

**CORRECT DEFINITION OF INTERNAL ENERGY
AT THE PHENOMENOLOGICAL CONSTRUCTION OF MODEL
OF MULTICOMPONENT CONTINUOUS MEDIUM
BY METHODS OF NONEQUILIBRIUM THERMODYNAMICS**

A.V. KOLESNICHENKO

¹Keldysh Institute of Applied Mathematics, Russian Academy of Science

*Corresponding author. E-mail: kolesn@keldysh.ru

DOI: 10.20948/mathmontis-2022-53-6

Summary. Taking into account the methods of thermodynamics of irreversible processes using the Onsager principle, a model of a multicomponent continuous medium is constructed, the internal energy of which is "free" of the kinetic energy of diffusion. The model is designed for an imperfect continuous medium with chemical reactions in the field of conservative external forces. Generalized Stefan–Maxwell relations are obtained, which represent a system of hydrodynamic equations of motion of a mixture with true inertial forces. The proposed thermodynamic technique made it possible to obtain a number of algebraic relations known from the kinetic theory of gases for the transfer coefficients, relating, in particular, the coefficients of multicomponent diffusion with binary diffusivities, thermal diffusion ratios with thermal diffusion coefficients and multicomponent diffusion coefficients, true (molecular) thermal conductivity coefficient for multicomponent mixture with partial thermal conductivity coefficient, which indicates their versatility. The results obtained are intended for modeling not only liquid imperfect solutions, but also gas-dust mixtures with a finely dispersed dust component.

1. INTRODUCTION

Currently, there is a need to revise the stable paradigm associated with the definition of the internal energy of a continuous medium at the phenomenological construction of multicomponent hydrodynamics. In whole number of classical monographs on the thermodynamics of non equilibrium processes, the authors, by analogy with the kinetic theory of multicomponent gases (see, for example, [1-7]), introduce into consideration the internal energy of a multicomponent medium, defining it as the difference between the total energy and mechanical energy, the latter being determined in the approximation of equal acceleration of all components of the mixture. The incorrectness of this definition is due to the fact that, with this approach, the internal energy of the mixture contains, in addition to the contributions from the thermal motion of molecules and short range molecular interactions, which is consistent with the usual understanding of internal energy, contains also and the kinetic energy of diffusion.

So, within the framework of the classical approach, at modeling physical and mechanical processes in a multicomponent medium, many authors (see, for example, [4-6, 8-18]) when deter-

2010 Mathematics Subject Classification: 80A20, 82B30, 94A24.

Key words and Phrases: Nonequilibrium thermodynamics, Stefan – Maxwell relation, Non-ideal multicomponent mixtures, Kinetic energy of diffusion.

mining the balance equation for the specific internal energy of a mixture usually proceed from the law of conservation of the total specific energy $u(\mathbf{x}, t)$

$$\frac{\partial}{\partial t}(\rho u) + \nabla \cdot \mathbf{J}_u = 0 \quad (1)$$

and the previously derived balance equation for the specific mechanical energy of the mixture, equal to the sum of the local kinetic energy of the center of mass and potential energy, $u_m^* \equiv \frac{1}{2} \mathbf{v}^2 + \varphi$. Here \mathbf{J}_u is the local flow of total energy; $\rho(\mathbf{x}, t)$ – total density, $\varphi(\mathbf{x}, t)$ – specific potential energy, $\mathbf{v}(\mathbf{x}, t)$ – velocity of the center of mass of a liquid element. These quantities are determined by the relations

$$\rho = \sum_{k=1}^N \rho_k, \quad \mathbf{v} = \rho^{-1} \sum_{k=1}^N \rho_k \mathbf{v}_k, \quad \varphi = \rho^{-1} \sum_{k=1}^N \rho_k \varphi_k, \quad (2)$$

where, $\rho_k(\mathbf{x}, t)$, $\mathbf{v}_k(\mathbf{x}, t)$ and $\varphi_k(\mathbf{x})$ are the density, velocity and potential energy of the mass unit of component k , respectively. In this case, the specific internal energy $\varepsilon^*(\mathbf{x}, t)$ of the mixture is determined by the ratio

$$\varepsilon^* \equiv u - u_m^* = u - \frac{1}{2} \mathbf{v}^2 - \varphi \quad (3)$$

However, the value of the internal energy $\varepsilon^*(\mathbf{x}, t)$, introduced in this way, as mentioned above, is not entirely correct, since the specific mechanical energy u_m^* contains only the macroscopic kinetic energy of the components of the mixture in the center of mass system.

At the same time, it is possible to determine another, more deserving of this name, internal energy $\varepsilon(\mathbf{x}, t)$ per unit mass of the mixture, which does not include the kinetic energy of diffusion, by subtracting the specific mechanical energy $u_m(\mathbf{x}, t)$ from the total energy $u(\mathbf{x}, t)$, equal to the sum of the specific potential energy $\varphi(\mathbf{x})$ and the kinetic energy $u_K(\mathbf{x}, t)$ of all com-

ponents, $u_m \equiv \varphi + u_K = \varphi + \frac{1}{2} \rho^{-1} \sum_{k=1}^N \rho_k \mathbf{v}_k^2$; as a result we will have

$$\begin{aligned} \varepsilon = u - u_m &= u - \varphi - \frac{1}{2} \rho^{-1} \sum_{k=1}^N \rho_k \mathbf{v}_k^2 = u - \varphi - \frac{1}{2} \mathbf{v}^2 - \frac{1}{2} \rho^{-1} \sum_{k=1}^N \rho_k (\mathbf{v}_k - \mathbf{v})^2 = \\ &= \varepsilon^* - \frac{1}{2} \rho^{-1} \sum_{k=1}^N \rho_k (\mathbf{v}_k - \mathbf{v})^2 = \varepsilon^* - \frac{1}{2} \sum_{k=1}^N c_k \mathbf{w}_k^2. \end{aligned} \quad (4)$$

Here, $\mathbf{w}_k(\mathbf{x}, t) \equiv (\mathbf{v}_k - \mathbf{v})$, $v(\mathbf{x}, t) \equiv 1/\rho$ and $c_k(\mathbf{x}, t) \equiv \rho_k/\rho$ are the diffusion rate, specific volume and concentration of the substance, respectively. It can be seen from relation (4) that the "internal" energy of the mixture $\varepsilon^*(\mathbf{x}, t)$ used in the literature is not quite correct, since it differs from the true internal energy $\varepsilon(\mathbf{x}, t)$ by an amount $\frac{1}{2} \sum_{k=1}^N c_k \mathbf{w}_k^2$, associated with the kinetic energy of diffusion (due to the diffusion velocities $\mathbf{w}_k(\mathbf{x}, t)$ of the components of the mixture relative

to the local center of mass). There is no doubt that in most cases the kinetic energy of diffusion can be neglected in comparison with the kinetic energy of the center of mass (the classical kinetic theory of multicomponent gas mixtures was just developed in this “diffusion approximation”), however, in a more general case, the difference between the quantities $\varepsilon(\mathbf{x}, t)$ and $\varepsilon^*(\mathbf{x}, t)$ should be taken into account (for example, in the phenomenological design of models of liquid multicomponent non ideal solutions, models of the movement of gas-dust mixtures, when the volume concentration of the dispersed phase is low, etc.).

It is important to keep this circumstance in mind also because classical multicomponent hydrodynamics is based on the fundamental Gibbs relation

$$TdS = d\varepsilon^* + pdv + \sum_{k=1}^N \mu_k dc_k, \quad (5)$$

written for a system in a state of "local" equilibrium (see [8]). In relation (5), the quantities $T(\mathbf{x}, t)$, $p(\mathbf{x}, t)$ and $\mu_k(\mathbf{x}, t)$ are, respectively, the equilibrium temperature, mixture pressure and specific chemical potential of the component k . However, this quasi-equilibrium relationship, which is, in essence, the relationship between the equilibrium entropy $S = S(\varepsilon^*, v, c_k)$ and local quantities $\varepsilon^*(\mathbf{x}, t)$, $v(\mathbf{x}, t)$ and $c_k(\mathbf{x}, t)$, it would be more correct to write it in a slightly different

form, namely $TdS = d\varepsilon + pdv + \sum_{k=1}^N \mu_k dc_k$, because at equilibrium the diffusion fluxes \mathbf{w}_k should

disappear. For this reason, the use of the fundamental Gibbs equation, which plays a central role in the theory of nonequilibrium processes, in the form (5) in the general case is not entirely correct (see, for example, [10], pp. 34-35; [14], p. 119).

In this work, an attempt is made to construct models of multicomponent media, free from the above disadvantage. The development of models was carried out by us for non-ideal continuous media with chemical reactions located in the field of conservative external forces. For simplicity of presentation, we did not take into account here the antisymmetric of the pressure tensor, which is possible for a medium of this type, associated with the presence of an “internal” angular momentum [14].

2. LAWS OF CONSERVATION

The stated goal of the work can be achieved only by applying Onsager's thermodynamic approach to simulate multicomponent and chemically reacting hydro-thermodynamic systems with consideration of the complete system of equations for conservation of mass, momentum, energy and entropy in both local and substantial form.

We write the local form of the balance equation for an arbitrary intense quantity \mathcal{A} in the form

$$\frac{\partial}{\partial t}(\rho a) + \nabla \cdot (\rho a \mathbf{v} + \mathbf{J}_a) = \sigma_a, \quad (6)$$

where $a(\mathbf{x}, t)$, $\mathbf{J}_a(\mathbf{x}, t)$, $\sigma_a(\mathbf{x}, t)$ – respectively the specific value, flux density and density of the source of the quantity (the parameter can be a scalar, vector, tensor of the second rank, etc.).

Usually, the source density $\sigma_a(\mathbf{x}, t)$ is divided into internal $\sigma_a^{(i)}(\mathbf{x}, t)$ and external $\sigma_a^{(e)}(\mathbf{x}, t)$ components in accordance with the ratio $\sigma_a = \sigma_a^{(i)} + \sigma_a^{(e)}$, and the value $\sigma_a^{(i)}$ is determined by inhomogeneities that exist locally inside the system, associated with the gradients of velocity, temperature, density, etc., and the value $\sigma_a^{(e)}$ arises from long-range nature of external forces affecting the inner part of the system under consideration. Using equation (6), we write down the basic laws of conservation of mass, momentum, energy, entropy, etc. for a multicomponent system, while identifying the quantities with the corresponding physical parameters, introducing the flux and source densities for them.

The mass balance equations for a reacting mixtures. To write the mass balance equation for a separate component, it is necessary to put in equation (6), $a \equiv c_k, \mathbf{J}_a \equiv \mathbf{J}_k, \sigma_a \equiv \Gamma_k$ where $\mathbf{J}_k(\mathbf{x}, t) = \rho_k \mathbf{w}_k$ is the diffusion flux of the mass of the k -th component relative to the center of mass, $\Gamma_k = \sum_{j=1}^r \nu_{kj} J_j$ is the mass of the k -component, that appears due to chemical reactions in a unit of volume per unit of time.

