions than in the previous representation according to formulae (5.1) and (5.2). The corresponding expressions for these coefficients and for the elements of the determinants, written in the form of linear combinations of Ω-integrals can be found in Refs. 12–14.

A comparison of Eq. (5.13) with Eq. (3.7), obtained within the framework of non-equilibrium thermodynamics, shows that the connection between the phenomenological and kinetic coefficients in this case is given by the relation

$$\Lambda_{ik} = \Lambda_{ki} = -\frac{pn_in_k}{n^2[\mathcal{D}_{ik}]_1}(1-\Delta_{ik}) \tag{5.15}$$

while for the coefficients Λ_{kq} and Λ_{qq} it is determined by relations (5.11) considered above.

The expressions for $[D_{ik}]_1$ and Δ_{ik} are symmetrical with respect to the subscripts i and k. Hence $\Lambda_{ik}=\Lambda_{ki}$. The equality of the cross coefficients ($\Lambda_{kq}=\Lambda_{qk}$) also follows from conditions (5.11). Hence, the results of kinetic calculations in this representation also ensure that the Onsager reciprocity relations are satisfied.

Note that Eq. (5.13) form a system of $N-1$ independent equations for determining the mass diffusion fluxes, which must be supplemented by condition (2.3). The solution of this system enables us, in particular, to express the diffusion and thermal diffusion coefficients of a multicomponent mixture in expressions (5.1) using the coefficients $[D_{ik}]_1$, Δ_{ik} and k_{Ti}.

When solving real gas-dynamic problems, however, it is not, as a rule, necessary to make such a transition to standard relations (5.1). On the contrary, the use of the diffusion equations in the Stefan–Maxwell form together with the parabolized Navier–Stokes equations when solving a number of problems of hypersonic aerodynamics and heat and mass transfer leads to systems of equations, that are solved for the first-order derivatives with respect to the normal coordinate to the body surface, of diffusion fluxes, heat fluxes, concentrations and temperature, i.e. to the equations represented in normal Cauchy form,[42] for which effective numerical methods have been developed.[43,44] Moreover, the equations of mass transport of the components, written in the form of Stefan–Maxwell relations, as if specially represented in this form, that is necessary to obtain explicit expressions of all the effective transport coefficients in the case of thermal by and chemically equilibrium flows of multicomponent mixtures gas and plasma.[45,46]

6. The generalized Stefan–Maxwell equations

The equations for determining the diffusion fluxes of the mixture components in the form of the Stefan–Maxwell relations (4.5) or the first equation of (5.13) can also be obtained if we use the equation of motion for a separate component of the mixture or the momentum balance equation of the component.[22,9] More general results, including also the equations for the heat fluxes and the viscous-stress tensor, are obtained using the method of moments.[9,10,14] Some generalization of Eq. (5.13) then turns out to be possible due to the additional contribution to them of the time and spatial derivatives of the fluxes having different types of tensors.[28–30] The equations obtained correspond to the recently developed extended irreversible thermodynamics.[23–25,27,30]

For a multicomponent gas mixture, the momentum balance equation of a component (the conservation equations) follows directly from Boltzmann's kinetic equation by multiplying the latter by the momentum of a molecule $m_i\mathbf{c}_i$ with subsequent integration over the velocities. The corresponding equation can be written in the form[22,9]

$$\frac{\partial}{\partial t}\rho_i v_{ir} + \frac{\partial}{\partial x_s}[\rho_i(v_{ir}v_s + v_{is}v_r - v_rv_s)] + \frac{\partial P_{irs}}{\partial x_s} - \rho_i F_{ir} = R_{ir} \tag{6.1}$$

Here $P_{irs}=p_i\delta_{rs}+\pi_{irs}$ are the components of the stress tensor for the i-th component of the mixture, p_i is the partial pressure, π_{irs} are the components of the partial viscous-stress tensor, δ_{rs} is the Kronecker delta, and R_{ir} is the value of the average momentum transmitted in collisions of particles of species i to all the particles of the remaining species of the mixture (also called the “diffusion force of friction”[38]).

