

## Diffusion by the Vacancy Mechanism in the Materials with the Large Number of Internal Surfaces

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### Abstract

The relationships for irreversible flows of matter, vacancies, surfaces, and heat are derived with the allowance for various cross effects on the basis of the model of a medium with additional parameters that determine structural features and availability of vacancies and internal surfaces. The generalized linearized relationships for the rates of chemical reactions, for the sources of vacancies and surfaces, as well as a generalization of the law of internal friction have been obtained. Analysis of various types of diffusive flows has been conducted for the diffusion that proceeds through the replacement mechanism. It was revealed, in particular, that the coefficient of volumetric diffusion in a polycrystalline material is other than the coefficient of self-diffusion for a single crystal that should be taken into account when interpreting experimental data for diffusion in fine structured materials.

### INTRODUCTION

The diffusion processes in solids are affected by many factors, including temperature, internal stresses, which can stem in its turn from the processes of mass transfer, the structural features, and external fields of the highly variable nature. Among the diversity of structural defects, the vacancies and internal surfaces (interfaces of grains and phases) play a special part in the processes of diffusive transfer thus defining on frequent occasions the mechanisms of many diffusion-controlled macroscopic (observed) phenomena. The large number of works is devoted to the description of diffusion processes in the solid media with the use of methods of thermodynamics of irreversible processes. Nevertheless there are many unresolved problems in this field. The works [1–3] suggest a generalization of thermodynamics of irreversible processes to the deformable media with diffusion and structural inhomogeneities of various types. Diffusion through the intrusion mechanism and various types of energy equations in the form of

thermal conductivity equation have been considered in detail. It has been demonstrated that the description of change in properties of materials with modification in their structure (accumulation of internal surfaces) may well be performed by methods of thermodynamic relaxation theory, which is inherently analogous to the thermodynamic theory of internal friction. A similar way of looking at the interaction between rheology and the transfer processes is developed in [4].

The present work concentrates most attention on the constructing of the equations for irreversible mass flows provided that diffusion proceeds through the vacancy mechanism. In multiphase metal systems, self-diffusion and interdiffusion occur with the vacancies involved. Moreover, according to the concepts of theoretical physics and thermodynamics, the crystal that is absolutely free of vacancies is an unstable system. When constructing the models of the multicomponent diffusion, which proceeds with the vacancies involved, the authors of numerous publications on this theme accept, as a rule, the condition

of the conserved sites of a crystal lattice or of the constant volume. Taking into account the influence of pressure and deformations on diffusion is realized under the condition of a vanishing deformation or in the hydrodynamic approximation. Despite the large number of the problems solved for the practical use and the attempts to explain many experimentally observed effects, the applicability of the familiar approaches [5–9] is limited. Mechanics of continuous media may treat the vacancies as the point defects and may involve such an additional parameter like the density of distribution of point defects that is rather convenient for the description of the problems of internal friction [10]. Generally, it is quite correct to treat the vacancies as the weight defect, as is the case when describing the diffusion creep [11].

#### GENERAL RELATIONSHIPS

The balance of weights and the balance of mass flows for a multicomponent body or for an ideal crystal with no damages are of the following form:

$$\sum_{k=1}^n \rho_k = \rho \quad \text{or} \quad \sum_{k=1}^n C_k = 1 \quad \text{and} \quad \sum_{k=1}^n \mathbf{J}_k = 0 \quad (1)$$

where  $\mathbf{J}_k = \rho_k(\mathbf{v}_k - \mathbf{v}) \equiv \rho_k \mathbf{w}_k$ ,  $\mathbf{v}_k$  is an individual speed of the component  $k$ ,  $\mathbf{v}$  is the barycentric speed defined by the relationship

$$\rho \mathbf{v} = \sum_{k=1}^n \rho_k \mathbf{v}_k \quad (2)$$

We will consider the imperfect crystal with vacancies as a multicomponent deformable continuous body, where one of the enclosed components controls the distribution of vacancies. Let us introduce into consideration the density of matter  $\rho_s$  in a given point of the body that it would be in the absence of vacancies, and the density  $\rho$  in this point for the real solid body. Then the positive magnitude

$$\rho_v = \rho_s - \rho > 0 \quad (3)$$

will define the density of vacancies, *i.e.* as contrasted to the known physical models where the negative density or the negative volume of vacancies is often spoken about, the vacancies here will be treated as the defect of weight. In

much the same way, we will derive for the multicomponent solid

$$\rho_v = \sum_{k=1}^n \rho_k - \rho > 0 \quad \text{или} \quad \sum_{k=1}^n C_k = 1 + C_v \quad (4)$$

that is different from (1).

The speed vector of centre of mass, unlike the relationship (2), will be defined by formulae

$$\rho \mathbf{v} = \rho_s \mathbf{v}_s - \rho_v \mathbf{v}_v > 0 \quad \text{and} \quad \mathbf{v} \rho = \sum_{k=1}^n \mathbf{v}_k \rho_k - \mathbf{v}_v \rho_v$$

or

$$\mathbf{v} = C_s \mathbf{v}_s - C_v \mathbf{v}_v > 0 \quad \text{and} \quad \mathbf{v} = \sum_{k=1}^n \mathbf{v}_k C_k - \mathbf{v}_v C_v \quad (5)$$

The general balance equations for the components remain unchanged and those for vacancies are similar to them.

The balance of mass flows for a crystal with vacancies also differs from (1) and takes the form

$$\sum_{k=1}^n \mathbf{J}_k - \mathbf{J}_v = 0 \quad (6)$$

The equations of mass balance for the components are identical. For example, in terms of mass concentrations, they take the form

$$\rho \frac{dC_k}{dt} = -\nabla \cdot \mathbf{J}_k + \sigma_k \quad (7)$$

where  $\sigma_k$  is the sum of sources and outlets of a component  $k$  under physicochemical transformations.

