METHODS OF CONTINUOUS MEDIUM MECHANICS FOR DEFINING POLYPHASE MULTICOMPONENT MIXTURES WITH CHEMICAL REACTIONS AND HEAT- AND MASS-TRANSFER

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Equations of mechanics of multicomponent two-phase compressible disperse mixture, in which heat and mass transfer processes and chemical reactions take place, are derived. Interphase energy transfer in particular during component transition from one phase to another is analyzed. Problems of allowance for phase imperfections and of conditions of thermodynamic equilibrium are considered. Explicit expression is derived for the dissipation function, linear phenomenological relationships are analyzed, and singularities of the structure of direct and cross effects which develop in the system are disclosed.

The state of investigations related to mechanics of heterogeneous mixtures is presented in the survey [1]. We would point out here that Rakhmatulin was the first to formulate a closed system of equations for determining mixtures of compressible phases [2]. The system included equations of mass and momenta of phases and equations for the over-all pressure. The proposed in it scheme for defining the force of interaction between phases is peculiar to a polyphase mixture and not to the multicomponent one. These concepts were applied to a saturated porous medium consisting of a mixture of two compressible phases without phase transitions. A scheme for defining energy exchange between phases and thermodynamic equations were proposed.

A system of hydromechanical equations for a two-phase single-component disperse mixture of compressible phases was considered in [4]. Phase transformations, which complicate the interphase exchange of energy and momentum, were assumed to be present in the mixture. This model was later supplemented by an allowance for surface effects and small scale flows around inclusions [5]. The equations of balance of mass, momentum and energy of components in a multi-speed form were formulated in [6-10]. No clear distinction between homogeneous and heterogeneous mixtures was made in a number of investigations of this kind [1], with the analysis reduced to that of equations of conservation of components.

It should be noted that in the case of a homogeneous mixture it is not necessary to have separate equations of momentum and energy for each component. Such separation (hence, also, the setting of momentum and energy exchange) must be made by phases only, i.e. in the case of a heterogeneous mixture in which in addition to other conditions it is necessary to take into account parts of volume and interphase surface of mixture occupied by each phase [1] (this problem does not arise in the case of homogeneous mixtures). An important aspect of the definition of a heterogeneous mixture is the correct determination

of the structure of terms which define the interaction between phases which takes place at interphase surfaces.

1. Basic assumptions. Let us consider a two-phase n-component medium in which chemical reactions occur inside each phase simultaneously with interphase transitions. The basic assumption is that the phases are homogeneous mixtures (solutions, mixtures of gases) and that the distances along which flow parameters change considerably (outside discontinuity surfaces) are substantially greater than the characteristic inhomogeneities or inclusions (drops, bubbles, particles) which define the mixture phase structure. This makes it possible to define the behavior of such mixture by using the concept of interpenetrating continua [1, 4].

Let ρ_{ik}° be the density of the k-th component $(k = 1, 2, \ldots, n)$ in the i-th phase averaged over the volume occupied by the i-th phase $(i = 1, 2)$. Then

$$\sum_{k=1}^{n} \rho_{ik}^{\circ} = \rho_i^{\circ}, \quad \rho_i = \alpha_i \rho_i^{\circ}, \quad \sum_{i=1}^{2} \alpha_i = 1 \quad (\alpha_i \geqslant 0), \quad \rho = \rho_1 + \rho_2$$

where ρ_i° and ρ_i are the true and the mean density of the i-th phase α_i is the volume of the i-th phase, and ρ is mixture density.

We define the velocity of a phase by its mass velocity

$$\mathbf{v}_i = \frac{1}{\rho_i} \sum_{k=1}^{n} \mathbf{v}_{ik} \rho_{ik}$$

where $\mathbf{v}_{ik}$ is the velocity of the k-th component in the i-th phase, averaged over components contained in that phase.

We assume that within each phase the hypothesis of local equilibrium is valid, hence it is possible to assign to each of these their individual temperature T_i, internal energy u_i, entropy s_i, enthalpy i_i, pressure p_i and other thermodynamic functions.

The multicomponent structure of phases implies that thermodynamic functions of each phase depend not only on the phase temperature T_i and its density ρ_i°, but also on the phase composition $c_{i1}, c_{i2}, \ldots, c_{in}$ $(c_{ik} = \rho_{ik} / \rho_i)$.

Let us consider a mixture of compressible phases in each of which strength effects are absent. We consider the first phase as the carrier and the second to be in the form of discrete inclusions (drops, bubbles, particles) of identical dimensions whose direct mechanical interaction can be neglected. Then $\alpha_2 = \eta m a^3$, where η is the particle form coefficient and m is the number of particles in a unit of mixture volume which in the absence of fractionation, coagulation and formation of new particles satisfies the equation [4]

$$\partial m / \partial t + \nabla (m \mathbf{v}_2) = 0$$

The carrier phase is simulated by a viscous fluid, whose surface force tensors σ_i^{ql} and those of viscous stresses τ_i^{ql} are defined by

$$\sigma_1^{ql} = -p_1 \delta^{ql} + \tau_1^{ql}, \quad \sigma_2^{ql} = 0, \quad \tau_1^{ql} = \lambda_1 \nabla \mathbf{v}_1 + 2\mu_1 e_1^{ql}$$

where δ^{ql} is the Kroneker delta, λ_1 and μ_1 are viscosity coeffcients and e_1^{ql} is the deformation rate tensor of the carrier phase. Values of λ_1 and μ_1 are affected by the presence of inclusions [4].