Then the continuity equation for the substance k has the form:

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k \mathbf{v} + \mathbf{J}_k) = \Gamma_k \equiv \sum_{j=1}^r \nu_{kj} J_j, \quad (k = 1, 2, \dots, N). \quad (7)$$

Note that the quantity $\nu_{kj} J_j$ is the rate of formation of the component k per unit volume in the j -th chemical reaction. The value ν_{kj} divided by the molecular mass m_k of the component k is proportional to the stoichiometric coefficient with which the substance k enters the equation of the j -th chemical reaction. The coefficients ν_{kj} are considered positive when the components k enter the right side, and negative when they enter the left side of the reaction equation. The scalar quantity $J_j(\mathbf{x}, t)$ is called the rate of the j -th chemical reaction. It has the dimension of mass per unit volume per unit of time.

Summing (7) over all k and taking into account the relations

$$\sum_{k=1}^N \mathbf{J}_k = 0, \quad \sum_{k=1}^N \Gamma_k = 0, \quad (8)$$

of which the latter expresses the law of conservation of mass as a result of all chemical reactions, we obtain the general continuity equation for the mixture in the divergent form usual for hydrodynamics

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (9)$$

In what follows, we will make extensive use of the operator relation

$$\rho \frac{da}{dt} = \frac{\partial}{\partial t}(\rho a) + \nabla \cdot (\rho a \mathbf{v}), \quad \frac{d}{dt}(\cdot) \equiv \frac{\partial}{\partial t}(\cdot) + \mathbf{v} \cdot \nabla(\cdot), \quad (10)$$

giving a connection between substantial and local changes in characteristics and allowing to write the differential balance equation (6) in the following substantial form

$$\rho \frac{da}{dt} = -\nabla \cdot \mathbf{J}_a + \sigma_a. \quad (6^*)$$

Note that relation (10) is a consequence of the continuity equation (9) and the definition of the total time derivative $da/dt \equiv \partial a/\partial t + \mathbf{v} \cdot \nabla a$ of the value $a(\mathbf{x}, t)$ in the accompanying coordinate system associated with an element of the medium moving with velocity $\mathbf{v}(\mathbf{x}, t)$.

Applying this relation to equation (7), we obtain the equation of the substitution mass balance of the k -th component

$$\rho \frac{dc_k}{dt} = -\nabla \cdot \mathbf{J}_k + \Gamma_k, \quad (k = 1, 2, \dots, N-1); \quad \sum_{k=1}^N c_k = 1. \quad (11)$$

The equation of motion for a multicomponent mixture. Setting in equation (6) $a \equiv \mathbf{v}$, $\mathbf{J}_a \equiv \mathbf{T}$, $\sigma_a \equiv \rho \mathbf{f}$, we obtain the law of conservation of specific impulse for any fluid continuum

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{T}) = \rho \mathbf{f} \quad (12)$$

where $\mathbf{T}(\mathbf{x}, t)$ is the symmetric tensor of pressures (or stresses) of the medium, caused by short-range interactions between the particles of the system; $\mathbf{f}(\mathbf{x}, t)$ – external force acting on a unit mass of the medium; $\mathbf{v} \mathbf{v}$ – dyadic product.

Using the operator relation (10), we can write the equation of motion (12) in the form

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \cdot \mathbf{T} + \rho \mathbf{f}. \quad (12^*)$$

Equation (12) is valid for any continuum, but the expressions for the pressure tensor and the density of external forces for different continua are not the same. We will further consider Eq. (12) as a balance equation for the continuum obtained by a superposition N of continuous continuous media, the equations of motion for which (similar in structure to Eq. (12)) have the form:

$$\frac{\partial}{\partial t}(\rho_k \mathbf{v}_k) + \nabla \cdot (\rho_k \mathbf{v}_k \mathbf{v}_k + \mathbf{T}_k) = \rho_k \mathbf{f}_k + \sum_{k \neq j=1}^N \mathbf{r}_{kj}, \quad (k = 1, 2, \dots, N). \quad (13)$$

Here $\mathbf{T}_k(\mathbf{x}, t)$ is the symmetric pressure tensor of the k -ith component, ($\mathbf{T}_k = \mathbf{T}_k^T$; this relationship is a mathematical expression of the second Cauchy law for a multicomponent mixture); $\mathbf{f}_k(\mathbf{x})$ - an external force acting on a unit mass of a substance k ; $\mathbf{r}_{kj}(\mathbf{x}, t)$ - a vector (intercomponent force) that determines the intensity of intercomponent exchange of momentum due to collisions and intercomponent transitions of an impulse as a result of chemical reactions, $\mathbf{r}_{kj} = -\mathbf{r}_{jk}$.

Next, an explicit vector expression \mathbf{r}_{kj} will be found.

Summing equation (13) over k and using the relation

$$\sum_{k=1}^N \rho_k \mathbf{v}_k \mathbf{v}_k = \rho \mathbf{v} \mathbf{v} + \sum_{k=1}^N \rho_k^{-1} \mathbf{J}_k \mathbf{J}_k, \quad (14)$$

we obtain the following equation for the momentum balance of the mixture [19]:

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot \left(\rho \mathbf{v} \mathbf{v} + \sum_{k=1}^N \rho_k^{-1} \mathbf{J}_k \mathbf{J}_k + \sum_{k=1}^N \mathbf{T}_k \right) = \sum_{k=1}^N \rho_k \mathbf{f}_k, \quad (15)$$

where $\sum_{k=1}^N \rho_k^{-1} \mathbf{J}_k \mathbf{J}_k$ is the stress arising from the relative motion of components of different kinds.

When writing equation (15), the equality $\sum_{k=1}^N \sum_{k \neq j=1}^N \mathbf{r}_{kj} = 0$ was taken into account, which is a

consequence of the fact that a change in the specific impulse $\mathbf{v}(\mathbf{x}, t)$ for a multicomponent continuum, occurring both as a result of collisions between particles of its individual continua (Newton's third postulate), and as a result of chemical reactions is equal to zero. Indeed, denoting through Γ_{kj} the mass of the component k , which is formed as a result of chemical reactions from the component j , we obtain the following expression for the corresponding change in the density

of the specific impulse $\mathbf{v}(\mathbf{x}, t)$ of the total continuum: $\sum_{k=1}^N \sum_{j=1}^N (\Gamma_{kj} \mathbf{v}_j - \Gamma_{jk} \mathbf{v}_k) = 0$.

Total energy conservation for a mixture. The total specific energy for the continuum modeling the mixture as a whole satisfies the local balance equation (1) without a source. We now obtain this equation by adding the equations for the transfer of the total specific energy for each component of the system

$$\frac{\partial}{\partial t}(\rho_k u_k) + \nabla \cdot \mathbf{J}_{u_k} = \sigma_{u_k}^{(i)}, \quad (k = 1, 2, \dots, N). \quad (16)$$

Here $u_k(\mathbf{x}, t)$ is the total specific (per unit mass) energy of the k -component; $\mathbf{J}_{u_k}(\mathbf{x}, t)$ – local

flow of total energy carried by matter k ; $\sigma_{u_k}^{(i)}(\mathbf{x}, t)$ – the density of the internal source of total energy of particles of a sort k , is equal, on the one hand, to the heat released in the gas of particles of a given sort due to collisions with particles of other kinds, and, on the other hand, to a change in the total energy of a component k , as a result of chemical reactions, given by the expression.

$\sum_{k=1}^N (\Gamma_{kj} u_j - \Gamma_{jk} u_k)$. The quantities $u_k(\mathbf{x}, t)$ and $\mathbf{J}_{u_k}(\mathbf{x}, t)$ satisfy the relations

$$u_k = \varepsilon_k + \frac{1}{2} \mathbf{v}_k^2 + \varphi_k, \quad (17)$$

$$\mathbf{J}_{u_k} = \rho_k u_k \mathbf{v}_k + \mathbf{T}_k \cdot \mathbf{v}_k + \mathbf{q}_k, \quad (18)$$

where $\varepsilon_k(\mathbf{x}, t)$ and $\varphi(\mathbf{x})$ – respectively, the internal and potential energy of the unit mass of the substance k ; $\mathbf{q}_k(\mathbf{x}, t)$ is the heat flux carried by the particles of the k -th component, determined precisely by the relation (18).

Recall that in our discussion, for simplicity, we limited ourselves to considering only conservative external fields, which can be characterized by a scalar potential $\varphi_k(\mathbf{x})$ per unit mass of a component k , i.e. the equations are assumed to be valid

$$\mathbf{f}_k = -\nabla\varphi_k, \quad \partial\varphi_k / \partial t = 0. \quad (19)$$

However, in the general case, forces \mathbf{f}_k can be of a different nature, in particular, associated with non-conservative electromagnetic external fields.

Now summing (16) over all k and using the natural equality $\sum_{k=1}^N \sigma_k^{(i)} = 0$, as well as the formulas

$$\frac{1}{2} \sum_{k=1}^N \rho_k \mathbf{v}_k^2 = \frac{1}{2} \rho \mathbf{v}^2 + \frac{1}{2} \sum_{k=1}^N \rho_k^{-1} \mathbf{J}_k^2, \quad (20)$$

$$\frac{1}{2} \sum_{k=1}^N \rho_k |\mathbf{v}_k|^2 \mathbf{v}_k = \frac{1}{2} \rho |\mathbf{v}|^2 \mathbf{v} + \frac{1}{2} \sum_{k=1}^N \rho_k^{-1} |\mathbf{J}_k|^2 \mathbf{v} + \frac{1}{2} \sum_{k=1}^N |\mathbf{v}_k|^2 \mathbf{J}_k, \quad (21)$$

$$\sum_{k=1}^N \mathbf{T}_k \cdot \mathbf{v}_k = p \mathbf{v} + \sum_{k=1}^N \rho_k^{-1} p_k \mathbf{J}_k - \sum_{k=1}^N \boldsymbol{\tau}_k \cdot \mathbf{v}_k, \quad (22)$$

$$\varepsilon = \sum_{k=1}^N c_k \varepsilon_k, \quad \varphi = \sum_{k=1}^N c_k \varphi_k, \quad \mathbf{q} = \sum_{k=1}^N \mathbf{q}_k, \quad (23)$$

$$u = \varepsilon + \frac{1}{2} \mathbf{v}^2 + \varphi + \frac{1}{2} \sum_{k=1}^N \frac{|\mathbf{J}_k|^2}{\rho \rho_k}, \quad \mathbf{J}_q = \mathbf{q} + \sum_{k=1}^N h_k \mathbf{J}_k \quad (24)$$

$$\mathbf{T}_k = p_k \mathbf{I} - \boldsymbol{\tau}_k, \quad p = \sum_{k=1}^N p_k, \quad h_k = \varepsilon_k + p_k \rho_k^{-1}, \quad (25)$$

we obtain the total energy conservation law for the total continuum

$$\frac{\partial}{\partial t} (\rho u) + \nabla \cdot \left\{ \rho u \mathbf{v} + p \mathbf{v} + \mathbf{J}_q + \sum_{k=1}^N \left(\varphi_k + \frac{1}{2} |\mathbf{v}_k|^2 \right) \mathbf{J}_k - \sum_{k=1}^N \boldsymbol{\tau}_k \cdot \mathbf{v}_k \right\} = 0. \quad (26)$$