Summation of Eq. (6.1) over i, taking the condition $\sum_i R_{ir}=0$ into account (the total momentum for collisions between molecules in the mixture is conserved) leads to an equation of motion of the mixture as a whole

$$\frac{\partial}{\partial t}\rho\upsilon_r+\frac{\partial}{\partial x_s}\rho\upsilon_r\upsilon_s+\frac{\partial P_{rs}}{\partial x_s}-\sum_i\rho_i F_{ir} = 0 \tag{6.2}$$

where $\mathbf{v}$ is the mean-mass velocity and $P_{rs}=\sum_i P_{irs}$ is the stress tensor of the mixture.

The initial Eq. (6.1) can be represented in a somewhat different form, if we write it with respect to the diffusion velocities of the components $\mathbf{V}_i=\mathbf{v}_i-\mathbf{v}$. By simple reduction, using Eq. (6.2), we obtain

$$\frac{d}{dt}\rho_i V_{ir}+\rho_i V_{ir}\frac{\partial\upsilon_l}{\partial x_l}+\rho_i V_{is}\frac{\partial\upsilon_r}{\partial x_s}+\frac{\partial P_{irs}}{\partial x_s}-\rho_i\left(F_{ir}-\frac{d\upsilon_r}{dt}\right) = R_{ir};\quad \frac{d}{dt} = \frac{\partial}{\partial t}+\upsilon_s\frac{\partial}{\partial\xi_s} \tag{6.3}$$

When linearizing Eq. (6.3) we can neglect the quadratic terms, proportional to the products of the diffusion fluxes $\rho_i V_{ir}$ by the derivatives with respect to the coordinate of the mean-mass velocity $\mathbf{V}$. Eliminating the derivative dv_r/dt from it using Eq. (6.2), we arrive at the equation

$$\frac{d}{dt}\rho_i V_{ir}+pd_{ir}^* = R_{ir};\quad pd_{ir}^* = pd_{ir}+\frac{\partial\pi_{irs}}{\partial x_s}-\frac{\rho_i}{\rho}\frac{\partial\pi_{rs}}{\partial x_s} \tag{6.4}$$

The quantity d_{ir} is defined by formula (3.4). Note that Eq. (6.4) can also be obtained if we use the linearized Boltzmann kinetic equation for the gas mixture[14,30] as the initial one for deriving the momentum balance equation of a component.

The right-hand side of Eq. (6.4) (the “diffusion force of friction”) can be written in the general case as[22,9]

$$\mathbf{R}_i = \sum_j m_i(\mathbf{c}_i'-\mathbf{c}_i)f_i f_j g\sigma_{ij}(g,\chi)d\Omega d\mathbf{c}_i d\mathbf{c}_j \tag{6.5}$$

Here f_i and f_j are the velocity distribution functions of the interacting molecules of the i-th and j-th components, $\mathbf{c}_i$ and $\mathbf{c}'_i$ are the velocities of the molecules of the i-th species before and after collision, $g=|\mathbf{c}'_i-\mathbf{c}_i|$ is the relative velocity of the molecules of the components on collision, and $\sigma_{ij}d\Omega$ is the differential scattering cross-section of the particles having a velocity $\mathbf{g}$ in a solid angle $d\Omega=\sin\chi d\chi$, where χ is the scattering angle.

The value of $\mathbf{R}_i$ can be calculated if we use a definite approximation to the distribution function. The simplest approximation corresponds to specifying f_i in the form of a local Maxwell distribution, shifted with respect to the proper macroscopic velocity of the component $\mathbf{v}_i$

$$f_i = n_i\left(\frac{m_i}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m_i}{2k_B T}(\mathbf{c}_i-\mathbf{v}_i)^2\right) \tag{6.6}$$

The diffusion velocity is assumed to be small compared with the average thermal velocity of the molecules or the adiabatic velocity of sound:

$$|\mathbf{V}_i| \ll (k_B T/m_i)^{1/2}$$

Hence, linearization of expression (6.6) gives

$$f_i = f_i^0\left(1+\frac{m_i}{k_B T}\mathbf{V}_i\cdot\mathbf{C}_i\right),\quad f_i^{(0)} = n_i\left(\frac{m_i}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m_i}{2k_B T}C_i^2\right),\quad \mathbf{C}_i = \mathbf{c}_i-\mathbf{v} \tag{6.7}$$