The analogous equation holds true for vacancies:

$$\rho \frac{dC_v}{dt} = -\nabla \cdot \mathbf{J}_v + \sigma_v \quad (8)$$

*When we deal with a polycrystalline material or the material with nanoinclusions (with the great quantity of internal interfaces), the state of the medium depends on one additional thermodynamic parameter that is specific area  $\eta$  of internal surfaces. The surfaces do not contain weight, but they possess energy. Therefore, they are not involved in the mass balance either for an «ideal» crystal or for a crystal with vacancies, but they comply with the equation of balance of the conventional type:*

$$\rho \frac{d\eta}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_s \quad (9)$$

and they are included in the energy balance or in the Gibbs equation together with the vacancies and component concentrations:

$$du = Tds + \sigma_{ij}^e p^{-1} d\epsilon_{ij} + \sum_{k=1}^n g_k dC_k - g_v dC_v - g_s d\eta \quad (10)$$

where  $u = u(s, \epsilon_{ij}, C_k, C_v, \eta)$  is the local internal energy,  $T$  is the temperature,  $\sigma_{ij}^e$  is an “elastic” part of the stress tensor components (that depends linearly on the components of the deformation tensor, on temperature, and on the other parameters),  $s$  is the local entropy. Generally, the additional parameter  $\eta$  may be a vector, all components of which match the various types of internal surfaces. In particular, the most part of the area of internal interfaces may result from mechanical activation. The specific superficial energy can be of the same nature.

Generally, to describe the behaviour of such medium and physicochemical transformations that proceed in it, we add continuity equations, movement equations, and energy equations to the equations written above:

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0 \quad (11)$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \cdot \boldsymbol{\sigma} \quad (12)$$

$$\rho \frac{du}{dt} = A + \boldsymbol{\sigma} \cdot \nabla \mathbf{v} \quad (13)$$

where  $A = -\nabla \cdot \mathbf{J}_T + \sum_{k=1}^n \mathbf{F}_k \cdot \mathbf{J}_k$ ,  $\mathbf{J}_T$  is a flow of

heat,  $\mathbf{F}_k$  is the component of an external force vector that acts upon the component with the number  $k$ . The equations (12), (13) include the full stress tensor  $\boldsymbol{\sigma}$ , which is represented as a sum of spherical tensor and the deviator:

$$\boldsymbol{\sigma} = -p\boldsymbol{\delta} + \mathbf{S}, \quad p = -\frac{1}{3} \sigma_{kk} \quad (14)$$

each being composed, in its turn, of “elastic” ( $e$ ) and “viscous” ( $i$ ) contributions:

$$p = p^i + p^e \quad \text{и} \quad \mathbf{S} = \mathbf{S}^i + \mathbf{S}^e$$

Then

$$\boldsymbol{\sigma} \cdot \nabla \mathbf{v} = -(p^i + p^e) \nabla \cdot \mathbf{v} + (\mathbf{S}^i + \mathbf{S}^e) \cdot \nabla \mathbf{v} \quad (15)$$

To close the system of equations we need to write down the equations of state and the determination relationships. They can be constructed in various manners or can be determined experimentally. *The general form of*

*the equations of state in thermodynamics of irreversible processes follows immediately from (10), which will be shown in the subsequent discussion.* The second relationships in thermodynamics follow from the condition of the non-negative produced entropy. Expression for the entropy production is derived on substitution of the derivatives with respect to time  $u$ ,  $C_k$ ,  $\eta$ , and  $C_v$  in (10). In the absence of external weight forces, with allowance made for (14), (15), we will obtain

$$\begin{aligned} \sigma_{en} = & \frac{1}{T} [g_v \sigma_v + g_s \sigma_s - \sum_{k=1}^n g_k \sigma_k - p^i \nabla \mathbf{v}] \\ & + \frac{1}{T} [-\mathbf{J}_T \frac{\nabla T}{T} - \sum_{k=1}^n \mathbf{J}_k \nabla (\frac{g_k}{T}) + \mathbf{J}_v \nabla (\frac{g_v}{T}) + \mathbf{J}_s \nabla (\frac{g_s}{T})] \\ & + \frac{1}{T} S^i \cdot \nabla \mathbf{v} + \frac{1}{T} \left[ S^e \cdot \nabla \mathbf{v} - S^e \frac{d\boldsymbol{\epsilon}}{dt} \right] \geq 0 \quad (16) \end{aligned}$$

Provided that the stress tensor is symmetric, the last summand in parentheses is equal to zero. Then, we deal only with a symmetric stress tensor. This expression distinguishes separately the scalar, vector, and tensor processes. In order that inequality (16) is complied with, it would suffice to assume that the relation between the generalized flows and thermodynamic forces that cause them is linear. According to the Curie’s principle, only magnitudes of the same tensor dimensionality can be linked by such linear relationships. Taking into consideration

$$\sigma_k = \sum_{i=1}^r v_{ki} m_k \varphi_i, \quad \sum_{k=1}^n g_k \sigma_k = - \sum_{i=1}^r A_i \varphi_i$$

where  $A_i = - \sum_{k=1}^n g_k v_{ki} m_k$  is the affinity of  $i$ -th

chemical reaction,  $\varphi_i$  is its rate,  $r$  is the number of chemical reactions running in the system,  $v_{ki}$  is the stoichiometrical coefficient of the component  $k$  in the reaction  $i$ ,  $m_k$  is its molar weight, we will write down for scalar processes

$$\begin{aligned} \varphi_i = & \sum_{j=1}^r l_{ij} A_{ch,j} + l_{iv} A_v + l_{is} A_s + l_{ip} A_p \\ \sigma_v = & \sum_{i=1}^r l_{vi} A_{ch,i} + l_{vv} A_v + l_{vs} A_s + l_{vp} A_p \quad (17) \end{aligned}$$

