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Jan Kubik

Thermodiffusion Flows in a Solid with a Dominant Constituent

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Herrn Prof. Dr.- Ing. Theodor Lehmann danke ich für groß - zügige Unterstützung und hilfreiche Anregungen.

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Summary

We consider mixtures of (n) constituents and assume that every part of the solid is occupied by particles of all constituents simultaneously. By means of an analysis of the balance equations we obtain the limiting process from mixture theory to thermo - diffusion. This is only possible if we propose the condition of the existence of a mixture constituent with a dominant density. The field equations of the thermomechanics concerning thermo - diffusion in solids are based on the balance equations relating to mass, impulse, energy and entropy.
As special cases of the theory we obtain :
- entropic diffusion
- kinematic diffusion
- filtration in solids
- classical thermodiffusion in solids.

Zusammenfassung

Wir betrachten Mischungen aus (n) Komponenten und nehmen an, daß jeder Punkt des Körpers gleichzeitig von Teilchen aller Komponenten besetzt ist. Mit Hilfe einer Analyse der Bilanz - gleichungen erhalten wir den Grenzübergang von der Mischtheorie zur Thermodiffusion. Dieses ist nur unter der Voraussetzung der Existenz einer Mischungskomponente mit einer dominanten Dichte möglich.
Die Feldgleichungen der Thermomechanik bei Thermodiffusion in Festkörpern basieren auf den Bilanzgleichungen bzgl. Masse, Impuls, Energie und Entropie.
Als Spezialfälle dieser Theorie erhalten wir :
- Entropische Diffusion
- Kinematische Diffusion
- Filtration in Festkörpern
- Klassische Thermodiffusion in Festkörpern.

C O N T E N T S

Notation

$x_i = x_i(X_k, t)$

(X_k, t) - point in E^4

V - volume

A - surface

t - time

$\rho = \sum_\alpha \rho^\alpha$ - density

c^α - concentration

R^α - mass source

v_i^α - velocity

$w_i = \frac{1}{\rho} \sum_\alpha v_i^\alpha \rho^\alpha$ - mass center velocity

$u_i^\alpha = v_i^\alpha - w_i$ - diffusion velocity

$j_i^\alpha = \rho^\alpha u_i^\alpha$ - diffusion fluxes

$V_i = \sum_\alpha a^\alpha v_i^\alpha$ - reference velocities $(\sum_\alpha a^\alpha = 1)$

$J_i^\alpha = \rho^\alpha (v_i^\alpha - V_i)$ - extra diffusion fluxes

$\rho F_i = \sum_\alpha \rho^\alpha F_i^\alpha$ - mass force

$\phi_i = \sum_\alpha \phi_i^\alpha = 0$ - momentum transmission

$P_i^\alpha = \sigma_{ij}^\alpha n_j$ - particul stress vector

T - temperature

$\rho U = \sum_{\alpha} \rho^{\alpha} U^{\alpha}$ - internal energy

$\rho K = \sum_{\alpha} \rho^{\alpha} K^{\alpha}$ - kinetic energy

$\rho A = \rho U + T \rho S$ - free energy

$q_i = \sum_{\alpha} q_i^{\alpha}$ - heat flux

$\rho r = \sum_{\alpha} \rho^{\alpha} r^{\alpha}$ - heat source

$\rho S = \sum_{\alpha} \rho^{\alpha} S^{\alpha}$ - entropy

$$\frac{d}{dt}(\ ) = \frac{\partial}{\partial t}(\ ) + V_k \frac{\partial}{\partial x_k}(\ \ )$$

$$\frac{d}{dt}(\ )^{\alpha} = \frac{\partial}{\partial t}(\ )^{\alpha} + V_k^{\alpha} \frac{\partial}{\partial x_k}(\ \ )^{\alpha}$$

Introduction

The processes of mass, energy, momentum and entropy exchanges appearing in a multi-constituent solid are of more complex thermodynamics problems. Then, the diffusion flows occur, as well as conversions between particular body constituents. These phenomena are typical for many capillary-porous media. They also appear in the majority of technological processes, where it comes to material structure rebuilding e.g. recrystallization. Moreover one can describe new material constituents generation, as a result of deformation processes, temperature changes, or to some extent of chemical reactions in a solid.

The possibility of description of the above mentioned processes is provided by the theory of mixtures, adapted to simulation of flows in a solid. On account of specifity of these flows it is necessary to distinguish a dominant constituent s.c. the skeleton, with regard to which the flows arise. Such an approach leads directly to the thermodiffusion descriptions which will be presented in this paper.

Firstly, the equations of theory of mixtures will be quoted.

We shall give a greater attention to the kinematics of mixture constituents. Indeed, the flows with regard to one of constituents will be of a great importance. Further, we shall present the fundamental sets of balances for various types of diffusion flows in a solid, ending on heterogeneous bodies discriptions excluding diffusion flows.

Chapter I

Kinematics in the theory of mixtures.

Let us assume that every particle X of medium (the point in $\mathcal{E}^3$) consists of (n) interacting elements of different densities ρ^{α} $\alpha=1,2,..n$ velocities V_i^{α} internal energies U^{α}, kinetic energies K^{α}, entropies S^{α}, e.t.c. Those elements interacte to one another and it comes to mutual flows of constituents and to conversions. Moreover, we assume that any particle X includes all elements Y^{α}. Thus we do not describe processes of segregation and so forth.

Let the Cartesian coordinate system of base vectors e_i is the reference one. We shall use the tensor notation with regard to Latin indices. The Greek ones will be refered to particular constituents of the mixture $\mathcal{S}^{\alpha}$ $\alpha = 1, 2, \ldots, n$.

If $v_k^{\alpha}(x_i, t)$ is the $\mathcal{S}^{\alpha}$ element velocity and ρ^{α} is its density at point (x_i, t), then

$$\rho = \sum_{\alpha} \rho^{\alpha} ,$$

$$\rho W_i = \sum_{\alpha} \rho^{\alpha} V_i^{\alpha} , \qquad U_i^{\alpha} = V_i^{\alpha} - W_i$$

where w_i denotes the X particle mass center velocity in a multi-constituent system, and u_i^{α} is its diffusion velocity, i.e. its motion velocity with regard to the mean one. In general, we shall relate a motion of medium to that mean velocity, One can, however, introduce the description in reference with a velocity of any constituent. These problem will be further analysed.

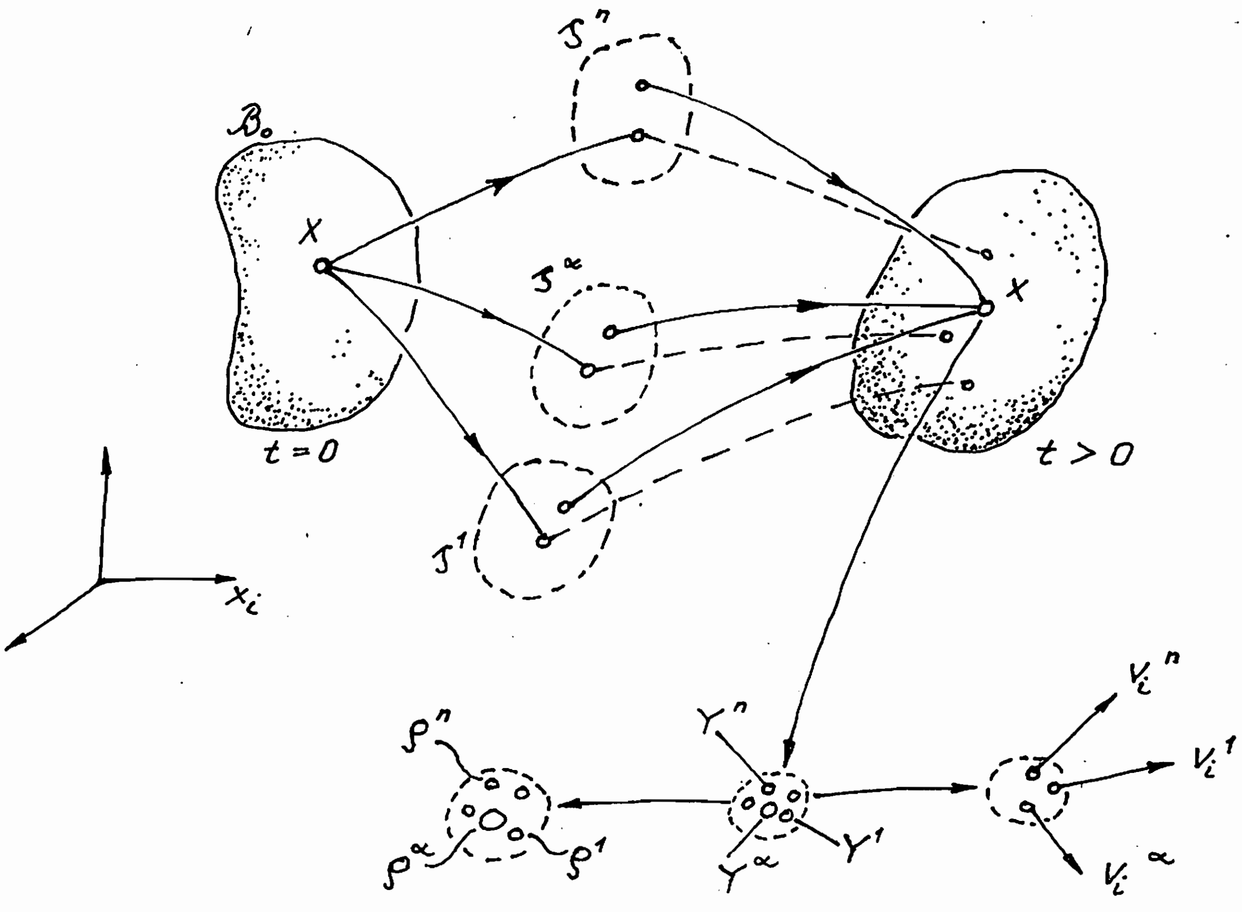


Fig.1

1. Reference systems

In the theory of mixtures the description of motion is, in general related to the mass center velocity. Sometimes it is convenient to describe it with regard to the given constituent.

In the general case, every vectorial field fulfiling the relations

(1.1) $$V_k = \sum_\alpha a^\alpha V_k^\alpha \;, \quad \sum_\alpha a^\alpha = 1 \;, \quad a^\alpha \geqslant 0 \;, \quad \alpha = 1, 2, \dots n$$

can be the reference velocity V_k

Hence

(1.2) $$a^\alpha V_i^\alpha = a^\alpha V_i + J_i^\alpha \frac{a^\alpha}{\rho^\alpha}$$

(1.3) $$J_i^\alpha = \rho^\alpha V_i^\alpha - \rho^\alpha V_i$$

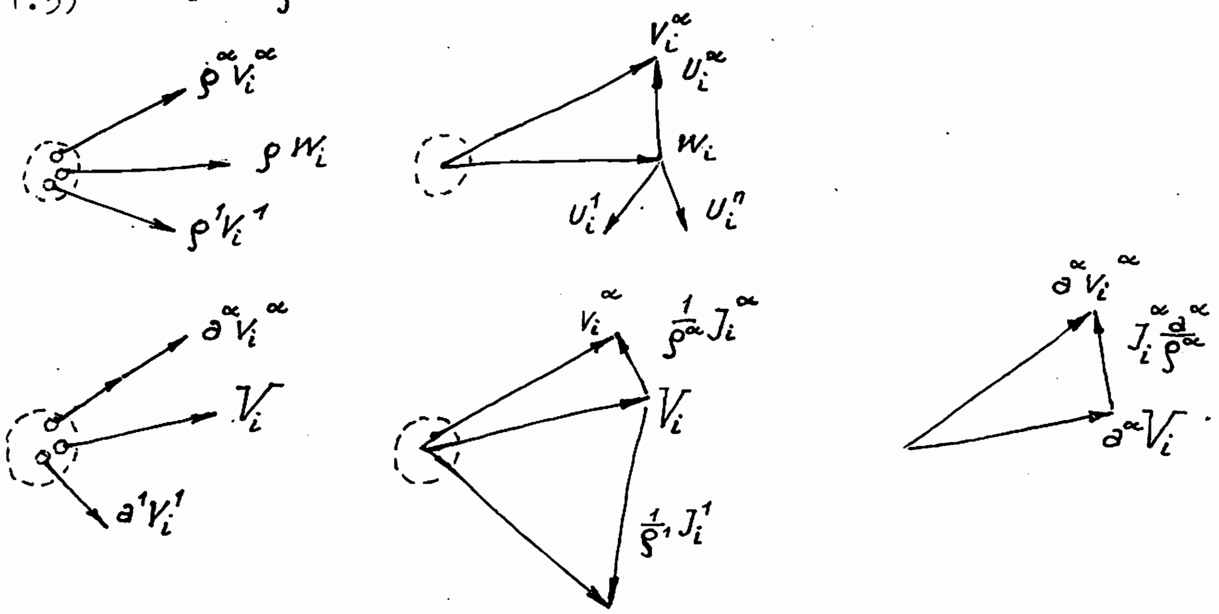


Fig.2

From the formula (1,3) it follows that each of diffusion fluxes is defined by the expression $J_i^\alpha = \rho^\alpha (V_i^\alpha - V_i)$ indepentdy on definition of the reference velocity, The sum of flows must then vanish

(1.4) $$\sum_\alpha \frac{a^\alpha}{\rho^\alpha} J_i^\alpha = 0$$

On account of an arbitrary choice of coeffcients a^α the conditions (1,1) lead to an infinitely large number of reference velocities V_k. It is found that all these possibilities are embraced in the transformation group G which we shall introduce in the next point.