2. Differential equations. We introduce for each phase the operator of the

substantive derivative (here and throughout the subsequent analysis summation is carried out only with respect to superscripts which relate to projections on coordinate axes) and define the diffusion stream of the k-th component in the i-th phase by

$$\frac{d_i}{dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}_i \nabla \equiv \frac{\partial}{\partial t} + v_i^q \frac{\partial}{\partial x^q} \equiv \frac{\partial}{\partial t} + v_i^q \nabla^q \qquad (2.1)$$

$$\mathbf{j}_{ik} = \rho_{ik}(\mathbf{v}_{ik} - \mathbf{v}_i) = \rho_{ik}\mathbf{w}_{ik}, \qquad \sum_{k=1}^{n} \rho_{ik}\mathbf{w}_{ik} = 0$$

where $\mathbf{w}_{ik}$ is the diffusion rate of the k-th component in the i-th phase.

The equation of mass conservation for the k-th component is of the form

$$d_i \rho_{ik}/dt + \rho_{ik}\nabla\mathbf{v}_i = -\nabla\mathbf{j}_{ik} + J_{k(ji)} - J_{k(ij)} + \sum_{r=1}^{N} v_{k(ir)}I_{(ir)} \qquad (2.2)$$

Here and in what follows subscript i is equal 1 and 2; the pair of subscripts (ij) assumes the values (12) and (21), respectively; $J_{k(ij)}$ is the "observed" macroscopic rate of the k-th component transfer through the phase separation boundary in the direction $i \rightarrow j$ (owing to phase transformation); $I_{(ir)}$ is the rate of the r-th chemical reaction ($r = 1, 2, \ldots, N$) in the i-th phase; $v_{k(ir)} = \beta_{k(ir)}M_k$; $\beta_{k(ir)}$ is the stoichiometric coefficient for the k-th component participating in the r-th chemical reaction in the i-th phase, and M_k is the molecular mass of the k-th component.

Passing to mass concentrations, we can write Eq. (2.2) as

$$\rho_i \frac{d_i c_{ik}}{dt} = -\nabla\mathbf{j}_{ik} + J_{k(ji)} - J_{k(ij)} + \sum_{r=1}^{N} v_{k(ir)}I_{(ir)} - c_{ik}(J_{(ji)} - J_{(ij)}) \qquad (2.3)$$

The first four terms in the right-hand parts of Eq. (2.3) take into account the change of concentration of the k-th component caused by its inflow to or outflow from the volume of the considered phase. The last terms relate to the change of concentration of the k-th component owing to the change of mass of the considered phase resulting from the overall streams of substance through the phase separation boundary. Summating (2.2) over all components, we obtain for the first and second phases the following equation of mass conservation:

$$d_i \rho_i / dt + \rho_i \nabla\mathbf{v}_i = J_{(ji)} - J_{(ij)} \qquad (2.4)$$

where allowance is made for

$$\sum_{k=1}^{n} \sum_{r=1}^{N} v_{k(ir)}I_{(ir)} = 0, \qquad J_{(ji)} = \sum_{k=1}^{n} J_{k(ji)}, \qquad J_{(ij)} = \sum_{k=1}^{n} J_{k(ji)}$$

The equations of motion for the first and second phase are of the form [4]

$$\rho_i \frac{d_i\mathbf{v}_i}{dt} = -\alpha_i \nabla p + \nabla^q \tau_i{}^q - \mathbf{f}_{(ij)} + J_{(ji)}(\mathbf{v}_{(ij)} - \mathbf{v}_i) - J_{(ij)}(\mathbf{v}_{(ij)} - \mathbf{v}_i) + \sum_{k=1}^{n} \rho_{ik}\mathbf{F}_{ik} \qquad (2.5)$$

(for the second phase the second term in the right-hand part is absent, $\mathbf{f}_{(21)} = -\mathbf{f}_{(12)}$). Here $\mathbf{F}_{ik}$ is the external mass force acting on particles of the k-th component in the i-th phase; $\mathbf{f}_{(ij)}$ is the force per unit of mixture volume produced by the phase velocity unbalance ($\mathbf{v}_1$ and $\mathbf{v}_2$ are different), and $\mathbf{v}_{(ij)}$ is the mean velocity of the mass passing through the phase separation boundary in the direction $i \rightarrow j$. Equations (2.5) are based

on the assumptions of the single-pressure model $(p_1 = p_2 = p)$ and of smallness of dynamic and inertial effects [1] of diffusion rates

$$\rho_{1k}\mathbf{w}_{1k}\mathbf{w}_{1k} \sim \rho_{2k}\mathbf{w}_{2k}\mathbf{w}_{2k} \sim 0$$

In formulating the equations of balance of the phase internal energy it is preferable [4, 11] to use equations of heat influx which in the considered case are of the form

$$\rho_i \frac{d_i u_i}{dt} = \frac{\alpha_i p}{\rho_i^\circ} \frac{d_i \rho_i^\circ}{dt} + \varkappa_i \mathbf{f}_{(ji)}(\mathbf{v}_j - \mathbf{v}_i) + \tau_i{}^{ql} e_i{}^{ql} + \qquad (2.6)$$

$$J_{(ji)} \frac{(\mathbf{v}_{(ji)} - \mathbf{v}_i)^2}{2} - J_{(ij)} \frac{(\mathbf{v}_{(ij)} - \mathbf{v}_i)^2}{2} + \sum_{k=1}^{n} \mathbf{F}_{ik}\mathbf{j}_{ik} -$$

$$\sum_{k=1}^{n} J_{k(ji)}x_{ik(ji)} - \sum_{k=1}^{n} J_{k(ij)}x_{ik(ij)} + q_{(ji)} - \nabla\mathbf{q}_i + \rho_i Q_i$$