$$\sigma_s = \sum_{i=1}^r l_{si} A_{ch,i} + l_{sv} A_s + l_{ss} A_s + l_{sp} A_p$$

$$p^i = \sum_{i=1}^r l_{pi} A_{ch,i} + l_{pv} A_v + l_{ps} A_s + l_{pp} A_p$$

where  $A_{ch,i} = A_i/T$ ,  $A_v = g_v/T$ ,  $A_s = g_s/T$ ,  $A_p = -\nabla \cdot \mathbf{v}/T$  are the scalar generalized thermodynamic forces (the temperature can be missed in the definition of thermodynamic force that is apparent from the equation (16));  $l_{ij} = l_{ji}$ ;  $l_{iv} = l_{vi}$ ;  $l_{ip} = l_{pi}$ ;  $l_{ch,j} = l_{j,ch}$ ;  $l_{vv}$  are the associated phenomenological coefficients that make up a symmetric positive definite matrix. Hence, *the rates of the solid phase chemical reactions and the sources and outlets for vacancies and internal surfaces depend on a diversity of scalar thermodynamic forces. The viscous component of hydrostatic pressure also includes summands of a variable physicochemical nature.* The last among the relationships (17) represents the generalized law of Newton's internal friction and the second takes into account that the sources and the outlets of vacancies can be related to chemical reactions, internal surfaces, and to a current of matter. If the number of additional parameters includes that one, which defines the behaviour of dislocations, additional summands will arise in these relationships.

For a special case of single chemical reaction and equilibrium vacancies, chemical affinity is represented by  $A = -(g_1 v_1 m_1 + g_2 v_2 m_2)$ . Then the first and the last expressions among (17) will assume the form  $\varphi = kA - k_p \nabla \cdot \mathbf{v}$ ,  $p^i = k_p A - \kappa \nabla \cdot \mathbf{v}$ , where the allowance is made for the symmetry of matrix of coefficients. Taking into consideration the fact that chemical potentials depend on the components of deformation tensor, we will find that the mobility of a medium can exert influence on the reaction rate through various channels.

For vector processes it is true

$$\begin{aligned} \mathbf{J}_k &= \sum_{j=1}^r L_{kj} \mathbf{X}_j + L_{kv} \mathbf{X}_v + L_{ks} \mathbf{X}_s + L_{kT} \mathbf{X}_T \\ \mathbf{J}_v &= \sum_{k=1}^r L_{vk} \mathbf{X}_k + L_{vv} \mathbf{X}_v + L_{vs} \mathbf{X}_s + L_{vT} \mathbf{X}_T \\ \mathbf{J}_s &= \sum_{k=1}^r L_{sk} \mathbf{X}_k + L_{sv} \mathbf{X}_v + L_{ss} \mathbf{X}_s + L_{sT} \mathbf{X}_T \\ \mathbf{J}_T &= \sum_{k=1}^r L_{Tk} \mathbf{X}_k + L_{Tv} \mathbf{X}_v + L_{Ts} \mathbf{X}_s + L_{TT} \mathbf{X}_T \end{aligned} \quad (18)$$

where  $\mathbf{X}_k = -\nabla(g_k/T)$ ,  $\mathbf{X}_v = -\nabla(g_v/T)$ ,  $\mathbf{X}_T = -\nabla T/T$  are the generalized vector thermodynamic forces. As well as in the foregoing, the matrix of  $L_{kj} = L_{jk}$ ,  $L_{kv} = L_{vk}$ , ... coefficients is positive definite.

The remaining summand represents the generalized Navier–Stokes law for viscous forces:

$$S_{kl}^j = C_{kl\alpha\beta} e_{\alpha\beta}, \quad e_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right)$$

#### ISOTHERMAL MULTICOMPONENT DIFFUSION IN CRYSTALS THROUGH THE REPLACEMENT MECHANISM AT CONSTANT STRESSES

Provided that  $d\sigma_{ij}^e = 0$ ,  $dT = 0$ ,  $d\eta = 0$  the Gibbs equation for the Gibbs energy  $g = u - Ts - \rho^{-1} \varepsilon_{ij} \sigma_{ij}^e$  takes the form

$$dg = \sum_{k=1}^n g_k dC_k - g_v dC_v \quad (19)$$

On the strength of additivity for thermodynamic parameters, we will derive

$$g = \sum_{k=1}^n g_k C_k - g_v C_v$$

where the first summand is the local specific Gibbs energy that it would be under the condition of no vacancies. Then the relationship

$$\sum_{k=1}^n C_k dg_k - C_v dg_v = 0$$

will be equivalent to Gibbs–Duhem relationship for the considered case.

By definition of diffusive flows (18), the following relationships hold true

$$\mathbf{J}_k = -\sum_{l=1}^n L_{kl} \nabla \left( \frac{g_l}{T} \right) + L_{kv} \nabla \left( \frac{g_v}{T} \right) \quad (20)$$

$$\mathbf{J}_v = -\sum_{l=1}^n L_{vl} \nabla \left( \frac{g_l}{T} \right) + L_{vv} \nabla \left( \frac{g_v}{T} \right)$$

from whence, taking into consideration (6), we will find

$$L_{vl} = \sum_{k=1}^n L_{kl}, \quad L_{vv} = \sum_{k=1}^n L_{kv}$$

In addition,  $L_{vl} = L_{lv}$ ,  $L_{kj} = L_{jk}$ . Consequently, the following relationship holds true for the flow of component  $k$

$$\mathbf{J}_k = -\sum_{j=1}^n L_{kj} \nabla \left( \frac{g_j - g_v}{T} \right) \quad (21)$$

Taking the definition for chemical potentials of components in an ordinary manner:  $g_k = g_k^{cm} + RTm_k^{-1} \ln(C_k \gamma_k)$ , and for chemical potentials of vacancies as

$$g_v = RTm_{cp}^{-1} \ln(C_v \gamma_v) \quad (22)$$

$$\gamma_v = (C_v^{eq})^{-1} = \gamma_v(C_k, \sigma_{ij}^e, T, \eta)$$

we can use the standard mathematical procedures in what follows. The definition (22) is different from a conventional one used when chemical potentials of vacancies are calculated for a unit volume. Theoretically, it is possible to define the vacancies with individual properties for each kind of diffusing particles. With the use of smoothed generalized description of vacancies as the weight defect, we introduce the average molar mass  $m_{av}$  of particles that relates also to vacancies.