Here $f_i^{(0)}$ is the locally-equilibrium Maxwell distribution (shifted with respect to the mean-mass velocity $\mathbf{v}$). Calculation of $\mathbf{R}_i$ using expression (6.7) leads to the following result[9]

$$\mathbf{R}_i = -\sum_k\frac{n_i n_k k_B T}{n[\mathcal{D}_{ik}]_1}(\mathbf{v}_i-\mathbf{v}_k) \tag{6.8}$$

The binary diffusion coefficient $[D_{ij}]_1$ is given by expression (5.14).

The generalized Stefan–Maxwell equation, following from Eq. (6.4), in this case takes the form

$$\frac{d\mathbf{J}_i}{dt} + p\mathbf{d}_i^* = -\sum_k \frac{n_i n_k k_B T}{n[\mathcal{D}_{ik}]_1}(\mathbf{v}_i - \mathbf{v}_k) \tag{6.9}$$

A more accurate calculation of $\mathbf{R}_i$, which enables us, in particular, to take into account the contribution of thermal diffusion, involves using a more complete approximation to the distribution function of the components of the mixture. In the well-known Grad's 13-moment approximation, for example, we obtain[22,9]

$$\begin{aligned} f_i &= f_i^{(0)}\left[1 + \gamma_i \mathbf{V}_i \cdot \mathbf{C}_i + \frac{1}{2}\gamma_i \frac{\pi_{irs}}{p_{i\alpha}}\left(C_{ir}C_{is} - \frac{1}{3}\delta_{rs}C_i^2\right) + \frac{1}{5}\gamma_i \frac{\mathbf{J}'_{qi} \cdot \mathbf{C}_i}{p_i}(\gamma_i C_i^2 - 5)\right] \\ \mathbf{J}'_{qi} &= \mathbf{J}_{qi} - \frac{5}{2}p_i\mathbf{V}_i \end{aligned} \tag{6.10}$$

Here $\gamma_i = m_i(Tk_BT)$ and $\mathbf{J}'_{qi}$ is the reduced partial heat flux.

In this case we have[9,10]

$$\begin{aligned} \mathbf{R}_i &= -\sum_k \frac{n_i n_k k_B T}{n[\mathcal{D}_{ik}]_1}(\mathbf{V}_i - \mathbf{V}_k) - \sum_k \xi_{ik}\left(\frac{\mathbf{J}'_{qi}}{\rho_i} - \frac{\mathbf{J}'_{qk}}{\rho_k}\right) \\ \xi_{ik} &= \frac{n_i n_k}{n[\mathcal{D}_{ik}]_1}\mu_{ik}\left(\frac{6}{5}C_{ik}^* - 1\right), \quad C_{ik}^* = \frac{\Omega_{ik}^{(1,2)}}{3\Omega_{ik}^{(1,1)}} \end{aligned} \tag{6.11}$$

The corresponding generalized Stefan–Maxwell equation can then be written in the following form[14,30]

$$\frac{d\mathbf{J}_i}{dt} + p\mathbf{d}_i^* = -\sum_k \frac{n_i n_k k_B T}{n[\mathcal{D}_{ik}]_1}(\mathbf{V}_i - \mathbf{V}_k) - \sum_k \xi_{ik}\left(\frac{\mathbf{J}'_{qi}}{\rho_i} - \frac{\mathbf{J}'_{qk}}{\rho_k}\right) \tag{6.12}$$

In the linearized 13-moment approximation, i.e. neglecting terms that are quadratic in the fluxes (momenta), the reduced partial heat fluxes $\mathbf{J}'_{qi}$ and the partial viscous-stress tensors with the components π_{irs} satisfy the system of relaxation equations[9,14]

$$\frac{dJ'_{qir}}{dt} + \frac{5}{2}\frac{k_B}{m_i}p_i\frac{\partial T}{\partial x_r} + \frac{k_B T}{m_i}\frac{\partial \pi_{irs}}{\partial x_s} = -\sum_k a_{ik}\frac{J'_{qkr}}{p_k} - \sum_k b_{ik}(V_{ir} - V_{kr}) \tag{6.13}$$

$$\frac{d\pi_{irs}}{dt} + 2p_i\varepsilon_{rs} = \sum_k c_{ik}\frac{\pi_{krs}}{p_k} \tag{6.14}$$

