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Thermal Effects in Mechanochemistry

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Abstract — Fundamental thermodynamic equations are presented for anisotropic bodies with account for thermal effects. Definitions for Gibbs energy and partial molar quantities with respect to a direction chosen in an anisotropic phase, as well as expressions for the chemical potential tensor of an immobile component of a solid and for the chemical affinity tensor for a physicochemical process (including chemical reactions) in terms of the strain tensor variables and mixed variables including one component of the stress tensor are proposed. Conditions of stationary affinity and phase equilibrium are deduced. The mechanochemistry of polymorphous transformations is formulated for the cases of first- and second-order phase transitions.

INTRODUCTION

Thermodynamic relationships of mechanochemistry related to isothermal processes have been derived in [1]. Aiming at the study of pure mechanical effects, we compared chemical affinity (starting any physicochemical process, chemical reactions inclusive) at different mechanical states, but at the same temperature. This means that either thermal equilibrium with the environment can be established during mechanical action on the system (i.e., the mechanical action is slow enough), or a physicochemical process at a given mechanical state of the system is observed for such a long time that the prehistory of the mechanical action (even if it fast enough) is of no significance any longer. Investigation of mechanochemical effects under such conditions is of principal importance: It will suffice to mention here the experiments on dissolution of bent crystalline plates [2]. Fast physicochemical processes that occur under fast mechanical action may involve temperature changes (naturally, we are interested in the mechanothermal effect produced by the mechanical action itself, but not in the trivial heat of chemical reaction). Note that the term “fast” is not necessarily understood as a “far-from-equilibrium.” If, for instance, one speaks about nanoparticles, the equilibrium in them is attained fast. Mechanical equilibrium is known to be attained with the sound velocity. For particles sized in the range 10–1000 nm at the sound velocity of order 1000 m/s, the time of attaining mechanical equilibrium will be of order 10^{-11}–10^{-9} s, which is considerably shorter than even fast (pulse) actions of order 10^{-8}–10^{-9} in a real process of mechanical treatment of particles [3]. Although phonons (if speaking about the phonon mechanism of heat conduction) also move with the sound velocity, thermal equilibrium will be attained with a slight delay, if for no other reason that the thermal (mechanothermal) effect is a consequence of the mechanical action. However, thermal equilibrium is also attained fast enough in small systems.

Though mechanothermal effect can be sufficiently strong, leading to local temperature pulses of up to 1000 K [3], it follows from above that, in the theoretical analysis of the problem, we may rely on equilibrium thermodynamics when dealing with small systems or small parts of a large system in the local equilibrium approximation. The form of thermodynamic relationships does not depend on whether the thermal effect is of mechanothermal origin or results from chemical reaction or even from direct thermal action. It is important for us that both mechanochemical and thermal effects will be taken into account together.

1. FUNDAMENTAL THERMODYNAMIC EQUATIONS AND PARTIAL MOLAR QUANTITIES

We start from the differential fundamental equation for free energy F that, under isothermal conditions, takes the form (see Eq. (6.2.3) in [1])

$$(dF)_T = \hat{E} : d\hat{V} + \hat{\mu}_j : d\hat{N}_j + \sum_i \mu_i dN_i, \qquad (1.1)$$

where T is temperature, $\hat{E}$ is the stress tensor with the components E_{lm}, $\hat{V}$ is the volume displacement tensor with the components V_{lm} (strain tensor multiplied by volume), $\hat{\mu}_j$ is the chemical potential tensor for an immobile component of a system (symbolized by j) with the components $\mu_{j(st)}$, $\hat{N}_j$ is the mass displacement

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tensor (volume displacement tensor multiplied by concentration) with the components $N_{j(st)}$, μ_i and N_i are the chemical potential and the amount (we will express it by the number of moles) of the *i*th mobile component of the system. The colon designates a biscalar product of tensors:

$$\hat{E}:d\hat{V} \equiv \sum_{l,m=1}^{3} E_{lm}dV_{lm} \equiv V\sum_{l,m=1}^{3} E_{lm}de_{lm}, \tag{1.2}$$

$$\hat{\mu}_j:d\hat{N}_j \equiv \sum_{s,t=1}^{3} \mu_{j(st)}dN_{j(st)}. \tag{1.3}$$

(e_{lm} are the components of the strain tensor $\hat{e}$).

The notions of the chemical potential tensor and the mass displacement tensor have been explained in detail in [1]. Mobile components are met in gases, liquids, and solids, and they characteristically migrate freely over the whole system. For such species, the chemical potential tensor turns to be spherical and may be written in a scalar form. Immobile components are characteristic of solids (crystalline or amorphous) whose particles are firmly fixed at their sites and form a lattice (regular for crystals and irregular for amorphous bodies). With no essential loss in generality, one may postulate that there is always a single immobile component consisting of the set of substances forming the lattice. The chemical potential of an immobile component is closely related to lattice stresses (always present in the lattice) whose anisotropy inevitably causes the anisotropy of the chemical potential of the immobile component. Therefore, together with the stress tensor, the tensor of the chemical potential of an immobile component automatically appears in Eq. (1.1). The interrelation between these tensors is given by the relationship [1]

$$\hat{\mu}_j = (f_j - v_j\sum_i \mu_i c_i)\hat{1} - v_j\hat{E}, \tag{1.4}$$

where f_j and v_j are the free energy and the system volume per 1 mol of an immobile component, respectively, c is concentration, and $\hat{1}$ is the unit tensor.