2. Transformation group $\mathcal{G}$

Set of relations (1.1) defining generally an arbitrary reference velocity field will be presented in a little different form

$$V_i = \sum_{\alpha} (\sqrt{a^{\alpha}})^2 V_i^{\alpha} = \sum_{\alpha} (b^{\alpha})^2 V_i^{\alpha} \tag{2.1}$$

$$\sum_{\alpha} (b^{\alpha})^2 = 1$$

Let us notice that the choice of the vector $b^T = [b^1, \dots b^{\alpha}, \dots b^n]$ fulfiling the condition $\sum_{\alpha} (b^{\alpha})^2 = 1$ leads directly to orthogonal group of transformations $\mathcal{O}(n, R)$

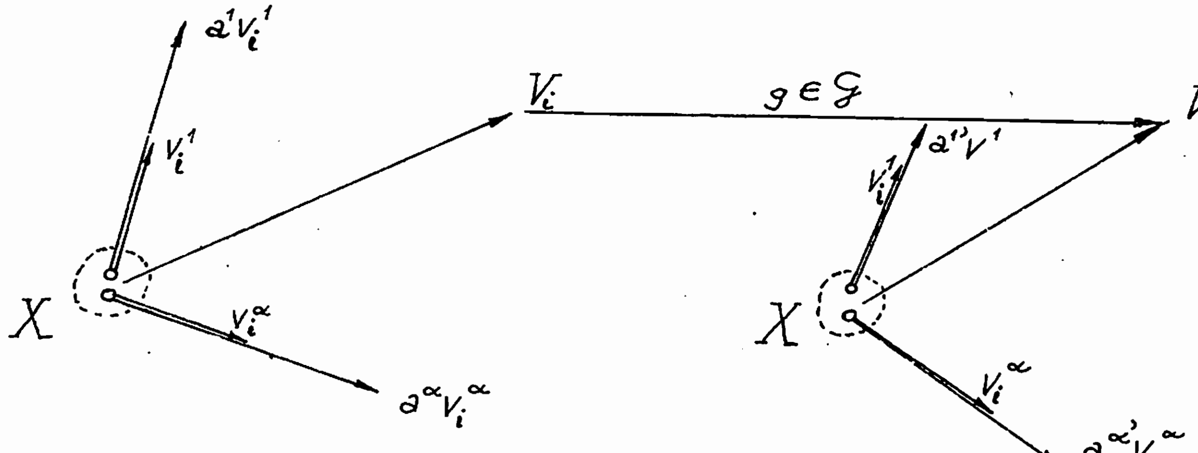


Fig.3

In general, the transformation of the vector $b \xrightarrow{o} b'$, $(b \in \mathcal{E}^n)$ is following

$$(b' = Ob) \Longrightarrow (V \longrightarrow V') \tag{2.2}$$

where

$$O^{-1} = O^T, \quad O = [\cos \alpha_{i'j}], \quad o \in \mathcal{O}(n, R)$$

is an orthogonal matrix.

Indeed, we have to do with the homomorfism of the group $\mathcal{O}$ into the group $\mathcal{G}$ of reference velocities transformation $V_i \xrightarrow{g} V_i'$, $g \in \mathcal{G}$

(2.3) $$\mathcal{O} \xrightarrow{hom} \mathcal{G}$$

Concluding we find that there exists an additional problem of invariantability towards the choice of reference velocity. It may be formulated as follows:
variation of the reference velocity V which is defined by the orthogonal group $\mathcal{O}(n,R)$ generates

($\mathcal{E}_1$) the transformation of diffusion fluxes

$$J_i \longrightarrow J_i' \quad , \quad J_i^{\alpha'} = A^{\alpha\delta} J_i^{\delta}$$

($\mathcal{E}_2$) the transformation of all balances equations.
The transformation of the vector $J_i \to J_i'$ is defined by the vector fulfiling the constraints (2.1).
Thus it is necessary to analyse the transformation of fluxes $J_i \to J_i'$ with the variation of reference velocity ($V_i \to V_i'$)

The velocity V_i^{α} is determined by help of the relation

(2.4) $$V_i^{\alpha} = V_i + \frac{1}{\rho^{\alpha}} J_i^{\alpha}$$
$$V_i^{\alpha} = V_i' + \frac{1}{\rho^{\alpha}} J_i^{\alpha'}$$

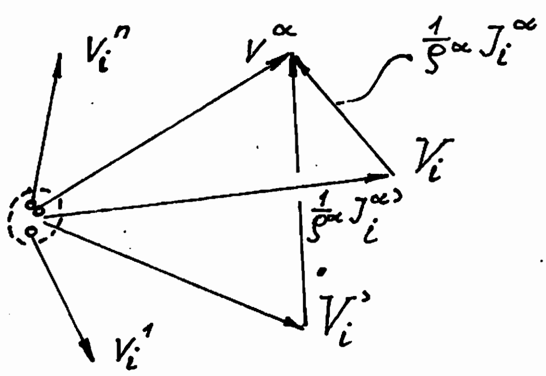


Fig.4

Comparing the left sides of the equations (2.4) we obtain

$$J_i^{\alpha'} = J_i^{\alpha} - \rho^{\alpha}(V_i' - V_i) \tag{2.5}$$

Assuming that $V_i' = \sum_{\beta} a'^{\beta} v_i^{\beta}$, $V_i = \sum_{\beta} a^{\beta} V_i^{\beta}$

we get

$$\begin{aligned} J_i^{\alpha'} &= J_i^{\alpha} - \rho^{\alpha}\Big[\sum_{\beta} a'^{\beta}(v_i^{\beta} - V_i)\Big] = \\ &= J_i^{\alpha} - \rho^{\alpha}\Big[\sum_{\beta} a'^{\beta}\frac{1}{\rho^{\beta}}\rho^{\beta}(V_i^{\beta} - V_i)\Big] = \\ &= J_i^{\alpha} - \rho^{\alpha}\Big[\sum_{\beta} \frac{a'^{\beta}}{a^{\beta}}\frac{a^{\beta}}{\rho^{\beta}} J_i^{\beta}\Big] \end{aligned} \tag{2.6}$$

In the end

$$\begin{aligned} J_i'^{\alpha} &= \delta^{\alpha\beta} J_i^{\beta} - \rho^{\beta}\Big[\sum_{\beta} \frac{a'^{\beta}}{\rho^{\beta}} J_i^{\beta}\Big] \\ J_i'^{\alpha} &= [A^{\alpha'\beta}]\, J_i^{\beta} \end{aligned} \tag{2.7}$$

$$\begin{bmatrix} J_i'^{1} \\ J_i'^{2} \\ \vdots \\ J_i'^{n} \end{bmatrix} = \begin{bmatrix} (1 - a'^{1}), & -\frac{1}{\rho^{2}}\rho^{1}a'^{2}, & \cdots & -\frac{1}{\rho^{n}}\rho^{1}a'^{n} \\ \frac{1}{\rho^{1}}\rho^{2}a'^{1}, & (1 - a'^{2}), & \cdots & -\frac{1}{\rho^{n}}\rho^{2}a'^{n} \\ \vdots & & & \vdots \\ -\frac{1}{\rho^{1}}\rho^{n}a'^{1}, & -\frac{1}{\rho^{2}}\rho^{n}a'^{2}, & \cdots & (1 - a'^{n}) \end{bmatrix} \begin{bmatrix} J_i^{1} \\ J_i^{2} \\ \vdots \\ J_i^{n} \end{bmatrix}$$

Each term o the matrix $A^{\alpha\beta}$ has the form

$$A^{\alpha\beta}=\begin{bmatrix} a^{\alpha\beta} & 0 & 0 \\ 0 & a^{\alpha\beta} & 0 \\ 0 & 0 & a^{\alpha\beta} \end{bmatrix} \tag{2.8}$$

When varying the reference velocity the mass source in the momentum balance stays constant. Admittedly, the mass balances for particular constituents decide on the form of the balances of momentum, angular momentum, energy e.t.c. So, for this reason all balances are affected by the transformation of the reference.system.

Chapter II

Balances of the mixtures

We shall here define mass, momentum, energy and entropy balances for a mixture composed of n interacting constituents. This approach will permit to use the equations describing the behaviour of mixtures for physical justification of the thermodiffusion. Of course comparision between the mixture and thermodiffusion equations should be independent on physical material properties. So, we postulate for that comparision of both theories to be the problem solved in the balances range only. Such procedure will be presented in the paper.

3. Mass balances

The mass balance equations for any material volume V of the constituent ζ_α have the form

$$\frac{d}{dt}\int_V \varrho^{\alpha}\, dV = \int_V R^{\alpha}\, dV \tag{3.1}$$

or after introducing the concentration $c^{\alpha} = \dfrac{\varrho^{\alpha}}{\varrho}$

$$\frac{d}{dt}\int_V \varrho c^{\alpha}\, dV = \int_V R^{\alpha}\, dV \tag{3.2}$$

In these equations R^{α} is the (α) constituent mass source, i.e. the velocity of mass supplying from another constituents.

The local form of the balance equations is following

$$\frac{\partial \varrho^{\alpha}}{\partial t} + \frac{\partial}{\partial x_k}\left(\varrho^{\alpha} V_k^{\alpha}\right) = R^{\alpha} \tag{3.3}$$

Summing the momentum balances over constituents (α) we attain

$$\begin{array}{ccccc}
\dfrac{\partial \varrho^{1}}{\partial t} & + & \dfrac{\partial}{\partial x_k}\left(\varrho^{1} V_k^{1}\right) & = & R^{1} \\
\vdots & & \vdots & & \vdots \\
\dfrac{\partial \varrho^{n}}{\partial t} & + & \dfrac{\partial}{\partial x_k}\left(\varrho^{n} V_k^{n}\right) & = & R^{n} \\
\hline
\end{array} \tag{3.4}$$

$$\frac{\partial}{\partial t}\left(\varrho^{1} + \ldots\ldots + \varrho^{n}\right) + \frac{\partial}{\partial x_k}\left(\varrho^{1} V_k^{1} + \ldots\ldots \varrho^{n} V_k^{n}\right) = R^{1} + \ldots\ldots + R^{n}$$

Finally

$$\frac{\partial \varrho}{\partial t} + \frac{\partial}{\partial x_k}\left(\varrho w_k\right) = 0 \tag{3.5}$$

$$\varrho = \sum_{\alpha} \varrho^{\alpha}, \quad \varrho w_k = \sum_{\alpha} \varrho^{\alpha} V_k^{\alpha}$$

Introducing the diffusion velocities U_k^α we obtain from Eg -(3.4)

$$\frac{\partial \varrho^1}{\partial t} + \frac{\partial}{\partial x_k}\left[\varrho^1(w_k + U_k^1)\right] = R^1 \longrightarrow$$

$$\longrightarrow \frac{\partial \varrho^1}{\partial t} + \frac{\partial}{\partial x_k}\left[\varrho^1 w_k + j_k^1\right] = R^1$$

(3.6)

$$\frac{\partial \varrho^n}{\partial t} + \frac{\partial}{\partial x_k}\left[\varrho^n(w_k + U_k^n)\right] = R^n \longrightarrow$$

$$\longrightarrow \frac{\partial \varrho^n}{\partial t} + \frac{\partial}{\partial x_k}\left[\varrho^n w_k + j_k^n\right] = R^n$$

$$j_k^\alpha \equiv \varrho^\alpha U_k^\alpha \quad \text{und} \quad \sum_\alpha \varrho^\alpha U_k^\alpha = 0$$

When changing the reference system $v_k \rightarrow v_k'$ and $j_u \rightarrow j_u$ we get

$$\frac{\partial \varrho^1}{\partial t} + \frac{\partial}{\partial x_k}\left(\varrho^1 V_k + J_k^1\right) = R^1$$

$$\vdots \qquad\qquad \vdots \qquad \vdots \qquad \vdots$$

(3.7)

$$\frac{\partial \varrho^n}{\partial t} + \frac{\partial}{\partial x_k}\left(\varrho^n V_k + J_k^n\right) = R^n$$

$$\frac{\partial \varrho}{\partial t} + \frac{\partial}{\partial x_k}\left(\varrho V_k\right) + \underline{\underline{\frac{\partial}{\partial x_k}\left(\sum_\alpha J_k^\alpha\right) = 0}}$$

where the transformations of both reference velocities w_n v_k and fluxes are defined by help of relations (2.4) and (2.8). In particular, the given transformations can describe the motion with regard to the dominant constituent.

It is necessary to emphasize that further we shall deal with a motion, whose velocity almost coincides the mean one. Such an approach will lead to the thermodiffusion.

4. Balanced flows

In the previous point we indicated that for the same set of particle constituent velocities $\rho^{\alpha} V_k^{\alpha}$ it is possible to define infinitely many reference velocities. This implies the definitions of the rest and flows in media. It comes out that the diffusion fluxes can be vanish although the flow towards one of constituents occurs. $(\mathcal{E}_1)$ we find that the rest may occur then when

$$(4.1) \qquad \bigvee_{\alpha} \left(\rho^{\alpha} V_k^{\alpha} = 0 \right) \longrightarrow \bigvee_{\alpha} \left(V_k^{\alpha} = 0 \right)$$

$(\mathcal{E}_2)$ On the other hand the case $V_i = 0$ in the presence of $V_i^{\alpha} = V_i + \frac{1}{\rho^{\alpha}} J_i^{\alpha}$ leads to the relation $V_i^{\alpha} = \frac{1}{\rho^{\alpha}} J_i^{\alpha}$ and for $V_i = \sum_{\alpha} a^{\alpha} V_i^{\alpha} = 0$ we obtain $\sum_{\alpha} \frac{a^{\alpha}}{\rho^{\alpha}} J_i^{\alpha} = 0$

It means that the diffusion flow coincides each of velocities

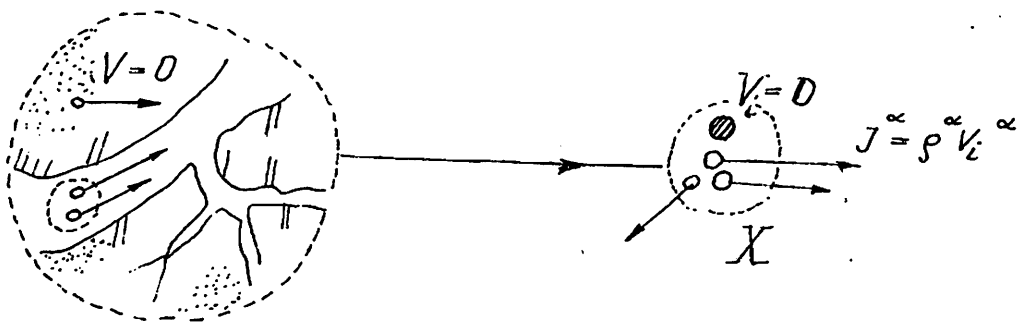


Fig.5

$(\mathcal{E}_3)$ If however $V_i^{\beta} = V_i$, otherwise $\frac{1}{\rho^{\beta}} \dot{J}_i^{\beta} = 0$ then
$\rho^{\alpha} V_i^{\alpha} = J_i^{\alpha *} + \rho^{\alpha} V_i^{\beta}$ and $\bigwedge\limits_{\alpha} J^{\alpha} = 0$

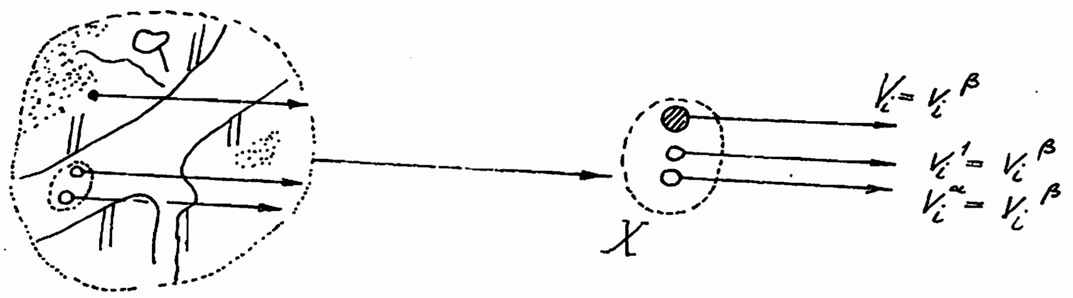


Fig.6

Let us notice that case $(\mathcal{E}_2)$ implies existing of a such set of coefficients $\{a^{\alpha}\}$ which must lead to vanishing of V_i. Then the diffusion flows occur in spite of the apparent equlibrium.