The components of the shear rate tensor ε_{rs} are defined by (2.2). Expressions for the coefficients a_{ik}, b_{ik} and c_{ik}, which are linear combinations of $\Omega_{ij}^{(l,r)}$ (T)-integrals, can be found in Refs. 9,10, where

$$b_{ik} = (5/2)(k_B T/m_i)^2\xi_{ik}$$

The relaxation form of the equations for $\mathbf{J}'_i = \rho_i\mathbf{V}_i$, $\mathbf{J}'_{qi}$ and π_{irs} enables us to carry out a more justified analysis of the propagation of small concentration, thermal and shear perturbations in gases and gas mixtures[23–27,30] (taking into account processes that occur in a time of the order of the time between collisions between molecules). Here the corresponding differential equations for the concentration, temperature and velocity, obtained using the generalized transport equations in the equations of continuity, motion and energy, become hyperbolic. One can thereby solve the paradox of the infinite propagation velocity of small perturbations, which arises when using ordinary linear relations of non-equilibrium thermodynamics or kinetic theory, discussed previously. As is well known, the use of the usual Navier–Stokes equations to solve these problems leads precisely to such paradoxes.[23–25]

As an example we will consider the problem of the propagation of concentration waves in a binary gas mixture.[26,30,47] The use of the equation of continuity for the i-th component of the mixture (and for the mixture as a whole) enables us to write the equation for the mass concentration ($c_i = \rho_i/\rho$) in the form

$$\rho\left(\frac{\partial c_i}{\partial t} + (\mathbf{v}\cdot\nabla)c_I\right) + \nabla\cdot\mathbf{J}_i = 0 \tag{6.15}$$

The quantity $\nabla\cdot\mathbf{J}_i$ can be obtained using the generalized Stefan–Maxwell relaxation equation. We will use this equation in its simplest form (6.9), neglecting the convective term ($d\mathbf{J}_i/dt \approx \partial\mathbf{J}_i/\partial t$) and the contribution from the viscous stresses ($\mathbf{d}_i^* = d_i$). For a binary mixture this equation can be rewritten as

$$\frac{\partial\mathbf{J}_1}{\partial t} + p\mathbf{d}_1 = -\gamma_{12}\mathbf{J}_1; \quad \gamma_{12} = \frac{k_BT}{n[\mathcal{D}_{12}]_1}\frac{\rho^2}{m_1m_2} \tag{6.16}$$

Neglecting the barodiffusion ($p = \text{const}$) and the external forces, the expression for $\mathbf{d}_1$ can be represented in the form

$$\mathbf{d}_1 = \nabla\frac{n_1}{n} = \frac{1}{m_1m_2}\frac{\rho^2}{n^2}\nabla c_1$$

We will write the equality of the divergence of the left- and right-hand sides of Eq. (6.16)

$$\frac{\partial\nabla\cdot\mathbf{J}_1}{\partial t} + \frac{1}{m_1m_2}\frac{\rho^2}{n^2}p\nabla^2c_1 = -\gamma_{12}\nabla\cdot\mathbf{J}_1 \tag{6.17}$$

Expressing $\nabla\cdot\mathbf{J}_1$ from Eq. (6.15) with the condition $\mathbf{v} = 0$ (a gas at rest) and substituting the result into Eq. (6.17), we arrive at an equation for the concentration c_1, which takes the form of the telegraph equation

$$\nabla^2c_1 = \frac{1}{\upsilon_c^2}\frac{\partial^2c_1}{\partial t^2} + \frac{1}{\beta_{12}}\frac{\partial c_1}{\partial t}; \quad \upsilon_c = \sqrt{\frac{\rho k_BT}{nm_1m_2}}, \quad \beta_{12} = \frac{\rho}{p}[\mathcal{D}_{12}]_1 \tag{6.18}$$

The parameter υ_c in this case corresponds to a finite propagation velocity of the concentration perturbations, and the attenuation of these perturbations is related to the parameter β_{12}.