We now have to cancel the isothermal condition and to discuss the term $-SdT$ (S is entropy and T is temperature) that naturally suggests itself on the right-hand side of Eq. (1.1). The question arises of whether the thermal term should also be written in a tensorial form? Stuke [4] was the first to declare temperature to be a tensor. Indeed, if we remember that entropy fluxes are vectors and that several fluxes can attack a system simultaneously, why not to introduce a tensorial temperature as we have done with the chemical potential of an immobile component when considering matter flux vectors [1]? However, in that work we dealt with an immobile component. Once a component becomes mobile, its chemical potential acquires isotropy even if the anisotropy of stresses is maintained. The surface layer of a liquid can be a good example: The normal and transverse pressures are different in the surface layer (because of which surface tension arises), whereas the chemical potentials of species are isotropic. All-pervading heat can scarcely remind an immobile component, but it can be compared with a mobile component. The analogy between heat and a mobile component becomes absolute if one turns to the phonon theory of dielectrics whose thermal properties are determined by the behavior of a gas of quasi-particles, phonons. Phonons move freely over the whole system and are undoubtedly mobile components, the temperature playing the role of their chemical potential. When passing from dielectrics to metals, electrons (to be more exact, their part forming the electron gas) join phonons in the process of heat conduction, but the electrons are also typical mobile components. Thus, the arguments relating to the nature of heat make us to draw the following conclusion: Even if temperature is really a tensor, it should be a spherical tensor, so that the additional, thermal term in Eq. (1.1) may be written in a scalar form. We now proceed to a more general equation for the free energy of a uniform system (1.5)

$$dF = -SdT + V\hat{E}:d\hat{e} + \hat{\mu}_j:d\hat{N}_j + \sum_i \mu_i dN_i. \tag{1.5}$$

If the amount of an immobile component is fixed (the system being closed all round for this component, so that $d\hat{N}_j = 0$) and equals 1 mol, Eq. (1.5) is written as Eq. (1.6)

$$\begin{aligned} df_j &= -s_j dT + v_j\hat{E}:d\hat{e} + \sum_i \mu_i dN_{i(j)} \\ &= -s_j dT + v_j\sum_{l,m=1}^{3} E_{lm}de_{lm} + \sum_i \mu_i dN_{i(j)}, \end{aligned} \tag{1.6}$$

where $s_j \equiv S/N_j$ and $N_{i(j)} \equiv N_i/N_j$ are, respectively, the system entropy and the number of moles of the *i*th mobile component, both per 1 mol of the immobile component. By cross differentiation in Eq. (1.6), we obtain Eq. (1.7)

$$\begin{aligned} &\left(\frac{\partial s_j}{\partial e_{lm}}\right)_{T,e_{st\neq lm},\hat{N}_j,N_i} \\ &= -v_j\left(\frac{\partial E_{lm}}{\partial T}\right)_{\hat{v},\hat{N}_j,N_i} \equiv -v_j\eta_{lm}, \end{aligned} \tag{1.7}$$

where, at fixed quantities, dummy indices run all possible values (restrictions, if any, are pointed out; for example, the condition of constancy $e_{st\neq lm}$ means that s and t run all possible values except for l and m, respectively, i.e. all the components of the strain tensor are fixed except for e_{lm}; the constancy of the tensor itself is indicated if all its components are fixed simultaneously). In Eq. (1.7), η_{lm} is the thermal stress coefficient showing what additional stress, in a direction chosen, arises in a closed system of a fixed configuration (therefore, v_j acts as a constant here) when the temperature is changed by one degree. The value of this coefficient is determined by the state equation of the system. The set of the coefficients η_{lm} (l, m = 1, 2, 3) forms the tensor of thermal stress coefficients $\hat{\eta}$ that can be defined as the temperature derivative of the stress tensor:

$$\hat{\eta} \equiv \left(\frac{\partial \hat{E}}{\partial T}\right)_{\hat{e},\hat{N}_j,N_i}. \qquad (1.8)$$

Together with the tensor of thermal strain coefficients $\hat{\theta}$ (analog of the thermal dilatation coefficient for isotropic systems)

$$\hat{\theta} \equiv \left(\frac{\partial \hat{e}}{\partial T}\right)_{\hat{E},\hat{N}_j,N_i} \qquad (1.9)$$

the tensor of thermal stress coefficients serves as a main index of the thermomechanical effect.

Passing now from free energy F to internal energy U, according to Eq. (1.10)

$$U \equiv F + TS \qquad (1.10)$$

and differentiating Eq. (1.10) with subsequent substituting Eq. (1.5), we obtain

$$dU = TdS + \hat{E}:d\hat{V} + \hat{\mu}_j:d\hat{N}_j + \sum_i \mu_i dN_i. \qquad (1.11)$$

The term TdS has the meaning of the amount of heat dQ transferred to the system from outside. Under adiabatic conditions, $dQ = 0$ and Eq. (1.11) becomes

$$(dU)_Q = \hat{E}:d\hat{V} + \hat{\mu}_j:d\hat{N}_j + \sum_i \mu_i dN_i. \qquad (1.12)$$

Comparison of Eqs. (1.1) and (1.12) shows that the variation in free energy under isothermal conditions and the variation in internal energy under adiabatic conditions are given by the same expression. This is not surprising, since the above characteristic functions both serve as thermodynamic potentials under the specified conditions, i.e. they are quantities whose change yields the work of a process. According to [1], the consequences of Eq. (1.1) for free energy are the same as the consequences of Eq. (1.12) for internal energy, so there is no need to analyze Eq. (1.12) in detail.

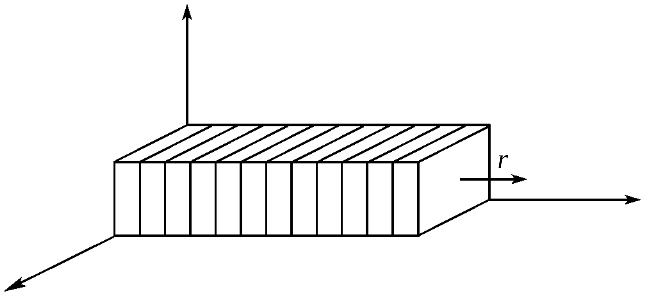

Fig. 1. To the calculation of thermodynamic functions by integration in the r direction.

