

## THERMODYNAMICS OF THE ACTIVATED STATE OF MATERIALS

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*The thermodynamics of irreversible processes is extended to deformable materials whose state and behavior under nonequilibrium conditions are determined by the value and evolution of the additional parameter — the activation parameter. General thermodynamic relations are presented. The concept of the time of existence of a nonequilibrium state is introduced, and the phase coexistence conditions are generalized taking into account the properties of the interface. Methods are described to generalize the relations for irreversible flows, thermodynamic forces, and the equations of state.*

**Key words:** *irreversible processes, activation parameter, nonequilibrium conditions, thermodynamics.*

**Introduction.** Substances (materials) in nonequilibrium states, including nanostructural ones possessing unique properties have attracted great interest, resulting in the development of methods for purposefully modifying the state of materials. Modern technologies of processing and modifying material surface by the action of high-energy beams are focused on the production of nonequilibrium states of materials aimed at increasing their operational characteristics.

The theoretical basis of the modern technologies for purposefully modifying the states of materials is nonequilibrium thermodynamics, which makes it possible not only to explain changes in the properties of materials due to external actions but also to predict the character of the changes.

Modern thermodynamics describes the behavior of complex media under nonequilibrium conditions using additional parameters which are variously introduced into the model of the medium. In fact, the additional parameters describe the inclusion of additional degrees of freedom in the formation of the state of the system. The need to introduce additional parameters can be due to various physical phenomena. For example, the damage parameter in mechanics is convenient for describing the failure and change in the structure of materials under external actions. The inelastic behavior of materials is explained by the existence of internal parameters, whose equilibrium value is determined by the stress and strain levels in the sample. The dislocation distribution density in dislocation theories of plasticity can be considered as an additional parameter. A detailed analysis shows that the presence and evolution of additional parameters are required to describe irreversible processes such as diffusion (generally, mass transfer), especially if these processes occur under nonequilibrium conditions typical of modern methods of surface processing.

As an additional parameter describing the degree of deviation of the system from the equilibrium state, we consider the activation parameter (a parameter of the nonequilibrium state) determined from the deviation of the atomic volume from the equilibrium value [1, 2]. This is due to the fact that, in the construction of phase diagrams, the atomic volume can be treated as a thermodynamic variable [3, 4]. The generation of excess volume as a result of external actions can lead to the formation of nonequilibrium phase and structural states that can be treated as a certain activated state of the medium. From a physical point of view, the activated state can be directly related

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to the concept of the activation volume. For example, in the theory of the activated complex, any system whose total energy is higher than the zero energy of the activated complex is active by the definition, and the Gibbs free activation energy depends on the averaged differences between the volume of the activated complex and the volume of the molecules entering this complex. In simplified form, the activation volume can be defined as the effective volume occupied by an atom (molecule) should (due to enhanced oscillations in the vicinity of the equilibrium state) before it enters a reaction, leaves the equilibrium state, etc.

**Activation Parameter.** Let  $V_{\text{eq}}$  be the maximum volume of an atom (molecule) in the equilibrium state, and let  $V'$  be the volume of the atom (molecule) in the nonequilibrium (activated) state. Then,

$$\eta = \frac{V - V_{\text{eq}}}{V' - V_{\text{eq}}} \quad (1)$$

is a parameter (degree) of activation. In the equilibrium state  $V = V_{\text{eq}}$  and  $\eta = 0$ . Thus, near the equilibrium state,  $\eta \ll 1$ , and in the completely nonequilibrium state ( $V = V'$ ), we have  $\eta = 1$ . With this definition, this parameter corresponds to the notion of excess volume, and, hence, in the thermodynamic description of the influence of external actions on the state of materials and the processes occurring in them, it can be treated as an additional parameter [3, 4]. We show that, in an activated layer in the surface electron- and ion-beam processing of materials, the presence of this parameter affects the acceleration of transfer processes and changes in the macroscopic properties and kinetics of physicochemical transformations.

It be noted that, in real materials, the excess volume can be due to the generation of local structural distortions (protodefects) under external actions. Such local structural distortions were first found in studies [5, 6] of the response of a material with an initial ideal crystal lattice to high-rate actions over a wide temperature range. The calculations were performed using the molecular dynamics method with multiparticle potentials of interatomic interaction obtained using the immersed atom method. The possibility of the thermofluctuation mechanism of generation of regions with local structure changes was shown. From an analysis of the results, it follows that there is a threshold strain value for which a sudden increase in the regions with local structural changes begins. Investigation of the conditions of formation of local structural changes shows that this process is accompanied by a local change in the atomic volume by a value comparable to the volume jump during melting. This may be due to the loss of structural stability during melting. In view of the aforesaid, it can be assumed that, during activation, the quantity  $V' - V_{\text{eq}}$  in expression (1) should also be close to the volume change during melting.