In the steady case or for slow processes, when the characteristic time of the problem is considerably greater than the characteristic time between particle collisions (which enables us to neglect derivatives with respect to time of the corresponding quantities in Eqs. (6.12)–(6.14)), the expressions for $\mathbf{J}'_{qi}$ and π_{irs} are found from the solution of systems of algebraic equations. If we neglect the contribution of viscous stresses in Eqs. (6.12) and (6.13), substitution of the solutions for $\mathbf{J}'_{qi}$ and $\mathbf{J}'_{qk}$ obtained into the right-hand side of Eq. (6.14) leads to the Stefan–Maxwell Eq. (5.13)

$$-p\mathbf{d}_i = \sum_{k\neq i}^{N}\frac{n_in_kk_BT}{n[\mathcal{D}_{ik}]_1}[1-\Delta_{ik}(2)]\left(\frac{\mathbf{J}_i}{\rho_i} - \frac{\mathbf{J}_k}{\rho_k}\right) + pk_{Ti}(2)\nabla\ln T \tag{6.19}$$

The use of the 13-moment approximation to distribution function (6.10) when calculating the diffusion and thermal diffusion coefficients will correspond in this case to the complete second approximation of the Chapman–Cowling method ($\xi = 2$).

By taking into account the contribution of the derivatives if the viscous-stress tensors in the expression for $\mathbf{d}_i^*$ we can consider one more particular form of the Stefan–Maxwell equations, which is obtained in the case of a steady viscous flow of a mixture.[22] The solution of Eq. (6.14) with the condition $d\pi_{irs}/dt = 0$ gives

$$\pi_{irs} = -2\eta_i\varepsilon_{rs} \tag{6.20}$$

where η_i is the partial coefficient of viscosity (not to be confused with the viscosity of the i-th component). Using the equation of motion of the mixture (6.2), which in this case takes the form

$$\frac{\partial p}{\partial x_r} + \frac{\partial\pi_{rs}}{\partial x_s} - \sum_k\rho_kF_k = 0$$

and omitting the derivative dV_{ir}/dt in Eq. (6.12), we can represent the latter as[22,9]

$$-p\mathbf{d}_i^v = \sum_k \frac{n_i n_k k_B T}{n[\mathcal{D}_{ik}]_1}(\mathbf{V}_i - \mathbf{V}_k) + \sum_k \xi_{ik}\left(\frac{\mathbf{J}'_{qi}}{\rho_i} - \frac{\mathbf{J}'_{qk}}{\rho_k}\right) \tag{6.21}$$

Here

$$\mathbf{d}_i^v = \nabla x_i + \left(x_i - \frac{\eta_i}{\eta}\right)\nabla \ln p - \frac{1}{p}\left(\rho_i \mathbf{F}_i - \frac{\eta_i}{\eta}\sum_{k=1}^{N} \rho_k \mathbf{F}_k\right) \tag{6.22}$$

and $x_i = n_i/n$ is the relative molar concentration of the i-th component of the mixture.

After using the solutions for $\mathbf{J}'_{qi}$, $\mathbf{J}'_{qk}$, the right-hand side of Eq. (6.21) takes the same form as the right-hand side of (6.19). Replacing the thermodynamic diffusion force $p\mathbf{d}_i$ by $p\mathbf{d}_i^v$ on the left-hand side of the equations leads to overdetermination of the barodiffusion coefficients and terms with the external field in the expressions for the diffusion fluxes of the of the mixture components, following from the solution of Eq. (6.21). Thus, for the case of a binary gas mixture, when there are no external fields, we can obtain from Eq. (6.21) the following expression for the mass diffusion flux of the first component[22]

$$\mathbf{J}_1 = -m_1 m_2 \frac{n^2}{\rho}[\mathcal{D}_{12}]_2(\nabla x_1 + [\alpha_p^v]_2 x_1 x_2 \nabla \ln p + [\alpha_T]_2 x_1 x_2 \nabla \ln T) \tag{6.23}$$

where

$$[\mathcal{D}_{12}]_2 = \frac{[\mathcal{D}_{12}]_1}{1-\Delta_{12}}, \quad [\alpha_p^v]_2 = [\alpha_p^v]_1(1-\Delta_p) - \frac{2}{5}[\alpha_T]_2, \quad [\alpha_p^v]_1 = \frac{1}{\eta}\left(\frac{\eta_2}{x_2} - \frac{\eta_1}{x_1}\right) \tag{6.24}$$