Here $p_k(\mathbf{x}, t) = k T n_k$, $n_k(\mathbf{x}, t) = \rho_k / m_k$, m_k , $h_k(\mathbf{x}, t)$ and $\boldsymbol{\tau}_k(\mathbf{x}, t)$ – respectively, hydrostatic pressure, number density, molecular weight, tensor of viscous stresses of the substance k ; $T(\mathbf{x}, t)$, $\mathbf{J}_q(\mathbf{x}, t)$, $\mathbf{q}(\mathbf{x}, t)$ – respectively, the temperature, the density of the total heat flux and the

reduced heat flux in the total continuum; $p = \sum_{k=1}^N p_k$ – the hydrostatic pressure of the mixture at a

given temperature (Dalton's law); k is the Boltzmann constant. When using the operator relation (10), equation (26) can be given the form:

$$\rho \frac{du}{dt} = -\nabla \cdot \left\{ \mathbf{J}_q + p\mathbf{v} + \sum_{k=1}^N \mathbf{J}_k \left(\varphi_k + \frac{1}{2} |\mathbf{v}_k|^2 \right) - \sum_{k=1}^N \boldsymbol{\tau}_k \cdot \mathbf{v}_k \right\}. \quad (26^*)$$

Potential energy balance. Multiplying the non-discontinuity equation (7) for the substance k by φ_k , summing over k and using (19) and (23), we obtain the equation for the local balance of the potential energy φ of the mixture in the form

$$\frac{\partial}{\partial t} (\rho\varphi) + \nabla \cdot \left\{ \rho\varphi\mathbf{v} + \sum_{k=1}^N \varphi_k \mathbf{J}_k \right\} = - \sum_{k=1}^N \rho_k \mathbf{f}_k \cdot \mathbf{v}_k + \sum_{k=1}^N \varphi_k \Gamma_k. \quad (27)$$

If we turn to equation (6), then such a comparison allows us to conclude that the first term on the right-hand side of (27) should be considered as a term corresponding to “external” sources, and the second term should be considered a term corresponding to an “internal” source of potential energy. Note that the density of the internal source $\sigma_\varphi^{(i)} = \sum_{k=1}^N \varphi_k \Gamma_k$ vanishes in all those cases when, due to chemical reactions, the equality

$$\sum_{k=1}^N \varphi_k v_{kj} = 0, \quad (j = 1, 2, \dots, r). \quad (28)$$

The fulfillment of this equality for the gravitational field is ensured by the conservation of mass. Taking into account the condition $\sigma_\varphi^{(i)} = 0$, the substantial form of the balance equation for the potential energy of the mixture takes the form

$$\rho \frac{d\varphi}{dt} = -\nabla \cdot \left\{ \sum_{k=1}^N \varphi_k \mathbf{J}_k \right\} - \rho \mathbf{v} \cdot \mathbf{f} - \sum_{k=1}^N \mathbf{f}_k \cdot \mathbf{J}_k. \quad (27^*)$$

Equation of the balance of the kinetic energy of the mixture. The derivation of the equation for the balance of kinetic energy is carried out as follows. Let us preliminarily rewrite the equation of motion of a multicomponent medium (15) in the form

$$\sum_{k=1}^N \left\{ \frac{\partial}{\partial t} (\rho_k \mathbf{v}_k) + \nabla \cdot (\rho_k \mathbf{v}_k \mathbf{v}_k - \boldsymbol{\tau}_k) \right\} = -\nabla p + \sum_{k=1}^N \rho_k \mathbf{f}_k, \quad (29)$$

or in substantial form

$$\sum_{k=1}^N \left\{ \rho_k \frac{d^{(k)} \mathbf{v}_k}{dt} \right\} = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{f} - \sum_{k=1}^N \Gamma_k \mathbf{v}_k. \quad (30)$$

Here $d^{(k)}/dt$ is the total time derivative (substantial differential operator) for the component k , which is determined by the relation

$$\rho_k \frac{d^{(k)}(..)}{dt} = \rho_k \left\{ \frac{\partial(..)}{\partial t} + \mathbf{v}_k \cdot \nabla(..) \right\} = \rho_k \frac{d(..)}{dt} + \mathbf{J}_k \cdot \nabla(..). \quad (31)$$

Note that in deriving (30) we used the identity

$$\begin{aligned} \nabla \cdot (\rho_k \mathbf{v}_k \mathbf{v}_k) &= \rho_k (\mathbf{v}_k \cdot \nabla \mathbf{v}_k) + \mathbf{v}_k \nabla \cdot (\rho_k \mathbf{v}_k) = \\ &= \rho_k (\mathbf{v}_k \cdot \nabla \mathbf{v}_k) + \mathbf{v}_k (\partial \rho_k / \partial t - \Gamma_k) \end{aligned} \quad (32)$$

Now multiplying equation (30) scalarly by $\mathbf{v} = \mathbf{v}_k - \rho_k^{-1} \mathbf{J}_k$ and taking into account definition (31), as a result we obtain

$$\sum_{k=1}^N \left\{ \rho_k \frac{d|\mathbf{v}_k|^2 / 2}{dt} \right\} = \sum_{k=1}^N \mathbf{J}_k \cdot \left\{ \frac{d^{(k)} \mathbf{v}_k}{dt} - \frac{1}{2} \nabla |\mathbf{v}_k|^2 \right\} + \mathbf{v} \cdot \left(-\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{f} - \sum_{k=1}^N \Gamma_k \mathbf{v}_k \right). \quad (33)$$

Finally, for the final derivation of the equation for the balance of specific kinetic energy, we calculate the substantial derivative with respect to time du_K / dt , using equations (11) and (33) for this; as a result we will have

$$\begin{aligned} \rho \frac{du_K}{dt} &= \sum_{k=1}^N \rho_k \frac{d}{dt} \left(\frac{|\mathbf{v}_k|^2}{2} \right) + \sum_{k=1}^N \frac{|\mathbf{v}_k|^2}{2} (\Gamma_k - \nabla \cdot \mathbf{J}_k) = \\ &= -\nabla \cdot \left(\frac{1}{2} \sum_{k=1}^N \mathbf{J}_k |\mathbf{v}_k|^2 \right) + \sum_{k=1}^N \mathbf{J}_k \cdot \left\{ \frac{d^{(k)} \mathbf{v}_k}{dt} + \frac{\Gamma_k}{2\rho_k^2} \mathbf{J}_k \right\} + \mathbf{v} \cdot (-\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{f}). \end{aligned} \quad (34)$$

Mechanical energy balance for a mixture. Let us define the total mechanical energy per unit mass of the mixture as the sum of kinetic energy $u_K(\mathbf{x}, t)$ and potential energy $\varphi(\mathbf{x}, t)$. Adding (27*) and (34), we obtain the following equation of the substantial balance of the quantity $u_m(\mathbf{x}, t)$

$$\begin{aligned} \rho \frac{du_m}{dt} &= -\nabla \cdot \left\{ \sum_{k=1}^N \mathbf{J}_k \left(\frac{1}{2} |\mathbf{v}_k|^2 + \varphi_k \right) \right\} + \\ &+ \sum_{k=1}^N \mathbf{J}_k \cdot \left\{ \frac{d^{(k)} \mathbf{v}_k}{dt} - \mathbf{f}_k + \frac{1}{2} \rho_k^{-1} \sum_{j=1}^N (\Gamma_{kj} - \Gamma_{jk}) (\mathbf{v}_k - \mathbf{v}_j) \right\} - \mathbf{v} \cdot \nabla p + \mathbf{v} \cdot (\nabla \cdot \boldsymbol{\tau}). \end{aligned} \quad (35)$$

When writing this equation, the transformation was used

$$\begin{aligned} \frac{1}{2} \sum_{k=1}^N \rho_k^{-2} \Gamma_k |\mathbf{J}_k|^2 &= \frac{1}{2} \sum_{k=1}^N \mathbf{J}_k \cdot \left\{ \sum_{j=1}^N \rho_k^{-2} \mathbf{J}_k (\Gamma_{kj} - \Gamma_{jk}) \right\} = \\ &= \frac{1}{2} \sum_{k=1}^N \mathbf{J}_k \cdot \left\{ \sum_{j=1}^N \rho_k^{-1} (\Gamma_{kj} - \Gamma_{jk}) \left(\frac{\mathbf{J}_k}{\rho_k} - \frac{\mathbf{J}_j}{\rho_j} \right) + \sum_{j=1}^N \mathbf{J}_j \rho_k^{-1} \rho_j^{-1} (\Gamma_{kj} - \Gamma_{jk}) \right\} = \end{aligned}$$

$$= \frac{1}{2} \sum_{k=1}^N \mathbf{J}_k \cdot \left\{ \rho_k^{-1} \sum_{j=1}^N (\Gamma_{kj} - \Gamma_{jk}) (\mathbf{v}_k - \mathbf{v}_j) \right\}. \quad (36)$$

The internal energy balance equation for a medium. Subtracting equation (35) from equation (26 *), we find the internal energy $\varepsilon(\mathbf{x}, t)$ balance equation in the following form:

$$\rho \frac{d\varepsilon}{dt} = -\nabla \cdot \mathbf{J}_q - \sum_{k=1}^N \mathbf{J}_k \cdot \left\{ \frac{d^{(k)} \mathbf{v}_k}{dt} - \mathbf{f}_k - \rho_k^{-1} \nabla \cdot \boldsymbol{\tau}_k + \rho_k^{-1} \sum_{j=1}^N \frac{\Gamma_{kj} - \Gamma_{jk}}{2} (\mathbf{v}_k - \mathbf{v}_j) \right\} -$$

$$-p \nabla \cdot \mathbf{v} - \sum_{k=1}^N \boldsymbol{\tau}_k : \nabla \mathbf{v}_k. \quad (37)$$

By the way, we note that the above phenomenological derivation of the balance equation for the specific internal energy of the mixture (when taken into account in the kinetic energy of diffusion) was not previously known (see the remark on p. 119 in the cited monograph I. Gyarmati[14]).