In different technologies of material processing and production, the activation and subsequent generation of defects occur under the action of different factors — particle flows, rapid heating by radiation, shock-wave loading, acoustic perturbations, different types of oscillations in tribotechnical systems, etc. In a particular physical situation with the deviation of the system from the equilibrium state, this leads to the need for a special description of the evolution of the new parameter.

It is obvious that the specific volume of the material  $\gamma = \rho^{-1}$  depends directly on the volume of the atoms and molecules. Thus, if  $m\rho^{-1}$  is the molar volume ( $m$  molar mass), then  $V = m/(\rho N_A)$  is the volume of one atom or one molecule. In multicomponent mixtures, this relation holds for each element of the mixture  $V_k = m_k/(\rho_k N_A)$ , where  $m_k/\rho_k$  is the partial molar volume of the component with number  $k$  and  $\rho_k$  is its partial density. Summation of all  $k$  gives

$$\sum_{(k)} V_k = \frac{1}{N_A \rho} \sum_{(k)} \frac{m_k}{C_k},$$

where  $C_k = \rho_k/\rho$  is the mass concentration of the component. By the definition,  $\rho = \sum_{(k)} \rho_k$  and, hence,  $\sum_{(k)} C_k = 1$ .

It is obvious that  $\gamma^{-1} = \sum_{(k)} \gamma_k^{-1}$  ( $\gamma_k = \rho_k^{-1}$ ).

For each component, the activation parameter can be introduced by the formula

$$\eta_k = \frac{V_k - V_{k,\text{eq}}}{V'_k - V_{k,\text{eq}}},$$

where the quantities are similar to the quantities in Eq. (1). Hence,

$$\sum_{(k)} V_k = \sum_{(k)} V_{k,\text{eq}} + \sum_{(k)} \eta_k (V'_k - V_{k,\text{eq}}).$$

Generally, the effective average volume of a conditional molecule can be defined as follows:

$$V \equiv \tilde{V} = \frac{1}{nN_A\rho} \sum_{k=1}^n \frac{m_k}{C_k}.$$

Then, setting

$$V = V_{\text{eq}} + \frac{1}{n} \sum_{(k)} \eta_k (V'_k - V_{k,\text{eq}}), \quad \eta = \frac{1}{V - V_{\text{eq}}} \sum_{k=1}^n \eta_k (V'_k - V_{k,\text{eq}})$$

to describe the activated state of a multicomponent system, we use the generalized parameter  $\eta$ .

**General Thermodynamic Relations.** We consider a multicomponent deformable thermodynamic system in which mass transfer processes can proceed. In the equilibrium state, the internal energy of the system is a function of the entropy  $s$ , the strain tensor components  $\varepsilon_{ij}$ , and the concentrations of the components  $C_k$ . Using the relations of thermodynamics of irreversible processes [7], we characterize the system by the additional parameter  $\eta$  the activation parameter (1). Then, the local Gibbs equation for the internal energy in which the stress and strain tensors are used as local analogs of pressure and volume becomes

$$du = T ds + \sigma_{ij}^e \rho^{-1} d\varepsilon_{ij} + \sum_{k=1}^n g_k dC_k - A d\eta, \quad (2)$$

where  $u$  is the local internal energy,  $s$  is the local entropy,  $g_k$  are the chemical potentials of the components,  $\sigma_{ij}^e$  are the components of the elastic stress tensor (in the thermodynamics and mechanics of a continuous medium [8, 9], inelastic stresses are introduced by a special method; in relation (2) and its consequences, restrictions on the value and type of strain are absent);  $A$  is the generalized thermodynamic force which depends on the energy required for the activation of the system. In the thermodynamics of irreversible processes, the quantity  $A$  is a thermodynamic force that tends to return the system to the equilibrium state. From relation (2), we obtain

$$T \frac{ds}{dt} = \frac{du}{dt} - \sigma_{ij}^e \rho^{-1} \frac{d\varepsilon_{ij}}{dt} - \sum_{k=1}^n g_k \frac{dC_k}{dt} + A \frac{d\eta}{dt}, \quad (3)$$

and from relations (2) and (3), we have

$$A = T \left( \frac{\partial s}{\partial \eta} \right)_{u, \varepsilon, C_k}, \quad A = - \left( \frac{\partial u}{\partial \eta} \right)_{s, \varepsilon, C_k}. \quad (4)$$