If however $V_i = W_i = 0$ then the mass center. is at rest and the convectional flow dees not occur.

5. The momentum and angular momentum balances.

We postulate for the momentum balance completed by the momentum transmission from remaining constituents to be fulfiled for each of constituents $\mathcal{J}^{\alpha}$ of a mixture.
It is

$$(5.1) \qquad \frac{d}{dt} \int\limits_V \rho^{\alpha} V_i^{\alpha} dV = \int\limits_V (\rho^{\alpha} F_i^{\alpha} + \varphi_i^{\alpha}) dV + \int\limits_A P_i^{\alpha} dA$$

where $\rho^{\alpha} F_i^{\alpha}$, φ_i^{α}, $P_i^{\alpha} = \sigma_{ij}^{\alpha} n_j$ are the mass force component, momentum transmission from remaining constituents and particul strees vector respectively.

Using the theorem on divergency we obtain

$$(5.2) \qquad \int_V \left[\frac{\partial}{\partial t}(\rho^\alpha v_i^\alpha) + \frac{\partial}{\partial x_k}(\rho^\alpha v_i^\alpha v_k^\alpha)\right] dV = \int_V \left[\rho^\alpha F_i^\alpha + \varphi_i^\alpha + \sigma_{ij,j}^\alpha\right] dV$$

but accounting for the mass balance leads here to the relation

$$(5.3) \qquad \rho^\alpha \frac{dv_i^\alpha}{dt} = -v_i^\alpha R^\alpha + \varphi_i^\alpha + \rho^\alpha F_i^\alpha + \sigma_{ij,j}^\alpha$$

Let us notice that only a constituent dependent on the mass source and the momentum transmission $\varphi_i^\alpha = \sum_\beta \tilde{\varphi}_i^{\alpha\beta}$, $\varphi^{\alpha\alpha} = 0$, differ this balance from that for the homogenous system.
Also the global balance for the sum of all constituents must be fulfiled

$$(5.4) \qquad \sum_\alpha \frac{d}{dt} \int_V \rho^\alpha v_i^\alpha dV = \sum_\alpha \int_V (\rho^\alpha F_i^\alpha + \varphi_i^\alpha) dV + \sum_\alpha \int_A P_i^\alpha dA$$

Let us transform the quality occuring on the left side of balance as follows

$$\sum_\alpha \frac{d}{dt} \int_V \rho^\alpha v_i^\alpha dV = \sum_\alpha \int_V \left[\frac{\partial}{\partial t}(\rho^\alpha v_i^\alpha) + \frac{\partial}{\partial x_k}(\rho^\alpha v_i^\alpha v_k^\alpha)\right] dV =$$

$$= \sum_\alpha \int_V \frac{\partial}{\partial t}(\rho^\alpha v_i^\alpha) + \frac{\partial}{\partial x_k}\left[\rho^\alpha (w_i + u_i^\alpha)(w_k + u_k^\alpha)\right] dV =$$

$$= \sum_\alpha \int_V \left\langle \frac{\partial}{\partial t}(\rho w_i) + \frac{\partial}{\partial x_k}\left[\rho w_i w_k + \rho^\alpha w_i u_k^\alpha + \rho^\alpha u_i^\alpha w_k + \right.\right.$$

$$\left.\left. + \rho^\alpha u_i^\alpha u_k^\alpha\right]\right\rangle dV = \sum_\alpha \int_V \left\langle w_i \left[\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho w_k)\right] + \right.$$

$$\left. + \rho\left[\frac{\partial w_i}{\partial t} + w_k \frac{\partial w_i}{\partial x_k}\right] + \frac{\partial}{\partial x_k}\left[\rho^\alpha u_i^\alpha u_k^\alpha\right]\right\rangle dV =$$

$$= \int_V \left\langle \rho \frac{dw_i}{dt} + \sum_\alpha \frac{\partial}{\partial x_k}\left[\rho^\alpha u_i^\alpha u_k^\alpha\right]\right\rangle dV$$

In the efect the local form of momentum balance for the whole mixture is following

$$(5.5)\qquad \int_V \left(\varrho \frac{dW_i}{dt} - \sum_\alpha \varrho^\alpha F_i^\alpha\right) dV = \int_A \sum_\alpha \left(\sigma_{ik}^\alpha - \varrho^\alpha v_i^\alpha v_k^\alpha\right) n_k \, dA$$

or

$$(5.6)\qquad \varrho \frac{dW_i}{dt} = \varrho F_i + \sigma_{ik,k} - \underline{\frac{\partial}{\partial x_k} \sum_\alpha \varrho^\alpha v_i^\alpha v_k^\alpha}$$

where $\sigma_{ik} = \sum_\alpha \sigma_{ik}^\alpha$ and $\varrho F_i = \sum_\alpha \varrho^\alpha F_i^\alpha$

In this balance there occurs a constituent $\sum_\alpha \varrho^\alpha v_i^\alpha v_k^\alpha$ describing the diffusion flows and its interactions. It comes out that the description towards the mass center leads to the simplest results.

Let us build up now the momentum balance for a constituent and for the whole mixture in the case of an arbitrary reference velocity .

The momentum balance for a constituent (α) can be expressed as follows.

$$(5.7)\qquad \frac{d}{dt} \int_V \varrho^\alpha V_i^\alpha dV = \int_V \left(\varrho^\alpha F_i^\alpha + \varphi_i^\alpha\right) dV + \int_A P_i^\alpha dA$$

When transformed we get

$$\int_V \frac{\partial}{\partial t}(\varrho^\alpha V_i^\alpha) + \frac{\partial}{\partial x_k}(\varrho^\alpha V_i^\alpha V_k^\alpha)\, dV = \int_V \langle V_i^\alpha \left(\frac{\partial \varrho^\alpha}{\partial t} + \frac{\partial}{\partial x_k}(\varrho^\alpha V_k^\alpha)\right)$$

$$+ \varrho^\alpha \left[\frac{\partial V_i}{\partial t} + V_k^\alpha \frac{\partial V_i^\alpha}{\partial x_k} \right] \rangle dV = \int_V \left(\varrho^\alpha \frac{dV_i^\alpha}{dt} + V_i^\alpha R^\alpha \right) dV$$

Finally the local form of balance is conventional and the same in every reference system.

$$(5.8)\qquad \varrho^\alpha \frac{dV_i^\alpha}{dt} = \left(-V_i^\alpha R^\alpha + \varphi_i^\alpha\right) + \varrho^\alpha F_i^\alpha + \sigma_{ij,j}^\alpha$$

The different result is obtained in the momentum balance for all constituents

$$\sum_\alpha \frac{d}{dt}\int_V \rho^\alpha V_i^\alpha \, dV =$$

$$=\sum_\alpha \int_V \frac{\partial}{\partial t}(\rho w_i) + \frac{\partial}{\partial x_k}\left[\rho^\alpha \left(V_i + \frac{1}{\rho^\alpha} J_i^\alpha\right)\left(V_k + \frac{1}{\rho^\alpha} J_k^\alpha\right)\right] dV =$$

$$=\sum_\alpha \int_V \frac{\partial}{\partial t}(\rho w_i) + \frac{\partial}{\partial x_k}\left[\rho^\alpha \left(V_i V_k + V_i \frac{1}{\rho^\alpha} J_k^\alpha + \frac{1}{\rho^\alpha} J_i^\alpha V_k + \left(\frac{1}{\rho^\alpha}\right)^2 J_i^\alpha J_k^\alpha\right)\right] dV =$$

$$=\sum_\alpha \int_V \left\langle \frac{\partial}{\partial t}(\rho w_i) + V_k \left[\rho V_{i,k} + (\rho V_{l,l} + J_{l,l}^\alpha)\delta_{ik} + J_{i,k}^\alpha\right] + J_k^\alpha (V_{i,k} + V_{l,l}\,\delta_{ik}) + \left(\frac{1}{\rho^\alpha} J_i^\alpha J_k^\alpha\right)_{,k} \right\rangle dV$$

Finally we abtain

$$\sum_\alpha \frac{d}{dt}\int_V \rho^\alpha V_i^\alpha dV = \sum_\alpha \int_V \rho^\alpha F_i^\alpha dV + \sum_\alpha \int_A P_i^\alpha dA \longrightarrow$$

(5.10)

$$\longrightarrow \frac{\partial}{\partial t}[\rho(V_i + d_i) + V_k[\rho V_{i,k} + (\rho V_{l,l} + J_{l,l}^\alpha)\delta_{ik} + J_{i,k}^\alpha] +$$

$$+ J_k^\alpha (V_{i,k} + V_{l,l}\delta_{ik}) = \rho F_i + \sigma_{ij,j} - \sum_\alpha \left(\frac{1}{\rho^\alpha} J_i^\alpha J_k^\alpha\right)_{,k}$$

For $V_i = const.$ we obtain $V_{i,k} = 0$, $V_{i,i} = 0$, $w_i = V_i + d_i$

$$\frac{\partial}{\partial t}[\rho(V_i + d_i)] + V_k\left[J_{l,l}^\alpha \delta_{ik} + J_{i,k}^\alpha\right] =$$

(5.11)

$$= \rho F_i + \sigma_{ij,j} - \sum_\alpha \left(\frac{1}{\rho^\alpha} J_i^\alpha J_j^\alpha\right)_{,j}$$

Let us consider an interesting case, when one of mixture constituents is at rest (e.g. V_i^β) and its velocity is assumed to be the reference velocity $V_i^\beta = V_i$. We obtain $V_i^\beta = V_i = 0$ (the zero velocity towards the outer reference system).

$$\sum_{\alpha} \frac{d}{dt}\int_V \rho^{\alpha} V_i^{\alpha}\, dV = \int_V \frac{\partial}{\partial t}(\rho W_i)\, dV + \int_A \sum_{\alpha} \frac{1}{\rho^{\alpha}} J_i^{\alpha} J_k^{\alpha} n_k\, dA \tag{5.12}$$

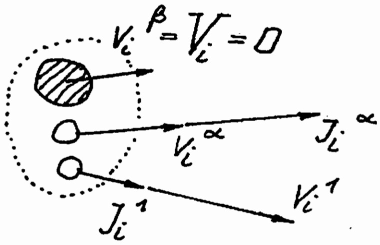


Fig.7

Finally the momentum balance for the whole mixture, in which one of constituents is motionless, has the form

$$\sum_{\alpha}{}' \frac{d}{dt}\int_V \rho^{\alpha} V_i^{\alpha}\, dV = \sum_{\alpha}\int_V (\rho^{\alpha} F_i^{\alpha} + \varphi_i^{\alpha})\, dV + \sum_{\alpha}\int_A P_i^{\alpha}\, dA$$

$$\longrightarrow \quad \frac{\partial}{\partial t}(\rho W_i) = \rho F_i + \sigma_{ij,j} - \frac{\partial}{\partial x_k}\Big(\sum_{\alpha} \frac{1}{\rho^{\alpha}} J_i^{\alpha} J_k^{\alpha}\Big) \tag{5.13}$$

From this formula it follows, that if $\rho^{\alpha} V_k^{\alpha} = \rho^{\alpha} V_k + J_k^{\alpha} \longrightarrow J_k^{\alpha} = \rho^{\alpha} V_k^{\alpha}$ other-wise $\sum_{\alpha} \frac{1}{\rho^{\alpha}} J_i^{\alpha} J_k^{\alpha} = \sum_{\alpha} \rho^{\alpha} V_i^{\alpha} V_k^{\alpha} = k_{ik}$ is constant in the space $k_{ik} \neq k_{ik}(x_k)$ or its change in the space is negligible, i.e. $(\sum_{\alpha} \rho^{\alpha} V_i^{\alpha} V_k^{\alpha})_{,k} \approx 0$ in comparison to $\rho F_i + \sigma_{ik,k}$, then the equations for the whole mixture have the form of the clasical motion ones.

$$\frac{\partial}{\partial t}(\rho W_i) = \rho F_i + \sigma_{ij,j} \tag{5.14}$$

In general, however, we have

$$\frac{\partial}{\partial t}(\rho W_i) = \rho F_i + \sigma_{ij,j} - \Big(\sum_{\alpha} \rho^{\alpha} V_i^{\alpha} V_j^{\alpha}\Big)_{,j} \tag{5.15}$$

Assuming the stress tensor symmetry $\sigma_{ij}^{\alpha} = \sigma_{ji}^{\alpha}$ we satisfy identically the angular momentum conservation principle. When analysing the equations (5.6),(5.13), and (5.15) we find that relatively simple equations near the classical momentum ones for one - constituent media cam be obtained neglecting terms $\frac{\partial}{\partial x_k}\left(\sum_\alpha \rho^\alpha u_i^\alpha u_k^\alpha\right)$ in the e.g.(5.6) and analogically $\rho \dot{W}_i$, $\frac{\partial}{\partial x_k}\left(\sum_\alpha \rho^\alpha V_i^\alpha V_k^\alpha\right)$ in the e.g.(5.15).

6. The static equllibrium of a mixture.

The equilibrium of each of constituents is possible, i.e.

$$\frac{dV_i^{\alpha}}{dt} = 0 \longrightarrow \frac{\partial V_i}{\partial t} + V_k \frac{\partial V_i}{\partial x_k} = 0$$

It leads to the relation

$$\sigma_{ij,j}^{\alpha} + \rho^{\alpha} F_i^{\alpha} + \varphi_i^{\alpha} - V_i^{\alpha} R^{\alpha} = 0 \tag{6.1}$$

for every α.

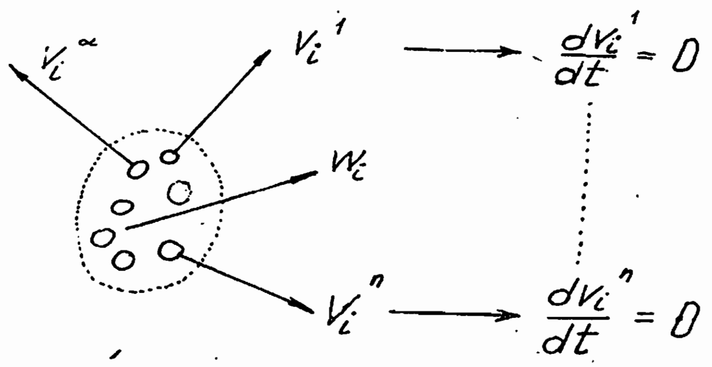


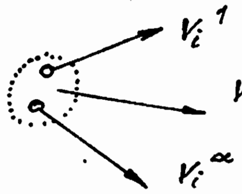
Fig.8

$\left.\frac{dV_i^{\alpha}}{dt}\right|_0 = \left.\frac{dV_i^{\alpha}}{dt}\right|_t$ for any t.