(for the second phase the third term in the right-hand part is absent; $q_{(12)} = -q_{(21)}$; if $i = 1$, then $j = 2$ and vice versa). In this equation the first five terms at the right in the first equation ($i = 1$) and the four in the second equation ($i = 2$) represent the work of internal forces per unit of time in a unit of volume of the first and second phase, respectively. Coefficients $\varkappa_i$ ($\varkappa_1 + \varkappa_2 = 1$) show the part of dissipated energy of the mixture produced by the phase force interaction which is directly converted into internal energy of the i-th phase. Terms of the first summations in both equations define the power output of external mass forces for component diffusion within the limits of the first and second phases. The remaining terms, viz., heat influx with $x_{ik(ji)}$ and $x_{ik(ij)}$ are the quantities of heat transfered from the i-th phase to the substance of the k-th component per unit of its mass, when it effects the transitions $j \to i$ and $i \to j$, respectively; $q_{(ji)}$ is the intensity of (contact) heat exchange between phases; $\mathbf{q}_i$ is the heat flux within the i-th phase, and $\rho_i Q_i$ is the output of external heat sources acting in the volume of the i-th phase.

3. Energy transfer at interphase heat and mass exchange. Assuming the additivity of entropy and total energy related to the mass of mixture phases and local equilibrium within a phase, we introduce for the phase mixture the specific entropy s and (neglecting second powers of the diffusion rate within phases) the specific total energy E

$$\rho s = \rho_1 s_1 (p, T_1, c_{11}, \ldots, c_{1n}) + \rho_2 s_2 (p, T_2, c_{21}, \ldots, c_{2n})$$
$$\rho E = \rho_1 u_1 (p, T_1, c_{11}, \ldots, c_{1n}) + \rho_2 u_2 (p, T_2, c_{21}, \ldots, c_{2n}) +$$
$${}^1/_2 \rho_1 v_1{}^2 + {}^1/_2 \rho_2 v_2{}^2$$

The concept of the substantive derivative for a quantity Φ which defines the mixture as a whole and is additive with respect to the masses of mixture components

$$\rho \frac{D\Phi}{Dt} = \sum_{i=1}^{2}\left[\rho_i \frac{d_i\Phi_i}{dt} + \Phi_i \sum_{j=1}^{2}(J_{(ji)} - J_{(ij)})\right] \qquad (3.1)$$

was introduced in [4]. This derivative determines the variation of Φ in a fixed volume of the medium, which is unaffected by mass inflow through the boundaries of that volume. Let us determine with the use of (3.1) the accommodation conditions which must be satisfied by $x_{ik(ji)}$ and $x_{ik(ij)}$ in the equation of heat influx (2.6). To do this we

write the derivative of (3.1) for the total energy of the two-phase mixture $E = \Phi$ and $\Phi_i = u_i + \frac{1}{2} v_i^2$.

Substituting into this the equations of heat influx (2.6) and the equations of balance for the kinetic energy, which follow from (2.5), we obtain

$$\rho \frac{DE}{Dt} = \Sigma_{(21)} - \Sigma_{(12)} - \nabla(\alpha_1 p \mathbf{v}_1 + \alpha_2 p \mathbf{v}_2) + \nabla^q(\tau_1^{ql} v_1^l) - \qquad (3.2)$$

$$\nabla(\mathbf{q}_1 + \mathbf{q}_2) + \rho_1 Q_1 + \rho_2 Q_2 + \sum_{k=1}^{n} \rho_{1k} \mathbf{F}_{1k} \mathbf{v}_{1k} + \sum_{k=1}^{n} \rho_{2k} \mathbf{F}_{2k} \mathbf{v}_{2k}$$

$$\left(\Sigma_{(ij)} = \sum_{k=1}^{n} J_{k(ij)} \left[u_1 - u_2 + (-1)^j (x_{1k(ij)} + x_{2k(ij)}) + p \left(\frac{1}{\rho_1^\circ} - \frac{1}{\rho_2^\circ} \right) \right] \right)$$

By the definition of the derivative DE / Dt the variation of total energy of a fixed mass of mixture, which is defined by that derivative, is determined only by the external effects (defined by the last nine terms) and not by any internal processes. Hence expressions of the kind of energy sources owing to the transfer of matter from phase to phase in the right-hand part of (3.2) (the first and second sums there) must vanish. Introducing the enthalpies of phases $i_i = u_i + p / \rho_i^\circ$, we obtain

$$\sum_{k=1}^{n} J_{k(ji)} (x_{1k(ji)} + x_{2k(ji)}) = \sum_{k=1}^{n} J_{k(ji)} (i_i - i_j) = J_{(ji)} (i_i - i_j)$$

The specific definition of the model requires data on that part of energy $J_{(ij)} (i_j - i_i)$ which is expended or absorbed individually by the first and second phase at transition of mass in directions $2 \to 1$ and $1 \to 2$, i.e. accommodation relationships for $x_{ih(ij)}$ and $x_{ih(ji)}$ must be specified. Let us specify these additional relationships. If we assume that $x_{i1(ij)}, \ldots, x_{in(ij)}$ are independent of $J_{1(ij)}, \ldots, J_{n(ij)}$, it becomes possible to replace $x_{ih(ij)}$ by $i_{h(ij)}$ which determine $x_{ih(ij)}$ and distribute the energy $i_2 - i_1$ between phases so that

$$x_{1k(12)} = i_{k(12)} - i_1, \qquad x_{2k(12)} = i_2 - i_{k(12)} \qquad (3.3)$$
$$x_{1k(21)} = i_1 - i_{k(21)}, \qquad x_{2k(21)} = i_{k(21)} - i_2$$