To deduce an integral expression for energy, we use the following method. Let us choose a direction r in space (with one of the axes of Cartesian coordinates along the direction, see Fig. 1) and move the body boundary in this direction simultaneously with adding matter only along this direction. For such process, Eq. (1.11) takes the form

$$dU = TdS + E_{rr}dV_{rr} + \mu_{j(rr)}dN_{j(rr)} + \sum_i \mu_i dN_i, \qquad (1.13)$$

where all the rest components of the volume and mass displacement tensors are zero. Integration of Eq. (1.13) at a fixed physical state of the system yields

$$U = TS + E_{rr}V + \mu_{j(rr)}N_j + \sum_i \mu_i N_i. \qquad (1.14)$$

The value of the energy of a system should be independent of the way of calculation and, in particular, independent of the choice of integration direction (then it follows from Eq. (1.14) that the sum $E_{rr}V + \mu_{j(rr)}N_j$ is invariant) or of fixing some variables. Equation (1.14) is valid for any variations and, therefore, may be differentiated irrespective of any conditions. Having performed this operation, we obtain

$$dU = TdS + SdT + E_{rr}dV + VdE_{rr} + \mu_{j(rr)}dN_j$$
$$+ N_j d\mu_{j(rr)} + \sum_i \mu_i dN_i + \sum_i N_i d\mu_i. \qquad (1.15)$$

Taking into account that the perfect differentials of volume and number of moles are composed from their directed variations:

$$dV = \sum_{l=1}^{3} dV_{ll} = \sum_{l=1}^{3} Vde_{ll}, \qquad (1.16)$$

$$dN_j = \sum_{s=1}^{3} dN_{j(ss)}, \tag{1.17}$$

we may rearrange Eq. (1.15) to obtain

$$dU = TdS + SdT + E_{rr} \sum_{l=1}^{3} Vde_{ll} + VdE_{rr}$$

$$+ \mu_{j(rr)} \sum_{s=1}^{3} dN_{j(ss)} + N_j d\mu_{j(rr)} + \sum_i \mu_i dN_i + \sum_i N_i d\mu_i. \tag{1.18}$$

Equating now the right-hand sides of Eqs. (1.11) and (1.18) and taking into account Eqs. (1.2) and (1.3), we come to

$$\sum_{l,m=1}^{3} (E_{lm} - \delta_{lm}E_{rr})Vde_{lm} - VdE_{rr} = SdT$$

$$-\sum_{s,t=1}^{3} (\mu_{j(st)} - \delta_{st}\mu_{j(rr)})dN_{j(st)} + N_j d\mu_{j(rr)} + \sum_i N_i d\mu_i, \tag{1.19}$$

where δ_{lm} is Kronecker's symbol (the components of the unit tensor $\hat{1}$). If the amount of the immobile component does not change from any side ($dN_{j(st)} = 0$) and changes are restricted to the mechanical state, Eq. (1.19) takes the form

$$\sum_{l,m=1}^{3} (E_{lm} - \delta_{lm}E_{rr})Vde_{lm} - VdE_{rr}$$

$$= SdT + N_j d\mu_{j(rr)} + \sum_i N_i d\mu_i, \tag{1.20}$$

where, as in Eq. (1.19), summation is carried out in reality with respect to five and not six components of the strain tensor, since the coefficient of de_{rr} is zero (the fundamental equation (1.20) has been formed in such a manner that the independent variable e_{rr} has been replaced by the independent variable E_{rr}). Dividing Eq. (1.20) by the system volume V, we obtain

$$\sum_{l,m=1}^{3} (E_{lm} - \delta_{lm}E_{rr})de_{lm} - dE_{rr}$$

$$= s_v dT + c_j d\mu_{j(rr)} + \sum_i c_i d\mu_i \tag{1.21}$$

(s_v is the bulk density of entropy) or, using the tensorial notation,

$$(\hat{E} - \hat{1}E_{rr}) : d\hat{e} - dE_{rr} = s_v dT + c_j d\mu_{j(rr)} + \sum_i c_i d\mu_i. \tag{1.22}$$

When passing to an isotropic fluid system, the conditions $\hat{E} = E_{rr}\hat{1} = -p\hat{1}$ (i.e. $E_{lm} = -p\delta_{lm}$ where p is hydrostatic pressure) and $N_j = 0$ are fulfilled, and Eq. (1.20) changes to the Gibbs–Duhem equation which is well known in chemical thermodynamics

$$Vdp = SdT + \sum_i N_i d\mu_i. \tag{1.23}$$

Therefore, the fundamental equation (1.20) may be considered a generalization of the Gibbs–Duhem equation for mechanically anisotropic states. Naturally, solid can also be present in a mechanically isotropic state. Then we again arrive at the Gibbs–Duhem equation, the immobile component being included in the sum standing in the equation.

In the absence of mobile components, the fundamental equation (1.20) gives directly the expression for the differential of the component of the chemical potential tensor for an immobile component in a direction chosen

$$d\mu_{j(rr)} = -s_j dT$$

$$+ v_j\left[\sum_{l,m=1}^{3} (E_{lm} - \delta_{lm}E_{rr})de_{lm} - dE_{rr}\right], \tag{1.24}$$

where $s_j \equiv S/N_j$ and $v_j \equiv V/N_j$ are the molar entropy and volume of the immobile component, respectively (the reader can make sure that Eq. (1.24) is also obtained by direct differentiation of Eq. (1.4) with use of Eq. (1.6) in the absence of mobile components). The chemical potentials of mobile components are controllable, and, if they are fixed, Eq. (1.20) again changes to Eq. (1.24). In this case, however, s_j and v_j should be called not the molar entropy and volume of an immobile component, but the entropy and volume of a system per 1 mol of an immobile component (as in Eq. (1.4)). Herewith, the quantity v_j maintains its meaning as the molar volume of an immobile component, provided mobile components do not escape the lattice formed by the immobile component. If, however, mobile components escape the lattice (as it occurs, for example, with the electron gas in metals), then, firstly, such effects are of surface character and may be often neglected at a high mass of the system, and, secondly, the system boundary may be strictly defined just along the lattice surface (with metals, however, this will cause that inconvenience that the system will no longer be electroneutral).

We have written above the fundamental equations for energy and free energy which play the role of thermodynamic potentials at constant strain tensor, amounts of all components, and entropy or temperature, respectively. For mechanically isotropic systems, the constancy of the strain tensor is reduced to the constancy of volume, but in practice, because of the approximate constancy of atmospheric pressure, isothermal–isobaric conditions are met more often. Replacement of the constancy of volume V by the constancy of pressure p results in that the Gibbs energy

$$G \equiv F + pV, \tag{1.25}$$

becomes a thermodynamic potential. For this reason, the Gibbs energy is so popular in the thermodynamics of solutions. The definition of the Gibbs energy becomes not unique for mechanically anisotropic states, since pressure (as well as stress) is different along different directions. The quantity $-E_{rr}$ plays the role of pressure in the r direction, and we may define the Gibbs energy G in an anisotropic system as

$$G_r \equiv F - E_{rr}V \equiv U - TS - E_{rr}V, \tag{1.26}$$

to relate it, in this manner, to the choice of direction (this is marked by the subscript at G). It will be emphasized that the Gibbs energy does not therewith become a directed quantity and remains, like any energy, a typical scalar.