The equilibrium in the „mean" sense denotes that each of constituents (or only several ones) moves, with that

$$\frac{dW_i}{dt} = 0 \longrightarrow \rho F_i + \sigma_{ik,k} - \frac{\partial}{\partial x_k}\left(\sum_\alpha \rho^\alpha u_i^\alpha u_k^\alpha\right) = 0 \tag{6.2}$$

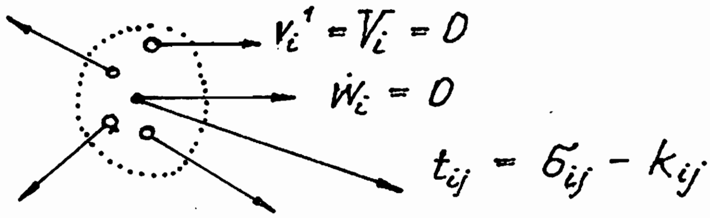
i.e. constituents displace arbitrary but the mean velocity remains constant (the rigid displacement)

Fig.9 

$$\longrightarrow \quad \frac{dW_i}{dt} = 0 \;, \quad \frac{dV_i^\alpha}{dt} \neq 0$$

Analogously if one of constituents V_i^1 is at rest $V_i^1 = V_i = 0$ and it is assumed to be the reference velocity, then for $\dot{W}_i$ and $\dot{\varrho}$ we get relations (comp.(5.15))

$$\begin{aligned} \sigma_{ij,j} - \Big(\sum_\alpha \varrho^\alpha V_i^\alpha V_j^\alpha\Big)_{,j} + \varrho F_i &= 0 \\ (\sigma_{ij} - k_{ij})_{,j} + \varrho F_i &= 0 \qquad (6.3) \\ t_{ij,j} + \varrho F_i &= 0 \end{aligned}$$

Fig.1o 

It is worth to notice, that the distribution of these stresses follows from the motion equations and not from physical postulates. To analogous results one can come at assuming that $\varrho W_i = 0$ Then, the equations (6.2) and (6.3) are identical.

At the momentum balances we conclude the problem analysis related to an arbitrary coordinate system.

7. Energy balance

Now, we present the energy balance for the whole mixture. It includes additional mutuably well-balanced flows of energy between constituents.

This balance has the form

$$\sum_{\alpha} \frac{d}{dt} \int_V \varrho^{\alpha}(U^{\alpha}+K^{\alpha})dV = \sum_{\alpha} \int_V (\varrho^{\alpha} r^{\alpha} + \varrho^{\alpha} F_i^{\alpha} V_i^{\alpha} + E^{\alpha})dV$$

(7.1)

$$+ \sum_{\alpha} \int_A (\sigma_{ij}^{\alpha} V_j^{\alpha} + q_i^{\alpha}) n_i \, dA$$

In the addition

$$\sum_{\alpha} \frac{d}{dt} \int_V \varrho^{\alpha} U^{\alpha} dV = \sum_{\alpha} \int_V \frac{\partial}{\partial t}(\varrho^{\alpha} U^{\alpha}) + \frac{\partial}{\partial x_k}[\varrho^{\alpha} U^{\alpha} V_k^{\alpha}] dV =$$

(7. 2)

$$= \int_V \varrho \frac{dU}{dt} dV + \int_V \sum_{\alpha} \frac{\partial}{\partial x_k}[\varrho^{\alpha} U^{\alpha} u_i^{\alpha}] dV$$

$$\frac{1}{2} \sum_{\alpha} \frac{d}{dt} \int_V \varrho^{\alpha} V_i^{\alpha} V_i^{\alpha} dV = \frac{1}{2} \sum_{\alpha} \int_V \frac{\partial}{\partial t}(\varrho^{\alpha} V_i^{\alpha} V_i^{\alpha}) + \frac{\partial}{\partial x_k}[\varrho^{\alpha} V_i^{\alpha} V_i^{\alpha} V_k^{\alpha}] dV =$$

(7.3)

$$= \int_V \frac{\partial}{\partial t}(\varrho K) + \frac{\partial}{\partial x_k}[\varrho K w_k + \sum_{\alpha} \frac{\partial}{\partial x_k} \varrho^{\alpha} K^{\alpha} u_i^{\alpha}] dV =$$

$$= \int_V \varrho \frac{dK}{dt} + \sum_{\alpha} \frac{\partial}{\partial x_k} [\varrho^{\alpha} K^{\alpha} u_i^{\alpha}] dV$$

Thus, the energy balance has the form

$$\varrho \frac{d}{dt}(U+K) = \varrho r + \varrho F_i w_i + \sum_{\alpha} \varrho^{\alpha} F_i^{\alpha} u_i^{\alpha} + \sum_{\alpha} E^{\alpha}$$

(7.4)

$$- q_{i,i} + (\sigma_{ij} w_j)_{,i} + \sum_{\alpha} [\sigma_{ij}^{\alpha} u_j^{\alpha} - \varrho^{\alpha}(U^{\alpha}+K^{\alpha}) u_i^{\alpha}]_{,i}$$

The energy balance expressed by (7.4) will be used below to an analysis of thermodiffusion processes. In the balance (7.4) we introduce the following quantities

(7.5) $\sum_\alpha \varrho^\alpha F_i^\alpha V_i^\alpha = \varrho F_i W_i$, $\sum_\alpha \varrho^\alpha r^\alpha = \varrho r$, $\sum_\alpha \varrho^\alpha U^\alpha = \varrho U$, $\sum_\alpha q_i^\alpha = q_i$

Let us notice the fact that the condition $V_i^1 = V_i^2 = \ldots\ldots = V_i^n$ leads to the relation

$$\sum_\alpha \frac{d}{dt}\int_V \varrho^\alpha (U^\alpha + K^\alpha)\,dV = \int_V \varrho \frac{d}{dt}(U+K)\,dV \tag{7.6}$$

Then the diffusion fluxes $j_i^\alpha = \varrho^\alpha U_i^\alpha$ vanish.
Moreover, the condition $\sum_\alpha j_i^\alpha (U^\alpha + K^\alpha - \frac{1}{\varrho^\alpha}\sigma_{ii}^\alpha) = 0$ shows that the mixture and homogeneous body are indistinguishable (on the energy level,), when the velocities of particular particles are different

$$\sum_\alpha j_i^\alpha \left(\sigma_{ii}^\alpha \frac{1}{\varrho^\alpha} - U^\alpha - K^\alpha\right) = \sum_\alpha j_i^\alpha M^\alpha \,, \quad M^\alpha = 0 \rightarrow \frac{\sigma_{ii}^\alpha}{\varrho^\alpha} = U^\alpha + K^\alpha \tag{7.7}$$

If the mass unit of each of constituents has the same both internal and kinetic energies and if it is $\frac{1}{\varrho^1}\sigma_{ii}^1 = \ldots\ldots = \frac{1}{\varrho^n}\sigma_{ii}^n$, then the diffusion does not occur in the mixture.

8. Entropy balance.

The starting point is here inequality of entropy growth given in the form

$$\sum_\alpha \frac{d}{dt}\int_V \varrho^\alpha S^\alpha dV \geqslant \sum_\alpha \int_V \frac{\varrho^\alpha r^\alpha}{T^\alpha} dV - \sum_\alpha \int_A \frac{q_i^\alpha}{T^\alpha} n_i\, dA \tag{8.1}$$

Determining the derivative $\sum_\alpha \frac{d}{dt}\int_V \varrho^\alpha S^\alpha dV$ we obtain

$$\begin{aligned}
\sum_\alpha \frac{d}{dt}\int_V \varrho^\alpha S^\alpha dV &= \sum_\alpha \int_V \frac{\partial}{\partial t}(\varrho^\alpha S^\alpha) + \frac{\partial}{\partial x_k}(\varrho^\alpha S^\alpha V_k^\alpha)\,dV = \\
&= \int_V \frac{\partial}{\partial t}(\varrho S) + \frac{\partial}{\partial x_k}\left[\varrho S W_k + \sum_\alpha \varrho^\alpha S^\alpha U_k^\alpha\right] dV = \\
&= \int_V \left\langle \varrho \frac{dS}{dt} + \sum_\alpha \frac{\partial}{\partial x_k}(\varrho^\alpha S^\alpha U_k^\alpha)\right\rangle dV .
\end{aligned} \tag{8.2}$$

So, the entropy inequality takes on the form

$$(8.3) \qquad \rho \frac{dS}{dt} \geqslant \sum_{\alpha} \frac{\rho^\alpha r^\alpha}{T^\alpha} - \sum_{\alpha} \left(\frac{q_i^\alpha}{T^\alpha}\right)_{,i} - \sum_{\alpha} \left(\rho^\alpha u_i^\alpha S^\alpha\right)_{,i}$$

The expression $\sum_{\alpha} \frac{\rho^\alpha r^\alpha}{T^\alpha}$, $\sum_{\alpha} \left(\frac{q_i^\alpha}{T^\alpha}\right)_{,i}$ can be prescribed as follows

$$(8.4) \qquad \begin{aligned} \sum_{\alpha} \frac{\rho^\alpha r^\alpha}{T^\alpha} &= \frac{\rho r}{T} + \sum_{\alpha} \frac{\rho^\alpha r^\alpha}{T^\alpha} \frac{T - T^\alpha}{T} \\ \sum_{\alpha} \left(\frac{q_i^\alpha}{T^\alpha}\right)_{,i} &= \left(\frac{q_i}{T}\right)_{,i} + \sum_{\alpha} \left(\frac{q_i^\alpha}{T^\alpha} \frac{T - T^\alpha}{T}\right)_{,i} \end{aligned}$$

In the consequence we get inequalities

$$(8.5) \qquad \begin{aligned} \rho T \frac{dS}{dt} \geqslant \rho r - q_{i,i} &+ \frac{q_i T_{,i}}{T} - T \sum_{\alpha} \left(\rho^\alpha u_i^\alpha S^\alpha\right)_{,i} \\ &+ T \left[\sum_{\alpha} \left(\frac{\rho^\alpha r^\alpha}{T^\alpha} \frac{T - T^\alpha}{T}\right) - \sum_{\alpha} \left(\frac{q_i^\alpha}{T^\alpha} \frac{T - T^\alpha}{T}\right)_{,i} \right]. \end{aligned}$$

When assuming that the temperature $T \to T_b$ $(t \to \infty)$ tends towards balanced one, then the terms in the buckle parentheses vanish.

Let us notice that in both cases there occurs a coefficent $k^\alpha = \frac{T - T^\alpha}{T}$

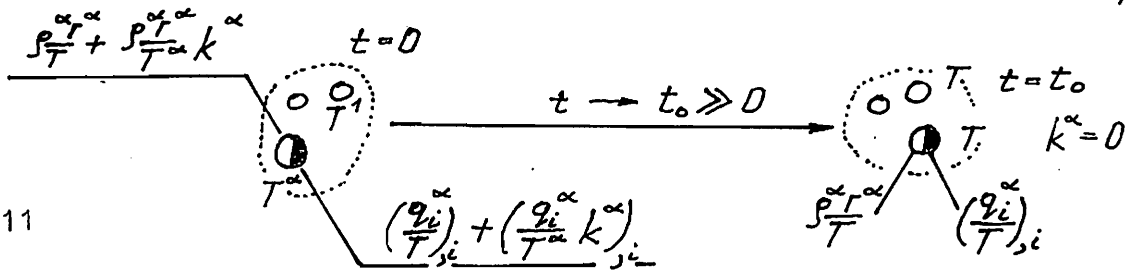


Fig.11

definning extinction of dissipation following from different temperatures of constituents (the source and fluxes).

In the simpler case of the mixture holding an equal temperature we obtain

$$(8.6) \qquad \rho T \frac{dS}{dt} \geqslant \rho r - q_{i,i} + \frac{q_i T_{,i}}{T} - \sum_{\alpha} \left(\rho^\alpha u_i^\alpha S^\alpha\right)_{,i}$$

If we assume that the mass unit of each of constituent holds an equal temperature and the same entropy $S^1 = \ldots\ldots = S^\alpha = \ldots\ldots = S^n$

then the component $\sum_{\alpha} \rho^{\alpha} u_i^{\alpha} s^{\alpha} = s \sum_{\alpha} \rho^{\alpha} u_i^{\alpha} = 0$

9. The system of process balances and the residual inequality.

We present now the fundamental set of the thermomechanics processes balances in the local form

The balances:

- of mass for a constituent (α)

(9.1) $$\frac{\partial \rho^{\alpha}}{\partial t} + \frac{\partial}{\partial x_k}(\rho^{\alpha} v_k^{\alpha}) = R^{\alpha}$$

$$\left(\frac{\partial \rho^{\alpha}}{\partial t} + \frac{\partial}{\partial x_k}(\rho^{\alpha} V_k + J_k^{\alpha}) = R^{\alpha} \right)$$

(9.2) $$\rho \frac{dc^{\alpha}}{dt} + \frac{\partial}{\partial x_k}(\dot{j}_k^{\alpha}) = R^{\alpha}, \quad c^{\alpha} = \frac{\rho^{\alpha}}{\rho}$$

$$v_k^{\alpha} = w_k + u_k^{\alpha}, \quad \dot{j}_k^{\alpha} = \rho^{\alpha} u_k^{\alpha}$$

- and for the whole mixture

(9.3) $$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho w_k) = 0 \quad \left(\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho V_k) + \frac{\partial}{\partial x_k}\left(\sum_{\alpha} J_k^{\alpha}\right) = 0 \right)$$

- the balance of momentum

(9.4) $$\rho^{\alpha} \frac{dv_i^{\alpha}}{dt} = -v_i^{\alpha} R^{\alpha} + \varphi_i^{\alpha} + \rho^{\alpha} F_i^{\alpha} + \sigma_{ij,j}^{\alpha} \qquad \sigma_{ij}^{\alpha} = \sigma_{ji}^{\alpha}$$

(9.5) $$\rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ij,j} - \sum_{\alpha} (\rho^{\alpha} u_i^{\alpha} u_j^{\alpha})_{,j}$$

and for an arbitrarily chosen reference velocity

(9.6) $$\frac{\partial}{\partial t}[\rho(V_i + d_i)] + V_k[\rho V_{i,k} + (\rho V_{l,l} + J_{l,l}^{\alpha})\delta_{ik} + J_{i,k}^{\alpha}]$$
$$+ J_k^{\alpha}(V_{i,k} + V_{l,l}\delta_{ik}) = \rho F_i + \sigma_{ik,k} - \sum_{\alpha}\left(\frac{1}{\rho^{\alpha}} J_i^{\alpha} J_k^{\alpha}\right)_{,k}$$

