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Recommended form of bibliographic references: Kolesnichenko A.V. Derivation by methods of thermodynamics irreversible processes of generalized Stefan−Maxwell relations for multicomponent diffusion flows in turbulent continuous medium // Keldysh Institute Preprints. 2015. No. 2. 40 p. URL: http://library.keldysh.ru/preprint.asp?id=2015-2&lg=e

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Derivation by methods of thermodynamics irreversible processes of generalized Stefan–Maxwell relations for multicomponent diffusion flows in turbulent continuous medium

Moscow — 2015

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Вывод методами термодинамики необратимых процессов обобщённых соотношений Стефана–Максвелла для потоков многокомпонентной диффузии в турбулентной сплошной среде.

В рамках феноменологической теории турбулентности сжимаемого многокомпонентного газового континуума рассмотрен термодинамический подход к проблеме замыкания осреднённых гидродинамических уравнений смеси на уровне моделей первого порядка. Онзагеровский формализм неравновесной термодинамики позволяет получить наиболее общую структуру замыкающих соотношений для турбулентных потоков диффузии и турбулентного потока тепла в многокомпонентной газовой смеси, в частности, в виде обобщённых соотношений Стефана–Максвелла для турбулентных потоков диффузии и соответствующего им выражения для турбулентного потока тепла. В качестве примера рассмотрен детальный вывод этих соотношений для развитой мелкомасштабной турбулентности, когда в потоке наблюдается тенденция к установлению локальной статистической изотропности. На рассматриваемом уровне замыкания полученные определяющие соотношения «силы через потоки» наиболее полно описывают турбулентный массо- и теплоперенос в многокомпонентной газовой смеси.

Ключевые слова: необратимая термодинамика, многокомпонентная сплошная среда, развитая турбулентность, модели замыкания первого порядка.

Aleksander Kolesnichenko

Derivation by methods of thermodynamics irreversible processes of generalized Stefan–Maxwell relations for multicomponent diffusion flows in turbulent continuous medium.

Within the framework of the phenomenological theory of turbulence of compressible chemically active gas continuum the thermodynamic approach to the problem of closure of hydrodynamic equations of average motion of a mixture at the level of the first-order models is considered. The Onzager formalism of nonequilibrum thermodynamics allows to obtain the most common structure of rheological relations for turbulent flows of diffusion and turbulent flow of heat in a multicomponent mixture, in particular, in the form of the generalized Stefan–Maxwell relations for turbulent flows of milticomponent diffusion. As an example, the detailed derivation of similar relations for a small-scale turbulence is considered, when the tendency to establishment of a local statistical isotropy in a flow is observed. On the considered level closing closure obtained defining relations of "forces through flows" most fully describe the turbulent heat- and mass transfer in multicomponent gas mixture

Key words: irreversible thermodynamics, multicomponent continuum, developed turbulence, model circuit of the first order**.**

Introduction

In theoretical construction of models of developed turbulence of multicomponenet chemically active gas medium the closure of system of averaged equations of hydrodynamics of a mixture [12] requires additional linear relations, i.e. so-called constitutive (rheological) relations, which associate the turbulent flows of diffusion $\mathrm{J}^{turb}_{\alpha j}(\mathrm{x}_j, t) \equiv \bar{\rho}\langle z''_\alpha u''_j \rangle$ $(\alpha = 1, 2, ..., N)$ and heat $\mathrm{q}^{turb}_j(\mathrm{x}_j, t) \equiv \bar{\rho}\langle H'' u'' \rangle$, the tensor of Reynolds' stresses $\mathrm{R}_{ij}(\mathrm{x}_j, t) \equiv -\bar{\rho}\langle u''_i u''_j \rangle$ as well as the averaged rates of chemical reactions $\bar{\xi}_s$, with the gradients of averaged hydrodymanical parameters. If we estimate the state of the first-order closure problem as whole, we should recognize that at present, in fact, there is no general phenomenological theory of turbulent conductivity and turbulent diffusion for multicomponent mixtures [11, 18, 22, 23, 26]. The gradient relations existing in the literature (see [13] for example) are not general enough and were obtained, mainly, either for turbulent flows with a prominent dominating direction [1], or under strong (and not always justified) assumptions, such as, for instance, the equality of mixture ways for processes of turbulent transport of momentum, heat and mass of various substances [11], [13].

Some problems of motion of multicomponent gas mixtures in the atmosphere, for which the processes of convective and diffusive turbulence transport are important, were analyzed in monograph [12]. These problems can be solved by means of second-order models, in which the model differential equations for second correlation moments are considered and some mechanisms responsible for generation of these moments are taken into account accurately enough. However, the system of equations for second-order moments is not closed and must be supplemented by one or several equations for average characteristics of turbulent motion, which are to some extent equivalent to a three-dimensional scale of turbulence L. In such an approach the additional model expressions for some higher-order terms in these equations are required. However, the approximation expressions used for these purposes (i.e. gradient relations with some proportionality constants universal for this class of problems) often are not accurate enough. This finally leads to the situation, when the appropriate second-order models, in spite of their mathematic complexity, occur to be not better than more simple first-order models.

In this connection, the given work presents the phenomenological approach to the problem of closure of Favre-averaged hydrodynamic equations of multicomponent mixture for a developed turbulent motion at the level of first-order moments. This approach allows, in particular, to describe more completely (with using non-equilibrium thermodynamics methods) the processes of turbulent heat- and mass-transport in a similar medium and to obtain more general rheological relations for turbulent flows of diffusion, heat and momentum as compared to those derived, for example, in well-known monographs [11, 13] by the standard method with using the notion of mixture way. In this case the balance semi-empirical equations for second-order correlation moments of structural parameters pulsating in a flux (derived with using the mean-weighted Favre averaging in [8]) may be considered for the purpose of modeling the turbulent exchange coefficients appeared in rheological relations obtained above (see [2, 12]).

1. Balance equations for enthropy in a turbulent flow of the multicomponent gas mixture

Prior to applying the non-equilibrium continuum thermodynamics formalism for description of processes of heat- and mass-transport in a turbulent flow of the multicomponent mixture, we shall briefly discuss the essence of those principal postulates, which underlie this theory and can be practically used in thermodynamic analysis of any irreversible process, including those for turbulent continuum.

1.1. The Onzager principle

As known [3, 4], in the linear non-equilibrium thermodynamics the phenomenological relations of irreversible processes (*the Onzager relations*) are used as basic relations, which supplement the system of hydrodynamic equations of conservation. These relations are as follows:

$$\Im_k(\mathrm{x}_j,t)=\sum_{k=1}^{f}L_{kl}(\mathrm{x}_j,t)\mathrm{X}_l(\mathrm{x}_j,t), \qquad (k=1,2,\ldots,f), \quad (1.1)$$

where f is the number of independent physical processes, $L_{kl}(\mathrm{x}_j,t)$ is the martix of phenomenological (kinetic) coefficients, which interrelate the flows $\mathfrak{I}_k(\mathrm{x}_j,t)$ and thermo-dynamic forces $\mathrm{X}_l(\mathrm{x}_j,t)$. The formers correspond to the rates of variation of extensive quantities (such as mass, energy), for which the conservation laws exist), or transportable quantities (such as heat) associated with the flows in conservation laws. The second ones are proportional to gradients of intensive parameters which deviate the thermodynamic system from the equilibrium. The flows and thermodynamic forces in (1.1) are, in the general case, tensor quantities of any rank. Within the phenomenological theory framework the explicit form of kinetic coefficients in (1.1) is not deciphered; however, their physical meaning (for example, for a mixture of single-atomic gases) can be clarified within the framework of the kinetic theory of gases [12, 19]. The number of non-zero kinetic coefficients in (1.1) is limited by the *Curie principle* [3], according to which, in virtue of symmetry properties of the material medium under consideration, the components of flows do not depend on all components of thermodynamic forces. So, in the particular case of isotropic system (whose properties are the same in all directions at the equilibrium state) the processes of different tensor dimensionality do not interact with each other. Besides, in the axiomatic approach the *Onzager–Kazimir relations* of symmetry (*the mutuality principle*) are used as an independent postulate,

$$L_{kl}(\mathbf{B},\mathbf{\Omega})=\varepsilon_k\varepsilon_l L_{kl}(-\mathbf{B},-\mathbf{\Omega}), \qquad (k,l=1,2,\ldots,f). \tag{1.2}$$

These relations allow to minimize the number of phenomenological coefficients in linear relations (1.1) [3]. Here $\mathbf{B}(\mathrm{x}_j,t)$ is the magnetic induction, $\mathbf{\Omega}$ is the angular velocity of system rotation, $\varepsilon_l=1$ for even (energy, concentrations) and $\varepsilon_k=-1$ – for odd (momentum density) macroscopic parameters (even or odd functions of particles' velocities). For an isotropic, non-rotating system in the absence of an outer magnetic field the symmetry relations (1.2) take a more simple form [3, 4]:

$$L_{kl}=\varepsilon_k\varepsilon_l L_{lk}, \qquad (k,l=1,2,\ldots,f), \tag{1.3}$$

where L_{kl} are scalar quantities. The symmetry relations (1.2) may be considered to be an empirically stable axiom regardless of their proof within the statistic mechanics framework [25]. According to Meison [24], the experimental confirmation of the mutuality principle is so convincing, as the confirmation of the 1st, 2nd and 3rd principles of thermodynamics. This gives a reason to raise postulate (1.2) to the paradigm status and to use it as a basis for describing a wide circle of phenomena.

For determination of flows and thermodynamic forces conjugated with them one usually applies the specific presentation of the rate of production (of source density) $\sigma_{(S)}(\mathrm{x}_j,t)$ of entropy $S(\mathrm{x}_j,t)$ inside the system in the irreversible process under consideration as a bilinear form

$$\sigma_{(S)}(\mathrm{x}_j,t)=\sum_{k=1}^{f}\Im_k\,\mathrm{X}_k\geq 0. \qquad (1.4)$$

In this case, when the flows $\Im_k(\mathrm{x}_j,t)$ are determined, the conjugated forces $\mathrm{X}_l(\mathrm{x}_j,t)$ are found uniquelly as the coefficients at appropriate flows in this expression.

To decipher the formula for the entropy source density (1.4) within the phenomenological theory framework it is necessary to obtain in the explicit form the equation for evolution of a specific entropy $S(\mathrm{x}_j,t)$ of the system

$$\rho\frac{d}{dt}S\equiv\frac{\partial}{\partial t}\left(\rho S\right)+\frac{\partial}{\partial \mathrm{x}_j}\left(\rho S u_j\right)=-\frac{\partial}{\partial \mathrm{x}_j}\mathrm{J}_{(S)j}+\sigma_{(S)},\quad (\sigma_{(S)}\geq 0), \qquad (1.5)$$

in which $\mathrm{J}_{(S)j}(\mathrm{x}_j,t)$ are components of the vector of substantional entropy flow density, and the divergence $\partial\mathrm{J}_{(S)j}/\partial\mathrm{x}_j$ describes the reversible heat exchange between the system being considered and the external medium.

Equation (1.5) can be obtained with regard to balance equations for specific volume $v(\mathrm{x}_j,t)$ $(\equiv 1/\rho)$, specific concentrations of chemical components $z_\alpha(\mathrm{x}_j,t)\equiv n_\alpha/\rho$ and specific internal energy of a mixture $E(\mathrm{x}_j,t)$ from the *Gibbs identity* for these quantities, written along the trajectory of motion of physical unit volume's center of masses:

$$T\frac{d}{dt}S=\frac{d}{dt}E+p\frac{d}{dt}\left(\frac{1}{\rho}\right)-\sum_{\alpha=1}^{N}\mu_\alpha\frac{d}{dt}\left(\frac{n_\alpha}{\rho}\right) \qquad (1.6)$$

Here $\mu_\alpha(x_j,t)$ is the chemical potential of component α calculated for one particle of substance, $\mu_\alpha = h_\alpha - Ts_\alpha$, [16]; $h_\alpha(x_j,t)$, $s_\alpha(x_j,t)$ are, respectively, the partial enthalpy and the partial entropy α of a component. We also note that a widely used expression for *Gibbs' specific free energy* (specific thermodynamic potential) follows from:

$$G = \sum_{\alpha=1}^{N} z_\alpha \mu_\alpha = E + pv - TS = H - TS, \tag{1.7}$$

in which

$$E = \sum_{\alpha=1}^{N} z_\alpha e_\alpha, \quad H = \sum_{\alpha=1}^{N} z_\alpha h_\alpha, \quad v \equiv 1/\rho = \sum_{\alpha=1}^{N} z_\alpha v_\alpha, \quad S = \sum_{\alpha=1}^{N} z_\alpha s_\alpha . \tag{1.8}$$

For the mixture of perfect gases obeying the state equation $p = k_B \rho T \sum_{\alpha=1}^{N} z_\alpha$ we have: $v = (k_B T/p) \sum_{\beta=1}^{N} z_\beta$, wherefrom $v_\beta = k_B T/p = 1/n$ (here k_B is the Boltzmann constant) [16].

The derivation and analysis of the explicit form of equation (1.5) for turbulent motion of a multicomponent gas mixture will be considered below.

With regard to the applicability of the Gibbs identity within the non-equilibrium theory framework we note the following. According to the quasilocal equilibrium principle (the basic postulate of non-equilibrium thermodynamics) the whole system can be broken into sufficiently small macroscopic regions, every of which may be considered as an equilibrium (more correctly, quasi-equilibrium) thermodynamic system. In the event, if the specific density of internal energy $E(x_j,t)$, the specific volume $v(x_j,t)$ and specific concentrations $z_\alpha(x_j,t)$ $(\alpha = 1,2,...,N)$ of various chemical components are chosen as characteristic variables, then the thermodynamic state of a physically unit volume in the vicinity of point x_1, x_2, x_3 at time moment t is described by specific entropy $S(x_j,t) = S\left(E,\ v,\ z_1,...,\ z_N\right)$, for which the Gibbs identity (1.6) is valid. Based on this identity the conjugated quantities

$$1/T \equiv \left(\frac{\partial S}{\partial E}\right)_{v,\{z_\alpha\}}, \quad p/T \equiv \left(\frac{\partial S}{\partial v}\right)_{E,\{z_\alpha\}}, \quad -\mu_\alpha/T \equiv \left(\frac{\partial}{\partial z_\alpha}\right)_{E,v,\{z_\beta \neq z_\alpha\}} \quad (\alpha = 1,2,...,N)$$

can be supposed to have a meaning of the local temperature $T(x_j, t)$, local pressure $p(x_j, t)$ and local chemical potentials $\mu_\alpha(x_j, t)$ of components α $(\alpha = 1, 2, \ldots, N)$. Within the framework of phenomenological approach the applicability region of a local thermodynamical equilibrium postulate is determined experimentally. Usually, this postulate is valid, if dissipative processes in a system play essential part and exclude the appearance of high gradients of characteristic variables.