By differentiating Eq. (1.26) with use of Eq. (1.16), we obtain

$$dG_r = dF - E_{rr}\sum_{l=1}^{3} dV_{ll} - VdE_{rr} \tag{1.27}$$

and, after substituting Eq. (1.5) in Eq. (1.27) with accounting for Eqs. (1.2) and (1.3), we arrive at the differential fundamental equation for the Gibbs energy of a uniform anisotropic system

$$\begin{aligned} dG_r = {} & -SdT + V\sum_{l,m=1}^{3}(E_{lm} - \delta_{lm}E_{rr})de_{lm} \\ & - VdE_{rr} + \sum_{s,t=1}^{3}\mu_{j(st)}dN_{j(st)} + \sum_i \mu_i dN_i. \end{aligned} \tag{1.28}$$

Using tensorial notation, Eq. (1.28) may be written as

$$\begin{aligned} dG_r = {} & -SdT + V(\hat{E} - \hat{1}E_{rr}) : d\hat{e} - VdE_{rr} \\ & + \hat{\mu}_j : d\hat{N}_j + \sum_i \mu_i N_i. \end{aligned} \tag{1.29}$$

If the amount of the immobile component is fixed on all sides ($d\hat{N} = 0$) and equals 1 mol, from Eq. (1.28) we may deduce the equation for the Gibbs energy $g_{r(j)}$ per mole of the immobile component:

$$\begin{aligned} dg_{r(j)} = {} & -s_j dT + v_j \sum_{l,m=1}^{3}(E_{lm} - \delta_{lm}E_{rr})de_{lm} \\ & - v_j dE_{rr} + \sum_i \mu_i dN_{i(j)} \end{aligned} \tag{1.30}$$

(the notation is the same as in Eq. (1.6)). From Eq. (1.30) we obtain the following cross relationships:

$$\begin{aligned} & \left(\frac{\partial s_j}{\partial e_{lm}}\right)_{T,e_{\substack{st\neq lm \\ st\neq rr}},E_{rr},\hat{N}_j,N_i} \\ & = -\left(\frac{\partial[v_j(E_{lm} - \delta_{lm}E_{rr})]}{\partial T}\right)_{e_{st\neq rr},E_{rr},\hat{N}_j,N_i}, \end{aligned} \tag{1.31}$$

$$\begin{aligned} & \left(\frac{\partial s_j}{\partial E_{rr}}\right)_{T,e_{lm\neq rr},E_{rr},\hat{N}_j,N_i} \\ & = \left(\frac{\partial v_j}{\partial T}\right)_{e_{lm\neq rr},E_{rr},\hat{N}_j,N_i} \equiv v_j\theta_{rr}, \end{aligned} \tag{1.32}$$

$$\begin{aligned} & \left(\frac{\partial[v_j(E_{lm} - \delta_{lm}E_{rr})]}{\partial E_{rr}}\right)_{T,e_{st\neq rr},\hat{N}_j,N_i} \\ & = -\left(\frac{\partial v_j}{\partial e_{lm}}\right)_{T,e_{\substack{st\neq lm \\ st\neq rr}},E_{rr},\hat{N}_j,N_i}. \end{aligned} \tag{1.33}$$

Introducing the thermal coefficient of linear dilatation in the r direction (all other directions are blocked by the conditions of fixation of the strain tensor components):

$$\theta_{rr} \equiv \frac{1}{v_j}\left(\frac{\partial v_j}{\partial T}\right)_{e_{lm\neq rr},E_{rr},\hat{N}_j,N_i}. \tag{1.34}$$

the thermal stress coefficient under the condition that the normal stress in the r direction is kept constant

$$\eta_{lm(rr)} \equiv \left(\frac{\partial E_{lm}}{\partial T}\right)_{e_{st\neq rr},E_{rr},\hat{N}_j,N_i}. \tag{1.35}$$

and the isothermal compressibility in the r direction

$$\chi_{rr} \equiv \frac{1}{v_j}\left(\frac{\partial v_j}{\partial E_{rr}}\right)_{T,e_{lm\neq rr},E_{rr},\hat{N}_j,N_i}. \quad (1.36)$$

we rewrite Eqs. (1.31)–(1.33) in the form

$$\left(\frac{\partial s_j}{\partial e_{lm}}\right)_{T,e_{\substack{st\neq lm\\ st\neq rr}},E_{rr},\hat{N}_j,N_i}$$

$$= -\theta_{rr}v_j(E_{lm} - \delta_{lm}E_{rr}) - v_j\eta_{lm(rr)}, \quad (1.37)$$

$$\left(\frac{\partial s_j}{\partial E_{rr}}\right)_{T,e_{lm\neq rr},\hat{N}_j,N_i} = v_j\theta_{rr}, \quad (1.38)$$

$$\left(\frac{\partial E_{lm}}{\partial E_{rr}}\right)_{T,e_{st\neq rr},\hat{N}_j,N_i}$$

$$= \delta_{lm} - \frac{1}{v_j}\left(\frac{\partial v_j}{\partial e_{lm}}\right)_{T,e_{\substack{st\neq lm\\ st\neq rr}},E_{rr},\hat{N}_j,N_i}$$

$$- \chi_{rr}(E_{lm} - \delta_{lm}E_{rr}). \quad (1.39)$$

In accordance with Eq. (1.16), the volume change is contributed exclusively by the normal components of the strain tensor. Therefore, only a small (because of the low compressibility) term $-\chi_{rr}E_{lm}$ remains for the shear components of the stress tensor E_{lm} ($l \neq m$) on the right-hand side of Eq. (1.39). For the normal component E_{ll} ($ll \neq rr$), in view of the fixation of the strain tensor component in the third direction, we have

$$\frac{1}{v_j}\left(\frac{\partial v_j}{\partial e_{lm}}\right)_{T,e_{\substack{st\neq lm\\ st\neq rr}},E_{rr},\hat{N}_j,N_i}$$

$$= \frac{\partial(e_{ll} + e_{rr})}{\partial e_{ll}} = 1 - \kappa_{rl}, \quad (1.40)$$

where κ_{rl} is a two-dimensional Poisson's ratio in the rl plane. In this case, Eq. (1.39) is rearranged to the form

$$\left(\frac{\partial E_{ll}}{\partial E_{rr}}\right)_{T,e_{st\neq rr},\hat{N}_j,N_i} = \kappa_{rl} - \chi_{rr}(E_{ll} - E_{rr}). \quad (1.41)$$

For an incompressible medium ($\kappa_{rl} = 1$, $\chi_{rr} = 0$), Eq. (1.41) yields equal variations of the acting stress and the transverse stress at a one-sided compression (the result is known in the theory of elasticity when using an ordinary Poisson's ratio). The same result directly follows from Eq. (1.39) at v = const.