- the balance of energy

$$\rho \frac{d}{dt}(U+K) = \rho r + \rho F_i w_i - q_{i,i} + (\sigma_{ij} w_j)_{,i} + \tag{9.7}$$
$$+ \sum_{\alpha} [\frac{1}{\rho^\alpha} \sigma_{ii}^\alpha - U^\alpha - K^\alpha) \rho^\alpha u_i^\alpha]_{,i}$$

and the inequality of entropy

$$\rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - \frac{q_{i,i}}{T} + \frac{q_i T_{,i}}{T^2} + \sum_{\alpha} [\frac{\rho^\alpha r^\alpha}{T^\alpha} k^\alpha - \rho^\alpha u_i^\alpha S^\alpha - (\frac{q_i^\alpha}{T^\alpha} k^\alpha)_{,i}] \tag{9.8}$$

From the equations (9.2), (9.4), (9.7) and from the condition (9.8) we derive the residual inequality

$$\rho \frac{dU}{dt} = \rho r - q_{i,i} + \sigma_{ij} d_{ij} - w_i \sum_{\alpha} (\rho^\alpha u_i^\alpha u_k^\alpha)_{,k}$$
$$+ \sum_{\alpha} [(\frac{1}{\rho^\alpha} \sigma_{ii}^\alpha - U^\alpha - K^\alpha) \rho^\alpha u_i^\alpha]_{,i}$$

$$\rho T \frac{dS}{dt} - \rho r + q_{i,i} - \frac{q_i T_{,i}}{T}$$
$$+ T \sum_{\alpha} [\frac{\rho^\alpha r^\alpha}{T^\alpha} k^\alpha - (\frac{q_i^\alpha}{T^\alpha} k^\alpha)_{,i} + (\rho^\alpha u_i^\alpha S^\alpha)_{,i}] \geqslant 0$$

$$-\rho \frac{dU}{dt} + \rho T \frac{dS}{dt} + \sigma_{ik} d_{ik} - w_i \sum_{\alpha} (\rho^\alpha u_i^\alpha u_k^\alpha)_{,k} - \frac{q_i T_{,i}}{T} \tag{9.9}$$
$$+ \sum_{\alpha} [(\frac{1}{\rho^\alpha} \sigma_{ii}^\alpha + T S^\alpha - U^\alpha - K^\alpha) \rho^\alpha u_i^\alpha]_{,i} - T \sum_{\alpha} [\frac{\rho^\alpha r^\alpha}{T^\alpha} k^\alpha - (\frac{q_i^\alpha}{T^\alpha} k^\alpha)_{,i}] \geqslant 0$$

For the free energy the inequality (9.9) take on the form

$$-\rho \frac{dA}{dt} - \rho S \frac{dT}{dt} + \sigma_{ij} d_{ij} - w_i \sum_{\alpha} (\rho^\alpha u_i^\alpha u_j^\alpha)_{,j} - \frac{q_i T_{,i}}{T} \tag{9.10}$$
$$- \sum_{\alpha} [\frac{1}{\rho^\alpha} \sigma_{ii}^\alpha + T S^\alpha - U^\alpha - K^\alpha) \rho^\alpha u_i^\alpha]_{,i} - T \sum_{\alpha} [\frac{\rho^\alpha r^\alpha}{T^\alpha} k^\alpha - (\frac{q_i^\alpha}{T^\alpha} k^\alpha)_{,i}] \geqslant 0$$

Introducing the mass flux $\dot{j}_i^{\alpha} = \rho^{\alpha} v_i^{\alpha}$ and $M^{\alpha} = \left(\frac{1}{\rho^{\alpha}} \sigma_u^{\alpha} + TS^{\alpha} - U^{\alpha} - K^{\alpha}\right) = M_\sigma^{\alpha} + M_s^{\alpha} + M_u^{\alpha} + M_k^{\alpha}$ we obtain

$$-\rho \frac{dA}{dt} - \rho S \frac{dT}{dt} + \sigma_{ij} d_{ij} + \sum_{\alpha} \left(M^{\alpha} \dot{j}^{\alpha}_{i,i} + M^{\alpha}_{,i} \dot{j}_i^{\alpha} \right) - \frac{q_i T_{,i}}{T}$$

$$-T \left[\sum_{\alpha} \left(\frac{\rho^{\alpha} r^{\alpha}}{T^{\alpha}} k^{\alpha} \right) - \sum_{\alpha} \left(\frac{q_i^{\alpha}}{T^{\alpha}} k^{\alpha} \right)_{,i} \right] - w_i \sum_{\alpha} \left(\frac{1}{\rho^{\alpha}} \dot{j}_i^{\alpha} \dot{j}_k^{\alpha} \right)_{,k} \geqslant 0 \tag{9.11}$$

$$-\rho \frac{dA}{dt} - \rho S \frac{dT}{dt} + \sigma_{ij} d_{ij} - \sum_{\alpha} M^{\alpha} \rho \frac{dc^{\alpha}}{dt} + \sum_{\alpha} \left(R^{\alpha} M^{\alpha} + M^{\alpha}_{,i} \dot{j}_i^{\alpha} \right)$$

$$- \frac{q_i T_{,i}}{T} - w_i \sum_{\alpha} \left(\frac{1}{\rho^{\alpha}} \dot{j}_i^{\alpha} \dot{j}_k^{\alpha} \right)_{,k} - T \left[\sum_{\alpha} \frac{\rho^{\alpha} r^{\alpha}}{T^{\alpha}} k^{\alpha} - \sum_{\alpha} \left(\frac{q_i^{\alpha}}{T^{\alpha}} k^{\alpha} \right)_{,i} \right] \geqslant 0$$

For $t > t_0$

$$-\rho \frac{dA}{dt} - \rho S \frac{dT}{dt} + \sigma_{ij} d_{ij} - \sum_{\alpha} M^{\alpha} \rho \frac{dc^{\alpha}}{dt} + \tag{9.12}$$

$$- \sum_{\alpha} \left(R^{\alpha} M^{\alpha} + M^{\alpha}_{,i} \dot{j}_i^{\alpha} \right) - w_i \sum_{\alpha} \left(\frac{1}{\rho^{\alpha}} \dot{j}_i^{\alpha} \dot{j}_k^{\alpha} \right)_{,k} - \frac{q_i T_{,i}}{T} \geqslant 0$$

Analyzing the dissipation sources related to the mass flow $\dot{j}_i^{\alpha}$ **and its production** R^{α} **we find** $\sum_{\alpha} \left(M^{\alpha}_{,i} \dot{j}_i^{\alpha} + M^{\alpha} R^{\alpha} \right) \geqslant 0$ **but**

($\mathcal{E}_1$) $M^1_{,i} = M^2_{,i} = \ldots\ldots = M^n_{,i}$ **it is no dissipation**

$$\sum_{\alpha} M^{\alpha}_{,i} \dot{j}_i^{\alpha} = M_{,i} \sum_{\alpha} \dot{j}_i^{\alpha} = 0$$

($\mathcal{E}_2$) $M^1 = M^2 = \ldots\ldots = M^n$ **it is also no dissipation**

$$\sum_{\alpha} M^{\alpha} R^{\alpha} = M \sum_{\alpha} R^{\alpha} = 0$$

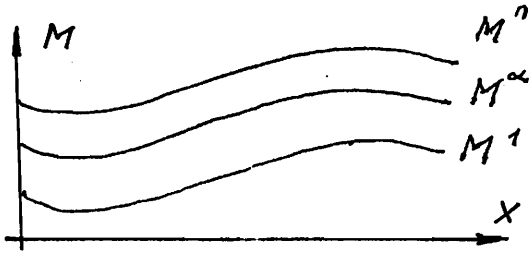
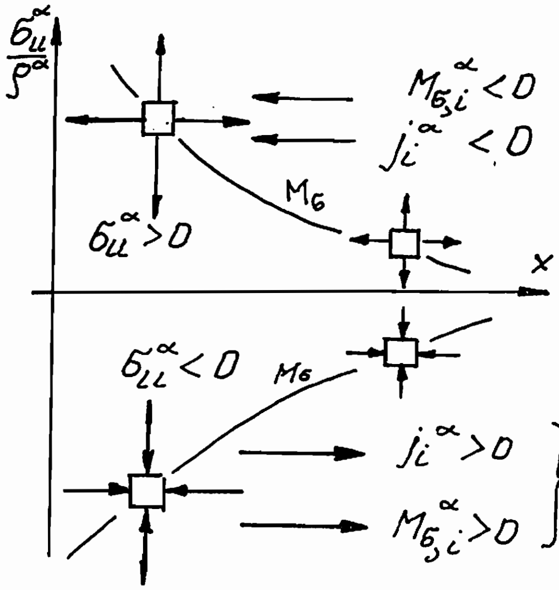


Fig.12

Analysis the dissipations sources

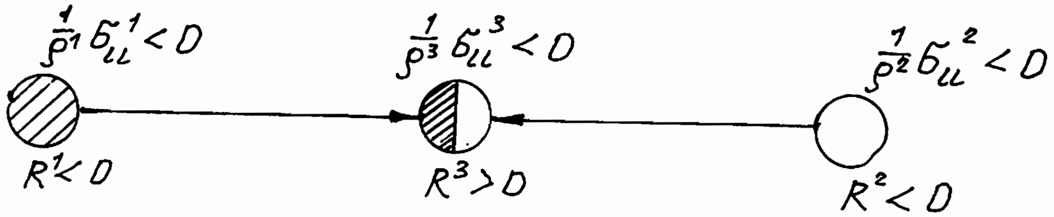
$$\sum_\alpha \left(M^\alpha_{,i} \dot{j}^\alpha_i + M^\alpha R^\alpha\right) \geqslant 0 \longrightarrow \begin{cases} \sum_\alpha M^\alpha_{,i} \dot{j}^\alpha_i \geqslant 0 \\ \sum_\alpha M^\alpha R^\alpha \geqslant 0 \end{cases}$$

1. $\boxed{M^\alpha \longrightarrow M^\alpha_\sigma = \frac{1}{\rho^\alpha}\sigma^\alpha_{ll}}$ $\quad \sum_\alpha \left(M^\alpha_{\sigma,i} \dot{j}^\alpha_i + M^\alpha_\sigma R^\alpha\right) \geqslant 0$



$$\left.\begin{matrix} M^\alpha_{\sigma,i} < 0 \\ \dot{j}^\alpha_i < 0 \end{matrix}\right\} \quad \sum_\alpha \left(-\frac{\sigma^\alpha_{ll}}{\rho^\alpha}\right)_{,i} \left(-\dot{j}^\alpha_i\right) \geqslant 0$$

$$\left.\begin{matrix} \dot{j}^\alpha_i > 0 \\ M^\alpha_{\sigma,i} > 0 \end{matrix}\right\} \quad \sum_\alpha \left(\frac{\sigma^\alpha_{ll}}{\rho^\alpha}\right)_{,i} \dot{j}^\alpha_i \geqslant 0$$

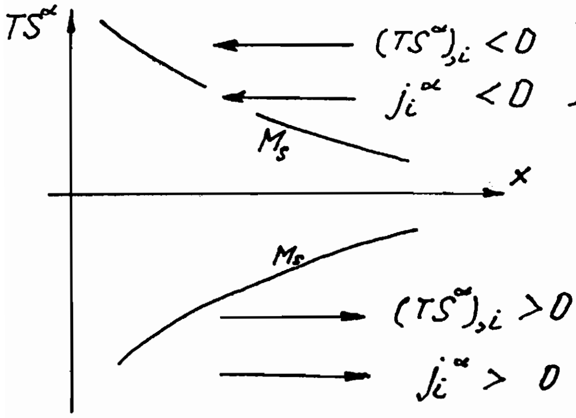


$$\sum_\alpha M^\alpha_\sigma R^\alpha \geqslant 0 \longrightarrow \frac{1}{\rho^1}\sigma^1_{ll} R^1 + \frac{1}{\rho^2}\sigma^2_{ll} R^2 - \frac{1}{\rho^3}\sigma^3_{ll} R^3 \geqslant 0$$

$$\frac{1}{\rho^1}\sigma^1_{ll} R^1 + \frac{1}{\rho^2}\sigma^2_{ll} R^2 \geqslant \frac{1}{\rho^3}\sigma^3_{ll} R^3$$

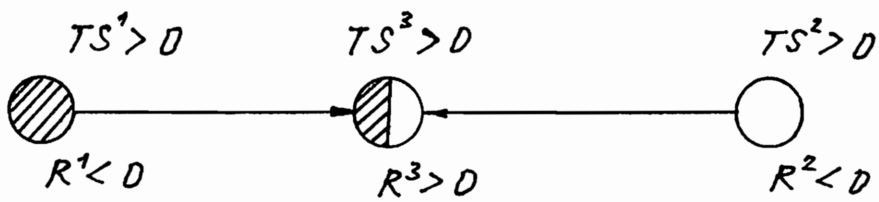
Fig.13

(2) $\boxed{M^\alpha \longrightarrow M_S^\alpha = TS^\alpha}$ $\qquad \sum_\alpha (TS^\alpha)_{,i} j_i^\alpha + TS^\alpha R^\alpha \geqslant 0$



$$\sum_\alpha -(T_{,i} S^\alpha + TS^\alpha_{,i})(-j_i^\alpha) \geqslant 0$$

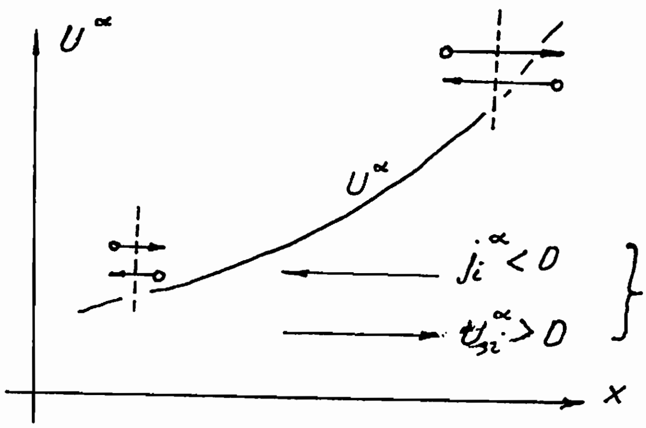
$$\sum (T_{,i} S^\alpha + TS^\alpha_{,i})(j_i) \geqslant 0$$



$$\sum_\alpha M_S^\alpha R^\alpha \geqslant 0 \longrightarrow (-S^1R^1 - S^2R^2 + S^3R^3)T \geqslant 0$$