For this elementary case, the set of equations of state can be presented as follows:

$$dg_k = \sum_{k=1}^n \beta_l^{(k)} dC_k - \beta_v^{(k)} dC_v$$

$$dg_v = \sum_{k=1}^n \beta_v^{(k)} dC_k + \beta_v dC_v \quad (23)$$

$$\text{where } \beta_l^{(k)} = \frac{RT}{m_k C_k} g_{kl}, \quad \beta_v^{(k)} = \frac{RT}{m_{cp} C_v} (g_{vk} + 1),$$

$$\beta_v = \frac{RT}{m_{cp} C_v} g_{vv}, \quad g_{vv} = 1 + \frac{\partial \ln \gamma_v}{\partial \ln C_v}.$$

The final relationship for the flow of component  $k$  assumes the form

$$\mathbf{J}_k = -\rho \sum_{i=1}^n D_{ki} \nabla C_i \quad (24)$$

where

$$D_{ki} = \sum_{j=1}^n \frac{RL_{kj}}{m_j C_j \rho} f_{ji} \quad (25)$$

$$f_{ji} = g_{ji} + \frac{m_j}{m_{cp}} \frac{C_j}{C_v} (g_{vi} + 1)$$

are the generalized thermodynamic multipliers that include the molar weight of diffusing

particles;  $g_{ji}$  are conventional thermodynamic multipliers:

$$g_{ji} = \delta_{ji} + \frac{C_j \partial \ln \gamma_i}{C_i \partial \ln C_i}; \quad g_{vi} \text{ are thermodynamic}$$

multipliers that relate to the interaction of

vacancies and components:  $g_{vi} = \delta_{vi} + \frac{C_v \partial \ln \gamma_v}{C_i \partial \ln C_i}$ .

Equation (6) holds true for the flow of vacancies.

Provided that  $m_k \approx m_{av}$ , i.e. in the case that diffusing particles have resembling sizes and weights, these equations give rise to all specific models known from the literature. The difference is but a definition of concentration for vacancies and, as a consequence, the signs in the definition of the generalized thermodynamic multipliers.

Relations (23)–(25) represent but a generalization of the known models in the theory of multicomponent diffusion.

#### DIFFUSION BY THE VACANCY MECHANISM IN THE MEDIUM WITH THE LARGE NUMBER OF INTERNAL INTERFACES

Let  $dT = 0$ ,  $d\sigma_{ij} = 0$  still hold true. However, the mass transfer occurs in the medium, which can be characterized by two additional parameters, specifically, the concentration of vacancies  $C_v$  and specific area of internal interfaces  $\eta$ . Then, having introduced the Gibbs energy into consideration, that is  $g = u - Ts - \rho^{-1} \sigma_{ij}^e \epsilon_{ij}$ , we will write down

$$dg = \sum_{k=1}^n g_k dC_k - g_s d\eta - g_v dC_v$$

$$g_k = \left( \frac{\partial g}{\partial C_k} \right)_{\eta, C_v}, \text{ and } g_s = - \left( \frac{\partial g}{\partial \eta} \right)_{C_k, C_v} \text{ instead of (10).}$$

The equations of balance for two additional parameters are of identical form. However, they exert the different influence on the mass transfer, as it will be apparent in what follows. Taking into consideration the relationships of symmetry and balance of flows (6) within the system of equations for the flows

$$\mathbf{J}_k = -\sum_{l=1}^n L_{kl} \nabla \left( \frac{g_l}{T} \right) + L_{ks} \nabla \left( \frac{g_s}{T} \right) + L_{kv} \nabla \left( \frac{g_v}{T} \right)$$

$$\mathbf{J}_s = -\sum_{l=1}^n L_{sl} \nabla \left( \frac{g_l}{T} \right) + L_{ss} \nabla \left( \frac{g_s}{T} \right) + L_{sv} \nabla \left( \frac{g_v}{T} \right) \quad (26)$$

$$\mathbf{J}_v = -\sum_{l=1}^n L_{vl} \nabla \left( \frac{g_l}{T} \right) + L_{vv} \nabla \left( \frac{g_v}{T} \right)$$

we will find:  $L_{kj} = L_{ik}$ ,  $L_{ks} = L_{sk}$ ,

$$L_{vj} = L_{jv} = \sum_{k=1}^n L_{kj} \quad , \quad L_{vs} = L_{sv} = \sum_{k=1}^n L_{ks} \quad ,$$

$$L_{vv} = \sum_{k=1}^n L_{kv} \quad .$$
 This significantly reduces the

number of independent phenomenological coefficients and allows representation of the equation (26) as

$$\mathbf{J}_k = -\sum_{j=1}^n \frac{L_{kj}}{T} \nabla (g_j - g_v) + \frac{L_{ks}}{T} \nabla g_s$$

$$\mathbf{J}_s = -\sum_{k=1}^n \frac{L_{sk}}{T} \nabla (g_k - g_v) + \frac{L_{ss}}{T} \nabla g_s \quad (27)$$

$$\mathbf{J}_v = \sum_{k=1}^n \mathbf{J}_k$$

This way of notation implies that the components and  $\eta$  have been selected as independent variables in the system from  $n$  components and vacancies. Therefore, the  $(g_j - g_v)$  and  $g_s$  magnitudes in (27) will depend on the concentration of components and the area of internal surfaces, *i.e.*

$$\nabla g_s = \sum_{k=1}^n \left( \frac{\partial g_s}{\partial C_k} \right) \nabla C_k + \left( \frac{\partial g_s}{\partial \eta} \right) \nabla \eta \quad \text{etc.}$$

Theoretically, we could choose  $n - 1$  concentrations, vacancies, and the additional parameter as independent variables. The result will be same.