One should note that the hypothesis on the local equilibrium is equivalent to the supposition, that not only the *Gibbs relation*, but all remaining thermostatic relations for infinitely small regions of non-equilibrium systems are valid. So, for example, the existence of specific thermodynamic potential (1.7) and the validity of the well-known relation $dG = -SdT - vdp + \sum_{\beta=1}^{N} \mu_\beta dz_\beta$, are allowed. Using (1.6) one can obtain from the latter relation the Gibbs–Dugem equation

$$\rho \sum_{\alpha=1}^{N} z_\alpha d\mu_\alpha = -\rho S dT + dp,$$

that is of fundamental significance for the thermodynamics of multicomponent systems.

So, the basic statements, which are assumed to be independent postulates in practical application of a linear non-equilibrium thermodynamics to any irreversible process, are reduced to the following ones:

- The quasi-local thermodynamic equilibrium principle is valid.
- For the entropy production, associated with irreversible processes in a system itself, the inequality $\sigma_{(S)} \geq 0$, that expresses the second principle of thermodynamics, is valid.
- If the analysis is restricted by a linear region, then the phenomenological relations (1.1) for flows and thermodynamic processes, appeared in expression (1.4) for entropy production, are valid.
- There exist the symmetry relations (1.2) for kinetic coefficients appeared in the linear laws (1.1).

1.2. The general form of evolution equation for a weighted average entropy

Now we pass to thermodynamic consideration of turbulent transport processes in a multicomponent mixture. Various methods of averaging physical quantities (time averaging, spatial averaging, statistical averaging over the ensemble of possible realizations, etc.), used in mixture turbulence theories, were analyzed in papers [7, 8]. In classical theories of homogeneous incompressible fluids turbulence, which have been developed rather completely till now, the averaging has usually been introduced in any similar manner and, as a rule, without weighting coefficients – for all hydrodynamic parameters without exception. However, in the case of a multicomponent turbulized continuum with variable density ρ this similar averaging for all variables leads not only to cumbersome hydrodynamic equations of the average motion, but to difficulties in physical interpretation of each individual term in such equations. By this reason, in [7, 8] in the development of a turbulence model for a chemically active gas flow the authors have used , along with the «usual» average value $\overline{\mathcal{A}}(\mathrm{x}_j,t)$ of some pulsating quantity $\mathcal{A}(\mathrm{x}_j,t)$, the so-called weighted average value of this quantity (*the Favre average*), which is specified, for example, by relation

$$\langle\mathcal{A}\rangle(\mathrm{x}_j,t)\equiv\overline{\rho\mathcal{A}(\mathrm{x}_j,t)}/\bar{\rho}=\left(\lim_{M\to\infty}\frac{1}{M}\sum_{p=1}^{M}\rho^{(p)}\mathcal{A}^{(p)}\right)\Big/\left(\lim_{M\to\infty}\frac{1}{M}\sum_{p=1}^{M}\rho^{(p)}\right), \qquad (1.9)$$

where summation is carried out over a set of relizations, and the corresponding average field of $\overline{\mathcal{A}}$ is determined as expected value of $\mathcal{A}$ for an ensemble of similar systems; and in this case: $\mathcal{A}=\overline{\mathcal{A}}+\mathcal{A}'$, $(\overline{\mathcal{A}'}=0)$, $\mathcal{A}=\langle\mathcal{A}\rangle+\mathcal{A}''$, $(\langle\mathcal{A}''\rangle=0,\ \overline{\mathcal{A}''}\neq 0)$; $\mathcal{A}'$, $\mathcal{A}''$ are corresponding turbulent pulsations.

The thermodynamic derivation of rheological relations for a turbulent medium will be carried out under supposition, that one-point correlation terms $\langle\mathcal{A}''\mathcal{B}''\rangle$ for any (but not equal to hydrodynamic velocity u_j) parameters $\mathcal{A}$ and $\mathcal{B}$, pulsating in a flow, are small as compared to first-order terms $\langle\mathcal{A}\rangle\langle\mathcal{B}\rangle$ and can be omitted [8, 12]:

$$\frac{\langle \mathcal{A}''\mathcal{B}''\rangle}{\langle \mathcal{A}\rangle\langle \mathcal{B}\rangle} << 1, \quad (\mathcal{A} \neq u_j,\ \mathcal{B} \neq u_j). \tag{1.10}$$

The presentation of a turbulized multicomponent continuum in form of thermodynamic complex consisting of two subsystems – the pulsation motion (*turbulent chaos*) subsystem and the average motion (averaged molecular chaos) subsystem [14, 15], allows then to obtain necessary expressions for turbulent flows of diffusion, heat and for the tensor of turbulent stresses, which generalize corresponding results of the homogeneous turbulized fluid hydrodynamics to the case of turbulized mixtures.

The balance equation for a weighted average specific entropy $\langle S\rangle \equiv \overline{\rho S}/\bar{\rho}$ of turbulized multicomponent mixture will be obtained by Favre averaging [21] of the evolution equation (1.5) for an instantaneous value of (pulsating in a flow) parameter S:

$$\bar{\rho}\frac{D\langle S\rangle}{Dt} \equiv \frac{\partial}{\partial t}\left(\bar{\rho}\langle S\rangle\right) + \frac{\partial}{\partial \mathrm{x}_j}\left(\bar{\rho}\langle S\rangle\langle u_j\rangle\right) = -\frac{\partial}{\partial \mathrm{x}_j}\left(\overline{\mathrm{J}_{(S)j}} + \mathrm{J}^{turb}_{\langle S\rangle j}\right) + \sigma_{\langle S\rangle}. \tag{1.11}$$

Here $\sigma_{\langle S\rangle}(\mathrm{x}_j,t) \equiv \bar{\sigma}_{(S)}$ is the local production of averaged entropy of a mixture, i.e. the appearance of quantity $\langle S\rangle(\mathrm{x}_j,t)$ per time unit in a medium volume unit; $\overline{\mathrm{J}_{(S)j}}(\mathrm{x}_j,t)$ and $\mathrm{J}^{turb}_{\langle S\rangle j}(\mathrm{x}_j,t) \equiv \overline{\rho S'' u''_j}$) are, respectively, the averaged substational density of a regular (molecular) flow of a mixture entropy and the density of a turbulent flow of the entropy of an averaged turbulent chaos subsystem; $D(..)/Dt \equiv \partial(..)/\partial t + \langle u_j\rangle \partial(..)/\partial \mathrm{x}_j$ is the substantional derivative for the average motion of a medium.

For obtaining (deciphering) the explicit form of expressions for mean values $\mathrm{J}^{turb}_{\langle S\rangle j}$, $\overline{\mathrm{J}_{(S)j}}$ and $\sigma_{\langle S\rangle}$ in (1.11) one of two techniques can be applied: either to average (over the ensemble of possible realizations) their corresponding instantaneous analogues, or to compare the averaged equation (1.11) with that equation, which is obtained from the averaged Gibbs identity with excluding from it corresponding substantional derivatives of mean parameters of the medium state $\langle v\rangle(\mathrm{x}_j,t)$, $\langle z_\alpha\rangle(\mathrm{x}_j,t)$ and $\langle E\rangle(\mathrm{x}_j,t)$. We shall use the latter technique here.

The averaged Gibbs identity. The averaging of the fundamental Gibbs identity (1.6) (written along the trajectory of motion of physical unit volume's center of masses), which is valid for micro-motions of a mixture, leads the following equation for weighted average entropy $\langle S\rangle(\mathrm{x}_j,t)$ and specific internal energy $\langle E\rangle(\mathrm{x}_j,t)$ of the mixture

$$\bar\rho\langle T\rangle\frac{D\langle S\rangle}{Dt}=\bar\rho\frac{D\langle E\rangle}{Dt}+\bar\rho\,\bar p\frac{D\langle v\rangle}{Dt}-\bar\rho\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\frac{D\langle z_\alpha\rangle}{Dt}+\mathbb{Q}. \qquad (1.12)$$

Here the following designation is introduced:

$$\mathbb{Q}\equiv-\overline{T''\rho\frac{dS}{dt}}-\langle T\rangle\frac{\partial}{\partial \mathrm{x}_j}\left(\overline{\rho S''u''_j}\right)+\frac{\partial}{\partial \mathrm{x}_j}\left(\overline{\rho E''u''_j}\right)+\overline{p\frac{\partial u''_j}{\partial \mathrm{x}_j}}-$$

$$-\sum_{\alpha=1}^{N}\overline{\mu''_\alpha\rho\frac{dz_\alpha}{dt}}-\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\frac{\partial}{\partial \mathrm{x}_j}\left(\overline{\rho z''_\alpha u''_j}\right). \qquad (1.13)$$

One can show that if for averaged values of thermodynamic parameters the same thermodynamic relations are valid, as for corresponding instantaneous values for micro-motions (and this takes place when condition (1.10) is met), and, in particular, the following basic thermodynamic identities are valid:

$$\langle G\rangle(\mathrm{x}_j,t)\equiv\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\langle z_\alpha\rangle=\langle E\rangle+\bar p\langle v\rangle-\langle T\rangle\langle S\rangle, \qquad (^1)$$

$$\langle S\rangle\delta\langle T\rangle+\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\delta\langle z_\alpha\rangle=\delta\langle E\rangle+\bar p\,\delta\langle v\rangle, \qquad (^2) \qquad (1.14)$$

(here δ is the increment symbol), then quantity $\Delta\equiv 0$, i.e. the fundamental Gibbs identity in a substantional form takes place for the averaged molecular chaos subsystem as well [7].

Indeed, averaging the identity

$$\delta(\rho\mathcal{A}E)-T\delta(\rho\mathcal{A}S)+p\,\delta\mathcal{A}-\sum_{\alpha=1}^{N}\mu_\alpha\delta(\rho\mathcal{A}z_\alpha)\equiv 0,$$

which is valid for any field quantity $\mathcal{A}(\mathrm{x}_j,t)$, over the ensemble of possible realizations, we shall have

$$0=\delta\left(\bar{\rho}\langle\mathcal{A}\rangle\langle E\rangle\right)-\langle T\rangle\delta\left(\bar{\rho}\langle\mathcal{A}\rangle\langle S\rangle\right)+\bar{p}\delta\langle\mathcal{A}\rangle-\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\delta\left(\bar{\rho}\langle\mathcal{A}\rangle\langle z_\alpha\rangle\right)=$$

$$=-\delta\left(\overline{\rho\mathcal{A}''E''}\right)+\langle T\rangle\delta\left(\overline{\rho\mathcal{A}''S}\right)+\overline{T''\delta\left(\rho S\mathcal{A}\right)}-\overline{p\delta\mathcal{A}''}+$$

$$+\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\delta\left(\overline{\rho z''_\alpha\mathcal{A}''}\right)+\sum_{\alpha=1}^{N}\overline{\mu''_\alpha\delta\left(\rho z_\alpha\mathcal{A}\right)}, \tag{1.15}$$

where, in virtue of assumption (1.14), the left-hand side of this equality is zero for any $\mathcal{A}(x_j,t)$. Letting in (1.15) successively $\mathcal{A}=1$ and $\mathcal{A}=u_j(x_j,t)$, we obtain, respectively, the following two identities:

$$\overline{T''\frac{\partial(\rho S)}{\partial t}}+\sum_{\alpha=1}^{N}\overline{\mu''_\alpha\frac{\partial(\rho z_\alpha)}{\partial t}}=0\ , \tag{^{1}}$$

$$-\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\overline{\frac{\partial}{\partial x_j}(\rho Z''_\alpha u''_j)}+\overline{\frac{\partial}{\partial x_j}(\rho E''u''_j)}-\langle T\rangle\overline{\frac{\partial}{\partial x_j}(\rho S''u''_j)}-$$

$$-\overline{T''\frac{\partial}{\partial x_j}(\rho S u''_j)}+\overline{p\frac{\partial u''_j}{\partial x_j}}-\sum_{\alpha=1}^{N}\overline{\mu''_\alpha\frac{\partial}{\partial x_j}(\rho z_\alpha u_j)}=0\ , \qquad (^2),$$

from which one can easily see that the identity $\mathbb{Q}\equiv 0.$ is just valid.