where $i_{h(ij)}$ define the accommodation properties of phases at transition $i \to j$. In the case of bulk chemical reactions it is possible to take for $i_{h(12)}$ and $i_{h(21)}$, as in [4], the specific enthalpies of equilibrium transition of the k-th component from one phase to another

$$i_{k(12)} = i_{2k, s} = i_{2k, s} (c_{21, s}, \ldots, c_{2n, s}, T_s), \quad i_{k(21)} = i_{1k, s} = \qquad (3.4)$$
$$i_{1k, s} (c_{11, s}, \ldots, c_{1n, s}, T_s)$$

where T_s is the temperature of equilibrium transition of the k-th component in the direction $1 \rightleftarrows 2$; $c_{1h,s}$ and $e_{2h,s}$ are equilibrium concentrations of the k-th component in phases 1 and 2, respectively. In some cases, such as for instance combustion [12], when the chemical reaction takes place at the interphase boundary, these accommodation relationships are of a more complex form.

Formulas (3.3) and (3.4) in fact imply that the i-th phase during transition $i \to j$ directly looses or absorbs the energy necessary for bringing at the ambient pressure the mass undergoing such transition, from a given state to the state of the j-th phase in equilibrium. The remaining energy required for bringing that mass from the equilibrium

to the working state of the j-th phase is lost or absorbed by the i-th phase itself.

Accommodation formulas (3.3) and (3.4) require the determination of partial specific enthalpies of phase components in equilibrium. In mixtures of gases (vapors) at not very high pressure , and also in liquid solutions,whose heat of component mixing is low, the partial properties of a mixture are close to the related properties of pure components. However, in imperfect mixtures (considerably deviating from Dalton's law for gases (vapors) or from the Raoult law for solutions of liquids) partial properties depend on the mixture composition. They are of the form [13]

$$i_{ik} = i_{ik}^{\circ} + \Delta i_{ik}, \qquad \Delta l_{ik} = RT_i \frac{\partial \ln \gamma_{ik}}{\partial T_i} \tag{3.5}$$

where Δi_{ik} is the "excess" enthalpy or correction for phase imperfection, which is a function of phase temperature and composition (the heat of mixing of the k-th component in the i-th phase); R is the gas constant; γ_{ik} is the measure of imperfection of the i-th phase or the activity coefficient of the k-th component in the i-th phase whose implicit relation to the equilibrium composition of the i-th phase (expressed in terms of molecular fractions C_{ik}, $k = 1, 2, \ldots, n$) for fixed pressure and temperature follows from the Gibbs-Duhem equation [13]

$$\sum_{k=1}^{n} C_{ik} \frac{\partial \ln \gamma_{ik}}{\partial C_{ik}} = 0 \tag{3.6}$$

Owing to the lack of an explicit analytic expression for the dependence of the activity coefficient on mixture composition, approximate formulas are normally used for defining the relation between these quantities. One of the most convenient forms of the expression for that relation is the one derived by Wilson [14] (for the liquid phase)

$$\ln \gamma_{1k} = 1 - \ln \left(\sum_{g=1}^{n} C_{1g} \Lambda_{kg} \right) - \sum_{l=1}^{n} \left(C_{1l} \Lambda_{kl} \Big/ \sum_{g=1}^{n} C_{1g} \Lambda_{lg} \right) \tag{3.7}$$

$$\Lambda_{kg} = \frac{V_{1g}}{V_{1k}} \exp \left[\frac{(\lambda_{kk} - \lambda_{kg})}{RT_1} \right]$$

where $(\lambda_{kk} - \lambda_{kg})$ is a constant parameter which defines the difference of cohesion energies of $k - k$ and $k - g$ molecular pairs and V_{ik} is the specific mole volume of the pure k-th component in the liquid phase. For a binary mixturw from (3.7) we obtain

$$\ln \gamma_{11} = - \ln (C_{11} + C_{12}\Lambda_{12}) + C_{12} \left(\frac{\Lambda_{12}}{C_{11} + C_{12}\Lambda_{12}} - \frac{\Lambda_{21}}{\Lambda_{21}C_{11} + C_{12}} \right) \tag{3.8}$$

$$\ln \gamma_{12} = - \ln (C_{12} + C_{11}\Lambda_{21}) - C_{11} \left(\frac{\Lambda_{12}}{C_{11} + C_{12}\Lambda_{12}} - \frac{\Lambda_{21}}{C_{11}\Lambda_{21} + C_{12}} \right)$$

It follows from (3.7) and (3.8) that sufficient experimental data on the equilibrium of binary component mixtures constituting a given multi-component mixture are available for the determination of Λ_{kg} and, consequently, of activity coefficients in the liquid phase. The activity coefficient of the k-th component of gas mixture in equilibrium with the liquid phase is determined by formula [13]

$$\gamma_{2k} = \varphi_{2k} / (\gamma_{1k} C_{1k} p_k^{\circ}) \tag{3.9}$$

where p_k° is the vapor pressure of a pure component whose dependence on temperature is usually approximated by a power polynomial or the Antoin equation [15]

$$\ln p_k^\circ (T_2) = a_1 + \frac{a_2}{a_3 + T_2} + a_4 T_2 + a_5 T_2{}^2 + a_6 \ln T_2 \qquad (3.10)$$

where $a_1, \ldots, a_6$ are constant coefficients and φ_{2k} is the fugacity coefficient defined
by the equality [16]

$$\ln \varphi_{2k} = \frac{1}{RT_2} \int\limits_0^p \left(\frac{\partial V_2}{\partial n_{2k}} - \frac{RT_2}{p} \right) dp \qquad (3.11)$$

The derivative of volume V_2 of gas mixture with respect to the number of moles n_{2k} of
the k-th component is taken at constant pressure and temperature, and the quantities
V_2, T_2, p and n_{2k} are interrelated by virial equations of state of real gases

$$\frac{pV_{2M}}{RT_2} = 1 + \frac{\psi_2}{V_{2M}} + \frac{\psi_3}{V_{2M}} + \cdots \quad \left(V_{2M} = V_2 \middle/ \sum_{k=1}^n n_{2k} \right) \qquad (3.12)$$

where $\psi_2, \psi_3, \ldots$ are the second, third, etc. virial coefficients which for an imperfect
mixture depend on the composition and temperature of the latter [16].