Using the designations introduced above, the system of equations of state on the basis of the Gibbs equation can be written as follows:

$$dg_k = \sum_{l=1}^n \beta_l^{(k)} dC_k - \gamma_s^{(k)} d\eta - \beta_v^{(k)} dC_v$$

$$dg_s = \sum_{k=1}^n \gamma_s^{(k)} dC_k + \Omega d\eta + \gamma_s^{(v)} dC_v \quad (28)$$

$$dg_v = \sum_{k=1}^n \beta_v^{(k)} dC_k + \gamma_s^{(v)} + \beta_v dC_v$$

where

$$\gamma_s^{(k)} = \left( \frac{\partial g_s}{\partial C_k} \right)_{T, \sigma, C_l, l \neq k, \eta} = - \left( \frac{\partial^2 g}{\partial C_k \partial \eta} \right) = - \left( \frac{\partial^2 g}{\partial \eta \partial C_k} \right)$$

$$= - \left( \frac{\partial g_k}{\partial \eta} \right)_{T, \sigma, C_l}$$

is a change in specific superficial energy under changes of the concentration of  $k$ -th component;

$$\Omega = \left( \frac{\partial g_s}{\partial \eta} \right)_{T, \sigma, C_k} = - \left( \frac{\partial^2 g}{\partial \eta^2} \right)_{T, \sigma, C_k}$$

is a change in energy of internal surfaces under changes of their area. These parameters introduced in [1] make quite clear physical sense. One more parameter, namely,

$$\gamma_s^{(v)} = \left( \frac{\partial g_s}{\partial C_v} \right) = - \left( \frac{\partial^2 g}{\partial C_v \partial \eta} \right) = - \left( \frac{\partial^2 g}{\partial \eta \partial C_v} \right) = \left( \frac{\partial g_v}{\partial \eta} \right)$$

defines the variation in the energy of internal surfaces under changes of concentration of vacancies.

Consequently, the equations for the flows of components and surfaces will take the following form

$$\mathbf{J}_k = -\rho \sum_{l=1}^n D_{kl} \nabla C_l - \rho D_{ks} \nabla \eta \quad (29)$$

$$\mathbf{J}_k = -\sum_{l=1}^n D_{sl} \nabla C_l - D_{ss} \nabla \eta$$

$$D_{kl} = \sum_{j=1}^n \frac{L_{kj} R}{\rho m_j C_j} f_{jl} - \frac{L_{ks} \gamma_s^{(l)}}{T \rho}$$

$$D_{ks} = -\frac{1}{T \rho} \left[ \sum_{j=1}^n L_{kj} \left( \gamma_s^{(l)} + \gamma_s^{(v)} \right) + L_{ks} \Omega \right] \quad (30)$$

$$D_{sl} = \sum_{k=1}^n \frac{L_{sk} R}{m_k C_k} f_{kl} - \frac{L_{ss} \gamma_s^{(l)}}{T}$$

$$D_{ss} = -\frac{1}{T} \left[ \sum_{k=1}^n L_{sk} \left( \gamma_s^{(k)} + \gamma_s^{(v)} \right) + L_{ss} \Omega \right]$$

Formulae derived for the diffusion coefficients differ from the formulae, which have been found in [1, 2] for an instance of diffusion through the intrusion mechanism, not only in the fact that they involve the generalized thermodynamic multipliers. *The diffusion*

coefficients along the interfaces and the coefficients for the migration of interfaces owing to their intrinsic curvature (or owing to the availability of a gradient of their specific area) depend on the energy that is transferred by the components and on the generalized energy, which is related to the transfer of vacancies. Similar to the case of [1–3], matrix of diffusion coefficients generally may be asymmetrical.

#### DIFFUSION AND STRESSES

With the proviso that a temperature is constant for a considered complex thermodynamic system, the Gibbs equation for the Gibbs energy is of the form

$$dg = -\rho^{-1}\varepsilon_{ij}d\sigma_{ij}^e + \sum_{k=1}^n g_k dC_k - g_s d\eta - g_v dC_v \quad (31)$$

Consequently, the components of deformation tensor, chemical potentials of components and vacancies, and specific superficial energy depend on variables  $\sigma_{ij}^e$ ,  $C_k$ ,  $\eta$ , and  $C_v$ .