3. THE PRODUCTION OF ENTROPY IN REACTING MIXTURES AND LINEAR KINEMATIC CONSTITUTIVE EQUATIONS

If we put in the general balance equation (6) $a \equiv S$, $\mathbf{J}_a \equiv \mathbf{J}_S$ and, $\sigma_a \equiv \sigma_S$ then we obtain the local equation of the balance of the entropy of the mixture, the substantial form of which will have the form:

$$\rho \frac{dS}{dt} + \nabla \cdot \mathbf{J}_S = \sigma_S \geq 0, \quad (38)$$

where $\sigma_S(\mathbf{x}, t)$ and $\mathbf{J}_S(\mathbf{x}, t)$ are the intensity of the "source" and the flux of entropy, respectively. To find an explicit form for these two quantities, we substitute in the fundamental Gibbs equation (5), previously written along the trajectory of the center of mass of the physical elementary volume and taking the form

$$T \frac{dS}{dt} = \frac{d\varepsilon}{dt} + p \frac{dv}{dt} - \sum_{k=1}^N \mu_k \frac{dc_k}{dt}, \quad (39)$$

derivatives $d\varepsilon/dt$, dv/dt and dc_k/dt , taken from equations (37), (10) and (11), respectively. As a result, we get

$$\rho \frac{dS}{dt} + \nabla \cdot \left\{ \left(\mathbf{J}_q - \sum_{k=1}^N \mu_k \mathbf{J}_k \right) / T \right\} =$$

$$= \frac{1}{T} \left\{ \sum_{k=1}^N \mathbf{J}_k \cdot \left(\boldsymbol{\Lambda}_k - T \nabla \frac{\mu_k}{T} \right) - \mathbf{J}_q \cdot \frac{\nabla T}{T} + \sum_{k=1}^N \boldsymbol{\tau}_k : \nabla \mathbf{v}_k - \sum_{j=1}^r J_j A_j \right\} \equiv \sigma_S. \quad (40)$$

Here the so-called chemical affinity for the j -th reaction is introduced, defined as follows:

$$A_j(\mathbf{x}, t) = \sum_{k=1}^N v_k \mu_k \quad (j = 1, \dots, r), \quad (41)$$

and thermodynamic forces

$$\Lambda_k(\mathbf{x}, t) \equiv \mathbf{f}_k - \frac{d^{(k)} \mathbf{v}_k}{dt} + \rho_k^{-1} \nabla \cdot \boldsymbol{\tau}_k - 1/2 \rho_k^{-1} \sum_{j=1}^N (\Gamma_{kj} - \Gamma_{jk}) (\mathbf{v}_k - \mathbf{v}_j). \quad (41^*)$$

It should be noted that in the general case, energy dissipation $T\sigma_S(\mathbf{x}, t) \geq 0$, which is a bilinear positive definite quantity, is determined by a set of generalized thermodynamic flows $\mathcal{Y}(\mathbf{x}, t)$ and the corresponding generalized thermodynamic forces $\mathcal{X}(\mathbf{x}, t)$

$$T\sigma_S(\mathcal{Y}, \mathcal{X}) = \sum_{j=1}^f \mathcal{Y}_j \mathcal{X}_j, \quad (42)$$

where f is the number of independent scalar flows $\mathcal{Y}_j(\mathbf{x}, t)$ and forces $\mathcal{X}_j(\mathbf{x}, t)$ [10]. In this case, thermodynamic flows and forces can be defined, generally speaking, in different ways. It is only necessary that they be coupled to each other by relation (42). The choice of their type in each specific case depends on the convenience of considering the problem. A consequence of the absence of interference of flows and thermodynamic forces of different tensor dimensions in an isotropic system (Curie principle) is the fact that vector phenomena of diffusion and heat conduction can be considered independently of scalar or tensor phenomena. In this work, we will focus on the derivation of the constitutive relations only for vector phenomena.

For energy dissipation due to diffusion and thermal conductivity, we have the following expression

$$T\sigma_S(\mathbf{x}, t) = -\mathbf{J}_q \cdot \mathbf{X}_q + \sum_{k=1}^N \mathbf{J}_k \cdot \mathbf{X}_k^*, \quad (43)$$

where

$$\mathbf{X}_q(\mathbf{x}, t) \equiv -\frac{1}{T} \nabla T, \quad \mathbf{X}_k^*(\mathbf{x}, t) \equiv \Lambda_k - T \nabla \frac{\mu_k}{T}, \quad (k = 1, 2, \dots, N). \quad (44)$$

In order to be able to compare the constitutive relations (derived further by methods of nonequilibrium thermodynamics) for the thermodynamic flows of diffusion $\mathbf{J}_k(\mathbf{x}, t)$ and heat $\mathbf{J}_q(\mathbf{x}, t)$ with analogous relations obtained by gas-kinetic methods (see, for example, [2,3]), we express gradients of chemical potentials $\mu_k(\mathbf{x}, t)$ through gradients of thermo-hydrodynamic parameters. Considering further the multicomponent medium as a non-ideal system, we write down the chemical potential $\mu_k(\mathbf{x}, t)$ per unit mass of the component k in the form [20].

$$\mu_k(T, p, x_k) = \mu_k^\ominus(T, p) + \frac{kT}{m_k} \ln a_k, \quad (k = 1, 2, \dots, N), \quad (45)$$

where $\mu_k^\circ(T, p)$ is the chemical potential of the pure component k at a given temperature T and pressure p ; $a_k = x_k \gamma_k$, $\gamma_k(T, p, x_k)$, n_k , $x_k = n_k / n$ – activity, activity coefficient, number density and molar concentration of the k -th component, respectively; $n = \sum_{k=1}^N n_k$ is the total numerical density of the system. For imperfect mixtures, activity $a_k = a_k(p, T, x_k)$ is determined from theory or experiment in the same way as function $\mu_k^\circ(T, p)$.

If we now use the well-known thermodynamic relations [20]

$$\left(\frac{\partial \mu_k}{\partial T} \right)_p = -\frac{h_k}{T^2}, \quad \left(\frac{\partial \mu_k}{\partial p} \right)_T = \frac{v_k^*}{m_k}, \quad (k=1, 2, \dots, N), \quad (46)$$

we get

$$T \nabla \left(\frac{\mu_k}{T} \right) = \frac{kT}{m_k} \frac{(\nabla a_k)_{p,T}}{a_k} + \frac{v_k^*}{m_k} \nabla p - \frac{h_k}{T} \nabla T, \quad (k=1, 2, \dots, N). \quad (47)$$

Here, $v_k^*(\mathbf{x}, t)$ and h_k are respectively the partial specific volume and specific enthalpy of the k -th component. Substituting (47) into (44) and (43), we find

$$T \sigma_S(\mathbf{x}, t) = \mathbf{q} \cdot \mathbf{X}_q - \sum_{k=1}^N \mathbf{J}_k \cdot \mathbf{X}_k, \quad (48)$$

where

$$\mathbf{X}_k(\mathbf{x}, t) \equiv \frac{h_k}{T} \nabla T - \mathbf{X}_k^*(\mathbf{x}, t) = \frac{kT}{m_k} (\nabla \ln a_k)_{p,T} + \frac{v_k^*}{m_k} \nabla p - \mathbf{\Lambda}_k \quad (k=1, 2, \dots, N). \quad (49)$$

Phenomenological relations for flows through forces for a multicomponent medium. In states close to equilibrium, flows can be represented as linear functions of forces (the main postulate of thermodynamics of irreversible processes):

$$q^\alpha(\mathbf{x}, t) = \mathcal{L}_{00}^{\alpha\beta} X_{q\beta} - \sum_{j=1}^N \mathcal{L}_{0j}^{\alpha\beta} X_{j\beta}, \quad (50)$$

$$J_k^\alpha(\mathbf{x}, t) = \mathcal{L}_{k0}^{\alpha\beta} X_{q\beta} - \sum_{j=1}^N \mathcal{L}_{kj}^{\alpha\beta} X_{j\beta}, \quad (k=1, 2, \dots, N). \quad (51)$$

The indices here $\alpha, \beta = 1, 2, 3$ refer to a rectangular coordinate system. Kinetic coefficients $\mathcal{L}_{kj}^{\alpha\beta}$ ($k, j = 1, 2, \dots, N$) are tensors that depend on the defining parameters characterizing the geometric symmetry of the medium. In what follows, we will consider isotropic media with respect to the full group of orthogonal coordinate transformations. According to the general theory of ten-

sors [12], the symmetry properties of isotropic media are fully characterized by the metric tensor $\mathbf{g}^{\alpha\beta}$; all tensors will be tensor functions of the metric tensor only:

$$\mathcal{L}_{kj}^{\alpha\beta} = \alpha_{kj} \mathbf{g}^{\alpha\beta}, \quad (k, j = 0, 1, 2, \dots, N).$$

For an isotropic medium in a rectangular coordinate system

$$\mathbf{g}^{\alpha\beta} = \delta^{\alpha\beta} = \begin{cases} 1, & \alpha = \beta; \\ 0, & \alpha \neq \beta \end{cases}$$

and the phenomenological equations connecting thermodynamic flows and forces take the form

$$\mathbf{q}(\mathbf{x}, t) = \alpha_{00} \mathbf{X}_0 - \sum_{j=1}^N \alpha_{0j} \mathbf{X}_j, \quad (52)$$

$$\mathbf{J}_k(\mathbf{x}, t) = \alpha_{k0} \mathbf{X}_0 - \sum_{j=1}^N \alpha_{kj} \mathbf{X}_j, \quad (k = 1, 2, \dots, N). \quad (53)$$

Once linear relations (52) and (53) are postulated, Onsager's theorem gives

$$\alpha_{kj} = \alpha_{jk}, \quad (k, j = 0, 1, 2, \dots, N). \quad (54)$$

A number of additional relationships follow from the fact of the independence of forces [10]

$$\sum_{j=1}^N \alpha_{kj} = 0, \quad (k = 0, 1, 2, \dots, N). \quad (55)$$

Thus, $(N+1)^2$ of the coefficients, there are $\frac{1}{2}N(N-1)$ independent phenomenological coefficients α_{ij} ($i, j = 0, 1, 2, \dots, N$).