Using other forms of the Gibbs equation, we represent the expression for the generalized thermodynamic force as

$$A = - \left( \frac{\partial h}{\partial \eta} \right)_{s, \sigma_{ij}^e, C_k} = - \left( \frac{\partial f}{\partial \eta} \right)_{T, \varepsilon, C_k} = - \left( \frac{\partial g}{\partial \eta} \right)_{T, \sigma_{ij}^e, C_k}, \quad (5)$$

where  $h = u - \sigma_{ij}^e \rho^{-1} \varepsilon_{ij}$  is the local enthalpy,  $f = u - Ts$  is the local Helmholtz energy, and  $g = h - Ts$  is the local Gibbs energy. In (2)–(5) and below, the thermodynamic potentials are calculated per unit mass and are expressed in joules per kilogram.

Obviously, the generalized thermodynamic force which will be called the activation potential can be associated with the specific activation energy for the initiation of a protodefekt [6, 10]. From relations (4) and (5), it follows that the activation potential depends on the thermodynamic conditions of the experiment performed.

In a multicomponent system, the following relations hold:

$$s = \sum_{(k)} s_k C_k, \quad h = \sum_{(k)} h_k C_k, \quad g = \sum_{(k)} g_k C_k, \quad \dots$$

Here  $s_k$ ,  $h_k$ , and  $g_k$  are the partial entropies, enthalpies, and Gibbs energies (or chemical potentials) of the components, respectively.

The choice of the components of the tensor  $\sigma^e$ , temperature  $T$ , and component concentration  $C_k$  as the basic thermodynamic variables of state implies that these quantities (at least, their macroscopic analogs) can be controlled during the experiment. In this case, the basic thermodynamic potential is the Gibbs energy  $g = g(T, \sigma_{ij}^e, C_k; \eta) = u - \sigma_{ij}^e \rho^{-1} \varepsilon_{ij} - Ts$ . Then, the Gibbs equation (2) becomes

$$dg = -s dT - \varepsilon_{ij} \rho^{-1} d\sigma_{ij}^e + \sum_{k=1}^n g_k dC_k - A d\eta. \quad (6)$$

We note that existing relaxation theories analyze the behavior of so-called two-parameter media, i.e., media whose state depends on two basic thermodynamic parameters. Then, the Gibbs equation (6) do not contain terms dependent on the component concentration. The variable describing the deviation of the thermodynamic system from the equilibrium state and some internal processes is characterized by the time of establishment of equilibrium which is much larger than the time of establishment of equilibrium in the degrees of freedom corresponding to external variables, in this case, temperature and stress tensor components. This is the case, for example, in Kneser's theory described in [11], which considers the establishment of equilibrium energy distribution between the internal and external degrees of freedom of molecules. In such theories, the concentrations of admixture and vacancies (lattice sites not occupied by particles) are treated as internal variables. The introduced parameter  $\eta$  can also be related to the vibrational degrees of freedom, whose presence leads to the deviation of the effective atomic volume from the equilibrium value. Hence, the general propositions of relaxation theory are also valid in the case considered. Thus, the instantaneous (equilibrium) and delayed isothermal compressibilities; the equilibrium and relaxation heat capacities; and the equilibrium and relaxation coefficients of thermal expansion take place. We note that a change in the activation parameter can be due to not only to temperature fluctuations.

Taking into account that  $\eta = \eta(\sigma_{ij}^e, T, C_k)$  and using the system of thermodynamic equations of state [11–13]

$$ds = \frac{C_\sigma}{T} dT + \rho^{-1} \alpha_{ij}^T d\sigma_{ij}^e + \sum_{k=1}^n s_k dC_k + \left( \frac{\partial s}{\partial \eta} \right)_{T, \sigma, C_k} d\eta,$$

$$d\varepsilon_{ij} = \alpha_{ij}^T dT + s_{ij\alpha\beta} d\sigma_{\alpha\beta}^e + \sum_{k=1}^n \alpha_{ij}^{(k)} dC_k + \left( \frac{\partial \varepsilon_{ij}}{\partial \eta} \right)_{T, \sigma, C_k} d\eta, \quad (7)$$