Representing  $\varepsilon_{ij}$ ,  $g_k$ ,  $g_s$ ,  $g_v$  as the total differentials, we will write down the system of equations of state that is analogous to (28):

$$dg_k = \sum_{l=1}^n \beta_l^{(k)} dC_k - \gamma_s^{(k)} d\eta - \beta_v^{(k)} dC_v - \rho^{-1}\alpha_{ij}^{(k)} d\sigma_{ij}^e$$

$$dg_s = \sum_{k=1}^n \gamma_s^{(k)} dC_k + \Omega d\eta + \gamma_s^{(v)} dC_v + \rho^{-1}\alpha_{ij}^{(s)} d\sigma_{ij}^e \quad (32)$$

$$dg_v = \sum_{k=1}^n \beta_v^{(k)} dC_k + \gamma_s^{(v)} d\eta + \beta_v dC_v + \rho^{-1}\alpha_{ij}^{(v)} d\sigma_{ij}^e$$

$$d\varepsilon_{ij} = \sum_{k=1}^n \alpha_{ij}^{(k)} dC_k + \alpha_{ij}^{(s)} d\eta + \alpha_{ij}^{(v)} dC_v + s_{ij\alpha\beta} d\sigma_{\alpha\beta}^e$$

where  $s_{ij\alpha\beta}$  are the ordinary coefficients of elastic compliance that make up the fourth rank tensor;  $\alpha_{ij}^{(k)}$  are the coefficients of concentration expansion or, if the case in point is crystals, the coefficients of dilatation of crystal lattice in the following form:

$$\alpha_{ij}^{(k)} = \left( \frac{\partial \varepsilon_{ij}}{\partial C_k} \right) = -\rho \left( \frac{\partial^2 g}{\partial C_k \partial \sigma_{ij}^e} \right) = -\rho \left( \frac{\partial^2 g}{\partial \sigma_{ij}^e \partial C_k} \right)$$

$$= -\rho \left( \frac{\partial g_k}{\partial \sigma_{ij}^e} \right);$$

coefficients  $\alpha_{ij}^{(s)}$  reflect the change in the components of the tensor of deformations upon the variation of the area of internal surfaces, or they reflect the change in the specific superficial energy upon the variation of components of elastic stress tensor [1–3]:

$$\alpha_{ij}^{(s)} = \left( \frac{\partial \varepsilon_{ij}}{\partial \eta} \right) = -\rho \left( \frac{\partial^2 g}{\partial \eta \partial \sigma_{ij}^e} \right)$$

$$= -\rho \left( \frac{\partial^2 g}{\partial \sigma_{ij}^e \partial \eta} \right) = \rho \left( \frac{\partial g_s}{\partial \sigma_{ij}^e} \right)$$

The newly derived  $\alpha_{ij}^{(v)}$  coefficients can be defined also in terms of thermodynamics:

$$\alpha_{ij}^{(v)} = \left( \frac{\partial \varepsilon_{ij}}{\partial C_v} \right) = -\rho \left( \frac{\partial^2 g}{\partial C_v \partial \sigma_{ij}^e} \right)$$

$$= -\rho \left( \frac{\partial^2 g}{\partial \sigma_{ij}^e \partial C_v} \right) = \rho \left( \frac{\partial g_v}{\partial \sigma_{ij}^e} \right)$$

The equations for the flows of components, surfaces, and vacancies are of the previous form (26), because according to thermodynamics, the vector processes can stem only from the forces of vector nature. However, taking into consideration the equations of state, we will derive that the final equations for the flows will include the summands of three types: those proportional to the concentration gradients, to a gradient of specific area of internal surfaces, and to the gradients of a component of elastic stress tensor:

$$\mathbf{J}_k = -\rho \sum_{l=1}^n D_{kl} \nabla C_l - \rho D_{ks} \nabla \eta + B_{lm}^{(k)} \nabla \sigma_{lm}^e \quad (33)$$

$$\mathbf{J}_s = -\sum_{l=1}^n D_{sl} \nabla C_l - D_{ss} \nabla \eta + B_{ij}^{(s)} \nabla \sigma_{ij}^e$$

where the coefficients of mass transfer under the effect of stresses and the coefficients of migration of surfaces under the effect of stresses, as is the case in [3], constitute not some new coefficients, but those calculated from the coefficients introduced previously. *Unlike the analogous coefficients for the case of diffusion through the intrusion mechanism, the transfer coefficients that have been found here depend on the dilatation coefficients of the crystal lattice, which are related to the availability of vacancies:*

$$B_{lm}^{(k)} = \sum_{j=1}^n \frac{L_{kj}}{T\rho} (\alpha_{lm}^{(j)} + \alpha_{lm}^{(v)}) + \frac{L_{ks}}{T\rho} \alpha_{lm}^{(s)} \quad (34)$$

$$B_{ij}^{(s)} = \sum_{k=1}^n \frac{L_{sk}}{T\rho} (\alpha_{ij}^{(k)} + \alpha_{ij}^{(v)}) + \frac{L_{ss}}{T\rho} \alpha_{ij}^{(s)}$$

If a medium is isotropic, which may be assumed the right characteristic for a polycrystalline body, we will derive

$$\alpha_{ij}^{(k)} = 3\alpha_k \delta_{ij}, \quad \alpha_{ij}^{(s)} = 3\alpha_s \delta_{ij}, \quad \alpha_{ij}^{(v)} = 3\alpha_v \delta_{ij}$$

where  $\alpha_k$ ,  $\alpha_s$ ,  $\alpha_v$  are the linear coefficients of structural and concentration "expansion".

Hence, instead of (34), we obtain

$$B_{ij}^{(k)} = \left[ \sum_{l=1}^n \frac{3L_{kl}}{T\rho} (\alpha_l + \alpha_v) + \frac{3L_{ks}}{T\rho} \alpha_s \right] \delta_{ij} \quad (35)$$

$$B_{ij}^{(s)} = \left[ \sum_{k=1}^n \frac{3L_{sk}}{T\rho} (\alpha_k + \alpha_v) + \frac{3L_{ss}}{T\rho} \alpha_s \right] \delta_{ij}$$