Diffusive thermodynamic forces. For further purposes, it is convenient to material relations (52) and (53) for thermodynamic flows $\mathbf{q}(\mathbf{x}, t)$ and $\mathbf{J}_k(\mathbf{x}, t)$ can be written using some other linearly dependent vectors $\mathbf{d}_k^{(a)}(\mathbf{x}, t)$, closely related to $\mathbf{X}_k(\mathbf{x}, t)$. This can be done, for example, as follows: put $\mathbf{d}_k^{(a)}(\mathbf{x}, t) \equiv \rho_k \mathbf{X}_k / p - \rho_k \mathbf{K} / p$ and define a vector \mathbf{K} common for all components k from the condition

$$\sum_{k=1}^N \mathbf{d}_k^{(a)}(\mathbf{x}, t) = 0; \quad (56)$$

then, taking into account (49), we obtain

$$\mathbf{K} = \sum_{k=1}^N c_k \mathbf{X}_k = \sum_{k=1}^N c_k \left(\frac{kT}{m_k} (\nabla \ln a_k)_{p,T} + \frac{v_k^*}{m_k} \nabla p - \mathbf{\Lambda}_k \right) = \frac{1}{\rho} \nabla p - \sum_{k=1}^N c_k \mathbf{\Lambda}_k. \quad (57)$$

When writing (57), the Gibbs–Duhem relation was taken into account for the case of constant pressure and temperature

$$0 = \sum_{k=1}^N \rho_k (\nabla \mu_k)_{p,T} = kT \sum_{k=1}^N \rho_k \frac{(\nabla \ln a_k)_{p,T}}{m_k} = p \sum_{k=1}^N x_j (\nabla \ln a_k)_{p,T}$$

and the property $\sum_{k=1}^N n_k v_k^* = 1$ for partial specific volumes v_k^* (see [10]; p. 225).

Using (49) and (57), vectors $\mathbf{d}_j^{(a)}(\mathbf{x}, t)$ can be given the form:

$$\mathbf{d}_j^{(a)}(\mathbf{x}, t) = x_j (\nabla \ln a_j)_{p,T} + n_j v_j^* \nabla \ln p - \frac{c_j}{p} \rho \mathbf{\Lambda}_j - \frac{c_j}{p} \sum_{k=1}^N \rho_k \mathbf{X}_k .$$

If we now exclude vectors $\mathbf{X}_k(\mathbf{x}, t)$ from this formula using expression (49), then as a result we will have

$$\mathbf{d}_j^{(a)}(\mathbf{x}, t) = x_j (\nabla \ln a_j)_{p,T} + \frac{n_j v_j^* - c_j}{p} \nabla p - \frac{c_j}{p} \left(\rho \mathbf{\Lambda}_j - \sum_{k=1}^N \rho_k \mathbf{\Lambda}_k \right), \quad (j = 1, 2, \dots, N). \quad (58)$$

These vectors are usually called the diffusive thermodynamic forces of the component (see, for example, [3,6]).

Finally, the vectors $\mathbf{d}_k^{(a)}(\mathbf{x}, t)$ written taking into account expressions (42) take the following final form

$$\mathbf{d}_k^{(a)}(\mathbf{x}, t) \equiv \frac{1}{p} \left\{ \rho_k \frac{d^{(k)} \mathbf{v}_k}{dt} - \nabla \cdot \boldsymbol{\tau}_k - \rho_k \mathbf{f}_k + \sum_{j=1}^N \frac{(\Gamma_{kj} - \Gamma_{jk})}{2} (\mathbf{v}_k - \mathbf{v}_j) + \right. \\ \left. + p x_k \frac{(\nabla a_k)_{p,T}}{a_k} + n_k v_k^* \nabla p \right\} \quad (59)$$

When writing this expression, we used, following from (30) and (42), the transformation

$$\sum_{k=1}^N \rho_k \mathbf{\Lambda}_k = \sum_{k=1}^N \left\{ \rho_k \mathbf{f}_k - \rho_k \frac{d^{(k)} \mathbf{v}_k}{dt} + \nabla \cdot \boldsymbol{\tau}_k - \sum_{j=1}^N \frac{(\Gamma_{kj} - \Gamma_{jk})}{2} (\mathbf{v}_k - \mathbf{v}_j) \right\} = \nabla p + \\ + \sum_{k=1}^N \mathbf{v}_k \Gamma_k - \sum_{k=1}^N \sum_{j=1}^N \frac{(\Gamma_{kj} - \Gamma_{jk})}{2} (\mathbf{v}_k - \mathbf{v}_j) = \nabla p + \sum_{k=1}^N \sum_{j=1}^N \frac{(\Gamma_{kj} - \Gamma_{jk})}{2} (\mathbf{v}_k + \mathbf{v}_j) = \nabla p .$$

Regarding expression (58) for vectors $\mathbf{d}_k^{(a)}$, it is important to note the following. In the case when the contribution of the kinetic energy of diffusion to the mechanical energy of the mixture (in this case $\mathbf{\Lambda}_k \equiv \mathbf{f}_k$) is not taken into account, and the multicomponent medium is a mixture of

ideal gases (for which $a_k = x_k$, $p = kTn$ the partial molar volume is also $v_k^* = 1/n$), this expression is reduced to the form

$$\mathbf{d}_k = \nabla x_k + \frac{x_k - c_k}{p} \nabla p - \frac{c_k}{p} \left(\rho \mathbf{f}_k - \sum_{j=1}^N \rho_j \mathbf{f}_j \right)$$

widely used in the kinetic theory of multicomponent gases [2,3].

Further, for brevity, in expression (59), we will further use the notation

$$\nabla_a p_k \equiv p_k \frac{(\nabla a_k)_{p,T}}{a_k} + n_k v_k^* \nabla p. \quad (60)$$

Substituting now vectors $\mathbf{X}_k = p \mathbf{d}_k^{(a)} / \rho_k + \mathbf{K}$ into equations (52) and (53) and taking into account relations (55), we obtain the transport equations in the form:

$$\mathbf{q}(\mathbf{x}, t) = \alpha_{00} \mathbf{X}_q - p \sum_{k=1}^N \frac{\alpha_{0k}}{\rho_k} \mathbf{d}_k^{(a)}, \quad (61)$$

$$\mathbf{J}_j(\mathbf{x}, t) = \alpha_{j0} \mathbf{X}_q - p \sum_{k=1}^N \frac{\alpha_{jk}}{\rho_k} \mathbf{d}_k^{(a)}, \quad (j = 1, 2, \dots, N). \quad (62)$$

We now use property (56) for vectors $\mathbf{d}_k^{(a)}$ and relations (54) and (55), introduce (by analogy with the kinetic theory of gases) generalized diffusion coefficients D_{ik} , generalized thermal diffusion coefficients D_i^T and a coefficient through which the thermal conductivity coefficient λ' will be further expressed λ . Then

$$\mathbf{q}(\mathbf{x}, t) = -\lambda' \nabla T - p \sum_{k=1}^N D_{Tk} \mathbf{d}_k^{(a)}, \quad (63)$$

$$\mathbf{J}_i(\mathbf{x}, t) = -\rho_i D_{Ti} \nabla \ln T - \rho_i \sum_{k=1}^N D_{ik} \mathbf{d}_k^{(a)}, \quad (j = 1, 2, \dots, N), \quad (64)$$

where, by definition, it is assumed

$$\lambda' \equiv \alpha_{00} / T, \quad D_{Tk} \equiv \alpha_{0k} / \rho_k = \alpha_{k0} / \rho_k, \quad (k = 1, 2, \dots, N), \quad (65)$$

$$D_{ik} = D_{ki} \equiv p \alpha_{ik} / \rho_i \rho_k, \quad (i, k = 1, 2, \dots, N). \quad (66)$$

According to relations (55) connecting the kinetic coefficients α_{0k} and α_{ik} , the generalized diffusion and thermal diffusion coefficients introduced by us are linearly dependent:

$$\sum_{k=1}^N \rho_k D_{Tk} = 0, \quad (1) \quad \sum_{k=1}^N \rho_k D_{ki} = 0, \quad (2) \quad (k = 1, 2, \dots, N). \quad (67)$$

Thus, we have $\frac{1}{2}N(N-1)$ independent multicomponent diffusion coefficients D_{ij} , which, together with independent thermal diffusion coefficients and the coefficient, will give independent transport coefficients in accordance with the general Onsager theory (see (52)-(55)). Expressions (63) and (64) in the particular case of ideal mixtures identically coincide with similar relations obtained phenomenologically, for example, in the monograph [13].

Thermal diffusion relations. It is known that thermal diffusion is an effect of the second order of smallness, important only in those cases when there is a large difference in the masses involved in the transfer of components. For further purposes, it is convenient to introduce new transfer coefficients to describe the effects of thermal diffusion – the so-called thermal diffusion ratios $k_{T\alpha}(\mathbf{x}, t)$:

$$\sum_{k=1}^N D_{ki} k_{Tk} = D_{Ti}, \quad (j = 1, 2, \dots, N), \quad (68)$$

$$\sum_{k=1}^N k_{Tk}(\mathbf{x}, t) = 0. \quad (69)$$

Thermal diffusion ratio $k_{Tk}(\mathbf{x}, t)$ characterizes a measure of the relative importance of thermal diffusion in relation to ordinary diffusion. Due to the correlation (67⁽²⁾), the determinant of the coefficients of the system of equations (68) vanishes. The only solution to the system of homogeneous equations corresponding to equations (68) is the N -component vector of mass concentrations $c_\alpha \equiv \rho_\alpha/\rho$, but, according to (67⁽¹⁾), this vector is orthogonal to the N -component vector of thermal diffusion coefficients. Thus, equations (68) have a solution in the form of a certain vector \mathbf{k}_T with components $k_{Tj}(\mathbf{x}, t)$ ($j = 1, 2, \dots, N$) determined up to some arbitrary constant multiplied by ρ_k ; condition (69) ensures the uniqueness of the vector \mathbf{k}_T .

When using coefficients k_{Tj} , expression (64) for the diffusion flux $\mathbf{J}_i(\mathbf{x}, t)$ can be written in the form of the following generalized Fick's law:

$$\mathbf{J}_i(\mathbf{x}, t) = -\rho_i \sum_{k=1}^N D_{ik} (\mathbf{d}_k + k_{Tk} \nabla \ln T), \quad (i = 1, 2, \dots, N). \quad (70)$$

We now make the following important remark regarding relation (63) for the heat flux $\mathbf{q}(\mathbf{x}, t)$. The coefficient λ' cannot be determined as a result of direct experimental measurement, since the temperature gradient in the gas mixture causes thermal diffusion and, therefore, leads to concentration gradients. Therefore, even in stationary processes, the vectors $\mathbf{d}_k^{(a)}$ are not equal to zero, which means that the heat flux due to the temperature gradient is always accompanied by

the heat flux due to the concentration gradients. Using relations (64), (66), and (70), it is possible to express vectors $\mathbf{d}_k^{(a)}$ in terms of diffusion fluxes and temperature gradient:

$$\sum_{k=1}^N D_{Tk} \mathbf{d}_k^{(a)} = \sum_{k=1}^N \sum_{j=1}^N D_{kj} k_{Tj} \mathbf{d}_k^{(a)} = - \sum_{j=1}^N k_{Tj} \left(\frac{1}{\rho_j} \mathbf{J}_j + D_{Tj} \nabla \ln T \right). \quad (71)$$

Substituting this expression in (63), we obtain the defining relation for the vector of the reduced heat flux in the form

$$\mathbf{q}(\mathbf{x}, t) = -\lambda \nabla T + p \sum_{k=1}^N \frac{k_{Tk}}{\rho_k} \mathbf{J}_k, \quad (72)$$

where $\lambda(\mathbf{x}, t)$ is the true (molecular) thermal conductivity coefficient of the multicomponent mixture,

$$\lambda(\mathbf{x}, t) \equiv \lambda' - k n \sum_{j=1}^N k_{Tj} D_{Tj}. \quad (73)$$

It is this coefficient that can be directly measured experimentally in a stationary system, since in the stationary case all diffusion fluxes $\mathbf{J}_j(\mathbf{x}, t)$ are equal to zero when the gas as a whole is at rest.