Formula for weighted average entropy production. Now we exclude substantional time derivatives from the right-hand side of averaged Gibbs' relation (1.12) by means of hyperbolic-type equations for determining the parameters of a medium $\langle v\rangle(x_j,t)$, $\langle z_\alpha\rangle(x_j,t)$ $(\alpha=1,2,\ldots,N)$ and $\langle E\rangle(x_j,t)$ (obtained, for example, in [10, 12]):

$$\bar{\rho}\frac{D}{Dt}\langle v\rangle=\frac{\partial\langle u_j\rangle}{\partial x_j}\ , \tag{1.16}$$

$$\bar{\rho}\frac{D}{Dt}\langle z_\alpha\rangle=-\frac{\partial}{\partial x_j}\left(\bar{J}_{\alpha j}+J^{turb}_{\alpha j}\right)+\sum_{s=1}^{r}\nu_{\alpha s}\bar{\xi}_s,\quad(\alpha=1,2,\ldots,N), \tag{1.17}$$

$$\bar{\rho}\frac{D}{Dt}\langle E\rangle=-\frac{\partial}{\partial x_j}\left(\overline{q_j}+q^{turb}_j-\overline{p'u''_j}\right)-\bar{p}\frac{\partial\langle u_j\rangle}{\partial x_j}+\bar{\tau}_{ij}\frac{\partial\langle u_i\rangle}{\partial x_j}+$$

$$+\sum_{\alpha=1}^{N}\overline{\mathrm{J}_{\alpha j}}\,\mathrm{F}_{\alpha j}-\overline{p'\frac{\partial u''_i}{\partial \mathrm{x}_i}}+\mathrm{J}_{v_j}^{turb}\frac{\partial \overline{p}}{\partial \mathrm{x}_j}+\overline{\rho}\langle\varepsilon_b\rangle, \qquad (1.18)$$

where $\mathrm{J}_{(v)j}^{turb}(\mathrm{x}_j,t))\equiv\overline{\rho v''\,u''_j}$, $\mathrm{J}_{\alpha j}^{turb}(\mathrm{x}_j,t)\equiv\overline{\rho z''_\alpha\,u''_j}$, $\mathrm{q}_j^{turb}(\mathrm{x}_j,t)\equiv\overline{\rho H'' u''_j}$ are, respectively, turbulent flows of specific volume, diffusion and heat, $\langle\varepsilon_b\rangle\equiv\overline{\tau_{ij}\partial u''_i/\partial \mathrm{x}_j}/\overline{\rho}$ is the average specific rate of turbulent kinetic energy dissipation into heat under an effect of molecular viscosity. As a result, we obtain the explicit form of substantional balance of weighted average entropy $\langle S\rangle(\mathrm{x}_j,t)$ for a subsystem of averaged motion of a turbulent multicomponent continuum

$$\overline{\rho}\langle T\rangle\frac{D\langle S\rangle}{Dt}=-\frac{\partial}{\partial x_j}\left(\overline{\mathrm{q}}_j+\mathrm{q}_j^{turb}-\overline{p'u''_j}\right)+\overline{\tau}_{ij}\frac{\partial\langle u_i\rangle}{\partial x_j}-\overline{p'\frac{\partial u''_j}{\partial x_j}}+\mathrm{J}_{(v)j}^{turb}\frac{\partial\overline{p}}{\partial x_j}+$$

$$+\sum_{\alpha=1}^{N}\overline{\mathrm{J}}_{\alpha j}\,\mathrm{F}_{\alpha j}-\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\frac{\partial}{\partial x_j}(\overline{\mathrm{J}}_{\alpha j}+\mathrm{J}_{\alpha j}^{turb})+\sum_{s=1}^{r}\langle A_s\rangle\overline{\xi}_s+\overline{\rho}\langle\varepsilon_b\rangle. \qquad (1.19)$$

Here, the averaged chemical affinities $\langle A_s\rangle(\mathrm{x}_j,t)$ of reactions "s" in a turbulized medium are introduced by means of relations

$$\langle A_s\rangle(\mathrm{x}_j,t)\equiv-\sum_{\alpha=1}^{N}\nu_{\alpha s}\langle\mu_\alpha\rangle, \quad (s=1,2,\ldots,r). \qquad (1.20)$$

Equation (1.19) by means of simple transformations

$$\frac{1}{\langle T\rangle}\frac{\partial \mathrm{q}_j^{\Sigma}}{\partial x_j}=\frac{\partial}{\partial x_j}\left(\frac{\mathrm{q}_j^{\Sigma}}{\langle T\rangle}\right)-\mathrm{q}_j^{\Sigma}\frac{\partial}{\partial x_j}\left(\frac{1}{\langle T\rangle}\right)=\frac{\partial}{\partial x_j}\left(\frac{\mathrm{q}_j^{\Sigma}}{\langle T\rangle}\right)+\frac{\mathrm{q}_j^{\Sigma}}{\langle T\rangle^2}\frac{\partial\langle T\rangle}{\partial x_j},$$

$$\frac{\langle\mu_\alpha\rangle}{\langle T\rangle}\frac{\partial \mathrm{J}_{\alpha j}^{\Sigma}}{\partial x_j}=\frac{\partial}{\partial x_j}\left(\frac{\langle\mu_\alpha\rangle\mathrm{J}_{\alpha j}^{\Sigma}}{\langle T\rangle}\right)-\mathrm{J}_{\alpha j}^{\Sigma}\frac{\partial}{\partial x_j}\left(\frac{\langle\mu_\alpha\rangle}{\langle T\rangle}\right),$$

where

$$\mathrm{q}_j^{\Sigma}\equiv\overline{\mathrm{q}}_j+\tilde{\mathrm{q}}_j^{turb}, \quad \tilde{\mathrm{q}}_j^{turb}\equiv\mathrm{q}_j^{turb}-\overline{p'u''_j}, \quad \mathrm{J}_{\alpha j}^{\Sigma}\equiv\overline{\mathrm{J}}_{\alpha j}+\mathrm{J}_{\alpha j}^{turb} \qquad (1.21)$$

(respectively, total heat and diffusion flows in a turbulent continuum) can easily be transformed into form (1.11) of the equation of averaged mixture entropy balance:

$$\bar{\rho}\frac{D\langle S\rangle}{Dt}+\frac{\partial}{\partial x_j}\left\{\frac{\mathrm{q}_j^{\Sigma}-\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle \mathrm{J}_{\alpha j}^{\Sigma}}{\langle T\rangle}\right\}=-\frac{\mathrm{q}_j^{\Sigma}}{\langle T\rangle}\frac{\partial\langle T\rangle}{\partial x_j}-$$

$$-\frac{1}{\langle T\rangle}\left\{\sum_{\alpha=1}^{N}\bar{\mathrm{J}}_{\alpha j}\left[\langle T\rangle\frac{\partial}{\partial x_j}\left(\frac{\langle\mu_\alpha\rangle}{\langle T\rangle}\right)-\mathrm{F}_{\alpha j}\right]-\sum_{\alpha=1}^{N}\mathrm{J}_{\alpha j}^{turb}\frac{\partial}{\partial x_j}\left(\frac{\langle\mu_\alpha\rangle}{\langle T\rangle}\right)+\overline{\tau}_{ij}\frac{\partial\langle u_i\rangle}{\partial x_j}+\right.$$

$$\left.+\sum_{s=1}^{r}\langle A_s\rangle\bar{\xi}_s-\overline{p'\frac{\partial u_j''}{\partial x_j}}-\frac{\overline{\rho' u_j''}}{\bar{\rho}}\frac{\partial\bar{p}}{\partial x_j}+\bar{\rho}\langle\varepsilon_b\rangle\right\}. \qquad (1.22)$$

Comparing now (1.22) with equation (1.11), we obtain for two diffusion entropy flows (the averaged molecular flow $\bar{\mathrm{J}}_{(S)j}$ and the turbulent flow $\mathrm{J}_{(S)j}^{turb}$), as well as for entropy production $\sigma_{\langle S\rangle}$ of an averaged molecular chaos subsystem, the following expressions:

$$\overline{\mathrm{J}_{(S)j}}(\mathrm{x}_j,t)\equiv\frac{1}{\langle T\rangle}\left(\bar{\mathrm{q}}_j-\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\,\bar{\mathrm{J}}_{\alpha j}\right)=\frac{1}{\langle T\rangle}\bar{\mathrm{J}}_{qj}+\sum_{\alpha=1}^{N}\langle S_\alpha\rangle\,\bar{\mathrm{J}}_{\alpha j}, \qquad (1.23)$$

$$\mathrm{J}_{\langle S\rangle j}^{turb}(\mathrm{x}_j,t)\equiv\frac{1}{\langle T\rangle}\left[\tilde{\mathrm{q}}_j^{\,turb}-\sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle\mathrm{J}_{\alpha j}^{turb}\right]=\frac{1}{\langle T\rangle}\tilde{\mathrm{J}}_{qj}^{turb}+\sum_{\alpha=1}^{N}\langle S_\alpha\rangle\,\mathrm{J}_{\alpha j}^{turb}, \qquad (1.24)$$

$$\sigma_{\langle S\rangle}=\sigma_{\langle S\rangle}^{(i)}+\sigma_{\langle S\rangle}^{(e)}, \qquad (1.25)$$

where

$$\sigma_{\langle S\rangle}^{(i)}(\mathrm{x}_j,t)\equiv\frac{1}{\langle T\rangle}\left\{-\tilde{\mathrm{J}}_{qj}^{\Sigma}\frac{\partial\ln\langle T\rangle}{\partial\mathrm{x}_j}+\overline{\tau}_{ij}\frac{\partial\langle u_i\rangle}{\partial\mathrm{x}_j}+\sum_{s=1}^{r}\langle A_s\rangle\bar{\xi}_s-\right.$$

$$-\sum_{\alpha=1}^{N} \mathrm{J}^{\Sigma}_{\alpha j}\left[\langle T\rangle \frac{\partial}{\partial \mathrm{x}_j}\left(\frac{\langle\mu_\alpha\rangle}{\langle T\rangle}\right)+\langle h_\alpha\rangle\frac{\partial \ln\langle T\rangle}{\partial \mathrm{x}_j}-\mathrm{F}_{\alpha j}\right]\Bigg]\Bigg\}\geq 0, \qquad (1.25^*)$$

$$\sigma^{(e)}_{\langle S\rangle}(\mathrm{x}_j,t)\equiv\frac{1}{\langle T\rangle}\left\{-\sum_{\alpha=1}^{N}\mathrm{J}^{turb}_{\alpha j}\mathrm{F}_{\alpha j}-\overline{p'\frac{\partial u''_j}{\partial \mathrm{x}_j}}+\mathrm{J}^{turb}_{(v)j}\frac{\partial\bar{p}}{\partial \mathrm{x}_j}+\bar{\rho}\langle\varepsilon_b\rangle\right\}\equiv\frac{\Im_{E,b}}{\langle T\rangle}. \qquad (1.25^{**})$$

Here

$$\tilde{\mathrm{J}}^{\Sigma}_{qj}\equiv\bar{\mathrm{J}}_{qj}+\tilde{\mathrm{J}}^{turb}_{qj}, \quad \bar{\mathrm{J}}_{qj}\cong\bar{\mathrm{q}}_j-\sum_{\alpha=1}^{N}\langle h_\alpha\rangle\overline{\mathrm{J}_{\alpha j}}, \quad \tilde{\mathrm{J}}^{turb}_{qj}\equiv\tilde{\mathrm{q}}^{turb}_j-\sum_{\alpha=1}^{N}\langle h_\alpha\rangle\mathrm{J}^{turb}_{\alpha j},$$

$$\tilde{\mathrm{J}}^{\Sigma}_{qj}\equiv\tilde{\mathrm{q}}^{\Sigma}_j-\sum_{\alpha=1}^{N}\langle h_\alpha\rangle\mathrm{J}^{\Sigma}_{\alpha j}, \qquad \tilde{\mathrm{q}}^{\Sigma}_j\equiv\bar{\mathrm{q}}_j+\tilde{\mathrm{q}}^{turb}_j=\mathrm{q}^{\Sigma}_j-\overline{p'u''_j}, \qquad (1.26)$$

$\sigma^{(i)}_{\langle S\rangle}(\mathrm{x}_j,t)$ is the rate of local production of averaged entropy $\langle S\rangle(\mathrm{x}_j,t)$ of the mixture, caused by irreversible processes inside the subsystem of averaged molecular chaos of a turbulent multicomponent continuum. Quantity $\sigma^{(e)}_{\langle S\rangle}(\mathrm{x}_j,t)$, as it will be clear from the following analysis, reflects the entropy exchange between the pulsation motion and average motion subsystems. This quantity can be different in sign depending on a specific turbulence regime. The energy transfer rate $\overline{p'(\partial u''_j/\partial \mathrm{x}_j)}$, which represents the work performed per time unit in a volume unit by the ambient medium over vortices, as a consequence of existence of pulsations of pressure p' and expansion $(\partial u''_j/\partial \mathrm{x}_j>0)$ or compression $(\partial u''_j/\partial \mathrm{x}_j<0)$ of vortices, may be different in sign. Quantity $\mathrm{J}^{turb}_{(v)j}(\partial p/\partial \mathrm{x}_j)\approx g\overline{\rho' u_3}$ which represents the rate of turbulence energy production under an effect of buoyancy forces, is positive in the case of small-scale turbulence and negative for large vortices [12]. The rate of average motion's potential energy conversion into the turbulent energy $\sum_{\alpha=1}^{N}\mathrm{J}^{T}_{\alpha j}\mathrm{F}_{\alpha j}$ can also be different in sign. Thus, it follows from (1.22) that in the general case the averaged entropy $\langle S\rangle(\mathrm{x}_j,t)$ of the averaged molecular chaos system can either grow or decrease, which is a typical feature of thermodynamically open systems.

1.3. Entropy balance equations and entropy production of an averaged turbulent chaos subsystem

The Favre-averaged mixture entropy $\langle S\rangle(\mathrm{x}_j,t)$, as a fundamental characteristics of a turbulized medium, does not determine fully enough the thermodynamic state of a system, since it does not depend on state variables characterizing the turbulent continuum structure (for example, on the turbulent energy $\langle b\rangle(\mathrm{x}_j,t)\equiv\overline{\rho u''_j u''_j}/2\overline{\rho}$). Following [20], we determine the structure of the pulsation motion subsystem (turbulent chaos) by specifying the state equation – the functional relation

$$S_{turb}(\mathrm{x}_j,t)=S_{turb}\Big(\langle b\rangle(\mathrm{x}_j,t),\langle v\rangle(\mathrm{x}_j,t)\Big)$$

between state variables $\langle b\rangle(\mathrm{x}_j,t)$, $S_{turb}(\mathrm{x}_j,t)$ and $\langle v\rangle$ (where S_{turb} is the so-called *turbulization entropy*). Then the fundamental Gibbs identity postulated in the form [7]

$$T_{turb}\frac{DS_{turb}}{Dt}=\frac{D\langle b\rangle}{Dt}+p_{turb}\frac{D\langle v\rangle}{Dt} \qquad (1.27)$$

introduces for a turbulent chaos subsystem (a turbulent overstructure) the so-called *turbulization temperature* $T_{turb}\equiv 1/\left\{\partial S_{turb}/\partial\langle b\rangle\right\}_{\langle v\rangle}$ and *turbulent (pulsation) pressure* $p_{turb}\equiv T_{turb}\left\{\partial S_{turb}/\partial\langle v\rangle\right\}_{\langle b\rangle}$ (it is supposed here that derivatives $\left\{\partial S_{turb}/\partial\langle b\rangle\right\}_{\langle v\rangle}>0$ and $\left\{\partial S_{turb}/\partial\langle v\rangle\right\}_{\langle b\rangle}>0$).