$$dg_k = -s_k dT - \alpha_{ij}^{(k)} \rho^{-1} d\sigma_{ij}^e + \sum_{j=1}^n \beta_j^{(k)} dC_j + \left( \frac{\partial g_k}{\partial \eta} \right)_{\sigma, T, C_k} d\eta,$$

$$dA = \left( \frac{\partial A}{\partial T} \right)_{\sigma, C_k, \eta} dT + \rho^{-1} \left( \frac{\partial A}{\partial \sigma_{ij}^e} \right)_{T, C_k, \eta} d\sigma_{ij}^e + \sum_{k=1}^n \left( \frac{\partial A}{\partial C_k} \right)_{T, \sigma, C_l, \eta} dC_k + \left( \frac{\partial A}{\partial \eta} \right)_{T, \sigma, C_k} d\eta,$$

obtained on the basis of the Gibbs equation (6) for the Gibbs energy and the differential of the additional variable

$$d\eta = \left( \frac{\partial \eta}{\partial T} \right)_{\sigma, C_k} dT + \left( \frac{\partial \eta}{\partial \sigma_{ij}^e} \right)_{T, C_k} d\sigma_{ij}^e + \sum_{k=1}^n \left( \frac{\partial \eta}{\partial C_k} \right)_{T, \sigma} dC_k, \quad (8)$$

which is slower, or inertial, compared to the basic variables, we find that, under nonequilibrium conditions, the formulas for the effective properties described by the second derivatives of thermodynamic potential consist of two terms. In this case, the second term is the contribution due to the change in the additional parameter.

In (7),  $C_\sigma$  is the heat capacity at a constant stress;  $\alpha_{ij}^T$  are the components of the tensor of the thermal-expansion coefficients,  $s_k$  are the partial entropies of the components,  $\alpha_{ij}^{(k)}$  are the components of the tensor of the concentration-expansion coefficients,  $s_{ij\alpha\beta}$  are the components of the tensor of the elastic compliance coefficients, and  $\beta_j^{(k)}$  are thermodynamic multipliers which depend on the structure of the solution or chemical compound and the method of its description. The coefficients not described above should be determined separately.

For linear relations to exist between the increments of the state variables and increments of their conjugate thermodynamic parameters, it is sufficient that the increment of the Gibbs energy  $dg$  be a polynomial of the second degree in the increments  $d\sigma_{ij}^e$ ,  $dT$ , and  $dC_k$ . This does not rule out the nonlinear dependence of  $g$  on the state variables  $\sigma_{ij}^e$ ,  $T$ , and  $C_k$ . In the case considered, the Gibbs equation (linear in the increments) implies that the chosen set of variables is complete in some sense and the Gibbs energy can be represented as the total differential for the chosen state variables. In the model considered, the deviation of the system from the equilibrium state is described by the parameter  $\eta$ , whose inclusion in the number of variables of state allows us to write the total differential for  $g$  (6).

By the definition,

$$\varepsilon_{ij} = -\left(\frac{\partial g}{\partial \sigma_{ij}^e}\right)_{T, C_k, \eta},$$

then, the strain tensor components  $\varepsilon_{ij}$  can be represented as the total differential with respect to the same state variables  $\sigma_{ij}^e$ ,  $T$ ,  $C_k$ , and  $\eta$ . This is also valid for the quantities  $s$ ,  $g_k$ , and  $A$ , which leads to the equations linear in the increments (7) but does not rule out a nonlinear dependence of  $s$ ,  $\varepsilon_{ij}$ ,  $g_k$ , and  $A$  on  $\sigma_{ij}^e$ ,  $T$ ,  $C_k$ , and  $\eta$ . To write relations (7), it is not required to know the form of the dependence of the potential on  $\sigma_{ij}^e$ ,  $T$ ,  $C_k$ , and  $\eta$ .