Let us return to Eq. (1.28). By integrating it along the r direction at constant E_{rr} or, still easier, by substituting Eq. (1.14) in Eq. (1.26), we obtain the integral expression for the Gibbs energy

$$G_r = \mu_{j(rr)}N_j + \sum_i \mu_i N_i. \quad (1.42)$$

Correspondingly, for the molar Gibbs energy, we have

$$g_r = \mu_{j(rr)}x_j + \sum_i \mu_i x_i, \quad (1.43)$$

where x is the molar fraction. Differentiating Eq. (1.42) and comparing the result with Eq. (1.28), we again arrive, as would be expected, at Eq. (1.19), from where Eqs. (1.21) and (1.22) follow, whose form does not depend on the choice of thermodynamic potential.

Equation (1.42), that is quite analogous in form to the expression for an ordinary Gibbs energy in the thermodynamics of solutions, shows that the Gibbs energy for a direction chosen is also composed of chemical potentials. In the thermodynamics of solutions, this circumstance leads to the representation of the chemical potential as a partial molar Gibbs energy. Thus we see that $\mu_{j(rr)}$ is a partial molar quantity of G_r. Indeed, from Eq. (1.28) we obtain

$$\mu_{j(rr)} = \left(\frac{\partial G_r}{\partial N_{j(rr)}}\right)_{T,e_{lm\neq rr},E_{rr},N_{j(st\neq rr)},N_i}. \quad (1.44)$$

from which it follows that the normal component of the chemical potential tensor of an immobile component in the r direction is the increment of the Gibbs energy corresponding to this direction, at adding 1 mol of the immobile component in the same direction to an infinitely large system. This addition is carried out at the constancy of the temperature and stress in the direction chosen, let alone that the variaion of the mass of species and of the system dimenions on all sides is forbidden. As a matter of fact, such addition of the immobile component (which means construction of a new portion of the lattice of the solid in the direction chosen) inevitably reduces the concentration of mobile components. As a consequence, the system state (including the mechanical state in other directions) changes, but this is a second-order effect for a macroscopic system.

If one replaces G_r by an arbitrary extensive quantity, the derivative in Eq. (1.44) symbolizes the definition of a partial molar quantity for a given direction. Since matter transfer is always directed, such extension of the notion of partial molar quantity is natural and turns to be useful for direction-dependent quantities. However, application of this definition to direction-independent quantities leads to ordinary partial molar quantities (chemical potentials of mobile components, volume, entropy, etc.). This can be illustrated by an example of entropy. Let us consider the system entropy S as a function of the independent variables indicated in Eq. (1.28) and write the exact differential of entropy in the form

$$dS = \frac{\partial S}{\partial T}dT + \sum_{\substack{l,m=1\\(lm\neq rr)}}^{3}\frac{\partial S}{\partial e_{lm}}de_{lm} + \frac{\partial S}{\partial E_{rr}}dE_{rr} + \sum_{s,t=1}^{3}\frac{\partial S}{\partial N_{j(st)}}dN_{j(st)} + \sum_i \frac{\partial S}{\partial N_i}dN_i. \tag{1.45}$$

At this choice of variables and under the conditions for the derivative $S/N_{j(st)}$, the r direction differs from all other directions in that respect that this direction is the only, along which geometrical dimensions of the system may vary. In this sense, the r direction can be called a free direction, while the others, restricted directions. Nevertheless, matter can be added from all sides, but it is not compressed when added in the free direction and is necessarily compressed when added in restricted directions (to return the system to the original size in each restricted direction). In a mechanically anisotropic system, compression in different directions leads to different states, including differences in entropy, so that the value of the derivative $\partial S/\partial N_{j(st)}$ depends on the choice of restricted direction. Let us now see whether the choice of free direction affects the value of the derivative $\partial S/\partial N_{j(st)}$.

In accordance with the terminology accepted in chemical thermodynamics, we call “open” those directions, along which matter exchange is possible, and “closed” those directions, along which matter exchange is forbidden. Let matter transfer be possible only along the open direction r and all other directions be closed. For this case, we write Eq. (1.45) as

$$dS = \frac{\partial S}{\partial T}dT + \sum_{\substack{l,m=1\\(lm\neq rr)}}^{3}\frac{\partial S}{\partial e_{lm}}de_{lm} + \frac{\partial S}{\partial E_{rr}}dE_{rr} + \bar{s}_{j(rr)}dN_{j(rr)} + \sum_i \bar{s}_i dN_i, \tag{1.46}$$

where $\bar{s}_{j(rr)}$ and $\bar{s}_i$ are the partial molar entropies of the immobile (in the r direction) and mobile components, respectively, defined, according to Eq. (1.44), as

$$\bar{s}_{j(rr)} = \left(\frac{\partial S}{\partial N_{j(rr)}}\right)_{T,e_{lm\neq rr},E_{rr},N_{j(st\neq rr)},N_i}, \tag{1.47}$$

$$\bar{s}_i \equiv \left(\frac{\partial S}{\partial N_i}\right)_{T,e_{lm\neq rr},E_{rr},N_{j(st)},N_{k\neq i}}, \tag{1.48}$$