Possible relations between parameters $\langle b\rangle(\mathrm{x}_j,t)$, $T_{turb}(\mathrm{x}_j,t)$, $p_{turb}(\mathrm{x}_j,t)$ and $S_{turb}(\mathrm{x}_j,t)$, which may be obtained in an usual manner from the formulae written above, can be interpreted as the equations of state of a turbulent chaos subsystem. Further we shall suppose that the relations obtained from (1.27) are similar in structure to various state equations for a perfect gas. In particular, we shall suppose that the following formulae for $\langle b\rangle(\mathrm{x}_j,t)$ and $S_{turb}(\mathrm{x}_j,t)$ are valid:

$$\langle b\rangle(\mathrm{x}_j,t)={}^3\!/_2\,\mathcal{R}^*T_{turb}={}^3\!/_2\,p_{turb}/\overline{\rho},\qquad p_{turb}(\mathrm{x}_j,t)=\mathcal{R}^*T_{turb}\overline{\rho},$$

$$S_{turb}(\mathrm{x}_j,t)={}^3\!/_2\,\mathcal{R}^{*} ln\left(\,p_{turb}\,/\,\overline{\rho}^{5/3}\right)+\,const\,,$$

$$\langle\mathcal{R}^{*}\rangle(\mathrm{x}_j,t)=k_B\sum_{\alpha=1}^{N}\langle z_\alpha\rangle=k_B\sum_{\alpha=1}^{N}\overline{n}_\alpha\,/\,\overline{\rho}=k_B\,\overline{n}\,/\overline{\rho}. \qquad (1.27^{*})$$

The corresponding balance equation for *turbulization entropy* S_{turb} is obtained from (1.27) by the method described above with using equation (1.16) for specific volume $\langle v\rangle$ and the balance equation for turbulent energy $\langle b\rangle$, which for a multicomponent turbulent mixture can be written as [10, 12]

$$\overline{\rho}\frac{D}{Dt}\langle b\rangle\equiv\frac{\partial}{\partial t}(\overline{\rho}\langle b\rangle)+\frac{\partial}{\partial\mathrm{x}_j}\left(\overline{\rho}\langle b\rangle\langle u_j\rangle\right)=-\frac{\partial}{\partial\mathrm{x}_j}\left(\mathrm{J}^{turb}_{\langle b\rangle j}\right)+\sigma_{\langle b\rangle}, \qquad (1.28)$$

$$\mathrm{J}^{turb}_{\langle b\rangle j}(\mathrm{x}_j,t)\equiv\overline{\rho(b+p'/\rho)u''_j-\tau_{ij}u''_i},$$

$$\sigma_{\langle b\rangle}(\mathrm{x}_j,t)\equiv\left\{\mathrm{R}_{ij}\frac{\partial\langle u_i\rangle}{\partial\mathrm{x}_j}+\overline{p'\frac{\partial u''_j}{\partial\mathrm{x}_j}}+\sum_{\alpha=1}^{N}\mathrm{J}^{turb}_{\alpha j}\mathrm{F}^{*}_j-\mathrm{J}^{turb}_{vj}\frac{\partial\overline{p}}{\partial\mathrm{x}_j}-\overline{\rho}\langle\varepsilon_b\rangle\right\},$$

where $\mathrm{J}^{turb}_{\langle b\rangle}(\mathrm{x}_j,t)$, $\sigma_{\langle b\rangle}(\mathrm{x}_j,t)$ – respectively turbulent-diffusion flow and local production (stock) averaged kinetic energy of turbulent fluctuations (turbulent energy). As a result, we shall have the following evolution equation for entropy S_{turb}:

$$\overline{\rho}\frac{D}{Dt}S_{turb}\;+\frac{\partial}{\partial\mathrm{x}_j}\mathrm{J}_{(S_{turb})j}=\sigma_{(S_{turb})}\equiv\sigma^{(i)}_{(S_{turb})}+\sigma^{(e)}_{(S_{turb})}, \qquad (1.29)$$

where

$$\mathrm{J}_{(S_{turb})j}(\mathrm{x}_j,t)\equiv\frac{1}{T_{turb}}\left\{\overline{\rho(u''_iu''_i/2+p'/\rho)u''_j-\tau_{ij}u''_i}\right\}=\frac{1}{T_{turb}}\mathrm{J}^{turb}_{\langle b\rangle j} \qquad (1.30)$$

is the entropy flow S_{turb} of a turbulent chaos subsystem,

$$0\le\sigma^{(i)}_{(S_{turb})}(\mathrm{x}_j,t)=\frac{1}{T_{turb}}\left\{-\mathrm{J}^{turb}_{\langle b\rangle j}\frac{\partial lnT_{turb}}{\partial\mathrm{x}_j}\;+\mathrm{R}_{ij}\frac{\partial\langle u_i\rangle}{\partial\mathrm{x}_j}+p_{turb}\frac{\partial\langle u_j\rangle}{\partial\mathrm{x}_j}\right\}, \qquad (1.31)$$

$$\sigma^{(e)}_{(S_{turb})}(\mathrm{x}_j,t)\equiv\frac{1}{T_{turb}}\left\{\sum_{\alpha=1}^{N}\mathrm{J}^{turb}_{\alpha j}\mathrm{F}^{\cdot *}_{\alpha j}+\overline{p'\frac{\partial u''_j}{\partial \mathrm{x}_j}}-\mathrm{J}^{turb}_{vj}\frac{\partial\overline{p}}{\partial \mathrm{x}_j}-\overline{\rho}\langle\varepsilon_b\rangle\right\}\equiv-\frac{\Im_{E,b}}{T_{turb}},\quad(1.32)$$

where quantities $\sigma^{(i)}_{(S_{turb})}(\mathrm{x}_j,t)$ and $\sigma^{(e)}_{(S_{turb})}(\mathrm{x}_j,t)$ have, respectively, a meaning of local production and effluence of pulsation entropy $S_{turb}(\mathrm{x}_j,t)$.

Now we transform quantity $T_{turb}\sigma^{(i)}_{(S_{turb})}$ to the form suitable for further analysis. For this purpose we shall separate tensor $\partial\langle u_i\rangle/\partial \mathrm{x}_j$ into symmetric and anti-symmetric parts

$$\partial\langle u_i\rangle/\partial \mathrm{x}_j=\left(\partial\langle u_i\rangle/\partial \mathrm{x}_j\right)^s+\left(\partial\langle u_i\rangle/\partial \mathrm{x}_j\right)^a=\mathrm{S}_{ij}+{}^1\!/_3\,\delta_{ij}\frac{\partial\langle u_k\rangle}{\partial \mathrm{x}_k}+\left(\frac{\partial\langle \mathrm{u}_i\rangle}{\partial \mathrm{x}_j}\right)^a,\quad(1.33)$$

Then, taking into account the state equation (1.27*) and introducing designations

$$\mathrm{S}_{ij}(\mathrm{x}_j,t)\equiv\overset{0}{\mathrm{D}}_{ij}(\mathrm{x}_j,t)\equiv\overset{0}{\left(\partial\langle \mathrm{u}_i\rangle/\partial \mathrm{x}_j\right)}^s=\mathrm{D}_{ij}-{}^1\!/_3\,\delta_{ij}\frac{\partial\langle u_k\rangle}{\partial \mathrm{x}_k}\qquad(1.34)$$

for a symmetric (with zero trace) part of a tensor of rates of deformations of a turbulized continuum $\mathrm{D}_{ij}(\mathrm{x}_j,t)\equiv\left(\partial\langle u_i\rangle/\partial \mathrm{x}_j\right)^s$ and

$$\overset{0}{\mathrm{R}}_{ij}(\mathrm{x}_j,t)\equiv\mathrm{R}_{ij}-{}^1\!/_3\left(\mathrm{R}_{lk}\delta_{lk}\right)\delta_{ij}=\mathrm{R}_{ij}+p_{turb}\delta_{ij}=\mathrm{R}_{ij}+{}^2\!/_3\,\overline{\rho}\langle b\rangle\delta_{ij}\qquad(1.35)$$

– for a part (with zero trace) of symmetric Reynolds' tensor R_{ij}, we shall have:

$$T_{turb}\sigma^{(i)}_{(S_{turb})}=-\mathrm{J}_{(S_{turb})j}\frac{\partial T_{turb}}{\partial \mathrm{x}_j}+\overset{0}{\mathrm{R}}_{ij}\overset{0}{\mathrm{D}}_{ij}.\qquad(1.36)$$

Here we used the fact that the scalar product of symmetric and anti-symmetric tensors is always zero.

Now we shall analyze the evolution equation (1.29) which, with regard to (1.31*) and (1.32), will be written as follows:

$$\overline{\rho}\frac{D}{Dt}S_{turb}+\frac{\partial}{\partial \mathrm{x}_j}\left(\frac{1}{T_{turb}}\mathrm{J}^{turb}_{\langle b\rangle j}\right)=\frac{1}{T_{turb}}\left\{-\mathrm{J}^{turb}_{\langle b\rangle j}\frac{\partial lnT_{turb}}{\partial \mathrm{x}_j}+\overset{0}{\mathrm{R}}_{ij}\overset{0}{\mathrm{D}}_{ij}-\Im_{E,b}\right\}.\quad(1.37)$$

1.4. Balance equation for full entropy of multicomponent turbulized continuum

The introduction of two entropies $\langle S\rangle(x_j,t)$ and $S_{turb}(x_j,t)$ corresponds to the presentation of turbulized continuum in the form of a thermodynamic complex consisting of two subsystems – a turbulent chaos subsystem and an averaged molecular chaos subsystem. The summary balance equation for a full entropy $S_\Sigma(x_j,t) = \langle S\rangle + S_{turb}$ of the turbulized mixture follows from (1.22) and (1.29):

$$\bar{\rho}\frac{D}{Dt}S_\Sigma + \frac{\partial}{\partial x_j}\left\{\frac{J^{turb}_{\langle b\rangle j}}{T_{turb}} + \frac{\left(q_j^\Sigma - \sum_{\alpha=1}^{N}\langle\mu_\alpha\rangle J^\Sigma_{\alpha j}\right)}{\langle T\rangle}\right\} = \sigma_\Sigma, \qquad (1.38)$$

where

$$0 \le \sigma_\Sigma \equiv \sigma^{(i)}_{\langle S\rangle} + \sigma^{(i)}_{S_{turb}} + \sigma_{\langle S\rangle, S_{turb}}, \qquad (1.39)$$

$$\sigma_\Sigma = \frac{1}{\langle T\rangle}\left\{-\tilde{J}^\Sigma_{qj}\frac{\partial ln\langle T\rangle}{\partial x_j} + \bar{\pi}\frac{\partial\langle u_k\rangle}{\partial x_k} + \overset{0}{\overline{\tau}}_{ij}\overset{0}{D}_{ij} + \sum_{s=1}^{r}\langle A_s\rangle\bar{\xi}_s - \right.$$

$$\left. - \sum_{\alpha=1}^{N} J^\Sigma_{\alpha j}\left[\langle T\rangle\frac{\partial}{\partial x_j}\left(\frac{\langle\mu_\alpha\rangle}{\langle T\rangle}\right) + \langle h_\alpha\rangle\frac{\partial ln\langle T\rangle}{\partial x_j} - F_{\alpha j}\right]\right\} +$$

$$+ \frac{1}{T_{turb}}\left\{-J^{turb}_{\langle b\rangle j}\frac{\partial ln T_{turb}}{\partial x_j} + \overset{0}{R}_{ij}\overset{0}{D}_{ij}\right\} + \Im_{E,b}\left(\frac{T_{turb} - \langle T\rangle}{T_{turb}\langle T\rangle}\right). \qquad (1.40)$$

Are here $\bar{\pi}(x_j,t) \equiv \tfrac{1}{3}\left(\overline{\tau}_{ij}\delta_{ij}\right)$ – so-called viscous pressure; then the scalar product of the tensor viscous stress and the velocity gradient tensor can be represented as: $\overline{\tau}_{ij}\frac{\partial\langle u_i\rangle}{\partial x_j} = \bar{\pi}\frac{\partial\langle u_k\rangle}{\partial x_k} + \overset{0}{\overline{\tau}}_{ij}\overset{0}{D}_{ij}$. The volume velocity of full entropy generation σ_Σ represents a bilinear form generated by generalized thermodynamic flows and forces.

2. Thermodynamic derivation of basic equations in multicomponent turbulized media

To find the basic relations for generalized thermodynamic flows and forces one can make use of *Onzager's formalism* of non-equilibrium thermodynamics proceeding from the growth of full entropy of a turbulized continuum and, thus, taking into account the interrelation between averaged molecular and turbulent characteristics [7].