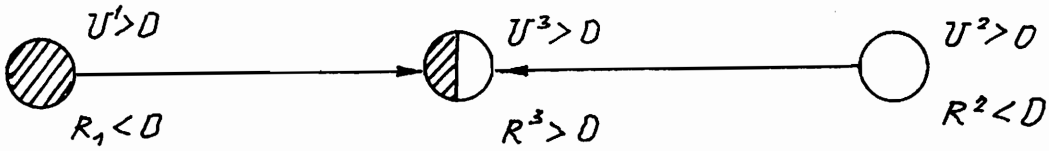
$$S^3R^3 \geqslant S^1R^1 + S^2R^2$$

(3) $\boxed{M^\alpha \longrightarrow M_U^\alpha = -U^\alpha}$ $\qquad -\sum_\alpha (U^\alpha_{,i} j_i^\alpha + U^\alpha R^\alpha) \geqslant 0$



$$-\sum_\alpha U^\alpha_{,i} j_i^\alpha \geqslant 0$$

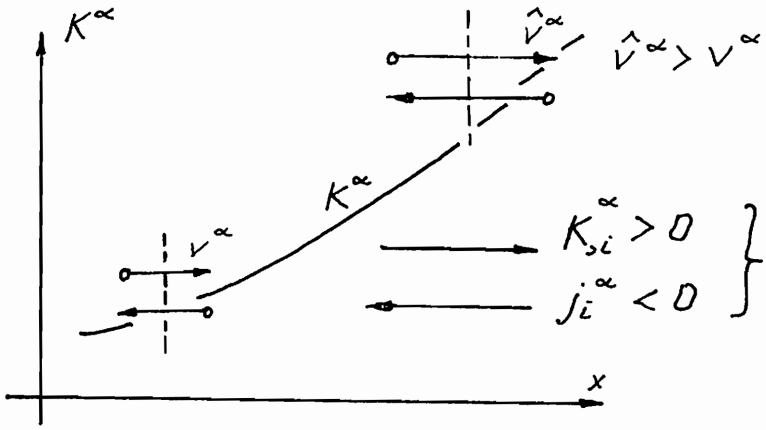
Fig.14



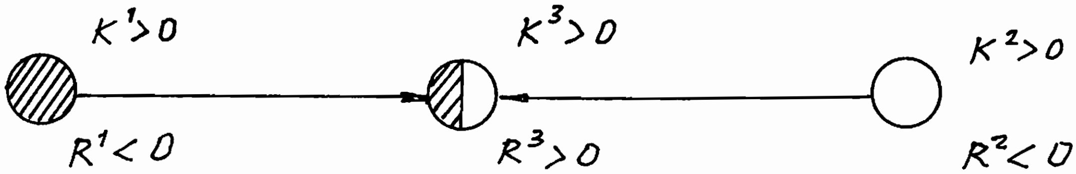
$$-\sum_\alpha U^\alpha R^\alpha \geqslant 0 \longrightarrow -(-U^1R^1 - U^2R^2 + U^3R^3) \geqslant 0$$

$$U^1R^1 + U^2R^2 \geqslant U^3R^3$$

4. $\boxed{M^\alpha \longrightarrow M_k^\alpha = -K^\alpha}$ $\quad -\sum_\alpha (K^\alpha_{,i} j_i^\alpha + K^\alpha R^\alpha) \geqslant 0$



$$-\sum_\alpha K^\alpha_{,i} j_i^\alpha \geqslant 0$$



$$-\sum_\alpha K^\alpha R^\alpha \geqslant 0 \longrightarrow -(-K^1R^1 - K^2R^2 + K^3R^3) \geqslant 0$$

$$K^1R^1 + K^2R^2 \geqslant K^3R^3$$

Fig.15

Chapter III

The flows in a solid

In this chapter various sets of balances describing diffusion processes in a solid will be presented. Each of these cases results logically from the mixture theory equations which were analysed in the previous chapter. In particular, the concept of the dominant constituent leads directly to searched diffusion equations in a solid. According to this idea the velocity of the distinguished constituent of the dominant density in the mixture is nearly indentical to the velocity of particle mass center.

We shall analyse the problems of diffusion flows induced by differences between

internal energies,

kinetic energies,

entropies and portional pressures

in particular constituents.

10. Diffusion treatment of mixtures.

We shall start to our considerations from balances equations giwen in the previous chapter.
We shall introduce, however, relations

$$\varrho^{\alpha} u_i^{\alpha} = j_i^{\alpha} \Longrightarrow \Big(\sum_{\alpha} \varrho^{\alpha} u_i^{\alpha} u_k^{\alpha} = \sum_{\alpha} \frac{1}{\varrho^{\alpha}} j_i^{\alpha} j_k^{\alpha}, \quad \sum_{\alpha} \sigma_{ij}^{\alpha} u_j^{\alpha} = \sum_{\alpha} \frac{1}{\varrho^{\alpha}} \sigma_{ik}^{\alpha} j_k^{\alpha}$$

$$\sum_{\alpha} \varrho^{\alpha} (TS^{\alpha} - U^{\alpha} - K^{\alpha}) u_i^{\alpha} = \sum_{\alpha} j_i^{\alpha} (TS^{\alpha} - U^{\alpha} - K^{\alpha}) \Big) \tag{10.1}$$

The balances equations have then the form

$$(10.2)\qquad \rho \frac{dc^{\alpha}}{dt} = R^{\alpha} - (j_i^{\alpha})_{,i}$$

$$(10.3)\qquad \rho \frac{dw_i}{dt} = \rho F_i + \Big(\sigma_{ik} - \sum_{\alpha} \frac{1}{\rho^{\alpha}} \dot{j}_i^{\alpha} \dot{j}_k^{\alpha}\Big)_{,k} \quad , \quad \sigma_{ik} = \sigma_{ki}$$

$$(10.4)\qquad \begin{aligned} \rho \frac{d}{dt}(U+K) &= \rho r + \rho F_i w_i + (\sigma_{ij} w_i)_{,j} - q_{i,i} \\ &+ \sum_{\alpha} \Big[\frac{1}{\rho^{\alpha}} \sigma_{ik}^{\alpha} \dot{j}_k^{\alpha} - j_i (U^{\alpha} + K^{\alpha}) \Big]_{,i} \end{aligned}$$

$$(10.5)\qquad \rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - \Big(\frac{q_i}{T}\Big)_{,i} - \sum_{\alpha} (j_i^{\alpha} S^{\alpha})_{,i}$$

In these equations the velocity w_i of the mass center occurs, and velocities of particular constituent express the mass fluxes $\dot{j}_i^{\alpha}$

The set of balances leads to the residual inequality

$$(10.6)\qquad \begin{aligned} &-\rho \frac{dU}{dt} + \rho T \frac{dS}{dt} + \sigma_{ik} w_{i,k} - w_i \Big(\sum_{\alpha} \frac{1}{\rho^{\alpha}} \dot{j}_i^{\alpha} \dot{j}_k^{\alpha} \Big)_{,k} \\ &+ \sum_{\alpha} \Big[\Big(\frac{1}{\rho^{\alpha}} \sigma_{il}^{\alpha} + T S^{\alpha} - U^{\alpha} - K^{\alpha} \Big) j_i^{\alpha} \Big]_{,i} - \frac{q_i T_{,i}}{T} \geqslant 0 \end{aligned}$$

The inequality (10.6) must be satisfied in every real process.

11. Diffusion in the dominant constituent

The given in the point 10 set of balances is valid for mixtures of gases holding equal temperatures of constituents. In a solid the thermodiffusion processes are also possible. Specifity of these processes depends on existing of the dominant constituent (of relatively large density), i.e. the skeleton (the solid phase) and of flows of constituents holding relatively small density. The migrating constituents decide, however, on the properties of deformation processes.They define orocesses of creep,plastic flow etc.

We begin the analysis of these processes from the momentum balance

(11.1) $$\rho \frac{dw_i}{dt} = \rho F_i + \left(\sigma_{ik} - \sum_\alpha \frac{1}{\rho^\alpha} \dot{j}_i^\alpha \dot{j}_k^\alpha\right)_{,k}$$

Occuring in this equation expression $\sum_\alpha \frac{1}{\rho^\alpha} \dot{j}_i^\alpha \dot{j}_k^\alpha$ differs it from the classical momentum balance.

Let us notice that if

(σ_1) $\rho^1 \gg \rho^\beta$, $\beta = 2, \ldots, n$, $\rho^1 \cong \rho = \sum_\alpha \rho^\alpha$

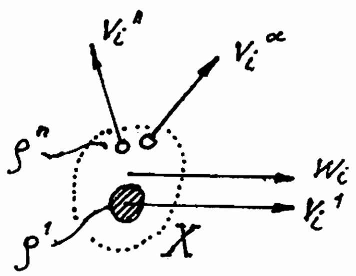


Fig. 16

then $$w_i = \sum_\alpha \frac{\rho^\alpha}{\rho} V_i^\alpha = \sum_\alpha \frac{\rho^1}{\rho} V_i^1 + \ldots + \frac{\rho^n}{\rho} V_i^n \cong V_i^1$$

(11.2) $$\sum_\alpha \frac{1}{\rho^\alpha} \dot{j}_i^\alpha \dot{j}_k^\alpha = \sum_\alpha \rho^1 u_i^1 u_k^1 + \ldots + \rho^n u_i^n u_k^n \cong 0$$

and

(σ_2)

$$\rho^1 + \rho^2 + \ldots + \rho^k = \rho^s, \quad \rho^s \gg \rho^{k+1} \ldots\ldots \rho^s \gg \rho^n$$
$$V_i^1 = V_i^2 = \ldots = V_i^k$$

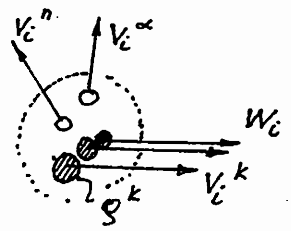


Fig. 17

(11.3) $$w_i = \sum_\alpha \frac{\rho^\alpha}{\rho} V_i^\alpha = \sum_\alpha \frac{1}{\rho}(\rho^1 + \ldots + \rho^k) V_i^k + \frac{\rho^{k+1}}{\rho} V_i^{k+1} + \ldots \cong V_i^1$$

$$\sum_\alpha \frac{1}{\rho^\alpha} \dot{j}_i^\alpha \dot{j}_k^\alpha \cong 0$$

The cases (σ_1) and (σ_2) and their combinations permit to comprise the majority of thermodiffusion processes in a solid.

From relations $\sum_\alpha \rho^\alpha u_i^\alpha u_j^\alpha = 0$ it follows

$$\sum_\alpha \rho^\alpha u_i^\alpha u_j^\alpha = 0 \longrightarrow \sum_\alpha \rho^\alpha (v_i^\alpha - w_i)(v_j^\alpha - w_j) =$$

(11.4)
$$= \sum_\alpha \rho^\alpha v_i^\alpha v_j^\alpha - \rho^\alpha v_j^\alpha w_i - \rho^\alpha v_i w_j + \rho^\alpha w_i w_j =$$

$$= \sum_\alpha \rho^\alpha v_i^\alpha v_j^\alpha - \rho w_i w_j \longrightarrow \rho w_i w_j = \sum_\alpha \rho^\alpha v_i^\alpha v_j^\alpha$$

In particular

(11.5) $$\frac{1}{2}\sum_\alpha \rho^\alpha u_i^\alpha u_i^\alpha = 0 \longrightarrow \frac{1}{2}\rho w_i w_i = \frac{1}{2}\sum_\alpha \rho^\alpha v_i^\alpha v_i^\alpha$$

From the relation (11.5) we conclude that in the energy balance also the constituent $\sum_\alpha \rho^\alpha u_i^\alpha K^\alpha = \sum_\alpha j_i^\alpha K^\alpha \longrightarrow 0$ should, in general, vanish.

Indeed

$$\frac{1}{2}\sum_\alpha \rho^\alpha v_i^\alpha v_i^\alpha = \frac{1}{2}\sum_\alpha \rho^\alpha (w_i + u_i^\alpha)(w_i + u_i^\alpha) =$$

(11.6)
$$= \frac{1}{2}\sum_\alpha \rho^\alpha (w_i w_i + 2 w_i u_i^\alpha + u_i^\alpha u_i^\alpha) =$$

$$= \frac{1}{2}\rho\, w_i w_i + \frac{1}{2}\sum_\alpha \rho^\alpha u_i^\alpha u_i^\alpha$$

The balances equations have here the form

(11.7) $$\rho \frac{dc^\alpha}{dt} = R^\alpha - (j_i^\alpha)_{,i}$$

(11.8) $$\rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ik,k} \quad , \quad \sigma_{ik} = \sum_\alpha \sigma_{ik}^\alpha$$

(11.9) $$\rho \frac{d}{dt}(U+K) = \rho r + \rho F_i w_i +$$

$$+ \left[\sigma_{ij} w_j - q_i + \sum_\alpha \left(\frac{1}{\rho^\alpha}\sigma_{ik}^\alpha j_k^\alpha - j_i U^\alpha\right)\right]_{,i}$$

(11.10) $$\rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - \left(\frac{q_i}{T}\right)_{,i} - \sum_\alpha (j_i^\alpha S^\alpha)_{,i}$$

In this case the residual inequality is defined by expression

$$(11.11)\qquad -\rho\frac{dU}{dt}+\rho T\frac{dS}{dt}+\sigma_{ik}w_{i,k}+\sum_{\alpha}\left[\left(\frac{1}{\rho^{\alpha}}\sigma_{ll}^{\alpha}+TS^{\alpha}-U^{\alpha}\right)j_i^{\alpha}\right]_{,i}-\frac{q_i T_{,i}}{T}\geq 0$$

The system of equations (11.7) - (11.11) is the most general set of balances for thermodiffusion processes occuring in a solid of equal temperature.

12. Seepage in a solid.

Seepage flows constitute a particular case of the diffusion with a dominant constituent.