Finally, it follows from (70) and (72) that the contribution of the effects of heat conduction and diffusion to expression (43) for the rate of entropy appearance is

$$\overset{(vektor)}{\sigma_{(S)}} = \lambda |\nabla \ln T|^2 + p \sum_{k=1}^N \sum_{j=1}^N D_{kj} \left(\mathbf{d}_k^{(a)} + k_{Tk} \nabla \ln T \right) \cdot \left(\mathbf{d}_j^{(a)} + k_{Tj} \nabla \ln T \right) \geq 0. \quad (74)$$

From the condition that one of the terms can be equal to zero, while the others are not equal to zero, it follows that the coefficient of thermal conductivity $\lambda > 0$, and for the coefficients of multicomponent diffusion, the inequality

$$\sum_{k=1}^N \sum_{j=1}^N D_{kj} \mathbf{y}_k \mathbf{y}_j \geq 0 \quad (75)$$

for any vectors \mathbf{y}_j satisfying the condition $\sum_j \mathbf{y}_j = 0$. From the properties of a nonnegative definite matrix of coefficients D_{kj} , one can indicate the following Sylvester conditions: $D_{kk} \geq 0$ – non negativity of all elements of the matrix D_{kj} on the main diagonal $D_{kj} D_{jk} \leq D_{kk} D_{jj}$; (each minor of a nonnegative definite matrix D_{kj} containing elements of its main diagonal as its own main diagonal must also be nonnegative), etc. Within the limits of these limitations, the diffusion

coefficients D_{kj} vary in a very wide range of values in accordance with the degree of connection between the processes of heat and mass transfer.

4. STEFAN-MAXWELL RELATIONS AND HEAT FLUX FOR MULTICOMPONENT NON-IDEAL MEDIUM

The use of constitutive relations (64) for diffusion fluxes $\mathbf{J}_k(\mathbf{x}, t)$ in the general multicomponent case is extremely difficult, since in the literature, with rare exceptions, there is no practical information on the generalized coefficients of multicomponent diffusion $D_{kj}(\mathbf{x}, t)$, and the existing experimental data refer mainly to diffusion coefficients in binary gas mixtures $\mathcal{D}_{kj}(\mathbf{x}, t)$. At the same time, the gas-kinetic theory of mixtures gives extremely cumbersome formulas connecting the diffusion coefficients $D_{kj}(\mathbf{x}, t)$ with binary coefficients $\mathcal{D}_{kj}(\mathbf{x}, t)$ for various pairs of mixture components. These formulas are usually difficult to use when solving specific problems. In addition, the system of diffusion equations obtained after substitution $\mathbf{J}_k(\mathbf{x}, t)$ from (64) into balance equations (11) turns out to be unresolved with respect to the higher derivatives. As is known, the numerical implementation of such systems is fraught with certain difficulties. Therefore, when analyzing diffusion processes in multicomponent gas mixtures, a different formulation of the problem is often advantageous, when constitutive relations (64) for diffusion flows $\mathbf{J}_k(\mathbf{x}, t)$ are used in a form that is resolved with respect to diffusion thermodynamic forces $\mathbf{d}_k(\mathbf{x}, t)$ through flows $\mathbf{J}_k(\mathbf{x}, t)$. Such an inverse transformation can be written in the form of the so-called generalized Stefan–Maxwell relations, which, instead of generalized coefficients of multicomponent diffusion $D_{kj}(\mathbf{x}, t)$, include molecular diffusion coefficients in binary gas mixtures $\mathcal{D}_{kj}(\mathbf{x}, t)$.

Generalized Stefan–Maxwell relations. For the phenomenological derivation of the Stefan–Maxwell relations, let us solve equations (61) and (62) with respect to generalized thermodynamic forces

$$\mathcal{X}_0 \equiv \mathcal{X}_q = -\frac{\nabla T}{T}, \quad \mathcal{X}_i = \mathcal{X}_i \equiv -p \frac{\mathbf{d}_i^{(a)}}{\rho_i}, \quad (i = 1, 2, \dots, N) \quad (76)$$

through flows $\mathbf{q}(\mathbf{x}, t)$ and $\mathbf{J}_k(\mathbf{x}, t)$ ($1, 2, \dots, N$). In relations (61) and (62), only N independent equations, since

$$\sum_{k=1}^N \mathbf{J}_k = 0, \quad (77)$$

$$\sum_{k=1}^N \alpha_{k0} = 0, \quad \sum_{k=1}^N \alpha_{kj} = 0, \quad (k = 1, 2, \dots, N). \quad (78)$$

Therefore, we omit the last equation from system (62) and write relations (61) and (62) in the form

$$\mathbf{q} - \alpha_{00}\boldsymbol{\mathcal{X}}_q = \sum_{k=1}^{N-1} \alpha_{0k}(\boldsymbol{\mathcal{X}}_k - \boldsymbol{\mathcal{X}}_N), \quad (79)$$

$$\mathbf{J}_j - \alpha_{j0}\boldsymbol{\mathcal{X}}_q = \sum_{k=1}^{N-1} \alpha_{jk}(\boldsymbol{\mathcal{X}}_k - \boldsymbol{\mathcal{X}}_N), \quad (j=1,2,\dots,N-1). \quad (80)$$

Solving system (80) with respect to $(\boldsymbol{\mathcal{X}}_k - \boldsymbol{\mathcal{X}}_N)$ ($j=1,2,\dots,N-1$), we find

$$\boldsymbol{\mathcal{X}}_j - \boldsymbol{\mathcal{X}}_N = \sum_{k=1}^{N-1} \beta_{jk}(\mathbf{J}_k - \alpha_{k0}\boldsymbol{\mathcal{X}}_0), \quad (j=1,2,\dots,N-1), \quad (81)$$

where the elements of the inverse matrix β_{jk} satisfy the relations

$$\sum_{k=1}^{N-1} \beta_{ik}\alpha_{kj} = \delta^{ij} = \begin{cases} 1, & i=j, \\ 0, & i \neq j. \end{cases} \quad (82)$$

The symmetry of the coefficients α_{ij} implies the symmetry of the coefficients β_{ij} :

$$\beta_{ij} = \beta_{ji}, \quad (i,j=1,2,\dots,N-1). \quad (83)$$

From relation (79), using (81), we find

$$\mathbf{q} = \left[\alpha_{00} - \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} \alpha_{0k}\beta_{kj}\alpha_{j0} \right] \boldsymbol{\mathcal{X}}_0 + \sum_{j=1}^{N-1} \left[\sum_{k=1}^{N-1} \alpha_{0k}\beta_{kj} \right] \mathbf{J}_j. \quad (84)$$

Multiplying each of the equations (81) by c_j and summing them from 1 to $(N-1)$, we find

$$\boldsymbol{\mathcal{X}}_N = \boldsymbol{\mathcal{X}}_0 \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} c_j \beta_{jk} \alpha_{k0} - \sum_{k=1}^{N-1} \mathbf{J}_k \left(\sum_{j=1}^{N-1} c_j \beta_{jk} \right), \quad (85)$$

$$\boldsymbol{\mathcal{X}}_i = \boldsymbol{\mathcal{X}}_0 \sum_{k=1}^{N-1} \left(\sum_{j=1}^{N-1} c_j \beta_{jk} - \beta_{ik} \right) \alpha_{k0} - \sum_{k=1}^{N-1} \left(\sum_{j=1}^{N-1} c_j \beta_{jk} - \beta_{ik} \right) \mathbf{J}_k, \quad (i=1,2,\dots,N). \quad (86)$$

The force can be found from expression (84). Equations (85) and (86) represent the sought inversion of relations (62).

In order to write these equations in the form of generalized Stefan - Maxwell relations with symmetric coefficients, we add to equations (84), (85), and (86) equation (77), respectively multiplied by the constants a_0, a_N and a_i ($i=1,2,\dots,N-1$), and determine the free parameters a_0 and a_i from symmetry conditions for the coefficients $\mathcal{A}_{ik} = \mathcal{A}_{ki}$. For this, it is necessary to put

$$a_0 = - \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} c_j \beta_{jk} \alpha_{k0}, \quad (87)$$

$$a_i = a_N - \sum_{k=1}^{N-1} c_k \beta_{ki}, \quad (i = 1, 2, \dots, N-1). \quad (88)$$

Then we get

$$\mathbf{q} = \mathcal{A}_{00} \boldsymbol{\chi}_0 + \sum_{k=1}^N \mathcal{A}_{0k} \mathbf{J}_k, \quad (89)$$

$$-\boldsymbol{\chi}_i = \mathcal{A}_{i0} \boldsymbol{\chi}_0 + \sum_{k=1}^N \mathcal{A}_{ik} \mathbf{J}_k, \quad (i = 1, 2, \dots, N), \quad (90)$$

where the coefficients \mathcal{A}_{ik} are

$$\mathcal{A}_{00} = \alpha_{00} - \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} \alpha_{0k} \beta_{kj} \alpha_{j0}, \quad (91)$$

$$\mathcal{A}_{0N} = \mathcal{A}_{N0} = a_0 = - \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} c_j \beta_{jk} \alpha_{k0}, \quad (92)$$

$$\mathcal{A}_{0i} = \mathcal{A}_{i0} = a_0 + \sum_{k=1}^{N-1} \alpha_{0k} \beta_{ki} = \sum_{k=1}^{N-1} \alpha_{0k} \left(\beta_{ki} - \sum_{j=1}^{N-1} c_j \beta_{jk} \right), \quad (i = 1, 2, \dots, N-1), \quad (93)$$

$$\mathcal{A}_{ik} = \mathcal{A}_{ki} = a_N + \sum_{j=1}^{N-1} c_j (\beta_{ji} + \beta_{jk}) - \beta_{ik}, \quad (i = 1, 2, \dots, N-1), \quad (94)$$

$$\mathcal{A}_{Ni} = \mathcal{A}_{iN} = a_N + \sum_{k=1}^{N-1} c_k \beta_{ki}, \quad (95)$$

$$\mathcal{A}_{NN} = -a_N, \quad (96)$$

and the identity

$$\sum_{\alpha=1}^N c_\alpha \mathcal{A}_{\alpha 0} = 0. \quad (97)$$

Thus, the coefficients \mathcal{A}_{ik} ($i, k = 0, 1, \dots, N$) are determined to within a constant a_N , which, generally speaking, can be chosen arbitrarily. Here we define it, assuming the flows $\mathbf{J}_i(\mathbf{x}, t)$ ($i = 1, 2, \dots, N$) are arbitrary.