2.1. Linear rheological relations

Expressing the gradient of a weighted average partial chemical potential $\langle\mu_\alpha\rangle(\mathrm{x}_j,t)$, taken for a turbulized ideal mixture of perfect gases in the form [16]

$$\langle\mu_\alpha\rangle=\mu_\alpha^\circ\left(\overline{p},\langle T\rangle\right)+k_B\langle T\rangle\ln\left(\overline{n}_\alpha/\overline{n}\right)\quad(\alpha=1,2,\ldots,N)\tag{2.1}$$

(here $\mu_\alpha^\circ(\mathrm{x}_j,t)$ is the chemical potential of a pure component α at temperature $\langle T\rangle$ and pressure $\overline{p}$), in terms of gradients of averaged hydrodynamic quantities $\langle T\rangle$, $\overline{p}$, $\overline{n}_\alpha/\overline{n}$ $(\alpha=1,2,\ldots,N)$, one can easily obtain for a volume velocity of generation of system's full entropy σ_Σ the bilinear form:

$$0\le\sigma_\Sigma=\overbrace{\sum_{s=1}^{r}\overline{\xi}_s\,Y_{A_s}+\widetilde{\mathrm{J}}_{qj}^{\Sigma}\mathrm{Y}_{qj}^{\Sigma}+\sum_{\alpha=1}^{N}\mathrm{J}_{\alpha j}^{\Sigma}\,\mathrm{Y}_{\alpha j}^{*}+\overline{\pi}\,Y_\pi+\overline{\overset{0}{\tau}}_{ij}\mathrm{Y}_{\mathrm{D}_{ij}}}^{\sigma_{\langle S\rangle}^{(i)}}+$$

$$+\overbrace{\mathrm{J}_{\langle b\rangle j}^{turb}\mathrm{Y}_{\langle b\rangle j}+\overset{0}{\mathrm{R}}_{ij}\mathrm{Y}_{\mathrm{R}_{ij}}}^{\sigma_{S_{turb}}^{(i)}}+\overbrace{\mathfrak{I}_{E,b}\,Y_{E,b}}^{\sigma_{\langle S\rangle,S_{turb}}},\tag{2.2}$$

where the following designations for generalized thermodynamic flows $\widetilde{\mathrm{J}}_{qj}^{\Sigma}(\mathrm{x}_j,t)$, $\overline{\xi}_s(\mathrm{x}_j,t)$, $\mathrm{J}_{\alpha j}^{\Sigma}(\mathrm{x}_j,t)$, $\overline{\pi}(\mathrm{x}_j,t)$, $\overline{\overset{0}{\tau}}_{ij}(\mathrm{x}_j,t)$, $\mathrm{J}_{\langle b\rangle j}^{turb}(\mathrm{x}_j,t)$, $p_{turb}(\mathrm{x}_j,t)$, $\overset{0}{\mathrm{R}}_{ij}(\mathrm{x}_j,t)$, $\mathfrak{I}_{E,b}(\mathrm{x}_j,t)$ and forces are introduced:

$$\mathrm{Y}_{qj}^{\Sigma}(\mathrm{x}_j,t)\equiv-\frac{1}{\langle T\rangle^2}\frac{\partial\langle T\rangle}{\partial\mathrm{x}_j}=\frac{\partial}{\partial\mathrm{x}_j}\left(\frac{1}{\langle T\rangle}\right),\quad\mathrm{Y}_{\langle b\rangle j}(\mathrm{x}_j,t)\equiv-\frac{1}{T_{turb}^2}\frac{\partial T_{turb}}{\partial\mathrm{x}_j},\tag{2.3}$$

$$Y_{A_s}(\mathrm{x}_j,t)\equiv\frac{\langle A_s\rangle}{\langle T\rangle}=-\sum_{\beta=1}^{N}\frac{\langle\mu_\beta\rangle}{\langle T\rangle}\nu_{\beta s},\quad (s=1,2,\ldots,r),\qquad(2.4)$$

$$Y_\pi(\mathrm{x}_j,t)\equiv\frac{1}{\langle T\rangle}\frac{\partial\langle u_k\rangle}{\partial\mathrm{x}_k},\quad \mathrm{Y}_{\mathrm{D}_{ij}}(\mathrm{x}_j,t)\equiv\frac{1}{\langle T\rangle}\overset{0}{\mathrm{D}}_{ij},\quad \mathrm{Y}_{\mathrm{R}_{ij}}(\mathrm{x}_j,t)\equiv\frac{1}{T_{turb}}\overset{0}{\mathrm{D}}_{ij},\qquad(2.5)$$

$$\mathrm{Y}^{*}_{\alpha j}(\mathrm{x}_j,t)\equiv-\frac{\partial}{\partial\mathrm{x}_j}\left(\frac{\langle\mu_\alpha\rangle}{\langle T\rangle}\right)+\langle h_\alpha\rangle\frac{\partial}{\partial\mathrm{x}_j}\left(\frac{1}{\langle T\rangle}\right)+\frac{\mathrm{F}_{\alpha j}}{\langle T\rangle},\qquad(2.6)$$

$$Y_{E,b}(\mathrm{x}_j,t)\equiv\left(\frac{T_{turb}-\langle T\rangle}{T_{turb}\langle T\rangle}\right).\qquad(2.7)$$

The Onzager formalism of non-equilibrium thermodynamics allows to find the basic relations between thermodynamic flows and forces for three main turbulent flow regions: for a laminar sub-layer region; for a buffer zone – an intermediate region, in which the molecular and turbulent transfer effects are compatible in their significance; and for the developed turbulent flow region, in which $\mathrm{R}_{ij} >> \overline{\tau_{ij}}$, $\mathrm{q}_j^{turb} >> \overline{\mathrm{q}}_j$, etc. At states close to local equilibrium the flows can be presented in the form of linear functions of thermodynamic forces (see formula (1.1)) $\mathfrak{I}_{\alpha i}=\sum_{\beta}L^{ij}_{\alpha\beta}\mathrm{X}_{\beta j}$ $(\alpha,\beta=1,2,\ldots,f)$. The matrix of coefficients $L^{ij}_{\alpha\beta}$ in the general case of turbulent field will depend only on state parameters and on parameters characterizing the geometric symmetry of a medium, but also on averaged characteristics of the field of pulsating velocities, i.e. on $\langle b\rangle$, $\langle\varepsilon_b\rangle$, etc. As seen from (2.2), as compared to regular multicomponent mixtures, in the case of turbulized multicomponent media the spectrum of cross effects ever expands. So, for example, thermodynamic forces, causing the transport of turbulent kinetic energy $\langle b\rangle$, have additional effect on averaged diffusion flows $\overline{\mathrm{J}}_{\alpha j}$. However, at present there are no experimental data confirming and quantitatively describing the cross effects of such a type. Besides, as usual, the contribution of any cross effect into the total rate of the process in an order of magnitude lower than the direct effects [3, 4]. Taking this fact into account, we shall use the requirement of positivity of intensities $\sigma^{(i)}_{\langle S\rangle}$, $\sigma^{(i)}_{S_{turb}}$, $\sigma_{\langle S\rangle,S_{turb}}$ independently of each other, supposing in this case that the turbulent chaos subsystem has no effect on corresponding linear relations, for example, between $\overset{0}{\overline{\tau}}_{ij}(x_j,t)$ and $\overset{0}{D}_{ij}$. We shall also further omit some cross effects in rheological relations without special explanations.

As an example, we shall consider in detail the derivation of basic relations for the case of small-scale turbulence, in which, as a rule, the tendency to establishing the local statistic isotropy (when statistical properties of a turbulized flow do not depend on the direction) is observed. The developed approach can easily be generalized to the case of non-isotropic large-scale turbulence as well [12].

According to the general theory of tensor functions [17], the symmetry properties of isotropic media are well characterized by metric tensor g^{ij}: all tensors will be tensor functions of a metric tensor only: $L^{ij}_{\alpha\beta} = L_{\alpha\beta} g^{ij}$ $(\alpha,\beta = 1,2,\dots f)$. Besides, because of the absence of interference between the flows and thermodynamic forces of various tensor dimensionality in the isotropic system (*the Curie principle*), one can consider, for example, the phenomena described by polar vectors (heat conductivity, diffusion) regardless of scalar, tensor and other phenomena [3]. Thus, assuming additional hypotheses usual for non-equilibrium thermodynamics, such as Markov's character of a system (according to which the flows at the given time moment depend only on generalized forces taken at the same moment) and the linearity of processes (according to which the flows are proportional to forces), we obtain from (2.2) in the rectangular coordinate system $(g^{ij} \equiv \delta_{ij})$ the following phenomenological relations:

$$\tilde{J}^{\Sigma}_{qj}(x_j,t) \equiv q^{\Sigma}_j - \overline{p'u''_j} - \sum_{\alpha=1}^{N} \langle h_\alpha \rangle J^{\Sigma}_{\alpha j} = L^{\Sigma}_{00} \frac{\partial}{\partial x_j}\left(\frac{1}{\langle T\rangle}\right) + \sum_{\beta=1}^{N} L^{\Sigma}_{0\beta} Y^{*}_{\beta j}, \qquad (2.8)$$

$$J^{\Sigma}_{\alpha j}(x_j,t) = L^{\Sigma}_{\alpha 0} \frac{\partial}{\partial x_j}\left(\frac{1}{\langle T\rangle}\right) + \sum_{\beta=1}^{N} L^{\Sigma}_{\alpha\beta} Y^{*}_{\beta j}, \qquad (2.9)$$

$$(\alpha = 1,2,\dots,N),$$

$$\overset{0}{\overline{\tau}}_{jk}(x_j,t) = L\, Y_{Djk}, \quad \overline{\pi}(x_j,t) = \frac{l_{\overline{\pi}\overline{\pi}}}{\langle T\rangle}\left(\frac{\partial\langle u_l\rangle}{\partial x_l} + \sum_{s=1}^{r} l_{\overline{\pi}s}\langle A_s\rangle\right) \qquad (2.10)$$

$$R_{jk}(x_j,t) = -\tfrac{2}{3}\overline{\rho}\langle b\rangle\delta_{jk} + L_{turb}\, Y_{R_{jk}}, \qquad (2.11)$$

$$\overline{\xi}_s(\mathrm{x}_j,t)=-l_{s\overline{\pi}}\frac{1}{\langle T\rangle}\frac{\partial\langle u_l\rangle}{\partial \mathrm{x}_l}+\sum_{m=1}^{r}l_{sm}\frac{\langle A_s\rangle}{\langle T\rangle},\quad (s=1,2,\ldots,r), \qquad (2.12)$$

$$\Im_{E,b}(\mathrm{x}_j,t)=l_{E,b}\left(\frac{T_{turb}-\langle T\rangle}{T_{turb}\langle T\rangle}\right). \qquad (2.13)$$

Here $\overline{\mu}(\mathrm{x}_j,t)\equiv\frac{L}{2\langle T\rangle}$, $\overline{\mu}_\vartheta(\mathrm{x}_j,t)\equiv\frac{l_{\overline{\pi}\overline{\pi}}}{\langle T\rangle}$, $\mu^{turb}\equiv\frac{L_{turb}}{2T_{turb}}$, $\nu^{turb}(\mathrm{x}_j,t)\equiv\frac{\mu^{turb}}{\overline{\rho}}$ are kinetic coefficients; and here, once the linear relations (2.8) and (2.9) are postulated, the Onzager theorem yields

$$L^{\Sigma}_{\alpha\beta}=L^{\Sigma}_{\beta\alpha}\quad(\alpha,\beta=1,2,\ldots N). \qquad (2.14)$$

Besides, the linear independence of thermodynamic forces gives rise to the following relations:

$$\sum_{\alpha=1}^{N}m_\alpha L^{\Sigma}_{0\alpha}=0,\quad \sum_{\alpha=1}^{N}m_\alpha L^{\Sigma}_{\alpha\beta}=0,\quad (\beta=1,2,..N). \qquad (2.15)$$

Taking into account relations (2.10) for an averaged tensor of viscous stresses, we obtain

$$\overline{\tau_{jk}}(\mathrm{x}_j,t)=\overline{\mu}\left\{\left(\frac{\partial\langle u_k\rangle}{\partial \mathrm{x}_j}+\frac{\partial\langle u_j\rangle}{\partial \mathrm{x}_k}\right)-\frac{2}{3}\delta_{jk}\frac{\partial\langle u_l\rangle}{\partial \mathrm{x}_l}\rangle\right\}+\overline{\mu}_\vartheta\delta_{jk}\frac{\partial\langle u_l\rangle}{\partial \mathrm{x}_l}, \qquad (2.16)$$

where $\overline{\mu}$ and $\overline{\mu}_\vartheta$ are, respectively, the viscosity coefficient and the second viscosity coefficient, which depend on averaged parameters of a turbulized medium $\langle T\rangle$, $\overline{\rho}$, $\langle z_\alpha\rangle$ $(\alpha=1,2,\ldots,N)$. Thus, the basic relation for tensor $\overline{\tau_{jk}}(\mathrm{x}_j,t)$ was obtained here directly by non-equilibrium thermodynamics methods without attracting an appropriate analog for molecular (instantaneous) quantities.

Similarly, using (2.11) and (1.35), we obtain for Reynolds'tensor the following most complete form, which is valid in the case of isotropic turbulence:

$$\mathrm{R}_{jk}(\mathrm{x}_j,t)=-\tfrac{2}{3}\overline{\rho}\langle b\rangle\delta_{jk}+L_{turb}\,\mathrm{Y}_{\mathrm{R}_{jk}}=$$

$$= -\tfrac{2}{3}\bar{\rho}\langle b\rangle\delta_{jk} + \mu^{turb}\left\{\left(\frac{\partial\langle u_k\rangle}{\partial x_j} + \frac{\partial\langle u_j\rangle}{\partial x_k}\right) - \frac{2}{3}\delta_{jk}\frac{\partial\langle u_l\rangle}{\partial x_l}\right\}, \qquad (2.17)$$

where μ^{turb} $(=\bar{\rho}\nu^{turb})$, ν^{turb} are, respectively, the scalar coefficient of turbulent viscosity and the coefficient of kinematic turbulent viscosity.

It should be noted, however, that relation (2.17) for Reynolds'stresses is not a single possible one (see, for example, [23]). In case if the anisotropy of turbulent pulsations is taken into account, this relation is additionally complicated, since it requires that the turbulent viscosity coefficient be replaced by the tensor (of the 4-th rank) [10, 12].