(the subscripts k and i refer to mobile components). Considering a uniform equilibrium system, we ideally select a rectangular parallelepiped in the form of a bar oriented along the r direction (Fig. 1) and calculate its entropy. To this end, we apply Eq. (1.46) to a parallelepiped slice of infinitesimal thickness in the r direction and integrate Eq. (1.46) along the r direction at a given physical state (at constant T, $e_{lm\neq rr}$, E_{rr}, $\bar{s}_{j(rr)}$, and $\bar{s}_i$). The integration result

$$S = \bar{s}_{j(rr)}N_j + \sum_i \bar{s}_i N_i \tag{1.49}$$

shows that $\bar{s}_{j(rr)}$ and $\bar{s}_i$ are really partial molar quantities. Formally, $\bar{s}_{j(rr)}$ is the partial molar quantity in the r direction, but, since the result (quantity S) must be independent of direction, the quantity $\bar{s}_{j(rr)}$ [the only direction-related quantity in Eq. (1.49)] should be the same for all directions. Thus, in contrast with the derivatives of entropy for restricted directions in Eq. (1.45), the derivative (1.47) for a free and open direction is independent of the choice of direction. Therefore, we may now omit the additional subscript rr from the quantity $\bar{s}_{j(rr)}$. The same applies to the partial molar volume (introduced in [1] as $v_{j(rr)}$)

$$\bar{v}_{j(rr)} = \left(\frac{\partial V}{\partial N_{j(rr)}}\right)_{T,V_{lm\neq rr},E_{rr},N_{j(st\neq rr)},N_i}, \tag{1.50}$$

However, it should be added here that the specific character of an immobile component (which forms the solid lattice accommodating mobile components) makes the partial molar volume of the immobile component almost undistinguishable from its molar volume. Thus, we may set $\bar{v}_{j(rr)} = v_j$.

We now make an essential clause. The aforesaid referred to uniform bulk (strictly speaking, infinitely large) phases. In nonuniform and small systems the partial molar quantities of the immobile component may well be direction-dependent. It is known, for example, that the state of small particles depends on their shape. Adding the immobile component (to build-up the solid lattice) from different sides can differently change the shape of the body, thereby leading to different states, including partial molar quantities.

2. EXPRESSIONS FOR CHEMICAL POTENTIALS

As a direct consequence of the Gibbs–Duhem equation, we gave above Eq.(1.24) for the chemical potential of an immobile component in the particular case of the absence of mobile components or the constancy of their chemical potentials. In practice, however, more typical is the case when the amounts, rather than the chemical potentials of mobile components are constant (say, in a single piece of a solid). So we have to find expressions for the chemical potentials of both immobile and mobile components under such conditions. This work has been performed in part in [1], but that analysis is rather incomplete. We will here not only complement the relationships obtained therein by accounting for thermal (entropy) effects, but also refine the mechanical part of the relationships.

General expressions for chemical potentials can be derived from fundamental equations for free energy and other characteristic functions. Turning first to free energy, let us write Eq. (1.5), with accounting for Eqs. (1.2) and (1.3), in the form

$$dF = -SdT + V\sum_{l,m=1}^{3} E_{lm}de_{lm} + \sum_{s,t=1}^{3} \mu_{j(st)}dN_{j(st)} + \sum_i \mu_i dN_i, \tag{2.1}$$

from which follow the relationships

$$S = -\left(\frac{\partial F}{\partial T}\right)_{\hat{e},\hat{N}_j,N_i}, \tag{2.2}$$

$$VE_{lm} = \left(\frac{\partial F}{\partial e_{lm}}\right)_{T,e_{st\neq lm},\hat{N}_j,N_i}, \tag{2.3}$$

$$\mu_{j(st)} = \left(\frac{\partial F}{\partial N_{j(st)}}\right)_{T,\hat{e},N_{j(lm\neq st)},N_i}, \tag{2.4}$$

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,\hat{e},\hat{N}_j,N_{k\neq i}}, \tag{2.5}$$

where the partial derivative with respect to one of the quantities standing in Eq. (2.1) under the differential symbol, is taken at the constancy of all others.

If the amount of an immobile component is fixed on all sides ($d\hat{N}_j = 0$), the quantities T, elm, and N_i remains as variables in Eq. (2.1); therewith, N_i acquire the character of intensive quantities. In these variables, the perfect differentials of the chemical potentials of immobile and mobile components are written as

$$d\mu_{j(st)} = \frac{\partial \mu_{j(st)}}{\partial T}dT + \sum_{l,m=1}^{3}\frac{\partial \mu_{j(st)}}{\partial e_{lm}}de_{lm} + \sum_i \frac{\partial \mu_{j(st)}}{\partial N_i}dN_i, \tag{2.6}$$

$$d\mu_i = -\frac{\partial \mu_i}{\partial T}dT + \sum_{l,m=1}^{3}\frac{\partial \mu_i}{\partial e_{lm}}de_{lm} + \sum_i \frac{\partial \mu_i}{\partial N_i}dN_i. \tag{2.7}$$

After substituting Eqs. (2.4) and (2.5), changing the order of differentiation, and subsequent using Eqs. (2.2) and (2.3), Eqs. (2.6) and (2.7) transform to

$$d\mu_{j(st)} = \frac{\partial S}{\partial N_{j(st)}}dT + \sum_{l,m=1}^{3}\frac{\partial E_{lm}}{\partial N_{j(st)}}Vde_{lm} + \sum_i \frac{\partial \mu_i}{\partial N_{j(st)}}dN_i, \tag{2.8}$$

$$d\mu_i = -\frac{\partial S}{\partial N_i}dT + \sum_{l,m=1}^{3}\frac{\partial E_{lm}}{\partial N_i}Vde_{lm} + \sum_i \frac{\partial \mu_i}{\partial N_i}dN_i. \tag{2.9}$$

All the derivatives in Eqs. (2.8) and (2.9) are taken under the conditions shown in Eqs. (2.4) and (2.5). In particular, these conditions include the constancy of strain tensor and, hence, the constancy of volume. This allows us to place V outside the derivative when differentiating VE_{lm}. Due to the constancy of volume, Eq. (2.9) for the chemical potential of a mobile component may be written as

$$d\mu_i = -\frac{\partial s_v}{\partial c_i}dT + \sum_{l,m=1}^{3}\frac{\partial E_{lm}}{\partial c_i}de_{lm} + \sum_i \frac{\partial \mu_i}{\partial c_i}dc_i, \tag{2.10}$$

where $s_v \equiv S/V$ is the entropy density and $c_i \equiv N_i/V$ is the concentration of the ith mobile component.