Let us rewrite relations (89), (90) in the form

$$\boldsymbol{\chi}_0 = \frac{1}{\mathcal{A}_{00}} \mathbf{q} - \sum_{k=1}^N \frac{\mathcal{A}_{0k}}{\mathcal{A}_{00}} \mathbf{J}_k, \quad (98)$$

$$\boldsymbol{\chi}_i = -\frac{\mathcal{A}_{i0}}{\mathcal{A}_{00}} \mathbf{q} + \sum_{k=1}^N \left(\frac{\mathcal{A}_{i0} \mathcal{A}_{0k}}{\mathcal{A}_{00}} - \mathcal{A}_{ik} \right) \mathbf{J}_k, \quad (i = 1, 2, \dots, N). \quad (99)$$

Using identity (56), notation (76), and the arbitrariness of vectors $\mathbf{J}_k(\mathbf{x}, t)$, taking into account (97)–(99), we obtain

$$\sum_{k=1}^N c_k \mathcal{A}_{ki} = 0, \quad (i = 1, 2, \dots, N). \quad (100)$$

Substituting the coefficients (94) and (95) into these relations, we find a_N :

$$a_N = - \sum_{k=1}^{N-1} \sum_{j=1}^{N-1} c_k c_j \beta_{kj}. \quad (101)$$

Thus, the constants in (94)–(96) are completely defined in terms of the elements of the symmetric matrix of phenomenological coefficients α_{ij} and the elements of the symmetric matrix β_{ij} inverse to it (see (83)).

Let us now bring expressions (90) to the form of the so-called generalized Stefan–Maxwell relations for multicomponent diffusion. For this we read from (90) the corresponding equality (100) multiplied by \mathbf{J}_i/c_i , then we find

$$-\mathbf{x}_i = \mathcal{A}_{i0} \mathbf{x}_0 + \sum_{k=1}^N \rho_k \mathcal{A}_{ik} (\mathbf{w}_k - \mathbf{w}_i), \quad (i = 1, 2, \dots, N), \quad (102)$$

or in more familiar notation

$$\mathbf{d}_i^{(a)} = \sum_{k=1}^N \frac{\rho_i \rho_k}{p} \mathcal{A}_{ik} (\mathbf{w}_k - \mathbf{w}_i) - \frac{\rho_i \mathcal{A}_{i0}}{p} \frac{\nabla T}{T}, \quad (i = 1, 2, \dots, N). \quad (103)$$

It remains to show that

$$\mathcal{A}_{i0} = - \sum_{k=1}^N \rho_k \mathcal{A}_{ik} \left(\frac{\alpha_{0k}}{\rho_k} - \frac{\alpha_{0i}}{\rho_i} \right), \quad (i = 1, 2, \dots, N). \quad (104)$$

Using (92)–(97) and identities (101) for this, we find

$$\begin{aligned} \sum_{k=1}^N \rho_k \mathcal{A}_{ik} \left(\frac{\alpha_{0k}}{\rho_k} - \frac{\alpha_{0i}}{\rho_i} \right) &= \sum_{k=1}^{N-1} \rho_k \left(\frac{\alpha_{0k}}{\rho_k} - \frac{\alpha_{0i}}{\rho_i} \right) \left[\alpha_N + \sum_{j=1}^{N-1} c_j (\beta_{ji} + \beta_{jk}) - \beta_{ik} \right] + \\ &+ \rho_N \left(\frac{\alpha_{0N}}{\rho_N} - \frac{\alpha_{0i}}{\rho_i} \right) \left(a_N + \sum_{k=1}^{N-1} c_k \beta_{ki} \right) = \sum_{k=1}^{N-1} \alpha_{0k} \left(\sum_{j=1}^{N-1} c_j \beta_{jk} - \beta_{ik} \right) - \\ &\frac{\alpha_{0i}}{c_i} \left(a_N + \sum_{k=1}^{N-1} c_k \beta_{ki} \right) - \sum_{k=1}^{N-1} \frac{c_k}{c_i} \alpha_{0i} \left(\sum_{j=1}^{N-1} c_j \beta_{jk} - \beta_{ik} \right) = \end{aligned}$$

$$= \sum_{k=1}^{N-1} \alpha_{0k} \left(\sum_{j=1}^{N-1} c_j \beta_{jk} - \beta_{ik} \right) = -\mathcal{A}_{i0}. \quad (105)$$

Substituting (104) into (103) and using notation (65) for the thermal diffusion coefficients, we finally find

$$\mathbf{d}_i^{(a)} = \sum_{k=1}^N \frac{\rho_k \rho_i \mathcal{A}_{ik}}{p} (\mathbf{w}_k - \mathbf{w}_j) + \frac{\nabla T}{T} \sum_{k=1}^N \frac{\rho_k \rho_i \mathcal{A}_{ik}}{p} (D_{Tk} - D_{Ti}), \quad (i = 1, 2, \dots, N), \quad (106)$$

which completely coincides for the case of ideal mixtures with the classical Stefan–Maxwell relations [6].

$$\mathbf{d}_i = \sum_{k=1}^N \frac{n_k n_i}{n^2 \mathcal{D}_{ik}} (\mathbf{w}_k - \mathbf{w}_j) + \nabla \ln T \sum_{k=1}^N \frac{n_k n_i}{n^2 \mathcal{D}_{ik}} (D_{Tk} - D_{Ti}), \quad (107)$$

if we identify the binary diffusion coefficients \mathcal{D}_{ik} of the kinetic theory with the expression

$$\mathcal{D}_{ik} = kT / m_i m_k n \mathcal{A}_{ik}. \quad (108)$$

Note that these coefficients are considered independent concentration x_k and there is no need to calculate them from the properties of molecules. You can use the experimental values measured on binary mixtures [7].

As noted above, very convenient parameters of thermodiffusion processes are thermal diffusion ratios k_{Tk} , which we define here through the phenomenological coefficients \mathcal{A}_{k0} by the formula

$$k_{Tk} = \rho_k \mathcal{A}_{k0} / p. \quad (109)$$

Then, by virtue of (97), equality (69) holds. In addition, using transformation (105), as well as definitions (108) and (109), it is easy to obtain the following system of equations

$$\sum_{k=1}^N \frac{n_i n_k}{\mathcal{D}_{ik} n^2} (D_{Ti} - D_{Tk}) = k_{Ti}(\mathbf{x}, t), \quad (i = 1, 2, \dots, N-1), \quad (110)$$

for finding thermal diffusion ratios k_{Ti} through binary diffusion coefficients \mathcal{D}_{ki} and thermal diffusion coefficients D_{Ti} . Thus, the thermal diffusion ratios k_{Tk} introduced earlier by formulas (68) and (69) completely coincide with the coefficients (109).

Finally, using formulas (108) and (110), we rewrite the generalized Stefan–Maxwell relations (103) for non ideal mixtures in the following final form:

$$\sum_{i=1}^N \frac{n_i n_k}{n^2 \mathcal{D}_{ik}} (\mathbf{v}_i - \mathbf{v}_k) - k_{Tk} \nabla \ln T = \mathbf{d}_k^{(a)}, \quad (k = 1, 2, \dots, N), \quad (111)$$

where

$$\mathbf{d}_k^{(a)} \equiv \frac{1}{p} \left\{ \rho_k \frac{d^{(k)} \mathbf{v}_k}{dt} - \nabla \cdot \boldsymbol{\tau}_k - \rho_k \mathbf{f}_k - \frac{1}{2} \sum_{i=1}^N (\Gamma_{ki} - \Gamma_{ik}) (\mathbf{v}_i - \mathbf{v}_k) + \nabla_a p_k \right\}. \quad (112)$$

This form of the Stefan–Maxwell relations, intended for finding the rates of relative diffusion, is most convenient for solving hydrodynamic problems, since the transfer coefficients $\mathcal{D}_{ki}(\mathbf{x}, t)$ and $\mathbf{k}_{Tk}(\mathbf{x}, t)$ have much simpler expressions for practical calculation than the multicomponent diffusion coefficients $D_{ik}(\mathbf{x}, t)$ and thermal diffusion coefficients $D_{Tk}(\mathbf{x}, t)$.

There is an interesting interpretation of the Stefan–Maxwell relation (111) as an equation of motion for a separate component of a non ideal mixture (see, for example, "Note I" in the monograph by Chapman and Cowling [1]). In this case, collisions between the molecules of the k -ith and i -th components lead to a force acting on each substance and tending to eliminate the relative velocity $(\mathbf{v}_i - \mathbf{v}_k)$. Substituting (112) into (111), we obtain

$$\begin{aligned} \rho_k \frac{d^{(k)}\mathbf{v}_k}{dt} = & -\nabla_a p_k + \nabla \cdot \boldsymbol{\tau}_k + \rho_k \mathbf{f}_k + \sum_{i=1}^N \theta_{ik} n_i n_k (\mathbf{v}_i - \mathbf{v}_k) + \\ & + \frac{1}{2} \sum_{i=1}^N (\Gamma_{ki} - \Gamma_{ik}) (\mathbf{v}_i - \mathbf{v}_k) + \mathbf{k} n \mathbf{k}_{Ti} \nabla T, \end{aligned} \quad (113)$$

where $\theta_{ki} = kT / n\mathcal{D}_{ki}$, and the parameter $\theta_{ki}(\mathbf{x}, t)$ (at least roughly) does not depend on the proportions of the mixture [1]; the penultimate term describes the change in the momentum of a component k during chemical reactions.

It should be noted that, in contrast to the analogous equation of motion obtained in the approximation of equal acceleration (when $d^{(k)}\mathbf{v}_k / dt \equiv d\mathbf{v} / dt$) by the methods of kinetic theory in the monograph cited above, system (113) is a system of hydrodynamic equations of a nonideal mixture with genuine inertial forces.