It is clear from $(3.5) - (3.12)$ that the knowledge of the equilibrium composition and
temperature of phases is required for the determination of partial specific enthalpies at
equilibrium. Computation of the vapor-liquid equilibrium of multicomponent systems
is based on the equality of component fugacity in phases $f_{1k} = f_{2k}$ [16] or on

$$f_{1k} = \gamma_{1k} C_{1k} f_{1k}^\circ = \varphi_{2k} C_{2k} p = f_{2k} \qquad (3.13)$$

where f_{1k}° is the fugacity of the k-th component in the liquid phase in a normal state
which is determined by the principle of corresponding states [17]. Physicochemical
properties of pure components and experimental data on the equilibrium of binary com-
ponent mixtures are used as the input information for computing multicomponent equi-
librium by formulas $(3.7) - (3.13)$. This is usually carried out on a computer with the
use of the iteration method [15, 17]. First, the activity coefficients of a multicomponent
mixture are determined for the specified temperature by Eq. (3.7) and then, the equilib-
rium composition of the system is computed by formula (3.13) with allowance for $(3.9)-$
(3.12). If this results in the sum of computed component concentration in the vapor
phase being different from unity by more than the specified ε, the equilibrium temper-
ature is corrected and the computation repeated.

4. Thermodynamic analysis. Entropy generation. The assumption
of local equilibrium within a phase (Sect. 1) makes it possible to obtain for an element
of the i-th phase moving along the mass center path the Gibbs formula

$$T_i \frac{d_i s_i}{dt} = \frac{d_i u_i}{dt} + p \frac{d_i}{dt} \left(\frac{1}{\rho_i^\circ} \right) - \sum_{k=1}^n \mu_{ik} \frac{d_i c_{ik}}{dt} \qquad (4.1)$$

where μ_{ik} is the chemical potential of the k-th component in the i-th phase.

Setting in (3.1) $\Phi = s$ and taking into account the Gibbs formula (4.1), we obtain
the expression for the substantive derivative Ds / Dt for the entropy of a two-phase
multicomponent medium in which chemical reactions and interphase transport processes
take place. We have

$$\rho \frac{Ds}{Dt} = \frac{\rho_1}{T_1} \frac{d_1 u_1}{dt} + \frac{\rho_2}{T_2} \frac{d_2 u_2}{dt} - \frac{\alpha_1 p}{\rho_1^\circ T_1} \frac{d_1 \rho_1^\circ}{dt} - \qquad (4.2)$$

$$\frac{\alpha_2 p}{\rho_2{}^\circ T_2}\frac{d_2\rho_2{}^\circ}{dt} - \frac{\rho_1}{T_1}\sum_{k=1}^{n}\mu_{1k}\frac{d_1 c_{1k}}{dt} - \frac{\rho_2}{T_2}\sum_{k=1}^{n}\mu_{2k}\frac{d_2 c_{2k}}{dt} + (J_{(12)} - J_{(21)})(s_2 - s_1)$$

Substituting (2.6) into (4.2) and taking into consideration formulas (3.3) and (3.4) and the thermodynamic equalities [18]

$$\sum_{k=1}^{n} c_{ik}\mu_{ik} = u_i + \frac{p}{\rho_i{}^\circ} - T_i s_i = i_i - T_i s_i \quad (i = 1, 2)$$

$$T_i d_i(\mu_{ik}/T_i) = (d\mu_{ik})_i - i_{ik} dT_i/T_i \quad (i = 1, 2)$$

$$(4.3)$$

where the subscript $i = 1, 2$ at parentheses implies that the differential is taken at the corresponding constant temperatures T_1 or T_2, we obtain for Ds/Dt an expression of the form

$$\rho\,\frac{Ds}{Dt} = \frac{\rho_1 Q_1}{T_1} + \frac{\rho_2 Q_2}{T_2} - \mathbf{V}\left[\frac{1}{T_1}\left(\mathbf{q}_1 - \sum_{k=1}^{n}\mu_{1k}\mathbf{j}_{1k}\right)\right] - \tag{4.4}$$

$$\mathbf{V}\left[\frac{1}{T_2}\left(\mathbf{q}_2 - \sum_{k=1}^{n}\mu_{2k}\mathbf{j}_{2k}\right)\right] + \frac{\tau_1^{ql}e_1^{ql}}{T_1} + \mathbf{f}_{(12)}(\mathbf{v}_1 - \mathbf{v}_2)\left(\frac{\varkappa_1}{T_1} + \frac{\varkappa_2}{T_2}\right) +$$

$$q_{(12)}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) - \mathbf{q}_1{}^*\mathbf{V}\left(\frac{1}{T_1}\right) - \mathbf{q}_2{}^*\mathbf{V}\left(\frac{1}{T_2}\right) -$$

$$\frac{1}{T_1}\sum_{k=1}^{n}\mathbf{j}_{1k}[(\mathbf{V}\mu_{1k})_1 - \mathbf{F}_{1k}] - \frac{1}{T_2}\sum_{k=1}^{n}\mathbf{j}_{2k}[(\mathbf{V}\mu_{2k})_2 - \mathbf{F}_{2k}] -$$