The change in the additional state variable which possesses special properties [7] can be represented as the total differential (8) of the basic state variables  $\sigma_{ij}^e$ ,  $T$ , and  $C_k$ . As the thermodynamic force  $A$ , the variable  $\eta$  is a scalar which can depend on the stress tensor components only through its invariants. Since the state variables are the stress tensor components (and not invariants), instead of (8) the following equality is valid:

$$\nabla \eta = w_T \nabla T + w_{ij}^\sigma \nabla \sigma_{ij}^e + \sum_{k=1}^n w_k \nabla C_k \quad (9)$$

or

$$\dot{\eta} = w_T \dot{T} + w_{ij}^\sigma \dot{\sigma}_{ij}^e + \sum_{k=1}^n w_k \dot{C}_k, \quad (10)$$

where the quantities  $w_T$ ,  $w_{ij}^\sigma$ , and  $w_k$  characterize the sensitivity of the activation parameter to a change in the thermodynamic state variables.

**Time of Life of the Nonequilibrium State.** If  $\eta < 1$ , then, upon removal of the external load, recovery of the equilibrium state of the system is theoretically possible. How and how long this will occur depends on the remoteness of the system from the equilibrium state and on the kinetic laws determined by the spatial and time scales of the corresponding physical phenomena. As a first approximation, this process can be described using thermodynamic relaxation theory [12], whose mathematical apparatus is well elaborate and whose analogs are available in various areas of physics and mechanics [7, 11, 14].

Indeed, the entropy production related to the evolution of the additional parameter is described by the relation

$$\left(\frac{ds}{dt}\right)_{in} = \frac{A}{T} \frac{d\eta}{dt} \geq 0.$$

According to Onsager theory, for the transition of the system from the activated state to the equilibrium state, the kinetic equation describing the evolution of the additional parameter can be written as

$$\frac{d\eta}{dt} = L \frac{A}{T}, \quad (11)$$

where  $L$  is the kinetic coefficient. Equation (11) also describes the evolution of this parameter under external actions. The thermodynamic force  $A$  depends on the parameter  $\eta$  and the thermodynamic state variables:

$$A = A(s, \varepsilon_{ij}, C_k; \eta).$$

The parameters  $T$ ,  $\sigma_{ij}^e$ , and  $g_k$  also depend on the thermodynamic state variables  $s$ ,  $\varepsilon_{ij}$ ,  $C_k$ , and  $\eta$ .

The constancy of the state variables is determined by specific conditions (for example, the conditions of the external action). In experimental studies, such conditions, as a rule, are the isothermal ( $T = \text{const}$ ) and adiabatic ( $s = \text{const}$ ) conditions and the conditions of constant volume or pressure. In a complex thermodynamic system, it is difficult to ensure constant entropy because of the presence of poorly controllable irreversible processes; therefore, by adiabatic conditions is meant the absence of heat exchange with the ambient medium. The constancy of particular macroscopic quantities (volume or pressure) does not imply the absence of fluctuations in their local analogs (strain and stress tensor components) due to irreversible processes since all local quantities are functions of coordinates and time.

In the equilibrium state,  $A = 0$  because, under equilibrium conditions, the entropy is maximal:

$$A_{\text{eq}} = T \left(\frac{\partial s}{\partial \eta}\right)_{\text{eq}} = 0.$$

We expand  $A$  in a series in the vicinity of an equilibrium state with accuracy up to terms of the second order of smallness in  $\eta - \eta_{\text{eq}}$ . Then, instead of (11) we obtain

$$\frac{d\eta}{dt} = \frac{L}{T} \left( \frac{\partial A}{\partial \eta} \right)_{\text{eq}} (\eta - \eta_{\text{eq}}). \quad (12)$$

Taking into account (3)–(5), we determine the values of the derivative  $(\partial A/\partial \eta)_{\text{eq}}$  for various observation conditions. For example, for (4) under adiabatic conditions with constant strain and component concentration, we have

$$\left( \frac{\partial A}{\partial \eta} \right)_{\text{eq}} = - \left( \frac{\partial^2 u}{\partial \eta^2} \right)_{s, \varepsilon_{ij}, C_k} < 0.$$

The positivity of the second partial derivative of the internal energy is a consequence of the condition of stability of thermodynamic equilibrium. Then, from (12) we have

$$\eta(t) - \eta_{\text{eq}}(s, \varepsilon_{ij}, C_k) = C_1 \exp(-t/\tau_{s, \varepsilon}), \quad (13)$$

where  $C_1$  is the integration constant which depends on the initial deviation from equilibrium;  $\tau_{s, \varepsilon}$  is the time of relaxation of the parameter  $\eta$  to its equilibrium value  $\eta_{\text{eq}}$  (the time of existence of the activated state):

$$\tau_{s, \varepsilon} = \frac{T}{L} \frac{1}{|(\partial A/\partial \eta)_{\text{eq}}|} > 0. \quad (14)$$

Using formulas (13) and (14), it is possible to determine the relaxation times  $\tau_{T, \sigma}$ ,  $\tau_{s, \sigma}$ , and  $\tau_{T, \varepsilon}$  corresponding to various observation conditions. From these relations, it follows that the time of existence of this nonequilibrium state depends on how it was reached and what where the subsequent conditions of existence of the system. For a multicomponent system for which the basic thermodynamic state variables include the component concentrations, there is a spectrum of relaxation times, which should be in definite relations [15].