The expressions for the thermal diffusion constant $[\alpha_T]_2$ and the corrections of the second approximation Δ_{12} and Δ_p are known.[22]

7. Conclusion

The results presented in this review enable the areas of effective application of the different methods of describing diffusion and heat transport in multicomponent gas mixtures and in plasma to be determined in specific problems. The advantage of writing the appropriate expressions using the "forces in terms of fluxes" representation compared with the classical "fluxes in terms of forces" representation, used in standard schemes of phenomenological non-equilibrium thermodynamics and in the traditional Chapman–Enskog method for the kinetic theory of gases, becomes obvious. This advantage becomes particularly noteworthy when using the equations of multicomponent diffusion in the Stefan–Maxwell form, in which the transport coefficients (the diffusion and thermal diffusion coefficients) are calculated with increased accuracy (i.e. taking into account higher approximations with respect to the number of Sonine polynomials, retained in the expansion of the distribution function of the particles of the mixture). Considerable simplifications are also obtained when using higher approximations in this case and in calculations of the heat fluxes.

One of the characteristic problems is related to calculations of the flows and heat and mass exchange in hypersonic flow around bodies. As was shown in Ref. 42, the use of the "forces in terms of fluxes" representation in this case leads to a system of equations, which is solved for the first derivatives of the concentrations and temperatures, along the normal to the surface around which the flow occurs, and also of the diffusion and heat fluxes, i.e. in the Cauchy normal form, for which effective numerical methods have been developed.[43,44]

Another example is related to the analysis of the effect of the separation of multicomponent (isotope) gas mixtures in high-speed gas centrifuges, where the use of the diffusion equations in the Stefan–Maxwell form also demonstrates its effectiveness.[48,49]

We can also cite another series of cases where the description of diffusion and heat transport in gases and plasma on the basis of the "forces in terms of fluxes" representation is the most optimum. The advantages of this approach for analysing diffusion and heat transport of heavy impurities in the hydrogen plasma of experimental devices for the magnetic containment of plasma, for example, have been considered in detail, as well as the separation of many varieties of ions in a rotating plasma.[9,10]

A further development in the use of extended or generalized non-equilibrium thermodynamics in gas-dynamic problems is also of undoubted interest.[23–30] This review has been confined to analysing the results which arise from Grad's 13-moment approximation for multicomponent mixtures of monatomic gases. The role of the relaxation equations of the higher approximations of this method so far remains not entirely clear. A further generalization of appropriate approaches to the case of polyatomic gases and gas mixtures is necessary. Some new results in this area can be found in a recent publication.[50]

Acknowledgements

This investigation was supported by the Russian Foundation for Basic Research (06-01-00374a, 06-01-00695a) and within the framework of the Program for the Support of the Leading Scientific Schools (NSh-835 2006-1).