2.2. Turbulent diffusion and heat flows in the developed turbulent flow

Rheological relations (2.8) and (2.9) for turbulent flows of diffusion $J^{\Sigma}_{\alpha j}(x_j,t)$ $(\alpha=1,2,...,N)$ and heat $\tilde{J}^{\Sigma}_{qj}(x_j,t)$, can be written in the following form:

$$J^{\Sigma}_{\alpha j}(x_j,t) = -\bar{n}_{\alpha}D^{\Sigma}_{T\alpha}\frac{\partial ln\langle T\rangle}{\partial x_j} - \bar{n}_{\alpha}\sum_{\beta=1}^{N}D^{\Sigma}_{\alpha\beta}\,d^{turb}_{\beta j}, \qquad (2.18)$$

$$(\alpha=1,2,...,N),$$

$$\tilde{J}^{\Sigma}_{qj}(x_j,t) = -\hat{\lambda}^{\Sigma}\frac{\partial\langle T\rangle}{\partial x_j} - \bar{p}\sum_{\beta=1}^{N}D^{\Sigma}_{T\beta}\,d^{turb}_{\beta j}, \qquad (2.19)$$

where the scalar phenomenological coefficients $\hat{\lambda}^{\Sigma}$, $D^{\Sigma}_{\alpha\beta}, D^{\Sigma}_{T\beta}$, which depend on averaged state parameters $\bar{\rho}$, $\langle T\rangle$, $\langle z_{\alpha}\rangle$ $(\alpha=1,2,...,N)$ and parameter $\langle b\rangle$, characterizing the physical nature of a turbulized medium, satisfy Onzager's conditions of symmetry (2.14) and conditions (2.15). By analogy with a laminary regime (see [9]), we have introduced: symmetric multicomponent coefficients of turbulent diffusion $D^{\Sigma}_{\alpha\beta}$ $(\alpha,\beta=1,2,...,N)$, turbulent thermodiffusion coefficients $D^{\Sigma}_{T\beta}$ $(\beta=1,2,...,N)$ and turbulent heat conductivity coefficient $\hat{\lambda}^{\Sigma}$ for a multicomponent gas by means of the following definitions:

$$\hat{\lambda}^{\Sigma} \equiv \frac{L^{\Sigma}_{00}}{\langle T\rangle^{2}}, \quad D^{\Sigma}_{T\beta} \equiv \frac{L^{\Sigma}_{0\beta}}{\langle T\rangle \bar{n}_{\beta}}, \quad D^{\Sigma}_{\alpha\beta} = D^{\Sigma}_{\beta\alpha} \equiv \frac{\bar{p}}{\langle T\rangle \bar{n}_{\alpha}\bar{n}_{\beta}} L^{\Sigma}_{\alpha\beta}. \qquad (2.20)$$

Coefficients $D^{\Sigma}_{T\beta}(\mathrm{x}_j, t)$ and $D^{\Sigma}_{\alpha\beta}(\mathrm{x}_j, t)$, in virtue of (2.15), satisfy the relations

$$\sum_{\alpha=1}^{N} \langle c_{\alpha}\rangle D^{\Sigma}_{T\alpha} = 0, \quad \sum_{\alpha=1}^{N} \langle c_{\alpha}\rangle D^{\Sigma}_{\alpha\beta} = 0, \quad (\alpha,\beta = 1,2,\dots,N). \qquad (2.21)$$

In order to introduce the turbulent exchange coefficients, which are similar to corresponding coefficients for regular (laminar) flow regimes (see [10]), we introduce are here, instead of linearly independent vectors $\mathrm{Y}^{*}_{\alpha j}$, a new set of linearly dependent vectors $\mathrm{d}^{turb}_{\beta j}(\mathrm{x}_j, t)$ $(\beta = 1,2,\dots,N)$ by letting

$$\mathrm{d}^{turb}_{\beta j}(\mathrm{x}_j, t) \equiv -\frac{\langle T\rangle \bar{n}_{\beta}}{\bar{p}} \mathrm{Y}^{*}_{\beta j} - \langle c_{\beta}\rangle \frac{\partial ln \bar{p}}{\partial \mathrm{x}_j} + \frac{\bar{\rho}_{\beta}}{\bar{p}} \sum_{\alpha=1}^{N} \langle z_{\alpha}\rangle \mathrm{F}_{\alpha j}, \qquad (2.22)$$

$$\sum_{\alpha=1}^{N} \mathrm{d}^{turb}_{\beta j}(\mathrm{x}_j, t) = 0 \qquad (2.23)$$

(here $\langle c_{\beta}\rangle = m_{\beta}\bar{n}_{\beta}/\bar{\rho}$). Then, with regard to formula (2.6) that determines vectors $\mathrm{Y}^{*}_{\beta j}$, we obtain the following expression for generalized thermodynamic forces:

$$\mathrm{d}^{turb}_{\beta j}(\mathrm{x}_j, t) \equiv \frac{\partial}{\partial \mathrm{x}_j}\left(\frac{\bar{n}_{\beta}}{\bar{n}}\right) + \left(\frac{\bar{n}_{\beta}}{\bar{n}} - \langle c_{\beta}\rangle\right)\frac{\partial ln \bar{p}}{\partial \mathrm{x}_j} - \frac{\bar{n}_{\beta}}{\bar{p}}\left\{\mathrm{F}_{\beta j} - m_{\beta}\sum_{\alpha=1}^{N}\langle z_{\alpha}\rangle \mathrm{F}_{\alpha j}\right\}, \qquad (2.24)$$

which is completely similar in structure to the appropriate expression for the case of regular motion of a mixture.

Herefrom, using formulae (1.26) and (2.19) for a normalized heat flow $\tilde{\mathrm{J}}^{\Sigma}_{qj}(\mathrm{x}_j, t)$, we finally find:

$$\mathrm{q}^{\Sigma}_{j}(\mathrm{x}_j, t) = -\frac{L^{\Sigma}_{qq}}{\langle T\rangle^{2}} \frac{\partial \langle T\rangle}{\partial \mathrm{x}_j} - \bar{p}\sum_{\beta=1}^{N} D^{\Sigma}_{T\beta}\, \mathrm{d}^{turb}_{\beta j} + \overline{p' u''_j} + \sum_{\alpha=1}^{N} \langle h_{\alpha}\rangle \mathrm{J}^{\Sigma}_{\alpha j}, \qquad (2.25)$$

$$\mathrm{J}^{\Sigma}_{\alpha j}(\mathrm{x}_j, t) = -\bar{n}_{\alpha} D^{\Sigma}_{T\alpha} \frac{\partial ln\langle T\rangle}{\partial \mathrm{x}_j} - \bar{n}_{\alpha}\sum_{\beta=1}^{N} D^{\Sigma}_{\alpha\beta}\, \mathrm{d}^{turb}_{\beta j}, \quad (\alpha = 1,2,\dots,N). \qquad (2.26)$$

Rheological relations (2.25) and (2.26) for flows of diffusion $\mathrm{J}_{\alpha j}^{\Sigma}(\mathrm{x}_j,t)$ and heat $\mathrm{q}_j^{\Sigma}(\mathrm{x}_j,t)$ most completely describe heat- and mass-transport in a turbulized gas mixture; but, unfortunately, in virtue of limited amount of experimental data on turbulent exchange coefficients, we are forced to use more simplified models at the given stage of multicomponent turbulence modeling.

3. Generalized Stefan–Maxwell relations and the heat flow for turbulent multicomponent continua

3.1. Stefan–Maxwell relations

It is very difficult to use the defining relations (2.26) for the diffusion fluxes $\mathrm{J}_{\alpha j}^{\Sigma}(\mathrm{x}_j,t)$ in the general, multicomponent case, because, with rare exception, there is no practical information on the generalized multicomponent coefficients of turbulent diffusion $D_{\alpha\beta}^{\Sigma}$ in the literature, while the available experimental data refer mainly to the coefficients of turbulent diffusion $\mathcal{D}_{\alpha\beta}^{\Sigma}$ in binary gas mixtures. In addition, the system of diffusion equations obtained after the substitution of $\mathrm{J}_{\alpha j}^{\Sigma}(\mathrm{x}_j,t)$ from (2.26) into the balance equations (1.17) turns out to be unresolvable with respect to the higher-order derivatives. A numerical realization of such systems is known to involve certain difficulties. Therefore, when the diffusion processes in multicomponent gas mixtures are analyzed, a different formulation of the problem where the defining relations (2.26) for the diffusion fluxes are used in a form resolved with respect to the diffusive thermodynamic forces $\mathrm{d}_{\beta j}^{turb}$ via the fluxes $\mathrm{J}_{\alpha j}^{\Sigma}$ is often more advantageous. Such an inverse transformation can be written in the form of the so-called generalized Stefan–Maxwell relations

$$d_{\beta j}^{\Sigma}=\sum_{\substack{\alpha=1\\ \alpha\neq\beta}}^{N}\frac{\overline{n}_{\beta}\,\mathrm{J}_{\alpha j}^{\Sigma}-\overline{n}_{\alpha}\,\mathrm{J}_{\beta j}^{\Sigma}}{\overline{n}^{2}\mathcal{D}_{\alpha\beta}^{\Sigma}}-\frac{\partial ln\langle T\rangle}{\partial x_j}\sum_{\alpha=1}^{N}\frac{\overline{n}_{\beta}\,\overline{n}_{\alpha}}{\overline{n}^{2}\mathcal{D}_{\alpha\beta}^{\Sigma}}\left(D_{T\beta}^{\Sigma}-D_{T\alpha}^{\Sigma}\right),\qquad(\beta=1,2,\ldots,N)$$

which include the coefficients of turbulent diffusion in binary gas mixtures

$\mathcal{D}^{\Sigma}_{\alpha\beta}$ instead of the generalized multicomponent coefficients of turbulent diffusion $D^{\Sigma}_{\alpha\beta}$. The advantage of these equations is that the quantity $\mathcal{D}^{\Sigma}_{\alpha\beta}$ in them is almost independent of the concentrations of the individual components in gas mixtures at low densities.

Historically, Stefan−Maxwell relations for regular flows (without thermal diffusion, $D_{T\alpha}=0$) were derived by Stefan (*1871*) and Maxwell (*1890*) phenomenologically by assuming that the force exerted on particles of type α from particles of type β was proportional to the difference of their diffusion velocities and that the total resistance force to the motion of particles of type α in a mixture was equal to the sum of the independent resistance forces from all the remaining particles (of other types). Generalized Stefan−Maxwell relations (including thermal diffusion and the effects of external mass forces) were derived by the methods of the kinetic theory of monoatomic gases in the book by Hirschfelder et al. [27] in the first approximation of the Chapman−Enskog theory for the multicomponent diffusion coefficients $D_{\alpha\beta}$ and in the second approximation for the thermal diffusion coefficients $D_{T\alpha}$. Muckenfuss and Curtiss [28] derived these relations in the full second approximation of the Chapman−Enskog. Subsequently, unsuccessful attempts were made in a number of works to obtain Stefan−Maxwell relations from the gas-kinetic theory in any approximation of the transport coefficients (see, [19, 27]). For this reason, Truesdell [29] suggested that the Stefan−Maxwell relations were not universal but were an approximate result of the kinetic theory. However, subsequently, these relations were first derived by Kolesnichenko and Tirskii [5] by the methods of nonequilibrium thermodynamics, thereby proving their absolute universality (i.e., the legitimacy of applying to any mutually diffusing media).

To derive the generalized Stefan–Maxwell relations [5] for turbulent media we resolve equations (2.18) and (2.19) with respect to generalized thermodynamic forces $\mathrm{X}_{0j}(\mathrm{x}_j,t)$ and $\mathrm{X}_{\beta j}(\mathrm{x}_j,t)$ $(\beta=1,2,\ldots,N)$ defined by the expressions

$$\mathrm{X}_{0j}(\mathrm{x}_j,t)\equiv \mathrm{Y}^{\Sigma}_{qj}(\mathrm{x}_j,t)=-\frac{1}{\langle T\rangle^2}\frac{\partial\langle T\rangle}{\partial \mathrm{x}_j},$$

$$X_{\beta j}(x_j,t) \equiv -\frac{\bar{p}}{\langle T\rangle \bar{n}_\beta}\, d^{turb}_{\beta j}, \qquad \left(\sum_{\beta=1}^{N}\langle z_\beta\rangle X_{\beta j}=0\right)$$

in terms of flows $J_{0j}(x_j,t)\equiv \tilde{J}^{\Sigma}_{qj}(x_j,t)$ and $J_{\alpha j}(x_j,t)\equiv J^{\Sigma}_{\alpha j}(x_j,t)$ $(\alpha=1,2,\dots,N)$

$$J_{0j}=L^{\Sigma}_{00}X_{0j}+\sum_{\beta=1}^{N}L^{\Sigma}_{0\beta}X_{\beta j},$$

$$J_{\alpha j}=L^{\Sigma}_{0\alpha}X_{0j}+\sum_{\beta=1}^{N}L^{\Sigma}_{\alpha\beta}X_{\beta j}, \quad (\alpha=1,2,\dots,N), \qquad (3.1)$$

This procedure is completely similar to that outlined in paper [9] for regular flows. For this purpose we omit the last equation of system (3.1) and re-write (3.1), using (2.15), in the form

$$J_{0j}-L^{\Sigma}_{00}X_{0j}=\sum_{\beta=1}^{N-1}L^{\Sigma}_{0\beta}\left[X_{\beta j}-\frac{m_\beta}{m_N}X_{Nj}\right], \qquad (3.2)$$

$$J_{\alpha j}-L^{\Sigma}_{0\alpha}X_{0j}=\sum_{\beta=\text{Б}}^{N-1}L^{\Sigma}_{\alpha\beta}\left[X_{\beta j}-\frac{m_\beta}{m_N}X_{Nj}\right], \quad (\alpha=1,2,\dots,N-1). \qquad (3.3)$$

Resolving the system (3.3) with respect to $X_{\beta j}-\left(m_\beta/m_N\right)X_{\beta Nj}$ we find

$$X_{\beta j}-\frac{m_\beta}{m_N}X_{Nj}=\sum_{\alpha=1}^{N-1}\mathcal{M}^{\Sigma}_{\beta\alpha}(J_{\alpha j}-L^{\Sigma}_{0\alpha}X_{0j}), \quad (\beta=1,2,\dots,N-1), \qquad (3.4)$$

where the elements of reverse matrix $\mathcal{M}^{\Sigma}_{\beta\alpha}$ satisfy the relations

$$\sum_{\alpha=1}^{N-1}\mathcal{M}^{\Sigma}_{\beta\alpha}L^{\Sigma}_{\alpha\gamma}=\delta_{\beta\gamma}=\begin{cases}1, & \beta=\gamma\\ 0, & \beta\neq\gamma.\end{cases} \qquad (3.5)$$

The symmetry of coefficients $\mathcal{M}^{\Sigma}_{\beta\alpha}$ follows from the symmetry of phenomenological coefficients $L^{\Sigma}_{\alpha\beta}$:

$$\mathcal{M}^{\Sigma}_{\alpha\beta}=\mathcal{M}^{\Sigma}_{\beta\alpha}, \quad (\alpha,\beta=1,2,\dots,N-1). \qquad (3.6)$$

Using (3.4), we find from equation (3.2):

$$\mathsf{J}_{0j} = \left[\mathcal{L}^{\Sigma}_{00} - \sum_{\alpha=1}^{N-1} \sum_{\beta=1}^{N-1} \mathcal{L}^{\Sigma}_{0\beta} \mathcal{M}^{\Sigma}_{\beta\alpha} \mathcal{L}^{\Sigma}_{0\alpha} \right] \mathsf{X}_{0j} + \sum_{\alpha=1}^{N-1} \left[\sum_{\beta=1}^{N-1} \mathcal{L}^{\Sigma}_{0\beta} \mathcal{M}^{\Sigma}_{\beta\alpha} \right] \mathsf{J}_{\alpha j} . \quad (3.7)$$

Multiplying each of equations (3.4) by $\langle z_\beta \rangle$ $(\sum_{\beta=1}^{N} m_\beta \langle z_\beta \rangle = 1,$ $\sum_{\beta=1}^{N} \langle z_\beta \rangle \, \mathsf{X}_{\beta j} = 0)$ and summing up them from 1 to N-1, we find the sought relations for vectors of diffusion forces:

$$\mathsf{X}_{Nj} = \left[m_N \sum_{\alpha=1}^{N-1} \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha} \mathcal{L}^{\Sigma}_{0\alpha} \right] \mathsf{X}_{0j} - m_N \sum_{\alpha=1}^{N-1} \left[\sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha} \right] \mathsf{J}_{\alpha j} , \quad (3.8)$$

$$\mathsf{X}_{\beta j} = \sum_{\alpha=1}^{N-1} \mathcal{L}^{\Sigma}_{0\alpha} \left[m_\beta \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha} - \mathcal{M}^{\Sigma}_{\beta\alpha} \right] \mathsf{X}_{0j} - \sum_{\alpha=1}^{N-1} \left[\mathcal{M}^{\Sigma}_{\beta\alpha} - m_\beta \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha} \right] \mathsf{J}_{\alpha j} .$$

$$(\beta = 0,1,\ldots,N-1) \qquad (3.9)$$

The thermodynamic force X_{0j} can be found from expression (3.7). Equations (3.8) and (3.9) represent the reversal of relations (3.3).