When describing the diffusion by the vacancy mechanism, it is supposed, as a rule, that the cross diffusive flows can be ignored as compared to the diagonal ones on an assumption that  $L_{ij} = L_{ji} \ll L_{kk}$ . This approximation is substantiated in thermodynamics [5, 6] and it allows a simplification of some coefficients in the considered case too:

$$D_{kl} = \frac{L_{lk}R}{\rho m_k C_k} f_{kl} - \frac{L_{ks}}{T\rho} \gamma_s^{(l)} \equiv D_k^0 f_{kl} - \frac{L_{ks}}{T\rho} \gamma_s^{(l)} \quad (36)$$

$$D_{ks} = - \left[ \frac{L_{kk}}{T\rho} (\gamma_s^{(k)} + \gamma_s^{(v)}) + \frac{L_{ks}}{T\rho} \Omega \right]$$

$$B_{ij}^{(k)} = \left[ \frac{3L_{kk}}{T\rho} (\alpha_k + \alpha_v) + \frac{3L_{sk}}{T\rho} \alpha_s \right] \delta_{ij} \equiv B_k \delta_{ij}$$

The other transfer coefficients remain unchanged. A correlation with vacancies (or the cross flows associated with the availability of the gradient in the concentration of vacancies that exceeds the equilibrium concentration) is taken into account through the generalized thermodynamic multipliers  $f_{kl}$ .

### SELF-DIFFUSION

Let a thermodynamic system is composed of atoms of one kind and of vacancies, which can move both in the bulk and along the internal interfaces. In this case, we need just one

equation for a mass flow (or for a flow of vacancies) and an equation for a flow of surfaces

$$\mathbf{J}_1 = -\rho D_{11} \nabla C_1 - \rho D_{1s} \nabla \eta + B_1 \nabla \sigma_{kk}^e \quad (37)$$

$$\mathbf{J}_s = -D_{s1} \nabla C_1 - D_{ss} \nabla \eta + B_s \nabla \sigma_{kk}^e$$

where

$$D_{11} = \frac{L_{11} R f_{11}}{\rho m_1 C_1} - \frac{L_{1s}}{T\rho} \gamma_s^{(1)}$$

$$D_{1s} = -\frac{1}{T\rho} \left[ L_{11} (\gamma_s^{(1)} + \gamma_s^{(v)}) + L_{1s} \Omega \right]$$

$$D_{s1} = \frac{L_{s1} R f_{11}}{m_1 C_1} - \frac{L_{ss}}{T} \gamma_s^{(1)} \quad (38)$$

$$D_{ss} = -\frac{1}{T} \left[ L_{s1} (\gamma_s^{(1)} + \gamma_s^{(v)}) + L_{ss} \Omega \right]$$

$$B_1 = \frac{3}{T\rho} \left[ L_{11} (\alpha_1 + \alpha_v) + L_{1s} \alpha_s \right]$$

$$B_s = \frac{3}{T\rho} \left[ L_{s1} (\alpha_1 + \alpha_v) + L_{ss} \alpha_s \right]$$

Among the six transfer coefficients do not all represent the independent ones.

So, if there exist an isolated crystal free of internal interfaces and if the vacancies are at equilibrium, then  $\mathbf{J}_1 = -\rho D_1^0 \nabla C_1$ , where  $D_1^0$  is a self-diffusion coefficient under equilibrium conditions with respect to vacancies. Thus, we derive

$$L_{11} = \frac{D_1^0 C_1 m_1 \rho}{R} \quad (39)$$

If the vacancies are the non-equilibrium ones, then  $\mathbf{J}_1 = -\rho D_1^0 f_{11} \nabla C_1$ . Supposing that the diffusion coefficient  $D_{1s}$  along the boundaries of polycrystal grains represents the known value and the coefficient of migration of boundaries under the effect of concentration gradient  $D_{s1}$  (these magnitudes can be determined experimentally on the basis of the appropriate concepts) is the known value too, we will define the phenomenological coefficients  $L_{1s} = L_{s1}$ :

$$L_{1s} = -\frac{T\rho}{\Omega} \left[ \frac{D_1^0 C_1 m_1}{RT} (\gamma_s^{(1)} + \gamma_s^{(v)}) + D_{1s} \right] \quad (40)$$

Using (39) and (40), we will determine the volumetric diffusion coefficient



$$D_{11} = D_1^0 f_{11} + \frac{\gamma_s^{(1)}}{\Omega} D_{1s} \left[ \frac{D_1^0 C_1 m_1}{D_{1s} RT} (\gamma_s^{(1)} + \gamma_s^{(v)}) + 1 \right] \quad (41)$$

Consequently, the volumetric diffusion coefficient in the polycrystalline system is different from the volumetric diffusion coefficient in an isolated crystal and depends on the ratio between two energy parameters: the change in specific superficial energy owing to a diffusion of component and the change in superficial energy owing to the changing surface curvature. This effect will be less pronounced for polycrystals with a larger grain size and actual investigations disregard the effect. This is correct when  $\gamma_s^{(1)}/\Omega \ll 1$ . However, this effect must be tangible and should be taken into account during the interpretation of experimental data for the materials with the large number of internal surfaces.

Now we can consecutively determine the remaining coefficients. Using  $L_{ss}$  phenomenological coefficient, which follows from (40) and from the expression for  $D_{s1}$

$$L_{ss} = -\frac{T}{\gamma_s^{(1)}} \left\{ \frac{f_{11}\rho}{\Omega} \left[ D_1^0 (\gamma_s^{(1)} + \gamma_s^{(v)}) + \frac{RT D_{1s}}{m_1 C_1} \right] + D_{s1} \right\}$$

we will first find the  $D_{ss}$  coefficient and then the coefficients of transfer under the effect of stresses:

$$D_{ss} = \frac{\Omega}{\gamma_s^{(1)}} D_{s1} + D_{1s} \left[ (\gamma_s^{(1)} + \gamma_s^{(v)}) \frac{\rho}{\Omega} + \frac{RT}{m_1 C_1} \frac{f_{11}\rho}{\gamma_s^{(1)}} \right] + D_1^0 (\gamma_s^{(1)} + \gamma_s^{(v)}) \left[ \frac{f_{11}\rho}{\gamma_s^{(1)}} + \frac{C_1 m_1}{RT} \frac{\rho}{\Omega} (\gamma_s^{(1)} + \gamma_s^{(v)}) \right] \quad (42)$$