We note that Eq. (13) can be written as

$$\eta(t) - \eta_{\text{eq}} = (\eta(t) - \eta_{\text{eq}})_0 \exp(-E_a/\Pi),$$

where  $E_a = m(\partial A/\partial \eta)_{\text{eq}}$  is the energy required to activate the thermodynamic system to the state with the current value of the additional parameter  $\eta$  (activation energy);  $\Pi = mT/(Lt)$  is the specific work that the system should perform to return to the equilibrium state. These quantities also depend on the activation conditions.

**Phase Coexistence Conditions.** The condition of the general thermodynamic equilibrium of a system that does not perform work can be written as

$$ds = \frac{du}{T} - \frac{\sigma_{ij}^e}{\rho T} d\varepsilon_{ij} - \frac{1}{T} \sum_{k=1}^n g_k dC_k + \frac{A}{T} d\eta = 0$$

or

$$ds = \frac{du}{T} + \frac{p_h}{T} d\gamma - \frac{1}{T} \sum_{k=1}^n g_k dC_k + \frac{s_{ij}}{\rho T} de_{ij} + \frac{A}{T} d\eta = 0, \quad (15)$$

where  $d\gamma = \rho^{-1} d\varepsilon_{ij}$  is the specific volume variation,  $p_h = -\sigma_{kk}^e/3$ ,  $s_{ij} = \sigma_{ij}^e - \sigma_{kk}^e/3$ , and  $e_{ij} = \varepsilon_{ij} - \varepsilon_{kk}/3$ . In (15), it is taken into account that  $s_{ij}d((1/3)\varepsilon_{kk}\delta_{ij}) \equiv 0$  and  $(1/3)\sigma_{kk}^e\delta_{ij}de_{ij} \equiv 0$ . If this system consists of three subsystems — two phases of the same substance and their interface — the Gibbs equations for each subsystem can be written as

$$du_k = T_k ds_k - p_k d\gamma_k + g_k dC_k + s_{ij}^{(k)} \rho_k^{-1} de_{ij}^{(k)} - A_k d\eta_k, \quad k = 1, 2,$$

$$du_f = T_f ds_f + \sigma_f d\Sigma, \quad (16)$$

where the subscript  $f$  corresponds to the quantities on the interface,  $\Sigma$  is the interfacial area,  $\sigma_f$  is the surface energy, and  $A_k$  is the thermodynamic force conjugate to the activation parameter in the phase  $k$ . In this approach, the surface is treated as a two-dimensional formation which does not have volume and, hence, mass.

For each phase (phases 1 and 2), the activation parameter depends on the thermodynamic variables of its state. Since  $u_k = u_k(s_k, \gamma_k, C_k, e_{ij}^{(k)})$  ( $k = 1, 2$ ), we have

$$d\eta_k = \left(\frac{\partial\eta_k}{\partial s_k}\right)_{\gamma, C_k, e} ds_k + \left(\frac{\partial\eta_k}{\partial\gamma_k}\right)_{s, C_k, e} d\gamma_k + \left(\frac{\partial\eta_k}{\partial e_{ij}}\right)_{s, C_k, \gamma} de_{ij} + \sum_{k=1}^n \left(\frac{\partial\eta}{\partial C_k}\right)_{s, e, \gamma} dC_k.$$

Hence, the Gibbs equations for phases (16) can be written as

$$du_k = T_k^a ds_k - p_k^a d\gamma_k + g_k^a dC_k + s_{ij}^{(k),a} \rho_k^{-1} de_{ij}^{(k)}, \quad k = 1, 2,$$

where  $T_k^a = T_k - A_k(\partial\eta_k/\partial s_k)_{\gamma_k, C_k, e^{(k)}}$  is the temperature,  $s_{ij}^{(k),a} = s_{ij}^{(k)} - A_k(\partial\eta_k/\partial e_{ij}^{(k)})_{s_k, C_k, \gamma_k}$  are the stress tensor deviator components,  $g_k^a = g_k - A_k(\partial\eta_k/\partial C_k)_{s_k, \gamma_k, e^{(k)}}$  are the chemical potentials of the phases,  $p_k^a = p_k + A_k(\partial\eta_k/\partial\gamma_k)_{s_k, C_k, e^{(k)}}$  is the pressure in the phases in the activated state.