The derivative $E_{lm}/N_{j(st)}$ implies that the lattice of an immobile component is built up under the condition of the constancy of volume and, therefore, under the condition of continuous compression. The relation of this derivative to the elastic properties of the lattice has been derived in [1] [Eq. (6.1.22)]:

$$\frac{\partial E_{lm}}{\partial N_{j(st)}} = -\frac{v_i}{V}\frac{\partial E_{lm}}{\partial e_{st}} \equiv -\frac{v_j}{V}\lambda_{lmst}, \tag{2.11}$$

where λ_{lmst} is the corresponding elasticity modulus. Substitution of Eq. (2.11) transforms Eq. (2.8) to the form

$$d\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}dT - v_i\sum_{l,m=1}^{3}\lambda_{lmst}de_{lm} + \sum_i \frac{\partial \mu_i}{\partial N_{j(st)}}dN_i. \tag{2.12}$$

Equation (2.12) is reduced to Eq. (6.2.31) (see [1]) at the constancy of temperature and of the amount of mobile components. Note that the derivatives of entropy in Eqs. (2.10) and (2.12) are not partial molar quantities. Indeed, these derivatives are taken at the constancy of the temperature and the strain tensor of a system (i.e. at the invariability of the whole boundary of the system). Under such conditions, introduction of an additional amount of the immobile component to the lattice along a certain direction means lattice compression and change in the mechanical state (stress) of the lattice even in this direction, let alone the others.

More convenient expressions can be obtained from the fundamental equation (1.28) for the Gibbs energy in the *r* direction, where, compared with Eq. (2.1), the independent variable e_{rr} is replaced by E_{rr}. From Eq. (1.28) we have

$$S = -\left(\frac{\partial G_r}{\partial T}\right)_{e_{lm\neq rr},E_{rr},\hat{N}_j,N_i}, \tag{2.13}$$

$$V(E_{lm} - \delta_{lm}E_{rr}) = \left(\frac{\partial G_r}{\partial e_{lm}}\right)_{T,e_{\substack{st\neq lm\\ st\neq rr}},E_{rr},\hat{N}_j,N_{i\,(lm\neq rr)}}, \tag{2.14}$$

$$V = -\left(\frac{\partial G_r}{\partial E_{rr}}\right)_{T,e_{lm\neq rr},E_{rr},\hat{N}_j,N_i}, \tag{2.15}$$

$$\mu_{j(st)} = \left(\frac{\partial G_r}{\partial N_{j(st)}}\right)_{T,e_{lm\neq rr},E_{rr},N_{j(lm\neq st)},N_i}, \tag{2.16}$$

$$\mu_i = \left(\frac{\partial G_r}{\partial N_i}\right)_{T,e_{lm\neq rr},E_{rr},\hat{N}_j,N_{k\neq i}}, \tag{2.17}$$

where the partial derivative with respect to one of the quantities standing in Eq. (1.28) under the differential symbol is taken at the constancy of all others.

If the amount of an immobile component is fixed on all sides ($d\hat{N} = 0$), chemical potentials become functions of temperature *T*, the components *elm*, except for e_{rr}, of the strain tensor, and the amounts (in moles) of mobile components N_i. Correspondingly, the differentials of chemical potentials $\mu_{j(st)}$ and μ_i are given by the expressions

$$d\mu_{j(st)} = -\frac{\partial \mu_{j(st)}}{\partial T}dT + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\frac{\partial \mu_{j(st)}}{\partial e_{lm}}de_{lm} + \frac{\partial \mu_{j(st)}}{\partial E_{rr}}dE_{rr} + \sum_i \frac{\partial \mu_{j(st)}}{\partial N_i}dN_i, \tag{2.18}$$

$$(d\mu_i)_{\hat{N}_j,N_i} = -\frac{\partial \mu_i}{\partial T}dT + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\frac{\partial \mu_i}{\partial e_{lm}}de_{lm} + \frac{\partial \mu_i}{\partial E_{rr}}dE_{rr} + \sum_i \frac{\partial \mu_i}{\partial N_i}dN_i, \tag{2.19}$$

where the partial derivatives are taken at the constancy of the quantities indicated in Eqs. (2.13)–(2.15) and (2.17). After substitution of Eqs. (2.16) and (2.17) in Eqs. (2.18) and (2.19), respectively, we now reverse the order of differentiation in the second partial derivatives and apply Eqs. (2.13)–(2.15) and (2.17). These operations lead to the expressions

$$d\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}dT + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\frac{\partial[V(E_{lm} - \delta_{lm}E_{rr})]}{\partial N_{j(st)}}de_{lm} + \frac{\partial V}{\partial N_{j(st)}}dE_{rr} + \sum_i \frac{\partial \mu_i}{\partial N_{j(st)}}dN_i, \tag{2.20}$$

$$d\mu_i = -\frac{\partial S}{\partial N_i}dT + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\frac{\partial[V(E_{lm} - \delta_{lm}E_{rr})]}{\partial N_i}de_{lm} + \frac{\partial V}{\partial N_i}dE_{rr} + \sum_i \frac{\partial \mu_i}{\partial N_i}dN_i. \tag{2.21}$$

It is of note that, under the condition of constancy of variables, the volume *V* in these expressions is no longer constant and is to be differentiated. By contrast, the stress E_{rr} is considered as a constant, and, therefore, the term $\delta_{lm}E_{rr}$ disappears on differentiation. As a result, Eqs. (2.20) and (2.21) take the form (the derivatives of entropy and volume may right away be replaced by partial molar quantities in the expression for mobile components):

$$d\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}dT + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\left[\frac{\partial V}{\partial N_{j(st)}}(E_{lm} - \delta_{lm}E_{rr}) + V\frac{\partial E_{lm}}{\partial N_{j(st)}}\right]de_{lm} - \frac{\partial V}{\partial N_{j(st)}}dE_{rr} + \sum_i \frac{\partial \mu_i}{\partial N_{j(st)}}dN_i, \tag{2.22}$$

$$d\mu_i = -\bar{s}_i dT + \sum_{\substack{l,m=1\\ lm\neq rr}}^{3}\left[\bar{v}_i(E_{lm} - \delta_{lm}E_{rr}) + V\frac{\partial E_{lm}}{\partial N_i}\right]de_{lm} - \bar{v}_i dE_{rr}. \tag{2.23}$$