$$\frac{1}{T_1}\sum_{r=1}^{N}B_{1r}I_{(1r)} - \frac{1}{T_2}\sum_{r=1}^{N}B_{2r}I_{(2r)} + \sum_{k=1}^{n}J_{k(12)}\left[\left(\frac{\mu_{1k}}{T_1} - \frac{\mu_{2k}}{T_2}\right) + \right.$$

$$\left. i_{2k,\,s}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{(\mathbf{v}_{(12)} - \mathbf{v}_2)^2}{2T_2} - \frac{(\mathbf{v}_{(12)} - \mathbf{v}_1)^2}{2T_1}\right] +$$

$$\sum_{k=1}^{n}J_{k(21)}\left[\left(\frac{\mu_{2k}}{T_2} - \frac{\mu_{1k}}{T_1}\right) + i_{1k,\,s}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \right.$$

$$\left. \frac{(\mathbf{v}_{(21)} - \mathbf{v}_1)^2}{2T_1} - \frac{(\mathbf{v}_{(21)} - \mathbf{v}_2)^2}{2T_2}\right]$$

$$\left(B_{ir} = \sum_{k=1}^{n}\mu_{ik}v_{k(ir)},\ \mathbf{q}_i{}^* = \mathbf{q}_i - \sum_{k=1}^{n}i_{ik}\mathbf{j}_{ik},\quad i = 1, 2\right)$$

In conformity with the second law of thermodynamics the derivative Ds/Dt can be presented in the form of the sum of two terms

$$Ds/Dt = D^{(e)}s/Dt + D^{(i)}s/Dt$$

where the first term defines the entropy increment of the mixture caused by entropy influx from outside which is produced by energy exchange with the external medium (the first four terms in the right-hand part of (4.4), while $D^{(i)}s/Dt$ (always nonnegative) determines the entropy increase produced by internal irreversible processes

$$\rho\,\frac{D^{(i)}s}{Dt} = \rho\,\frac{Ds}{Dt} - \rho\,\frac{D^{(e)}s}{Dt} = \sigma,\quad \sigma \geqslant 0$$

within and between phases. The dissipation function σ is represented by the last eleven

terms in formula (4.4) and is the sum of the product of thermodynamic forces

$$Z = \frac{e_1^{ql}}{T_1}, \quad X_1 = (\mathbf{v}_1 - \mathbf{v}_2)\left(\frac{\varkappa_1}{T_1} + \frac{\varkappa_2}{T_2}\right), \quad X_2 = -\frac{\nabla T_1}{T_1^2}, \quad X_3 = -\frac{\nabla T_2}{T_2^2}$$

$$X_4 = -\frac{(\nabla\mu_{11})_1 - \mathbf{F}_{11}}{T_1}, \quad \ldots, \quad X_{n+3} = -\frac{(\nabla\mu_{1n})_1 - \mathbf{F}_{1n}}{T_1}$$

$$X_{n+4} = -\frac{(\nabla\mu_{21})_2 - \mathbf{F}_{21}}{T_2}, \quad \ldots, \quad X_{2n+3} = -\frac{(\nabla\mu_{2n})_2 - \mathbf{F}_{2n}}{T_2}$$

$$Y_1 = \frac{1}{T_2} - \frac{1}{T_1}, \quad Y_2 = -\frac{B_{11}}{T_1}, \quad \ldots, \quad Y_{N+1} = -\frac{B_{1N}}{T_1}$$

$$Y_{N+2} = -\frac{B_{21}}{T_2}, \quad \ldots, \quad Y_{2N+1} = -\frac{B_{2N}}{T_2}, \quad Y_{2N+2} = \left(\frac{\mu_{11}}{T_1} - \frac{\mu_{21}}{T_2}\right) +$$

$$i_{21,s}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{(\mathbf{v}_{(12)} - \mathbf{v}_2)^2}{2T_2} - \frac{(\mathbf{v}_{(12)} - \mathbf{v}_1)^2}{2T_1}, \quad \ldots, \quad Y_{2N+2n+1} =$$

$$\left(\frac{\mu_{2n}}{T_2} - \frac{\mu_{1n}}{T_1}\right) + i_{1n,s}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{(\mathbf{v}_{(21)} - \mathbf{v}_1)^2}{2T_1} - \frac{(\mathbf{v}_{(21)} - \mathbf{v}_2)^2}{2T_2}$$

by thermodynamic fluxes

$$J_Z = \tau_1^{ql}, \quad J_{X1} = \mathbf{f}_{(12)}, \quad J_{X2} = \mathbf{q}_1{}^*, \quad J_{X3} = \mathbf{q}_2{}^*, \quad J_{X4} = \mathbf{j}_{11}, \quad \ldots, \quad J_{X,n+3} = \mathbf{j}_{1n}$$

$$J_{X,n+4} = \mathbf{j}_{21}, \quad \ldots, \quad J_{X,2n+3} = \mathbf{j}_{2n}, \quad J_{Y1} = q_{(12)}, \quad J_{Y2} = I_{(11)}, \quad \ldots, \quad J_{Y,N+1} =$$

$$I_{1N}, \quad J_{Y,N+2} = I_{(21)}, \quad \ldots, \quad J_{Y,2N+1} = I_{(2N)}, \quad J_{Y,2N+2} =$$

$$J_{1(12)}, \quad \ldots, \quad J_{Y,2N+n+1} = J_{n(12)}, \quad J_{Y,2N+n+2} =$$

$$J_{1(21)}, \quad \ldots, \quad J_{Y,2N+2n+1} = J_{n(21)}$$

For isotropic systems and small deviations from equilibrium the following linear kinetic relationships between fluxes and thermodynamic forces of equal tensor dimensions:

$$J_Z = E_{11}Z, \quad J_{X1} = \sum_{h=1}^{2n+3} L_{1h}X_h, \quad \ldots, \quad J_{X,2n+3} = \sum_{h=1}^{2n+3} L_{2n+3,h}X_h \qquad (4.5)$$

$$J_{Y1} = \sum_{\theta=1}^{2N+2n+1} D_{1\theta}Y_\theta, \quad \ldots, \quad J_{Y,2N+2n+1} = \sum_{\theta=1}^{2N+2n+1} D_{2N+2n+1,\theta}Y_\theta$$

are valid in virtue of the Curie principle.