We assume that

$$(12.1)\qquad \begin{aligned}&\bigwedge_{\alpha} U^{\alpha}=U \longrightarrow \sum_{\alpha}\rho^{\alpha}v_i^{\alpha}U^{\alpha}=U\sum_{\alpha}\rho^{\alpha}v_i^{\alpha}=0\\ &\bigwedge_{\alpha} T^{\alpha}=T\\ &\bigwedge_{\alpha} S^{\alpha}=S \longrightarrow \sum_{\alpha}j_i^{\alpha}S^{\alpha}=S\sum_{\alpha}j_i^{\alpha}=0\end{aligned}$$

$$(12.2)\qquad \frac{1}{\rho^{\alpha}}\sigma_{ik}^{\alpha}j_k^{\alpha}\Rightarrow\frac{1}{\rho^{\alpha}}\sigma_{ll}^{\alpha}\delta_{ik}j_k^{\alpha}=\frac{1}{\rho^{\alpha}}\sigma_{ll}^{\alpha}j_i^{\alpha}=\stackrel{df}{=}M_{\sigma}^{\alpha}j_i^{\alpha}$$

The balances equations have the form

$$(12.3)\qquad \rho\frac{dc^{\alpha}}{dt}=R^{\alpha}-(j_i^{\alpha})_{,i}$$

(12.4) $$\rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ij,j} \quad , \sigma_{ij} = \sum_\alpha \sigma_{ij}^\alpha \quad , \sigma_{ij} = \sigma_{ji}$$

(12.5) $$\rho \frac{d}{dt}(U+K) = \rho r + \rho F_i w_i + (\sigma_{ij} w_j)_{,i} - q_{i,i} + \sum_\alpha (M_\sigma^\alpha j_i^\alpha)_{,i}$$

(12.6) $$\rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - \left(\frac{q_i}{T}\right)_{,i}$$

When substituted (12.3) and (12.4) into (12.5) we obtain

(12.7) $$\rho \frac{dU}{dt} = \rho r - q_{i,i} + \sigma_{ij} d_{ij} + \sum_\alpha M_\sigma^\alpha \left(R^\alpha - \rho \frac{dc^\alpha}{dt}\right) + \sum_\alpha M_{\sigma,i}^\alpha j_i^\alpha \qquad \left(d_{ij} = \frac{1}{2}(w_{i,j} + w_{j,i})\right)$$

The residual inequality takes on the form

(12.8) $$\rho \frac{dU}{dt} + \rho T \frac{dS}{dt} + \sigma_{ij} d_{ij} - \sum_\alpha \rho \frac{dc^\alpha}{dt} M_\sigma^\alpha + \sum_\alpha (M_\sigma^\alpha R^\alpha + M_{\sigma,i}^\alpha j_i^\alpha) - \frac{q_i T_{,i}}{T} \geqslant 0$$

In the inequality (12.8) constituents

(12.9) $$\sum_\alpha (M_\sigma^\alpha R^\alpha + M_{\sigma,i}^\alpha j_i^\alpha) - \frac{q_i T_{,i}}{T} \qquad (\ldots \geqslant 0)$$

concern energy dissipation from the system.

On the other hand constituents

(12.10) $$-\rho \frac{dU}{dt} + \rho T \frac{dS}{dt} + \sigma_{ij} d_{ij} - \sum_\alpha \rho \frac{dc^\alpha}{dt} M_\sigma^\alpha$$

permit to define constitutive equations.

13. Classical thermodiffusion in a solid

Such flows also constitute a particular case of the diffusion ones with the dominant constituent. We introduce here a constraint

$$\bigwedge_\alpha s^\alpha = s \longrightarrow \sum_\alpha j_i^\alpha s^\alpha = s \sum_\alpha j_i^\alpha = 0$$

(13.1) $$\bigwedge_\alpha \frac{1}{\rho^\alpha}\sigma_{ll}^\alpha = \frac{1}{\rho^0}\sigma_{ll}^0 \longrightarrow \sum_\alpha \frac{1}{\rho^\alpha}\sigma_{ll}^\alpha j_i^\alpha = \frac{1}{\rho^0}\sigma_{ll}^0 \sum_\alpha j_i^\alpha = 0$$

$$\bigwedge_\alpha T^\alpha = T$$

The balances equations have the form

(13.2) $$\rho \frac{dc^\alpha}{dt} = R^\alpha - (j_i^\alpha)_{,i}$$

(13.3) $$\rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ik,k} \qquad \sigma_{ik} = \sum_\alpha \sigma_{ik}^\alpha$$

$$\sigma_{ki} = \sigma_{ik}$$

(13.4) $$\rho \frac{d}{dt}(U+K) = \rho r + \rho F_i w_i - q_{i,i} + (\sigma_{ij} w_j)_{,i} - \sum_\alpha (j_i^\alpha U^\alpha)_{,i}$$

(13.5) $$\rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - \left(\frac{q_i}{T}\right)_{,i}$$

After substitution (13.2) and (13.3) into (13.4), when assuming that

$$\sigma_{ij} w_{i,j} = \sigma_{ij}\left[\tfrac{1}{2}(w_{i,j} + w_{j,i}) + \tfrac{1}{2}(w_{i,j} - w_{j,i})\right] = \sigma_{ij}\,\tfrac{1}{2}(w_{i,j} + w_{j,i}) = \sigma_{ij} d_{ij}$$

we get

$$\rho \frac{dU}{dt} = \rho r - q_{i,i} + \sigma_{ij} d_{ij}$$

(13.6)
$$- \sum_{\alpha} U^{\alpha} \left(R^{\alpha} - \rho \frac{dc^{\alpha}}{dt} \right) + \sum_{\alpha} U^{\alpha}_{,i} j_i^{\alpha}$$

The form of the residual inequality is following

$$- \rho \frac{dU}{dt} + T \rho \frac{dS}{dt} + \sigma_{ij} d_{ij} + \sum_{\alpha} \rho \frac{dc^{\alpha}}{dt} U^{\alpha}$$

(13.7)
$$- \sum_{\alpha} \left(U^{\alpha} R^{\alpha} + U^{\alpha}_{,i} j_i^{\alpha} \right) - \frac{q_i T_{,i}}{T} \geqslant 0$$

Assuming that $U^{\alpha} = M_o^{\alpha}$ we obtain the residual inequality

$$- \rho \frac{dU}{dt} + T \rho \frac{dS}{dt} + \sigma_{ij} d_{ij} + \sum_{\alpha} \rho \frac{dc^{\alpha}}{dt} M_o^{\alpha} +$$

(13.8)
$$- \sum_{\alpha} \left(M_o^{\alpha} R^{\alpha} + M^{\alpha}_{o,i} j_i^{\alpha} \right) - \frac{q_i T_{,i}}{T} \geqslant 0$$

In this inequality constituents

$$- \rho \frac{dU}{dt} + T \rho \frac{dS}{dt} + \sigma_{ij} d_{ij} + \sum_{\alpha} M_o^{\alpha} \rho \frac{dc^{\alpha}}{dt}$$

serve to determination of physical equation, but constituents

$$- \sum_{\alpha} \left(M_o^{\alpha} R^{\alpha} + M^{\alpha}_{o,i} j_i \right) - \frac{q_i T_{,i}}{T} \qquad (\ldots \geqslant)$$

define the basic energy dissipation from a body.

14. Entropy diffusion in a solid

It is a very particular case of the diffusion with the dominant constituent. We assume here that

$$(14.1)\quad \begin{aligned} &\bigwedge_{\alpha} U^{\alpha} = U \longrightarrow \sum_{\alpha} j_i^{\alpha} U^{\alpha} = U \sum_{\alpha} j_i^{\alpha} = 0 \\ &\bigwedge_{\alpha} \frac{1}{\rho^{\alpha}} \sigma_{ii}^{\alpha} = \frac{1}{\rho^{0}} \sigma_{ii}^{0} \longrightarrow \sum_{\alpha} \frac{1}{\rho^{\alpha}} \sigma_{ii}^{\alpha} j_i^{\alpha} = 0 . \end{aligned}$$

The balances equations have here the form

$$(14.2)\qquad \rho \frac{dc^{\alpha}}{dt} = R^{\alpha} - (j_i^{\alpha})_{,i}$$

$$(14.3)\qquad \rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ik,k} \qquad\qquad \sigma_{ik} = \sigma_{ki}$$

$$(14.4)\qquad \rho \frac{d}{dt}(U+K) = \rho r + \rho F_i w_i + [\sigma_{ij} w_j - q_i]_{,i}$$

$$(14.5)\qquad \begin{aligned} \rho \frac{dS}{dt} \geqslant{}& \frac{\rho r}{T} - \left(\frac{q_i}{T}\right)_{,i} + \\ &+ \sum_{\alpha} \left[\left(\frac{\rho^{\alpha} r^{\alpha}}{T^{\alpha}} k^{\alpha}\right) - \left(\frac{q_i^{\alpha}}{T^{\alpha}} k^{\alpha}\right)_{,i} - (j_i^{\alpha} S^{\alpha})_{,i} \right] \end{aligned}$$

$$\bigwedge_{\alpha} T^{\alpha} \neq T \quad , \qquad k^{\alpha} = \frac{T - T^{\alpha}}{T} \neq 0$$

Substituting (14.2) and (14.3) into (14.4) we obtain

$$(14.6)\qquad \rho \frac{dU}{dt} = \rho r - q_{i,i} + \sigma_{ij} d_{ij}$$

The residual inequality takes on the form

$$(14.7)\qquad \begin{aligned} &-\rho \frac{dU}{dt} + T\rho \frac{dS}{dt} + \sigma_{ij} d_{ij} + T \sum_{\alpha} (j_i^{\alpha} S^{\alpha})_{,i} \\ &+ T \sum_{\alpha} (j_i^{\alpha} S^{\alpha})_{,i} - \\ &- T \sum_{\alpha} \left[\frac{\rho^{\alpha} r^{\alpha}}{T^{\alpha}} k^{\alpha} - \left(\frac{q_i^{\alpha}}{T^{\alpha}} k^{\alpha}\right)_{,i} \right] - \frac{q_i T_{,i}}{T} \geqslant 0 \end{aligned}$$

Introducing (14.2) to (14.7) we obtain

$$-\rho\frac{dU}{dt}+T\rho\frac{dS}{dt}+\sigma_{ij}d_{ij}-T\sum_{\alpha}\rho\frac{dc^{\alpha}}{dt}S^{\alpha}$$

$$(14.8)\quad +T\sum_{\alpha}S^{\alpha}R^{\alpha}+T\sum_{\alpha}j_i^{\alpha}S_{,i}^{\alpha}-$$

$$-T\sum_{\alpha}\left[\left(\frac{\rho^{\alpha}r^{\alpha}}{T^{\alpha}}k^{\alpha}\right)-\left(\frac{q_i^{\alpha}}{T^{\alpha}}k^{\alpha}\right)_{,i}\right]-\frac{q_i T_{,i}}{T}\geqslant 0$$

Introducing the potential $M_S^{\alpha}=TS^{\alpha}$ we get finally

$$-\rho\frac{dU}{dt}+T\rho\frac{dS}{dt}+\sigma_{ij}d_{ij}-\sum_{\alpha}\rho M_S^{\alpha}\frac{dc^{\alpha}}{dt}$$

$$(14.9)\quad +\sum_{\alpha}M_S^{\alpha}R^{\alpha}+\sum_{\alpha}j_i^{\alpha}T\left(\frac{M_S^{\alpha}}{T}\right)_{,i}$$

$$-T\sum_{\alpha}\left[\frac{\rho^{\alpha}r^{\alpha}}{T^{\alpha}}k^{\alpha}-\left(\frac{q_i^{\alpha}}{T^{\alpha}}k^{\alpha}\right)_{,i}\right]-\frac{q_i T_{,i}}{T}\geqslant 0$$

The process described in this point occurs, when constituents of mixture have different temperatures. Then, during the diffusion process it comes to rapid leveling of temperatures. On the other hand temperature leveling leads to occuring of diffusion flows.

15. Kinetic diffusion.

As a very particular case of the diffusion flow migration in a solid defined with the help of relations

$$(15.1)\quad \bigwedge_{\alpha}U^{\alpha}=U,\quad \bigwedge_{\alpha}S^{\alpha}=S,\quad \bigwedge_{\alpha}T^{\alpha}=T,\quad \bigwedge_{\alpha}\frac{1}{\rho^{\alpha}}\sigma_{ll}^{\alpha}=\frac{1}{\rho^{\circ}}\sigma_{ll}^{\circ}$$

$\sum_{\alpha}\rho^{\alpha}v_i^{\alpha}v_j^{\alpha}\cong 0$ but the sum $\sum_{\alpha}\rho^{\alpha}v_i^{\alpha}v_i^{\alpha}$ exists and it is comparable with another constituents of the energy balance.

The balances equations have the form

(15.2) $$\rho \frac{dc^{\alpha}}{dt} = R^{\alpha} - (j_i)_{,i}$$

(15.3) $$\rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ij,j} \quad , \quad \sigma_{ij} = \sigma_{ji}$$

(15.4) $$\rho \frac{d}{dt}(U+K) = \rho r - q_{i,i} + \rho F_i w_i + [\sigma_{ij} w_j - \sum_{\alpha} j_i^{\alpha} K^{\alpha}]_{,i}$$

(15.5) $$\rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - \left(\frac{q_i}{T}\right)_{,i}$$

In the issue of transformations we get the residual inequality

$$-\rho \frac{dU}{dt} + T\rho \frac{dS}{dt} + \sigma_{ij} d_{ij} + \sum_{\alpha} \rho K^{\alpha} \frac{dc^{\alpha}}{dt}$$

(15.6) $$-\sum_{\alpha} (K^{\alpha} R^{\alpha} + K^{\alpha}_{,i} j_i^{\alpha}) - \frac{q_i T_{,i}}{T} \geqslant 0$$

This flow appears in a solid, when diffusing particles hold a large kinetic energy, and in the skeleton cousiderable stresses arise.

16. The diffusion towards. a multi-constituent skeleton

Let us study now a case, when the dominant constituent a skeleton is multi-constituent. Convertions together with chemical reactions can appear between constituents. Problem concerns the case $(\mathcal{E}_2)$ of diffusion with a dominant constituent (comp. p.11).