For a closed system that does not perform work, we have

$$ds = ds_1 + ds_2 = 0, \quad d\gamma = d\gamma_1 + d\gamma_2 = 0, \quad dC_1 + dC_2 = 0, \quad d(u_1 + u_2) = -du_f, \quad (17)$$

$$\rho^{-1} de_{ij} = \rho_1^{-1} de_{ij}^{(1)} + \rho_2^{-1} de_{ij}^{(2)} = 0.$$

Expressing the differentials of the entropy from the Gibbs equations for the phases and using the general thermodynamic equilibrium condition ( $ds = 0$ ), we obtain

$$\left(\frac{1}{T_1^a} - \frac{1}{T_2^a}\right) du_1 + \left(\frac{p_1^a}{T_1^a} - \frac{p_2^a}{T_2^a}\right) d\gamma_1 - \left(\frac{g_1^a}{T_1^a} - \frac{g_2^a}{T_2^a}\right) dC_1 - \left(\frac{s_{ij}^{(1),a}}{T_1^a} - \frac{s_{ij}^{(2),a}}{T_2^a}\right) \frac{de_{ij}^{(1)}}{\rho_1} + \frac{\sigma_f}{T_f} d\Sigma_f = 0. \quad (18)$$

Hence, because the differentials included in expression (18) are independent of each other, the phases are in equilibrium if  $g_1^a = g_2^a$ ,  $T_1^a = T_2^a = T_f$ , and  $s_{ij}^{(1),a} = s_{ij}^{(2),a}$ . Since the differentials  $d\Sigma_f$  and  $d\gamma_1$  [or  $d\gamma_2$ ] cannot be considered independent, for the pressure in the phases we have

$$p_1^a = p_2^a - \frac{\sigma_f}{T} \frac{\partial\Sigma_f}{\partial\gamma_1}.$$

The conditions of equality the stress tensor deviator components of the phases are satisfied on the interface, where, according to (17), the following additional condition is valid:

$$de_{ij}^{(2)} = -\frac{\rho_2}{\rho_1} de_{ij}^{(1)}.$$

Because in local descriptions of phase transitions (when all thermodynamic parameters are functions of spatial coordinates and time), the notion of the interface is conditional, there is no need to introduce the interface in explicit form as a thermodynamic subsystem. Inner boundary surfaces, including interfacial surfaces, and their influence on the thermodynamic properties and states of equilibrium can be described by supplementing the model of the medium by additional parameters with special properties [13, 14].

Using the condition of equilibrium of the phases, similarly to [16], it is possible to obtain some simple generalizations of the Clausius–Clapeyron equation for phase transitions of the first kind in a deformable solid in the activated state.

**Other Generalizations.** For the activated state, it is possible to generalize different thermodynamic relations. Thus, using relation (8) and the above notation for the sensitivities of the activation parameter to changes in the basic thermodynamic state variables, the Gibbs equation (6) for the energy can be written as

$$dg = -(s - Aw_T) dT - \rho^{-1}(\varepsilon_{ij} + A\rho w_{ij}^\sigma) d\sigma_{ij}^e + \sum_{k=1}^n (g_k - Aw_k) dC_k$$

or

$$dg = -s^a dT - \varepsilon_{ij}^a \rho^{-1} d\sigma_{ij}^e + \sum_{k=1}^n g_k^a dC_k,$$

where the subscript “a” corresponds to the activated state.