The Onsager reciprocity relation implies that

$$L_{\beta h} = L_{h\beta} \quad (h, \beta = 1, 2, \ldots, 2n+3), \qquad D_{\theta\gamma} = D^{\gamma\theta} \quad (\theta, \gamma = 1, 2, \ldots, 2N+2n+1)$$

It will be seen from (4.5) that in the case of polyphase multicomponent systems (with chemical reactions, phase transformations, and heat and mass exchange) simulated by interpenetrating continua the cross effect-spectrum widens considerably in comparison with such effects in single-phase systems [18] (e. g. the Soret, Dufour and other effects). Thus the magnitude of diffusion and heat fluxes within a phase are affected by the relative motion of phases (coefficients $L_{21}, L_{31}, \ldots, L_{2n+3,1}$). The heat flux $q_{(12)}$ between phases is determined not only by the difference of their temperatures, but also by the driving forces of interphase transport of mass (coeffcients; $D_{1,2N+2}, \ldots, D_{1,2N+2n+1}$) and chemical transformations (coefficients $D_{12}, \ldots, D_{1,2N+1}$).

The rate of transport of the k-th component substance between phases is primarily determined by the driving force of interphase mass transport which is the resultant of

three components: the Planck difference of potentials $(\mu_{ik} / T_i - \mu_{jk} / T_j)$, the enthalpy driving force $i_{k(ij)}$ $(1/T_j - 1/T_i)$, and the imbalance of phase rates $(v_{(ij)} - v_j)^2 / 2 \ T_j - (v_{(ij)} - v_i)^2 / 2 \ T_i$.

In the structure of the driving force of mass transport the above factors are additive and are, consequently, equivalent as to their effect on the rate of mass exchange between phases. Under isothermic conditions (e. g. in the case of isothermic absorption or extraction) $T_1 = T_2 =$ const, and the rate of component transport between phases is determined only by the difference of chemical potentials and imbalance of rates between phases.

Besides the described direct effects the intensity of mass exchange between phases is affected by cross effects: temperature imbalance of phases (coefficients $D_{2N+k,1}$) and the imbalance of chemical transformations (coefficients $D_{2N+k,2} \cdots D_{2N+k,2N+1}$). Cross effects such as temperature and concentration gradients in phases, which affect the mechanical interaction of phases (coefficients $L_{12}, \ldots, L_{1,2n+3}$) should be noted.

5. The complete system of equations of motion for a disperse mixture.

The contribution of cross effects to the overall rate of a process is usually by one order lower than that of direct effects [18]. If the kinetic relationships (4.5) are restricted to direct effects only, the expressions for fluxes assume the form

$$\tau_1{}^{ql} = E_{11} \frac{e_1{}^{ql}}{T_1}, \quad \mathbf{f}_{(12)} = L_{11}(\mathbf{v}_1 - \mathbf{v}_2)\left(\frac{\varkappa_1}{T_1} + \frac{\varkappa_2}{T_2}\right), \quad \mathbf{q}_1{}^* = -\frac{L_{22}}{T_1{}^2}\nabla T_1 \quad (5.1)$$

$$\mathbf{q}_2{}^* = -\frac{L_{33}}{T_2{}^2}\nabla T_2, \quad \mathbf{j}_{1k} = -\frac{L_{1k}}{T_1}[(\nabla\mu_{1k})_1 - \mathbf{F}_{1k}]$$

$$\mathbf{j}_{2k} = -\frac{L_{2k}}{T_2}[(\nabla\mu_{2k})_2 - \mathbf{F}_{2k}]$$

$$q_{(12)} = \frac{D_{11}}{T_1 T_2}(T_1 - T_2), \quad I_{(1r)} = -\frac{D_{1r}}{T_1}B_{1r}, \quad I_{(2r)} = -\frac{D_{2r}}{T_2}B_{2r}$$

$$J_{k(12)} = D_{k(12)}Y_{k(12)}, \quad J_{k(21)} = D_{k(21)}Y_{k(21)}$$

$$(L_{1k} = L_{k+3,\,k+3}, \quad L_{2k} = L_{n+k+3,\,n+k+3}, \quad \underset{(r>1)}{D_{1r} = D_{r+1,\,r+1}}, \quad \underset{(r>1)}{D_{2r} =}$$

$$D_{N+r+1,\,N+r+1}, \quad D_{k(12)} = D_{2N+k+1,\,2N+k+1}, \quad D_{k(21)} = D_{2N+n+k+1,\,2N+n+k+1}$$

$$Y_{k(12)} = Y_{2N+k+1,\,2N+k+1}, \quad Y_{k(21)} = Y_{2N+n+k+1,\,2N+n+k+1})$$

The kinetic coefficients in (5.1) must be determined experimentally. Thus with allowance for (5.1), (3.4) and (4.1) the system of equations of thermohydrodynamics of multicomponent heterogeneous disperse mixtures assumes the form