References

1. Sedov LI. *Continuum Mechanics*, Vol. 1. Moscow: Nauka; 1973.
2. Landau LD, Lifshitz EM. *Fluid Dynamics*. Oxford: Pergamon; 1987.
3. de Groot SR, Mazur P. *Non-Equilibrium Thermodynamics*. Amsterdam: North-Holland; 1962.
4. Pilyugin NN, Tirskiy GA. *Dynamics of an Ionized Radiating Gas*. Moscow: Izd MGU; 1989.
5. Chapman S, Cowling TG. *The Mathematical Theory of Non-Uniform Gases*. Cambridge: Univ Press; 1952.
6. Hirschfelder JO, Curtiss CF, Bird RB. Molecular Theory of Gases and Liquids. New York Wiley; London: Chapman and Hall, 1954.
7. Ferziger JH, Kaper YG. *Mathematical Theory of Transport Processes in Gases*. Amsterdam; London: North-Holland; 1972.
8. Waldmann L. Transporterscheimmgen in Gasen von mittlerem Druck. *Hanbuch der Physik*. Bd. 12/Ed. S. Flugge, Berlin: Springer, 1958. P. 295–514.
9. Zhdanov VM. *Transport Phenomena in Multicomponent Plasma*. Moscow: Energoizdat; 1982.
10. Zhdanov VM. *Transport Processes in Multicomponent Plasma. L.* London: Taylor and Francis; 2002. p. 296.
11. Grad H. On the kinetic theory of rarefied gases. *Communs Pure and Appl Math* 1949;**2**(4):331–407.
12. Kolesnikov AF, Tirskiy GA. Hydrodynamic equations and transport equations for ionized multicomponent two-temperature mixtures of gases. In Models in Continuum Mechanics. Novosibirsk: Izd ITPM SO AN SSSR; 1979.
13. Kolesnikov AF, Tirskiy GA. *The equations of hydrodynamics for partially ionized multicomponent gas mixtures with transport coefficients in higher approximations. In Molecular Gas Dynamics*. Moscow: Nauka; 1982.
14. Zhdanov VM, Tirskiy GA. The use of the method of moments to derive the transport equations of a gas and a plasma with transport coefficients in higher approximations. *Prikl Mat Mekh* 2003;**67**(3):406–33.
15. Monchick L, Yun KS, Mason EA. Formal kinetic theory of transport phenomena in polyatomic gas mixture. *J Chem Phys* 1963;**39**(3):654–69.
16. Monchick L, Pereira ANG, Mason EA. Heat conductivity of polyatomic and polar gases and gas mixtures. *J Chem Phys* 1965;**42**(9):3241–56.
17. Monchick L, Aunn RJ, Mason EA. Thermal diffusion in polyatomic gases: a generalized Stefan- Maxwell diffusion equations. *J Chem Phys* 1966;**45**(8):3051–8.
18. Zhdanov VM, Aliyevskii MYa. *Transport and Relaxation Processes in Molecular Gases*. Moscow: Nauka; 1989.
19. Devoto RS. Transport properties of ionized monatomic gases. *Phys Fluids* 1966;**9**(6):1230–40.
20. Devoto RS. Transport coefficients of partially ionized argon. *Phys Fluids* 1967;**10**(2):354–64.
21. Mitchner M, Kruger Jr CH. *Partially lonized Gases*. New York: Wiley; 1973.
22. Zhdanov V, Kagan Y, Sazhkin A. The effect of viscous transport of momentum on diffusion in a gas mixture. *Zh Eksp Teor Fiz* 1962;**42**(3):857–67.
23. Muller I, Ruggeri T. *Extended Thermodynamics*. New York: Springer; 1993. p. 230.
24. Jou D, Casas-Vazquez J, Lebon G. Extended Irreversible Thermodynamics. *Rep Progr Phys* 1988;**51**:1105–79.
25. Jou D, Casas-Vazquez J, Lebon G. *Extended Irreversible Thermodynamics*. New York: Springer; 1993. p. 319.
26. Khon'kin AD. The equations of hydrodynamics of a gas mixture with finite propagation velocities of perturbations. *Modelirovaniye v Mekhanike* 1988;**2**(5):142–7.
27. Velasco RM, Garcia-Colin LS. The kinetic foundations of extended irreversible thermodynamics revisited. *J Stat Phys* 1992;**69**(1–2):217–29.
28. Zhdanov VM, Roldugin VI. The method of moments and non-equilibrium thermodynamics of rarefied gases. *Zh Eksp Teor Fiz* 1998;**113**(6):2081–95.
29. Zhdanov VM, Roldugin VI. Non-equilibrium thermodynamics and the kinetic theory of rarefied gases. *Usp Fiz Nauk* 1998;**168**(4):407–38.
30. Zhdanov VM, Roldugin VI. The kinetic basis of extended non-equilibrium thermodynamics of multicomponent systems. *Zh Eksp Teor Fiz* 2002;**122**(4(10)):789–804.
31. Landau LD, Lifshitz EM. *Statistical Physics. Pt. 1*. Oxford: Pergamon; 1980.
32. Galkin VS, Makashev NK. Modification of the first approximation of the Chapman–Enskog method for a gas mixture. *Izv Rass Akad Nauk MZhG* 1992;**4**:178–85.
33. Galkin VS. Conversions of the equations of the first approximation of the Chapman–Enskog methods and the vector transport relations for monatomic gas mixtures. *Prikl Mat Mekh* 2007;**71**(2):301–20.