Full heat flux in ideal multi-component environments. From relation (89), taking into account (109), the expression for the reduced heat flux $\mathbf{q}(\mathbf{x}, t)$ follows

$$\mathbf{q} = \mathcal{A}_{00} \boldsymbol{\chi}_0 + \sum_{k=1}^N \mathcal{A}_{0k} \mathbf{J}_k = -\lambda \nabla T + p \sum_{k=1}^N \mathbf{k}_{Tk} \mathbf{w}_k, \quad (114)$$

where by the formula

$$\lambda = \mathcal{A}_{00} / T \quad (115)$$

the so-called true thermal conductivity coefficient was determined, which is related to the previously introduced coefficient by the ratio

$$\lambda = \lambda' - kT \sum_{k=1}^N \mathbf{k}_{Tk} D_{Tk} = \lambda' - kT \sum_{k=1}^N \sum_{j=1}^N \mathbf{k}_{Tk} D_{kj} \mathbf{k}_{Tj}. \quad (116)$$

Indeed, by virtue of (82), (91) and the transformation $\sum_{k=1}^N \alpha_{jk} \mathcal{A}_{k0} = \alpha_{0k}$ easily deduced using formulas (92) and (93), we will have

$$\begin{aligned} \mathcal{A}_{00} \equiv \alpha_{00} - \sum_{j=1}^{N-1} \sum_{k=1}^{N-1} \alpha_{0k} \beta_{kj} \alpha_{0j} &= \alpha_{00} - \sum_{j=1}^{N-1} \sum_{k=1}^{N-1} \alpha_{0k} \beta_{kj} \left[\alpha_{0N} \mathcal{A}_{N0} + \right. \\ &\left. + \sum_{i=1}^{N-1} \alpha_{ji} \mathcal{A}_{i0} \right] = \alpha_{00} - \sum_{k=1}^{N-1} \alpha_{0k} \mathcal{A}_{k0} - \mathcal{A}_{N0} \alpha_{0N} = \alpha_{00} - \sum_{k=1}^N \alpha_{0k} \mathcal{A}_{k0}. \end{aligned} \quad (117)$$

Hence, when using definitions (65), (109) and (115), expression (116) follows.

Thus, the total heat flux in multicomponent media can be written as

$$\mathbf{J}_q = -\lambda \nabla T + p \sum_{k=1}^N k_{Tk} \rho_k^{-1} \mathbf{J}_k + \sum_{k=1}^N h_k \mathbf{J}_k \quad (118)$$

in full agreement with the kinetic theory of gases [3].

Determination of multicomponent diffusion coefficients in terms of binary diffusion coefficients. We now obtain algebraic equations that allow calculating multicomponent diffusion coefficients through binary diffusion coefficients. It is easy to check that the relation

$$\sum_{k=1; k \neq j}^N \mathcal{A}_{kj} (\rho_k \alpha_{ij} - \rho_j \alpha_{ik}) = \rho_i (\delta^{ji} - c_j), \quad (j, i = 1, 2, \dots, N). \quad (119)$$

Indeed, by virtue of (65), (66), (94), and (97), we have

$$\begin{aligned} \sum_{k=1; k \neq j}^N \mathcal{A}_{kj} (\rho_k \alpha_{ij} - \rho_j \alpha_{ik}) &= \sum_{k=1}^N \mathcal{A}_{kj} (\rho_k \alpha_{ij} - \rho_j \alpha_{ik}) = -\rho_j \sum_{k=1}^N \mathcal{A}_{kj} \alpha_{ik} = \\ &= -\rho_j \left(\sum_{k=1}^{N-1} \mathcal{A}_{kj} \alpha_{ik} + \mathcal{A}_{kN} \alpha_{iN} \right) = -\rho_j \left[\sum_{l=1}^{N-1} c_l \left(\sum_{k=1}^{N-1} \beta_{lk} \alpha_{ki} \right) - \sum_{k=1}^{N-1} \beta_{kj} \alpha_{ik} \right] = \\ &= -\rho_j \left(\sum_{k=1}^{N-1} c_k \delta^{ki} - \delta^{ji} \right) = \rho_i (\delta^{ji} - c_j). \end{aligned} \quad (120)$$

When using the notation (66) and (108) for the quantities $\mathcal{A}_{ik} = p/m_i m_k n^2 \mathcal{D}_{ik}$ and $\alpha_{ik} = \rho_i \rho_k D_{ki} / p$, relations (120) can be rewritten in the form of the following equations

$$\sum_{k=1; k \neq j}^N \frac{n_k n_i}{n^2 \mathcal{D}_{ik}} (D_{ji} - D_{ki}) = \delta^{ji} - c_i, \quad (i, j = 1, 2, \dots, N), \quad (121)$$

suitable for determining the multicomponent diffusion coefficients of a mixture D_{ij} ($i, j = 1, 2, \dots, N$) through binary diffusion coefficients \mathcal{D}_{ik} ($i, k = 1, 2, \dots, N$). Equations (121) are linearly dependent (since their summation over leads to identity), therefore, one more equation should be added to them, namely (67⁽²⁾).

Then equations (121) and (67⁽²⁾) can be given the following form:

$$\sum_{\substack{k=1 \\ k \neq i}}^N \left(\frac{n_i n_k}{\mathcal{D}_{ik}} + \sum_{\substack{l=1 \\ l \neq i}}^N \frac{n_i n_l}{\mathcal{D}_{il}} \right) D_{jk} = n^2 (c_i - \delta^{ji}) \quad (i, j = 1, 2, \dots, N), \quad (122)$$

which is very convenient for practical calculations of multicomponent diffusion coefficients $D_{jk}(\mathbf{x}, t)$.

In the particular case of a mixture consisting of three components, equations. (122) allow one to find the following expressions for the coefficients of multicomponent diffusion

$$D_{11} = \frac{n^2}{\rho^2 n_1^2} \left(\frac{n_1 n_3 m_3^2 \mathcal{D}_{23} \mathcal{D}_{31} + n_1 n_2 m_2^2 \mathcal{D}_{12} \mathcal{D}_{23} + (\rho_2 + \rho_3)^2 \mathcal{D}_{12} \mathcal{D}_{31}}{n_1 \mathcal{D}_{23} + n_2 \mathcal{D}_{31} + n_3 \mathcal{D}_{12}} \right), \quad (123)$$

$$D_{12} = \frac{n^2}{\rho^2} \left(\frac{n_3 m_3^2 \mathcal{D}_{23} \mathcal{D}_{31} - m_2 (\rho_1 + \rho_2) \mathcal{D}_{12} \mathcal{D}_{23} - m_1 (\rho_2 + \rho_3) \mathcal{D}_{31} \mathcal{D}_{11}}{n_1 \mathcal{D}_{32} + n_2 \mathcal{D}_{31} + n_3 \mathcal{D}_{12}} \right). \quad (124)$$

Expressions for the remaining coefficients can be obtained from (123) and (124) using the appropriate permutation of the indices.

It should be noted that relations of the type (111), (119), and (121) were first obtained in the kinetic theory of gases of monatomic gases in the first approximation of the Chapman–Enskog method in the well-known work [21]. Here, their phenomenological conclusion is given, and thus the universal character of this kind of relations is established.

CONCLUSION

We have already noted that in the literature, when determining the internal energy balance equation, they usually proceed from the law of conservation of the total energy of the mixture. This is apparently due to the fact that the balance equations for mechanical energy are usually derived earlier; and thus, it is possible to derive the equation for the balance of internal energy, using only them. In other words, until recently, the literature was limited to mechanical balance equations for energy quantities containing only the kinetic energy of the center of mass $\frac{1}{2} \rho \mathbf{v}^2$ and not including the kinetic energy of diffusion.

At the same time, the balance equations for the total specific kinetic energy of the system $\frac{1}{2} \sum_k \rho_k |\mathbf{v}_k|^2$ can be written directly only when it can be derived from the balance equations for the total momentum of the system. However, such a direct conclusion was not known until recently. In this work, we managed to overcome this difficulty and, as a result, obtain the correct balance equation for the correct value of the local internal energy for multicomponent systems. Taking this equation into account, the generalized Stefan – Maxwell relations were thermodynamically derived, which are, in fact, a system of hydrodynamic equations of a mixture with genuine inertial forces. In addition, it was possible to obtain thermodynamically a number of algebraic relations for the transfer coefficients, connecting, in particular, the thermal diffusion relations with the coefficients of thermal diffusion and multicomponent diffusion, true and partial

coefficients of thermal conductivity, multicomponent and binary diffusion coefficients, which indicates their universal character. The results obtained are intended for modeling liquid multicomponent non-ideal media, as well as gas-dust mixtures with a finely dispersed dust component.

REFERENCES

- [1] S. Chapman, T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases*. Cambridge (1939).
- [2] D. Hirschfelder, C. Curtiss and R. Bird, *Molecular Theory of Gases and Liquids*. John Wiley and Sons, New York and London (1954).
- [3] J. Ferziger, H. Kaper, *Mathematical Theory of Transport Processes in Gases*. North-Holland, Amsterdam (1972)
- [4] I. Prigogin, D. Kondepudi, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*. Wiley Inter Science, New York (1998).
- [5] M.Ya. Marov, A.V. Kolesnichenko, *Turbulence and Self-Organization. Modeling Astrophysical Objects*. Springer, New York-Heidelberg-Dordrecht-London (2013).
- [6] A.V. Kolesnichenko. *Continuous models of natural and space environments. Problems of thermodynamic design*, Lenand, Moscow (2017) (in Russian).
- [7] D.A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics*. Nauka, Moscow (1987) (in Russian).
- [8] S.R. de Groot, *Thermodynamics of Irreversible Processes*, Amsterdam (1951).
- [9] J. Meixner, H.G. Reik, *Thermodynamik der irreversiblen Prozesse. Handbuch der Physik, Bd. 3, T I. 2*, Berlin-Göttingen-Heidelberg (1959).
- [10] S.R. de Groot, P. Mazur, *Non-equilibrium Thermodynamics*. Amsterdam (1962). [11] E. Oran, J. Boris, *Numerical Simulation of Reactive Flow*. Cambridge University, Cambridge (2001).
- [12] L.I. Sedov, *Introduction to Continuum Mechanics*. Fizmatlit, Moscow (1962) (in Russian)
- [13] R. Haase, *Thermodynamik der irreversiblen Prozesse*, Darmstadt (1963).
- [14] I. Gyarmati, *Non-Equilibrium Thermodynamics. Field Theory and Variational Principles*, Springer-Verlag-Berlin-Heidelberg-New York (1970).
- [15] D.D. Pitts, *Nonequilibrium Thermodynamics*. New York - Toronto - London (1962).
- [16] A.V. Kolesnichenko, “Informational-thermodynamic conception of processes formation of self-organization in open systems under influence of external environment” *Math. Montis.*, **35**, 80-106, (2016).
- [17] P. Glansdorff and I. Prigogine, *Thermodynamic theory of structure, stability and fluctuations*. John Wiley & Sons, Ltd. London-New York-Sydney-Toronto (1971).
- [18] V.I. Mazhukin, A.V. Shapranov, V.E. Perezhigin, “Mathematical modeling of thermo-physical properties, heating and melting processes of metal with the molecular dynamics Method”, *Math. Montis.*, **24**, 47-66, (2012).

- [19] C. Truesdell, *Rational Thermodynamics*. Springer, New York. (1984).
- [20] I. Prigogine, R. Defay, *Chemical Thermodynamics*. Longmans Green and Co., London -New-York-Toronto (1954).
- [21] C.F. Curtiss, "Symmetric gaseous diffusion coefficients" *J. Chem. Phys.*, **49**, 2917-2919 (1968)

Received, December 8, 2021