In order to write down equations (3.8) and (3.9) in the Stefan–Maxwell form, we add the identity $\sum_{\alpha=1}^{N} m_\alpha \mathsf{J}_{\alpha j} = 0$, multiplied by a_0 , a_N and a_β $(\beta = 1,2,\ldots,N-1)$ to (3.7), (3.8) and (3.9), respectively, and determine constants a_0 and a_β from the condition of symmetry of coefficients $\mathcal{A}$. For this purpose one must let

$$a_0 = -\sum_{\alpha=1}^{N-1} \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha} \mathcal{L}^{\Sigma}_{0\alpha} , \quad (3.10)$$

$$a_\beta = \frac{m_\beta}{m_N} a_N - \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\beta} , \quad (\beta = 1,2,\ldots,N-1) . \quad (3.11)$$

Then we obtain

$$\mathsf{J}_{0j} = \mathcal{A}_{00} \, \mathsf{X}_{0j} + \sum_{\alpha=1}^{N} \mathcal{A}_{0\alpha} \mathsf{J}_{\alpha j} , \quad (3.12)$$

$$-X^{t}_{\beta j} = \mathcal{A}_{\beta 0}\,\mathsf{X}_{0j} + \sum_{\alpha=1}^{N} \mathcal{A}_{\beta\alpha}\,\mathsf{J}_{\alpha j}\,, \qquad (\beta = 1,2,\dots,N) \tag{3.13}$$

where coefficients $\mathcal{A}$ are equal to

$$\mathcal{A}_{00} = L^{\Sigma}_{00} - \sum_{\beta=1}^{N-1}\sum_{\gamma=1}^{N-1} L^{\Sigma}_{0\beta}\mathcal{M}^{\Sigma}_{\gamma\beta}L^{\Sigma}_{0\gamma}\,, \tag{3.14}$$

$$\mathcal{A}_{0N} = \mathcal{A}_{N0} = a_0 m_N = -m_N \sum_{\alpha=1}^{N-1}\sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha} L^{\Sigma}_{0\alpha}\,, \tag{3.15}$$

$$\mathcal{A}_{0\alpha} = \mathcal{A}_{\alpha 0} = a_0 m_\alpha + \sum_{\beta=1}^{N-1} L^{\Sigma}_{0\beta}\mathcal{M}^{\Sigma}_{\beta\alpha} = \sum_{\beta=1}^{N-1} L^{\Sigma}_{0\beta}\left[\mathcal{M}^{\Sigma}_{\beta\alpha} - m_\alpha \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\beta} \right], \tag{3.16}$$

$$(\alpha = 0,1,\dots,N-1),$$

$$\mathcal{A}_{\beta\alpha} = \mathcal{A}_{\alpha\beta} = -\frac{m_\alpha m_\beta}{m_N} a_N + \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \left(m_\alpha \mathcal{M}^{\Sigma}_{\gamma\beta} + m_\beta \mathcal{M}^{\Sigma}_{\gamma\alpha} \right) - \mathcal{M}^{\Sigma}_{\beta\alpha}\,, \tag{3.17}$$

$$(\alpha,\beta = 0,1,\dots,N-1),$$

$$\mathcal{A}_{N\alpha} = \mathcal{A}_{\alpha N} = -a_N m_\alpha + m_N \sum_{\gamma=1}^{N-1} \langle z_\gamma \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha}\,, \tag{3.18}$$

$$\mathcal{A}_{NN} = -a_N m_N\,, \tag{3.19}$$

where the identity

$$\sum_{\alpha=1}^{N} \langle z_\alpha \rangle \mathcal{A}_{\alpha 0} = 0 \tag{3.20}$$

takes place.

Thus, coefficients $\mathcal{A}_{\alpha\beta}$ $(\alpha,\beta = 0,1,\dots,N)$ are still determined to an accuracy of constant a_N, which can be chosen arbitrarily, generally speaking. Further we shall determine this constant supposing the diffusion flows $\mathsf{J}_{\alpha j}$ to be arbitrary.

Now we re-write relations (3.12) and (3.13) in the form

$$\mathsf{X}_{0j} = \left(1/\mathcal{A}_{00}\right)\mathsf{J}_{0j} - \sum_{\alpha=1}^{N} \left(\mathcal{A}_{0\alpha}/\mathcal{A}_{00} \right) \mathsf{J}_{\alpha j}\,, \tag{3.21}$$

$$\mathsf{X}_{\beta j} = -\left(\mathcal{A}_{\beta 0}/\mathcal{A}_{00}\right)\mathsf{J}_{0j} + \sum_{\alpha=1}^{N}\left[\left(\mathcal{A}_{\beta 0}\mathcal{A}_{0\alpha}/\mathcal{A}_{00}\right) - \mathcal{A}_{\beta\alpha}\right]\mathsf{J}_{\alpha j}, \qquad (3.22)$$
$$(\beta = 1,2,\ldots,N)$$

Using the identity $\sum_{\beta=1}^{N}\langle z_\beta\rangle \mathsf{X}_{\beta j} = 0$ and the arbitrary nature of vectors $\mathrm{J}^{\Sigma}_{\alpha j}$, we obtain with regard to (3.20):

$$\sum_{\beta=1}^{N}\langle z_\beta\rangle \mathcal{A}_{\beta\alpha} = 0, \; (\alpha = 1,2,\ldots,N). \qquad (3.23)$$

Substituting coefficients (3.17) and (3.18) into these relations, we find the coefficient a_N:

$$a_N = -m_N \sum_{\beta=1}^{N-1}\sum_{\gamma=1}^{N-1}\langle z_\beta\rangle\langle z_\gamma\rangle \mathcal{M}^{\Sigma}_{\gamma\beta}. \qquad (3.24)$$

Constants in (3.14)-(3.19) are, thus, completely determined in terms of the elements of a symmetric matrix of phenomenological coefficients $L^{\Sigma}_{\alpha\beta}$ and the elements of symmetric matrix $\mathcal{M}^{\Sigma}_{\alpha\beta}$, which is reverse to former one.

Now we transform equations (3.13) to the form of generalized Stefan–Maxwell relations for a multicomponent diffusion in the turbulent flow. For this purpose we subtract expression (3.23), multiplied by $\mathrm{J}^{\Sigma}_{\beta j}/\langle z_\beta\rangle$, from (3.13). Then we find

$$-\mathsf{X}_{\beta j} = \mathcal{A}_{\beta 0}\,\mathsf{X}_{0j} + \sum_{\substack{\alpha=1\\ \alpha\neq\beta}}^{N}\mathcal{A}_{\beta\alpha}\left(\mathsf{J}_{\alpha j} - \frac{\langle z_\alpha\rangle}{\langle z_\beta\rangle}\mathsf{J}_{\beta j}\right), \quad (\beta = 1,2,\ldots,N) \qquad (3.25)$$

or, in usual designations,

$$d^{t}_{\beta j} = \sum_{\substack{\alpha=1\\ \alpha\neq\beta}}^{N}\frac{\mathcal{A}_{\beta\alpha}}{\overline{p}}\left(\overline{n}_\beta \mathsf{J}_{\alpha j} - \overline{n}_\alpha \mathsf{J}_{\beta j}\right) - \frac{\mathcal{A}_{\beta o}\overline{n}_\beta}{\overline{p}\langle T\rangle}\frac{\partial\langle T\rangle}{\partial x_j}, \quad (\beta = 1,2,\ldots,N). \qquad (3.26)$$

What is remained now, is to show that

$$\mathcal{A}_{\beta 0} = -\sum_{\alpha=1}^{N} \mathcal{A}_{\beta\alpha}\left(L^{\Sigma}_{0\alpha} - \frac{\bar{n}_{\alpha}}{\bar{n}_{\beta}} L^{\Sigma}_{0\beta} \right), \quad (\beta = 1,2,\dots,N) . \qquad (3.27)$$

Using expressions (3.16) and (3.17) as well as identities (3.20) and (3.23), we find

$$\sum_{\alpha=1}^{N} \mathcal{A}_{\beta\alpha}\left(L^{\Sigma}_{0\alpha} - \frac{\bar{n}_{\alpha}}{\bar{n}_{\beta}} L^{\Sigma}_{0\beta} \right) = \sum_{\alpha=1}^{N} \mathcal{A}_{\beta\alpha} L^{\Sigma}_{0\alpha} - \frac{L^{\Sigma}_{0\beta}}{\bar{n}_{\beta}} \sum_{\alpha=1}^{N} \bar{n}_{\alpha} \mathcal{A}_{\beta\alpha} = \mathcal{A}_{\beta N} L^{\Sigma}_{0N} + \sum_{\alpha=1}^{N-1} \mathcal{A}_{\beta\alpha} L^{\Sigma}_{0\alpha} =$$

$$= \sum_{\alpha=1}^{N-1} L^{\Sigma}_{0\alpha} \left[\mathcal{A}_{\beta\alpha} - \frac{m_{\alpha}}{m_{N}} \mathcal{A}_{\beta N} \right] = \sum_{\alpha=1}^{N-1} L^{\Sigma}_{0\alpha} \left[-\mathcal{M}^{\Sigma}_{\beta\alpha} + m_{\beta} \sum_{\gamma=1}^{N-1} \langle z_{\gamma} \rangle \mathcal{M}^{\Sigma}_{\gamma\alpha} \right] = -\mathcal{A}_{0\beta} . \qquad (3.28)$$

Substituting (3.27) into (3.26) and using designations of (2.28), we finally find:

$$d_{\beta j} = \sum_{\substack{\alpha=1 \\ \alpha\neq\beta}}^{N} \frac{\mathcal{A}_{\beta\alpha}}{\bar{p}} \left(\bar{n}_{\beta} \mathsf{J}_{\alpha j} - \bar{n}_{\alpha} \mathsf{J}_{\beta j} \right) + \frac{\partial ln\langle T \rangle}{\partial x_{j}} \sum_{\substack{\alpha=1 \\ \alpha\neq\beta}}^{N} \frac{\bar{n}_{\beta}\bar{n}_{\alpha}}{\bar{p}} \mathcal{A}_{\beta\alpha} \left(D^{\Sigma}_{T\alpha} - D^{\Sigma}_{T\beta} \right) . \qquad (3.29)$$

$$(\beta = 1,2,\dots,N)$$

If we introduce the binary coefficients of turbulent diffusion $\mathcal{D}^{\Sigma}_{\alpha\beta}$ and turbulent thermodiffusion relations $\mathsf{k}^{\Sigma}_{T\alpha}$ by formulae

$$\mathcal{D}^{\Sigma}_{\alpha\beta} \equiv k_{B} \langle T \rangle / \bar{n} \mathcal{A}_{\alpha\beta} , \quad (\alpha,\beta = 1,2,\dots,N), \qquad (^{1})$$

$$\mathsf{k}^{\Sigma}_{T\beta} \equiv \bar{n}_{\beta} \mathcal{A}_{\beta 0} / \bar{p} , \quad (\beta = 1,2,\dots,N), \qquad (^{2}) \qquad (3.30)$$

then we obtain from (3.26) the following generalized form for Stefan–Maxwell relations in a developed turbulent flow:

$$\mathsf{d}^{turb}_{\beta j} \equiv \frac{\partial}{\partial \mathsf{x}_{j}} \left(\frac{\bar{n}_{\beta}}{\bar{n}} \right) + \left(\frac{\bar{n}_{\beta}}{\bar{n}} - \langle c_{\beta} \rangle \right) \frac{\partial ln\bar{p}}{\partial \mathsf{x}_{j}} - \frac{\bar{n}_{\beta}}{\bar{p}} \left\{ \mathrm{F}_{\beta j} - m_{\beta} \sum_{\alpha=1}^{N} \langle z_{\alpha} \rangle \mathrm{F}_{\alpha j} \right\} =$$

$$= \sum_{\substack{\alpha=1 \\ \alpha\neq\beta}}^{N} \frac{\bar{n}_{\beta} \mathrm{J}^{\Sigma}_{\alpha j} - \bar{n}_{\alpha} \mathrm{J}^{\Sigma}_{\beta j}}{\bar{n}^{2} \mathcal{D}^{\Sigma}_{\alpha\beta}} - \mathsf{k}^{\Sigma}_{T\beta} \frac{\partial ln\langle T \rangle}{\partial x_{j}} , \quad (\beta = 1,2,\dots,N-1) , \qquad (3.31)$$

$$\sum_{\alpha=1}^{N} m_{\beta}\,\mathrm{J}^{\Sigma}_{\alpha j} = 0 \,. \tag{3.32}$$

These relations are quite similar in structure to Stefan-Maxwell relations

$$\sum_{\substack{\alpha=1\\ \alpha\neq\beta}}^{N} \frac{n_{\beta}\,\mathrm{J}_{\alpha j} - n_{\alpha}\,\mathrm{J}_{\beta j}}{n^{2}\mathcal{D}_{\alpha\beta}} = d_{\beta j} + \mathsf{k}_{T\beta}\frac{\partial lnT}{\partial x_{j}}, \qquad (\beta = 1,2,\dots,N)$$

which have first been obtained thermodynamically for regular flows in [5].