34. Stefan J. Uber das Gleichgewicht und Bewegung, insbesonderc die Diffusion von Gasgemengeu. *Wien Acad Sitzungsber* 1871. Bd. 63. S. 63–124.
35. Maxwell JC. In: Niven WD, editor. *The Scientific Papers of James Clark Maxwell*, 1. Cambrige: Univ. Press; 1890. p. 377.
36. Kolesnichenko AV, Tirskiy GA. The Stefan–Maxwell relations and the heat flux for non-perfect multicomponent continua. In Numerical Methods of Continuum Mechanics. Novosibirsk: Izd VTs SO Akad Nauk SSSR; 1976; 7(4): 106–121.
37. Truesdell C. Mechanical basis of diffusion. *J Chem Phys* 1962;**37**(10):2336–44.
38. Frank-Kamenetskii DA. *Diffusion and Heat Exchange in Chemical Kinetics*. Princeton: Princeton Univ Press; 1955.
39. Curtiss CF. Symmetric gaseous diffusion coefficients. *J Chem Phys* 1968;**49**(7):2917–9.
40. Vasil'evskii SA, Sokolova IA, Tirskiy GA. Determination and calculation of the effective transport coefficients for chemically equilibrium flows of partially dissociated and ionized gas mixtures. *Zh Prikl Mekh Tekh Fiz* 1986;**1**:68–79.
41. Muckenfuss C, Curtiss CF. Thermal conductivity of multicomponent gas mixtures. *J Chem Phys* 1958;**29**(6):1273–7.
42. Tirskiy GA. The equations of motion of partially ionized multicomponent gas mixtures in normal Cauchy form with exact transport coefficients. *Nauch Trudy Inst Mekh MGU* 1974;**32**:6–22.
43. Suslov ON. The solution of the equations of a chemically non-equilibrium multicomponent boundary layer by a difference method with an increased accuracy of approximation. *Otchet Inst Mekh MGU* 1978;**2098**:41–54.
44. Kovalev VL, Suslov ON. A difference method with increased accuracy of approximation for integrating the equations of a chemically non-equilibrium multicomponent shock layer. In: Tirskiy GA, Gershbein EA, editors. *Hypersonic Three-Dimensional Flow when there are Physical-Chemical Transitions*. Moscow: Izd MGU; 1981.
45. Tirskiy GA. The equations of hydrodynamics for chemically equilibrium flows of a multielement plasma with exact transport coefficients. *Prikl Mat Mekh* 1999;**63**(6):899–922.
46. Tirskiy GA. Up-to-date gasdynamic models of hypersonic aerodynamics and heat transfer withieal gas properties. *Annu Rev Fluid Mech* 1993;**25**:151–81.
47. Khonkin AD, Orlov AV. Derivation of the modified diffusion equations in a gas mixture. *Phys Rev E* 1994;**49**(1):906–9.
48. Aisen EM, Borisevich VD, Levin YV. Modelling of flows and diffusion in a gas centrifuge for separating multicomponent isotope mixtures. *Mat Modelirovaniye* 1977;**9**(4):27–38.
49. Borisevich VD, Levin EV. Separation of multicomponent isotope mixtures by gas centrifuge. *Separation Sci and Technol* 2001;**36**(8/9): 1697–735.
50. Zhdanov VM. Generalized Stefan-Maxwell diffusion equations for multicomponent mixtures of polyatomic gases. 25th Intern. Symp. RGD. St.-Petersburg, Russia, 2006. Book of Abstracts. P. 6.

Translated by R.C.G.