Since the expansion of the thermodynamic system due to the introduction of additional parameters allows the use of the entire apparatus of thermodynamics, thermodynamic quantities such as the Gibbs energy, entropy, internal energy, and the other indicated above can be assumed to obey the additivity rule. Then, using the equality

$$g = \sum_{k=1}^n g_k^a C_k,$$

from the last relation we obtain the generalization of the Gibbs–Duhem equation

$$s^a dT + \varepsilon_{ij}^a \rho^{-1} d\sigma_{ij}^e + \sum_{k=1}^n C_k dg_k^a = 0.$$

In thermodynamics, the chemical potentials of the components are related not only to chemical reaction rates but also to transfer processes, which play an important role in the formation of material properties under external actions. Thus, according to the laws of thermodynamics, the chemical reaction rate is given by an equation similar to (11):

$$\varphi = \frac{l}{T} A_{\text{ch}}.$$

Here  $A_{\text{ch}} = -\sum_{i=1}^r \nu_i g_i$  is the affinity of the chemical reaction,  $\nu_i$  is the stoichiometric coefficient of the component  $i$  in the reaction, and  $r$  is the number of chemical reactions. Then, for the activated state, we have

$$\varphi = -\frac{l}{T} \sum_{i=1}^r \nu_i (g_i - Aw_i).$$

In [1, 2], based on the model of nonequilibrium thermodynamics with the additional parameter describing the deviation of the system from the equilibrium state, for the mass fluxes in multicomponent deformable media, equations are obtained that take into account the effect of the new parameter on the diffusion and other transfer coefficients under the action of stresses in nonequilibrium conditions. We analyzed various approximations typical of diffusion theory in solids (for example, the approximations of ideal and nonideal solutions; descriptions of diffusion by the intercalation and substitution mechanisms), particular models of diffusion in binary and ternary systems, etc. Thus, using (8), from the third relation of (7), we have

$$dg_k = -(s_k - \delta_k w_T) dT - (\alpha_{ij}^{(k)} - \rho \delta_k w_{ij}^\sigma) \rho^{-1} d\sigma_{ij}^e + \sum_{j=1}^n (\beta_j^{(k)} + \delta_j w_j) dC_j$$

or [in view of (9) and (10)]

$$\nabla g_k = -s_k^a \nabla T - \alpha_{ij}^{(k),a} \rho^{-1} \nabla \sigma_{ij}^e + \sum_{j=1}^n \beta_j^{(k),a} \nabla C_j, \quad (19)$$

where  $\delta_k$  is the energy required to activate the element with number  $k$ :

$$\delta_k = -\left(\frac{\partial g_k}{\partial \eta}\right)_{\sigma, C_j} = \left(\frac{\partial A}{\partial C_k}\right)_{\sigma, \eta}.$$

Using relation (19), the equations for the mass flux of the component  $k$  under nonisothermal conditions in the form

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

( $L_{kT}$  and  $L_{kl}$  are phenomenological coefficients) and performing transformations common in the theory of diffusion and thermodynamics of irreversible processes, we obtain

$$\mathbf{J}_k = -\rho \sum_{l=1}^n D_{kl}^a \nabla C_l - \rho \frac{D_{kT}^a}{T} \nabla T + \sum_{i,j=1}^3 B_{ij}^{(k),a} \nabla \sigma_{ij}^e. \quad (20)$$

The equations for the fluxes (20) contain partial diffusion coefficients  $D_{kl}^a$ , thermodiffusion coefficients  $D_{kT}^a$ , and the coefficients of mass transfer under the action of stresses (the relations linking the transfer coefficients  $D_{kl}^a$ ,  $D_{kT}^a$ ,



and  $B_{ij}^{(k),a}$  to the phenomenological coefficients and various physical quantities are not given here). The superscript  $a$  indicates that these coefficients correspond to the activated state of the substance, i.e., they differ from the coefficients known in diffusion theory. The coefficients  $D_{kl}^a$ ,  $D_{kT}^a$ , and  $B_{ij}^{(k),a}$  consist of the transfer coefficients and the values of their changes due to activation [1, 2]. The quantity and nature of the change in the additional terms due to changes in the physical quantities obviously depend on the method of producing the activated state (the character of the external action, thermodynamic states, etc.).

**Conclusions.** The thermodynamics of irreversible processes was extended to the nonequilibrium conditions occurring during surface processing of materials using various energy sources or to nonequilibrium conditions of material production. The activation parameter which characterizes the degree of deviation of the system from the equilibrium state is directly related to the deviation of the atomic volume from the equilibrium value and is included in all thermodynamic relations. The evolution of this parameter depends on the character of changes in the basic thermodynamic variables. The generality of the above relations and introduced concepts allows thermodynamic theory to be used to explain the various laws observed under nonequilibrium conditions: changes in the reaction rates, increases in transfer coefficients, etc.

An example of using the theory to describe the acceleration of diffusion in the surface layer observed during material surface processing by an electron flow is given in [17].

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