Using (3.30), (2.28) and (3.28), one can show that there also exist the expressions (similar to corresponding expressions for a regular motion):

$$\mathsf{k}^{\Sigma}_{T\beta} = \sum_{\alpha=1}^{N} \frac{\overline{n}_{\beta}\,\overline{n}_{\alpha}}{\overline{n}^{2}\mathcal{D}^{\Sigma}_{\alpha\beta}}\left(D^{\Sigma}_{T\beta} - D^{\Sigma}_{T\alpha}\right), \tag{3.33}$$

$$(\beta = 1,2,\dots,N)$$

which associate turbulent diffusion relations $\mathsf{k}^{\Sigma}_{T\beta}$ with turbulent thermodiffusion coefficients $D^{\Sigma}_{T\beta}$ of multicomponent mixtures.

In virtue of (3.20), the equality

$$\sum_{\alpha=1}^{N} \mathsf{k}^{\Sigma}_{T\alpha} = 0 \tag{3.34}$$

takes place.

Besides, one can easily prove the formula

$$\sum_{\beta=1}^{N} L^{\Sigma}_{\beta\alpha}\mathcal{A}_{\beta 0} = L^{\Sigma}_{0\alpha}, \quad (\alpha = 1,2,\dots,N). \tag{3.35}$$

from which, with regard to definitions (2.28) and (3.30$^{(2)}$), the system of equations follows for finding parameters $\mathsf{k}^{\Sigma}_{T\beta}$ in terms of parameters $D^{\Sigma}_{\alpha\beta}$ and $D^{\Sigma}_{T\alpha}$:

$$\sum_{\beta=1}^{N} D^{\Sigma}_{\alpha\beta}\mathsf{k}^{\Sigma}_{T\beta} = D^{\Sigma}_{T\alpha}, \quad (\alpha = 1,2,\dots,N). \tag{3.36}$$

Indeed, using relations (2.15), (3.5), (3.15) and (3.16), we find

$$\sum_{\beta=1}^{N} L^{\Sigma}_{\alpha\beta}\mathcal{A}_{\beta 0} = L^{\Sigma}_{\alpha N}\mathcal{A}_{N0} + \sum_{\beta=1}^{N-1} L^{\Sigma}_{\alpha\beta}\mathcal{A}_{\beta 0} = -a_{0}\sum_{\beta=1}^{N-1} m_{\beta}L^{\Sigma}_{\alpha\beta} +$$

$$+\sum_{\beta=1}^{N-1} L^{\Sigma}_{\alpha\beta}\left[a_0 m_\beta + \sum_{\gamma=1}^{N-1} L^{\Sigma}_{0\gamma}\mathcal{M}^{\Sigma}_{\gamma\beta}\right] = \sum_{\beta=1}^{N-1}\sum_{\gamma=1}^{N-1} L^{\Sigma}_{\alpha\beta}\mathcal{M}^{\Sigma}_{\gamma\beta}L^{\Sigma}_{0\gamma} = L^{\Sigma}_{0\beta}. \qquad (3.37)$$

Thus, relations (3.38), (3.34) and (3.36) for turbulent thermodiffusion ratios, which are valid, as shown in [6, 12, 19], for regular multicomponent flow as well, have universal character, i.e. they can be used for description of all regimes of motion in a fluid.

And, finally, using turbulent thermodiffusion relations, expressions (2.27) for turbulent diffusion flows $\mathrm{J}^{\Sigma}_{\alpha j}$ can be written in the following form convenient for practical applications:

$$\mathrm{J}^{\Sigma}_{\alpha j} = -\bar{n}_\alpha \sum_{\beta=1}^{N} D^{\Sigma}_{\alpha\beta}\left(d^{\Sigma}_{\beta j} + \mathrm{k}^{\Sigma}_{T\beta}\frac{\partial ln\langle T\rangle}{\partial x_j}\right), \quad (\alpha = 1,2,\ldots,N). \qquad (3.38)$$

3.2. Complete heat flow in turbulent multicomponent media

The complete heat flow of a mixture, caused by turbulent heat conductivity and turbulent diffusion $\tilde{\mathrm{q}}^{\Sigma}_j \equiv \bar{\mathrm{q}}_j + \tilde{\mathrm{q}}^{turb}_j = \mathrm{q}^{\Sigma}_j - \overline{p'u''_j}$, is equal to (see (1.26) and (2.25))

$$\tilde{\mathrm{q}}^{\Sigma}_j \equiv \mathrm{q}^{\Sigma}_j - \overline{p'u''_j} = -\hat{\lambda}^{\Sigma}\frac{\partial\langle T\rangle}{\partial \mathrm{x}_j} - \bar{p}\sum_{\beta=1}^{N} D^{\Sigma}_{T\beta}\,\mathrm{d}^{turb}_{\beta j} + \sum_{\alpha=1}^{N}\langle h_\alpha\rangle \mathrm{J}^{\Sigma}_{\alpha j}. \qquad (3.39)$$

From (3.12) with regard to (3.30$^{(2)}$) $\mathrm{k}^{\Sigma}_{T\beta} \equiv \bar{n}_\beta \mathcal{A}_{\beta 0}/\bar{p}$, one can obtain for a normalized turbulent heat flow $\mathrm{J}_{0j} \equiv \tilde{\mathrm{J}}^{\Sigma}_{qj}$ another expression corresponding to the Stefan–Maxwell relations (3.12):

$$\tilde{\mathrm{J}}^{\Sigma}_{qj} \equiv \mathrm{J}_{0j} = \mathcal{A}_{00}\mathrm{X}_{0j} + \sum_{\alpha=1}^{N}\mathcal{A}_{0\alpha}\mathrm{J}_{\alpha j} = -\lambda^{\Sigma}\frac{\partial\langle T\rangle}{\partial \mathrm{x}_j} + \bar{p}\sum_{\alpha=1}^{N}\frac{\mathrm{k}^{\Sigma}_{T\alpha}}{\bar{n}_\alpha}\mathrm{J}^{\Sigma}_{\alpha j}, \qquad (3.40)$$

or

$$\tilde{\mathrm{q}}^{\Sigma}_j \equiv \tilde{\mathrm{J}}^{\Sigma}_{qj} + \sum_{\alpha=1}^{N}\langle h_\alpha\rangle \mathrm{J}^{\Sigma}_{\alpha j} = -\lambda^{\Sigma}\frac{\partial\langle T\rangle}{\partial \mathrm{x}_j} + \bar{p}\sum_{\alpha=1}^{N}\frac{\mathrm{k}^{\Sigma}_{T\alpha}}{\bar{n}_\alpha}\mathrm{J}^{\Sigma}_{\alpha j} + \sum_{\alpha=1}^{N}\langle h_\alpha\rangle \mathrm{J}^{\Sigma}_{\alpha j}.$$

Here

$$\lambda^{\Sigma} = \mathcal{A}_{00}/\langle T\rangle^2 \qquad (3.41)$$

denotes a true turbulent heat conductivity coefficient, which is associated with coefficient $\hat{\lambda}^{\Sigma}$, introduced earlier, (see (2.28)) by the relation

$$\lambda^{\Sigma} = \hat{\lambda}^{\Sigma} - k_B \bar{n} \sum_{\beta=1}^{N} D^{\Sigma}_{T\beta} \mathrm{k}^{\Sigma}_{T\beta} = \hat{\lambda}^{\Sigma} - k_B \bar{n} \sum_{\beta=1}^{N} \sum_{\alpha=1}^{N} \mathrm{k}^{\Sigma}_{T\alpha} D^{\Sigma}_{\alpha\beta} \mathrm{k}^{\Sigma}_{T\beta} . \qquad (3.42)$$

Indeed, in virtue of (3.5), (3.14) and (3.31), we shall have

$$\mathcal{A}_{00} \equiv L^{\Sigma}_{00} - \sum_{\alpha=1}^{N-1} \sum_{\delta=1}^{N-1} L^{\Sigma}_{0\delta} \mathcal{M}^{\Sigma}_{\delta\alpha} L^{\Sigma}_{0\alpha} = L^{\Sigma}_{00} - \sum_{\alpha=1}^{N-1} \sum_{\delta=1}^{N-1} L^{\Sigma}_{0\delta} \mathcal{M}^{\Sigma}_{\delta\alpha} \Big[L^{\Sigma}_{0N} \mathcal{A}_{N0} +$$

$$+ \sum_{\beta=1}^{N-1} L^{\Sigma}_{\alpha\beta} \mathcal{A}_{\beta 0} \Big] = L^{\Sigma}_{00} - \sum_{\beta=1}^{N-1} L^{\Sigma}_{0\beta} \mathcal{A}_{\beta 0} - \mathcal{A}_{N0} L^{\Sigma}_{0N} = L^{\Sigma}_{00} - \sum_{\beta=1}^{N} L^{\Sigma}_{0\beta} \mathcal{A}_{\beta 0} , \qquad (3.43)$$

wherefrom, with using designations (2.28), (3.30$^{(2)}$) and (3.41), relation (3.42) is deduced.

Thus, the complete heat flow in turbulent multicomponent gas mixtures can be written as

$$\mathrm{q}^{\Sigma}_{j} = \overline{p' u''_j} - \lambda^{\Sigma} \frac{\partial \langle T \rangle}{\partial \mathrm{x}_j} + \bar{p} \sum_{\alpha=1}^{N} \frac{\mathrm{k}^{\Sigma}_{T\alpha}}{\bar{n}_{\alpha}} \mathrm{J}^{\Sigma}_{\alpha j} + \sum_{\alpha=1}^{N} \langle h_{\alpha} \rangle \mathrm{J}^{\Sigma}_{\alpha j} . \qquad (3.44)$$

This relation is completely similar (with the exception of the first term) to the corresponding expression for regular motion obtained both thermodynamically [5] and by methods of kinetic theory of multicomponent gases [12, 19].

The true turbulent heat conductivity coefficient λ^{Σ} can be directly measured experimentally for a steady regime of mixture motion, since in this case all turbulent diffusion flows $\mathrm{J}^{\Sigma}_{\alpha j}$ are zeroes (if the gas is rested, generally). As seen from (3.42), the difference between coefficients λ^{Σ} and $\hat{\lambda}^{\Sigma}$ is of the order of $(D^{\Sigma}_{T\beta})^2$. Since the turbulent thermodiffusion coefficients are small (this effect was not yet discovered experimentally), this difference can apparently be neglected under usual conditions. The term $k_B \bar{n} \sum_{\beta=1}^{N} \sum_{\alpha=1}^{N} \mathrm{k}^{\Sigma}_{T\alpha} D^{\Sigma}_{\alpha\beta} \mathrm{k}^{\Sigma}_{T\beta}$ in expression (3.42) for a heat flow vector corresponds to the turbulent diffusion heat flow.

One can also write down the system of equations (the analog of system (3.78) from paper [9]), which allows to determine turbulent multicomponent diffusion coefficients $D^{\Sigma}_{\alpha\beta}$ in terms of turbulent binary diffusion coefficients $\mathcal{D}^{turb}_{\alpha\beta}$.

Conclusion

Within the framework of the phenomenological theory of turbulence of a multicomponent chemically active gas continuum the thermodynamic approach to closure of hydrodynamic equations of the average motion is considered at the level of first-order models. This approach allows to find more general expressions for turbulent flows in a multicomponent medium, than those derived with using the mixture path notion. The presentation of a turbulized continuum in the form of thermodynamic complex consisting of two subsystems – the pulsation motion (turbulent chaos) subsystem and the average motion (averaged molecular chaos) subsystem – makes it possible to obtain, with using the non-equilibrium thermodynamics methods, the expressions for turbulent flows of heat and momentum, which generalize corresponding results of homogeneous fluid hydrodynamics for the case of multicomponent mixtures.

- The averaging of the fundamental Gibbs identity, which is valid for micro-motions of a multicomponent mixture, allowed to obtain a substantional form of the balance of a weighted average specific entropy for the subsystem of the average motion of a turbulized continuum and to find an explicit expression for averaged molecular and turbulent flows of entropy (associated with corresponding flows of heat and diffusion), for the rate of local production of averaged entropy (caused by irreversible processes inside the averaged molecular chaos subsystem) and for the rate of entropy exchange between pulsation and averaged motion subsystems. The state parameters for the turbulent chaos subsystem (such as turbulization temperature and pressure, for example) are introduced by means of postulating the corresponding Gibbs identity. The evolution balance equation for turbulization entropy (written in the substantional form) is analyzed; the explicit form of a pulsation entropy flow is found, as well as the expressions for a local production and effluence of turbulent chaos subsystem's entropy. The balance equation for a complete (turbulent and averaged molecular) entropy of a turbulized continuum is obtained, which allows to find rather accurate expressions for turbulent thermodynamic flows in multicomponent media.

- The Onzager formalism of non-equilibrium thermodynamics allows to find basic relations between thermodynamic flows and forces for three main regions of turbulized flow: the laminar sublayer region , the buffer zone – an intermediate region, in which the molecular and turbulent transport effects are comparable in their significance (in the atmosphere – the turbopause) and the developed turbulent flow region. As an example, the author presented a detailed derivation of these relations for the case of small-scale turbulence, for which there exists a tendency to establishing a local statistical isotropy, when statistic properties of a turbulized flow (and, thus, the turbulent transport coefficients) do not depend on the direction. The developed approach can easily be generalized for the case of non-isotropic large-scale turbulence.
- In the particular case of a local-stationary state of the developed turbulent field, when there exists some internal equilibrium in the turbulence structure, in which the turbulization entropy production approximately equals its effluence (as the measurements of turbulence energy budget in a homogeneous flow with the velocity gradient have shown, this situation takes place, for example, for a forced convection regime in the atmosphere); the Stefan–Maxwell relations for a multicomponent diffusion and the appropriate expression for the heat flow in a turbulized continuum are obtained, as well as the equations for determining turbulent multicomponent diffusion coefficients in terms of turbulent binary diffusion coefficients. The obtained relations of "forces through flows" most completely describe heat- and mass-exchange in a multicomponent turbulent medium; but, unfortunately, due to the lack of experimental data on turbulent transport coefficients, only simplified models have to be used at the given stage.

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