$$\frac{d_1\rho_{1k}}{dt} + \rho_{1k}\nabla\mathbf{v}_1 = -\nabla\mathbf{j}_{1k} + J_{k(21)} - J_{k(12)} + \sum_{r=1}^{N}v_{k(1r)}I_{(1r)} \ (k = 1, 2, ..., n) \quad (5.2)$$

$$\frac{d_2\rho_{2k}}{dt} + \rho_{2k}\nabla\mathbf{v}_2 = -\nabla\mathbf{j}_{2k} + J_{k(12)} - J_{k(21)} + \sum_{r=1}^{N}v_{k(2r)}I_{(2r)}$$

$$(k = 1, 2, \ldots, n)$$

$$\frac{\partial m}{\partial t} + \nabla(m\mathbf{v}_2) = 0$$

$$\rho_1\frac{d_1\mathbf{v}_1}{dt} = -\varkappa_1\nabla p + \nabla^q\tau_1{}^q - \mathbf{f}_{(12)} + J_{(21)}(\mathbf{v}_{(21)} - \mathbf{v}_1) -$$

$$J_{(12)}(\mathbf{v}_{(12)} - \mathbf{v}_1) + \sum_{k=1}^{n}\rho_{1k}\mathbf{F}_{1k}$$

$$\rho_2 \frac{d_2 \mathbf{v}_2}{dt} = -\alpha_2 \nabla p + \mathbf{f}_{(12)} + J_{(12)}(\mathbf{v}_{(12)} - \mathbf{v}_2) - J_{(21)}(\mathbf{v}_{(21)} - \mathbf{v}_2) + \sum_{k=1}^{n} \rho_{2k} \mathbf{F}_{2k}$$

$$\rho_1 \frac{d_1 u_1}{dt} = \frac{\alpha_1 p}{\rho_1^\circ} \frac{d_1 \rho_1^\circ}{dt} + \varkappa_1 \mathbf{f}_{(12)}(\mathbf{v}_1 - \mathbf{v}_2) + \tau_1^{ql} e_1^{ql} + J_{(21)} \frac{(\mathbf{v}_{(21)} - \mathbf{v}_1)^2}{2} -$$

$$J_{(12)} \frac{(\mathbf{v}_{(12)} - \mathbf{v}_1)^2}{2} - \sum_{k=1}^{n} J_{k(21)}(i_1 - i_{1k,\,s}) - \sum_{k=1}^{n} J_{k(12)}(i_{2k,\,s} - i_1) +$$

$$q_{(21)} - \nabla \mathbf{q}_1 + \rho_1 Q_1 + \sum_{k=1}^{n} \mathbf{F}_{1k} \mathbf{j}_{1k}$$

$$\rho_2 \frac{d_2 u_2}{dt} = \frac{\alpha_2 p}{\rho_2^\circ} \frac{d_2 \rho_2^\circ}{dt} + \varkappa_2 \mathbf{f}_{(12)}(\mathbf{v}_1 - \mathbf{v}_2) + J_{(12)} \frac{(\mathbf{v}_{(12)} - \mathbf{v}_2)^2}{2} -$$

$$J_{(21)} \frac{(\mathbf{v}_{(21)} - \mathbf{v}_2)^2}{2} - \sum_{k=1}^{n} J_{k(21)}(i_{1k,\,s} - i_2) - \sum_{k=1}^{n} J_{k(12)}(i_{2k,\,s} - i_2) -$$

$$q_{(21)} - \nabla \mathbf{q}_2 + \rho_2 Q_2 + \sum_{k=1}^{n} \mathbf{F}_{2k} \mathbf{j}_k$$

$$p_1 = p_2 = p, \quad \alpha_1 + \alpha_2 = 1, \quad \alpha_2 = \eta m a^3, \quad \varkappa_1 + \varkappa_2 = 1, \quad \rho_1^\circ = \rho_1/\alpha_1$$

$$\rho_2^\circ = \rho_2/\alpha_2, \quad \rho_1 = \sum_{k=1}^{n} \rho_{1k}, \quad \rho_2 = \sum_{k=1}^{n} \rho_{2k}, \quad \mathbf{j}_{1k} = \rho_{1k}(\mathbf{v}_{1k} - \mathbf{v}_1)$$

$$\mathbf{j}_{2k} = \rho_{2k}(\mathbf{v}_{2k} - \mathbf{v}_2)$$

Equations (5.2) together with Eqs. (2.4), the thermodynamic relationships (3.5)–(3.13), and the phenomenological equations (5.1) in which the kinetic coefficients are experimentally determined, constitute a closed system of equations of motion of a two-phase multicomponent disperse medium in which heat and mass exchange processes take place simultaneously with chemical reactions.

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DIFFUSION ON A PARTICLE IN A HOMOGENEOUS TRANSLATIONAL-SHEAR FLOW

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We consider the problem of a stationary convective diffusion of a substance, dissolved in an incompressible fluid flow on the surface of a particle moving with constant speed in a shear flow field. We assume that the flow over the particle is inertia-free and that there is total absorption of the dissolved component on its surface. In the diffusing boundary layer approximation we determine the concentration field and obtain expressions for the total diffusing stream of a substance on the surface of a solid spherical particle and on the surface of a spherical drop (bubble).

1. The flow field. In a rectangular Cartesian coordinate system fixed to the center of a moving spherical particle (drop) the velocity field of an unperturbed (at large distances from the particle) translational-shear flow can be written in the form

$$\mathbf{v} = \{v_x, v_y, v_z\} = \{-\alpha x, -\alpha y, U + 2\alpha z\} \qquad (1.1)$$

Here U is the speed of the unperturbed translational motion of the fluid, α is the shear motion intensity, which may assume both positive and negative values.