$$B_1 = 3(\alpha_1 + \alpha_v) \frac{D_1^0 C_1 m_1}{RT} - \frac{3\alpha_s}{\Omega} D_{1s} \left[ \frac{D_1^0 C_1 m_1}{D_{1s} RT} (\gamma_s^{(1)} + \gamma_s^{(v)}) + 1 \right] \quad (43)$$

$$B_s = -3 \left\{ D_{1s} \left( \frac{\alpha_1 + \alpha_v}{\Omega} + \frac{\alpha_s}{\gamma_s^{(1)}} \frac{f_{11}}{\Omega} \frac{RT}{m_1 C_1} \right) + \frac{\alpha_s}{\rho \gamma_s^{(1)}} D_{s1} + D_1^0 \frac{\gamma_s^{(1)} + \gamma_s^{(v)}}{\Omega} \right\} \times \left[ \frac{(\alpha_1 + \alpha_v) C_1 m_1}{RT} + \frac{\alpha_s}{\gamma_s^{(1)}} f_{11} \right] \quad (44)$$

Thus, only three from six transfer coefficients are independent, specifically,  $D_1^0$ ,  $D_{1s}$ ,  $D_{s1}$ . The others can be calculated or determined experimentally on the basis of concepts on the structure of crystal and of interfaces.

The formulae given in this section imply that if a body (a medium) is made up of the particles small in size so that we can assume  $\nabla\eta = 0$  (this corresponds to a uniform distribution of the area of internal interfaces), we are no longer able to speak about the diffusion coefficients in the bulk and along the grain boundaries. In this case, we should deal with some effective diffusion coefficients and effective transfer coefficients under the effect of pressure. Formulae (41) and (43) can be presented as

$$D_{11} = D_{\text{eff}} = D_1^0 f_{11} + \delta \frac{\gamma_s^{(1)}}{\Omega} D_{1s}$$

$$B_1 = B_{\text{eff}} = 3(\alpha_1 + \alpha_v) \frac{D_1^0 C_1 m_1}{RT} - \delta \frac{3\alpha_s}{\Omega} D_{1s}$$

$$\equiv B_1^0 - \delta \frac{3\alpha_s}{\Omega} D_{1s}$$

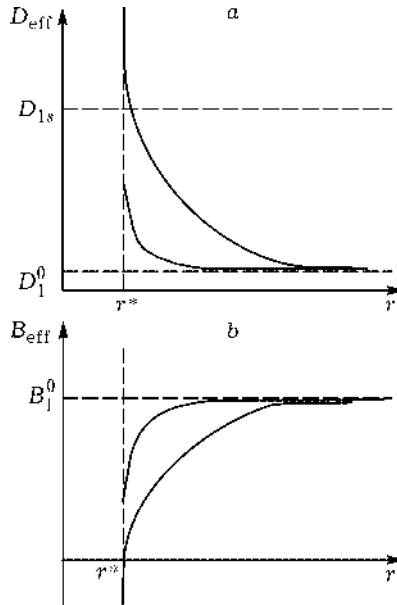


Fig. 1. Likely qualitative change in the effective transfer coefficients, which follows from the analysis of formulae (41) (a) and (43) (b).  $r^*$  is a minimum possible size of "particles" the system consists of.

where  $\delta = \frac{D_1^0 C_1 m_1}{D_{1s} RT} (\gamma_s^{(1)} + \gamma_s^{(v)}) + 1$ . By definition

$\Omega \geq 0$ , and  $\Omega \sim r^2$ . As  $D_1^0/D_{1s} \ll 1$ , it is worth expecting that  $\delta$  is a positive magnitude of the order of 1. Consequently, if  $\gamma_s^{(1)} > 0, D_{1s} > 0$  ( $r$  is an average size of the "particles" that make up the system), then the effective diffusion coefficient sharply increases with reduced  $r$ . Depending on the  $\gamma_s^{(1)}$  and  $\delta$  magnitudes, the effective diffusion coefficient may be theoretically both lower than is the coefficient of superficial diffusion and higher than this coefficient. The character of change in the effective transfer coefficient under the effect of pressure may be different depending on the sign of  $\alpha_s$  coefficient. This depends supposedly on the structure of interfaces. When

$$\left| \frac{RT}{C_1 m_1 \Omega} \frac{\alpha_s}{\alpha_1 + \alpha_v} \frac{D_{1s}}{D_1^0} \right| > 1$$

the coefficient  $B_1$  reverses sign. The likely qualitative behaviour of effective transfer coefficients depending on the size of particles, which make up the system, is illustrated in Fig. 1, a, b.

## CONCLUSIONS

Thus, the study shows the potentials of thermodynamics of irreversible processes as regards the simulation of chemical transformations and diffusion in solid, structurally non-uniform media. The relationships for mass flows in the media that include the large number of internal surfaces are analysed; the relationships are derived that link the various transfer coefficients for diffusion through the replacement mechanism with allowance made for stresses,

which accompany diffusion. The relationships for mass flows contain parameters, which make clear physical sense and are available from the experiment, for example, starting from the theory of internal friction. Generally, the model of the medium offered in [1–3] and developed in the present work may be useful to describe the mechanical behaviour of structurally non-uniform media, including nanostructured materials and creep processes. Within the limits of thermodynamics of irreversible processes, it is possible to perform estimates of change in macroscopic properties of a medium under changes of the additional parameters that characterize the structure [3]. These issues need for a special discussion.

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