The balances equations are here following

$$\rho \frac{dc^{\alpha}}{dt} = R^{\alpha} \quad , \quad \alpha = 1, 2, \ldots\ldots k$$

(16.1) $$\rho \frac{dc^\beta}{dt} = R^\beta - (j_i^{\ \beta})_{,i} \quad , \quad \beta = k+1, \ldots\ldots n$$

(16.2) $$\rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ik,k}$$

(16.3) $$\rho \frac{dU}{dt} = \rho r - q_{i,i} + \sigma_{ij} d_{ij} - \sum_\alpha M^\alpha (R^\alpha - \rho \frac{dc^\alpha}{dt}) - \sum_\beta M^\beta (R^\beta - \rho \frac{dc^\beta}{dt}) - \sum_\beta M^{\ \beta}_{,i} j_i^{\ \beta}$$

(16.4) $$\rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - (\frac{q_i}{T})_{,i} \quad , \quad \sum_\alpha S^\alpha = S$$

When transformed the residual inequality has the form

(16.5) $$-\rho \frac{dU}{dt} + \rho T \frac{dS}{dt} + \sigma_{ij} d_{ij} + \sum_\alpha M^\alpha \rho \frac{dc^\alpha}{dt} + \sum_\beta M^\beta \rho \frac{dc^\beta}{dt} - \sum_\alpha M^\alpha R^\alpha - \sum_\beta (M^\beta R^\beta + M_{,i}^{\ \beta} j_i^{\ \beta}) - \frac{q_i T_{,i}}{T} \geqslant 0$$

where

(16.6) $$M^\alpha = \frac{1}{\rho^\alpha} \sigma_{ii}^\alpha - U^\alpha - K^\alpha = M_\sigma^\alpha - M_0^\alpha - M_k^\alpha$$
$$M^\beta = \frac{1}{\rho^\beta} \sigma_{ii}^\beta - U^\beta - K^\beta = M_\sigma^\beta - M_0^\beta - M_k^\beta$$

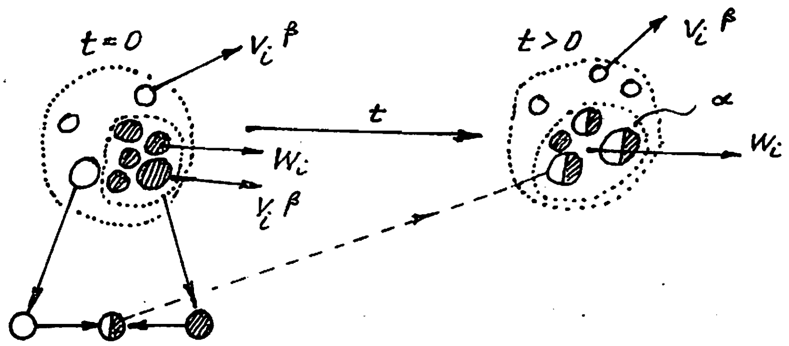


Fig.18

In the inequality (16.5) constituents

(16.7) $$-\rho \frac{dU}{dt} + \rho T \frac{dS}{dt} + \sigma_{ij} d_{ij} + \sum_\alpha \rho M^\alpha \frac{dc^\alpha}{dt} + \sum_\beta \rho M^\beta \frac{dc^\beta}{dt}$$

are related substantially with the constitutive equations, and quantities

$$(16.8) \qquad -\sum_{\alpha} M^{\alpha} R^{\alpha} - \sum_{\beta} (M^{\beta} R^{\beta} + M^{\beta}_{,i} \dot{j}_i^{\beta}) - \frac{q_i T_{,i}}{T}$$

with the dissipation ,

Let us notice that the description presented includes an apprehension of continous heterogeneous medium without diffusion as well as nonhomogeneous medium with thermodiffusion flows.

17. Comparision of various diffusion descriptions.

The given above equations of various kinds of diffusion in a solid do not occur, in general, independently,

As a rule various combinations of several diffusion flows can be observed. In the general case the potential M generating diffusion flows of mass and convertions have the form

$$(17.1) \qquad M^{\alpha} = M_{\sigma}^{\alpha} + M_{S}^{\alpha} - M_{o}^{\alpha} - M_{k}^{\alpha} = \frac{1}{\rho^{\alpha}} \sigma_{ii}^{\alpha} + TS^{\alpha} - U^{\alpha} - K^{\alpha}$$

It seems that the dominant components is in general, the internal energy U^{α}. Differences in the free energy between the particular components are the most often reason for flows $(\Delta U = U^{\alpha} - U^{\gamma})$. Comparatible quantity in the isothermic problems is the flow induced by differences between portional pressures $\Delta M_{\sigma}^{\alpha} = \frac{1}{\rho^{\alpha}} \sigma_{ii}^{\alpha} - \frac{1}{\rho^{\gamma}} \sigma_{ii}^{\gamma}$

The contribution of the difference of entropy of particular constituents in generation of flows is smaller. It follows from the rapid leveling of temperatures in a multi-constituent system of different temperature T for constituents $(T^{\alpha} \neq T^{\gamma})$.

Likely, the contribution of diffusion produced by the difference in kinetic energy $\Delta M_k = K^{\alpha} - K^{\gamma}$ for particular, migrating constituents. So, one can assume that

$$M^{\alpha} \cong M_{\sigma}^{\alpha} - M_{0}^{\alpha} = \frac{1}{\rho^{\alpha}} \sigma_{ll}^{\alpha} - U^{\alpha} \tag{17.2}$$

18. Linear theories.

Further particular cases of all considered hitherto diffusion flows in a solid are those in which convectional terms of derivatives are neglected. It is admissible when velocities are relatively small and the inequality $\frac{\partial c^{\alpha}}{\partial t} \gg V_k \frac{\partial c^{\alpha}}{\partial x_k}$, $\frac{\partial V_i}{\partial t} > V_k \frac{\partial V_i}{\partial x_k}, \ldots$ The set of balances can be here written

$$\rho \dot{c}^{\alpha} = R^{\alpha} - (j_i^{\alpha})_{,i} \tag{18.1}$$

$$\rho \dot{W}_i = \rho F_i + \sigma_{ij,j} \, , \quad \sigma_{ij} = \sigma_{ji} \tag{18.2}$$

$$\rho(\dot{U}+\dot{K}) = \rho r - q_{i,i} + (\sigma_{ij} W_j)_{,i} - \sum_{\alpha} \left(j_i^{\alpha}(U^{\alpha}+K^{\alpha}) + \frac{1}{\rho^{\alpha}} \sigma_{ll}^{\alpha} j_i^{\alpha} \right)_{,i} \tag{18.3}$$

$$\rho \dot{S} \geqslant \frac{\rho r}{T} - \left(\frac{q_i}{T} \right)_{,i} - \sum_{\alpha} (j_i^{\alpha} S^{\alpha})_{,i} \tag{18.4}$$

and the residual inequality is following

$$-\rho \dot{U} + \rho T \dot{S} + \sigma_{ij} \dot{\varepsilon}_{ij} + \sum_{\alpha} \rho M^{\alpha} \dot{c}^{\alpha} - \sum_{\alpha} (M^{\alpha} R^{\alpha} + M^{\alpha}_{,i} j_i^{\alpha}) - \frac{q_i T_{,i}}{T} \geqslant 0. \tag{18.5}$$

The system presented constitutes the base of linear equations describing diffusion in a solid.

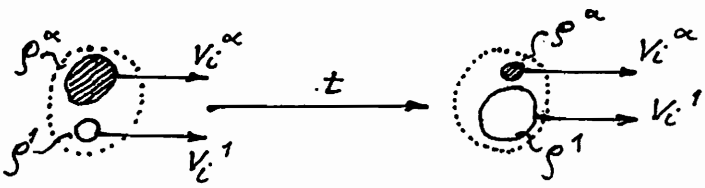
Of course, $M^{\alpha} = M_{\sigma}^{\alpha} + M_{s}^{\alpha} - M_{\theta}^{\alpha} - M_{k}^{\alpha} = \frac{1}{\rho^{\alpha}}\sigma_{ii}^{\alpha} + TS^{\alpha} - U^{\alpha} - K^{\alpha}.$

From those equations the most often applied descriptions of thermodiffusion processes result in which M^{α} is, in general, identified with U^{α}.

19. Heterogeneous bodies without diffusion

Let us analyse another particular case, when all mixture constituents hold the same velocity $v_i^{1} = v_i^{2} = \ldots\ldots\ldots = v_i^{n}$

Fig.19



In this body there can occur, however, conversions of particular constituents. Especially during deformation process a new constituent can arise holding different properties. Temperature or chemical potentials of particular constituents plays here a part analogous to the deformation process.

The balances can be now written as

(19.1) $$\rho \frac{dc^{\alpha}}{dt} = R^{\alpha} \qquad (j_{i,i}^{\alpha} = 0).$$

(19.2) $$\rho \frac{dw_i}{dt} = \rho F_i + \sigma_{ij,j} \quad , \quad \sigma_{ij} = \sigma_{ji}, \quad \sigma_{ij} = \sum_{\alpha} \sigma_{ij}^{\alpha}$$

(19.3) $$\rho \frac{d}{dt}(U+K) = \rho r - q_{i,i} + \sigma_{ij} d_{ij} + \sum_{\alpha}\left(\rho M^{\alpha} \frac{dc^{\alpha}}{dt} - M^{\alpha} R^{\alpha}\right)$$

(19.4) $$\rho \frac{dS}{dt} \geqslant \frac{\rho r}{T} - \left(\frac{q_i}{T}\right)_{,i}$$

(19.5) $$M^{\alpha} = \frac{1}{\rho^{\alpha}} \sigma_{ll}^{\alpha} + TS^{\alpha} - U^{\alpha}$$

The residual inequality has the form

$$-\rho \frac{dU}{dt} + \rho T \frac{dS}{dt} + \sigma_{ij} d_{ij} + \sum_{\alpha} \rho M^{\alpha} \frac{dc^{\alpha}}{dt}$$

(19.6) $$- \sum_{\alpha} M^{\alpha} R^{\alpha} - \frac{q_i T_{,i}}{T} \geqslant 0$$

The equations (19.1)- (19.5) seem to be useful as describing degradation processes of material, recristalization, and generally conversion without diffusion, when new phase of material arises in the issue of a thermomechanical process.

Those equations also permits to describe self-balanced stresses in a body. Then

(19.7) $$\sigma_{ij} = 0 \longrightarrow \sigma_{ij} = \sum_{\alpha} \sigma_{ij}^{\alpha} = 0 \text{ , } \underline{\sigma_{ij}^{\alpha} \neq 0}$$

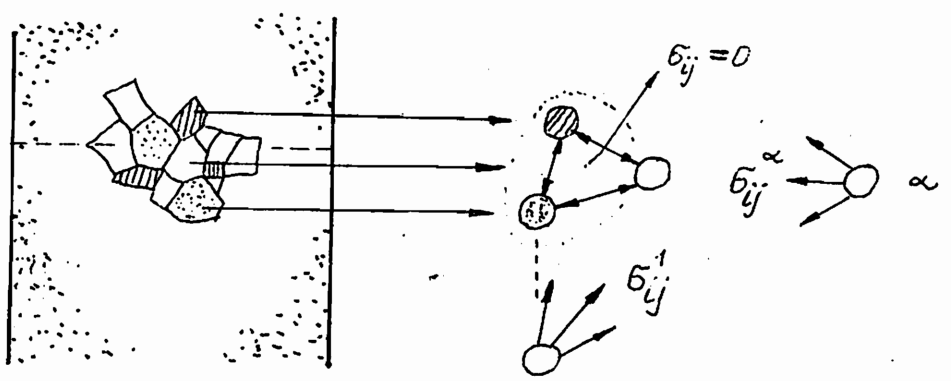
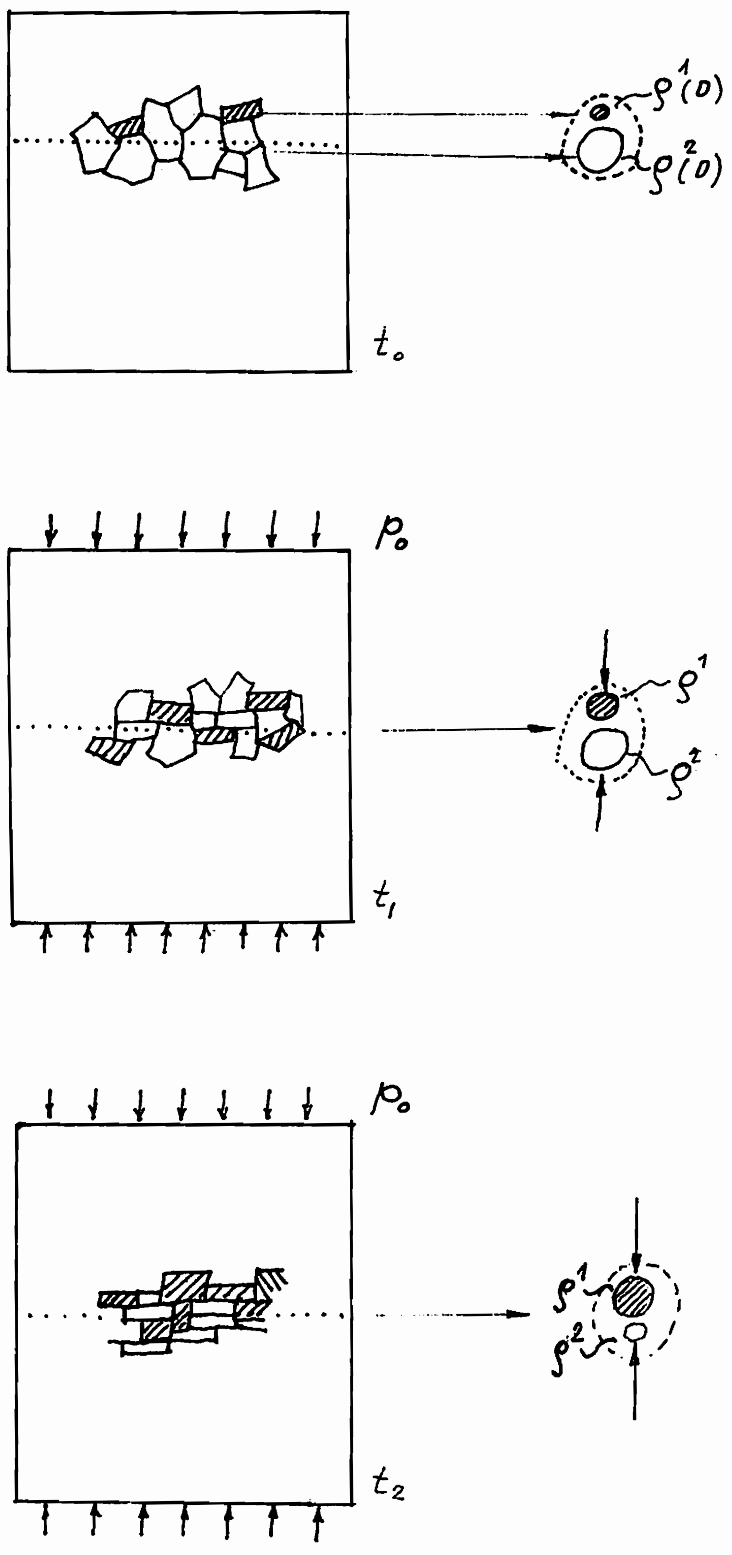


Fig.20

Material model



$$\sigma_{ij} = \sum_\alpha \sigma_{ij}^\alpha = 0$$
$$T = T_0$$
$$t = t_0$$

$$\rho^1(t_1) > \rho^1(0)$$
$$\rho^2(t_1) < \rho^2(0)$$
$$\sigma_{ij} > 0$$
$$T_1 > T_0$$
$$t_1 > t_0$$

$$\sigma_{ij} > 0$$
$$T > T_0$$
$$t_2 > t_1$$

$$M_1 R_1 + M_2 R_2 \geq 0$$
$$R_1 + R_2 = 0$$
$$\rho^1(t_2) > \rho^1(t_1)$$
$$\rho^2(t_2) < \rho^2(t_1)$$

Fig. 21

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