For the sake of further transformation of Eq. (2.22), we detail the derivatives $\partial V/\partial N_{j(st)}$ and $\partial E_{lm}/N_{j(st)}$ which should be now treated with accounting for that the *r* direction is free. The expression for the first of these derivatives we derived earlier {see [1], Eqs. (6.1.26) and (6.1.30)}

$$\frac{\partial V}{\partial N_{j(st)}} = \delta_{st}\kappa_{sr}v_j, \tag{2.24}$$

where $\kappa_{sr} \equiv -de_{rr}/de_{ss}$ is a two-dimensional Poisson's ratio in the *sr* plane. As for the derivative $\partial E_{lm}/\partial N_{j(st)}$, we may again use Eq. (2.11) with the specification that the modulus λ_{lmst} is now of another meaning (we will mark it with a prime). Indeed, since the *r* direction is free, addition of matter along another (always restricted) direction will mean not only compression of the matter in this direction, but also dilatation in the *r* direction in accordance with Poisson's ratio. If, however, matter is introduced along the free direction, intensive parameters of the system do not change at all, and the derivative $\partial E_{lm}/\partial N_{j(st)}$ becomes zero. In view of the aforesaid, we write Eq. (2.22) at $st \neq rr$ as

$$d\mu_{j(st)} = -\frac{\partial S}{\partial N_{j(st)}}\,dT + v_j \sum_{\substack{l,m=1\\ lm\neq rr}}^{3} [\delta_{st}\kappa_{sr}(E_{lm} - \delta_{lm}E_{rr}) - \lambda'_{lmst}]de_{lm} - \delta_{st}\kappa_{sr}v_j dE_{rr} + \sum_i \frac{\partial\mu_i}{\partial N_{j(st)}}\,dN_i. \quad (2.25)$$

The simplest expression for the chemical potential of an immobile component results at $st = rr$. Then, according to the definition of partial molar quantities, the derivatives of entropy and volume are replaced by their partial molar values for the immobile component (herewith, the partial molar volume may be replaced by the molar volume, as it was said above), whereas λ'_{lmrr} becomes zero (this circumstance was not taken into account in [1]). As a result, we have

$$d\mu_{j(rr)} = -\bar{s}_j dT + v_j \sum_{\substack{l,m=1\\ lm\neq rr}}^{3} (E_{lm} - \delta_{lm}E_{rr})de_{lm} - v_j dE_{rr} + \sum_i \frac{\partial\mu_i}{\partial N_{j(rr)}}\,dN_i. \quad (2.26)$$

By comparing Eq. (2.26) at fixed amounts of mobile components ($dN_i = 0$) with Eq. (1.24), we note that the only difference is that molar entropy is replaced by partial molar entropy. The conditions of applicability of Eq. (2.26) are of practical significance, since matter is most frequently transferred along a free direction (other conditions may take place, for example, in the presence of rigid semipermeable walls).

3. EXPRESSIONS FOR CHEMICAL AFFINITY AND CONDITION OF STATIONARITY

Knowing the expressions for chemical potentials, we may now write expressions for the chemical affinity of an arbitrary physicochemical process, including chemical reactions. The chemical affinity tensor $\hat{A}$ is defined as [1]

$$\hat{A} \equiv \sum_k (\nu'_k\hat{\mu}'_k - \nu''_k\hat{\mu}''_k) \equiv \Delta\sum_k \nu_k\hat{\mu}_k, \quad (3.1)$$

where ν_k are stoichiometric coefficients, and summation is carried out over all components of the system. The quantities related to the initial and final states of the process (they can differ in space and time) are marked with a single prime and a double prime, respectively. In the second, more compact form of Eq. (3.1), Δ symbolizes the difference of quantities marked with single and double primes. If a component is absent in the initial or final state, its corresponding stoichiometric coefficient is zero. Dividing immobile (symbol j) and mobile (symbol i) components, we may write Eq. (3.1) as

$$\hat{A} \equiv \Delta\sum_j \nu_j\hat{\mu}_j + \hat{1}\Delta\sum_i \nu_j\mu_i \quad (3.2)$$

or, for the components of the chemical affinity tensor,

$$A_{st} \equiv \Delta\sum_j \nu_j\mu_{j(st)} + \delta_{st}\Delta\sum_i \nu_i\mu_i. \quad (3.3)$$

We here have to admit the existence of several immobile components, as it happens, for instance, in heterogeneous systems even under the condition that each phase contains only one immobile component.

To bring into the picture the effects of temperature and mechanical state on the components of chemical affinity (at specified amounts of all substances in the initial and final states of a physicochemical process), one should write Eq. (3.3) in a differential form

$$dA_{st} = \Delta\sum_j \nu_j d\mu_{j(st)} + \delta_{st}\Delta\sum_i \nu_i d\mu_i \quad (3.4)$$

and apply any of the above expressions for the chemical potentials of immobile and mobile components (2.10), (2.12) or (2.23), (2.25). If the transport of matter proceeds in the r direction, the most important for practice turns to be the expression

$$dA_{rr} = \Delta\sum_j \nu_j d\mu_{j(rr)} + \Delta\sum_i \nu_i d\mu_i. \quad (3.5)$$

Substituting first Eqs. (2.10) and (2.12), and then Eqs. (2.23) and (2.26) in Eq. (3.5), we obtain two expressions for the chemical affinity differential with different sets of variables:

$$(dA_{rr})_{\hat{N}_j,N_i} = -\Delta\sum_j \nu_j\Big(\frac{\partial S}{\partial N_{j(rr)}}\,dT + v_j\sum_{l,m=1}^{3}\lambda_{lmrr}de_{lm}\Big) - \Delta\sum_i \nu_i\Big(\frac{\partial s_v}{\partial c_i}\,dT - \sum_{l,m=1}^{3}\frac{\partial E_{lm}}{\partial c_i}\,de_{lm}\Big), \quad (3.6)$$

$$(dA_{rr})_{\hat{N}_j,N_i} = -\Delta\sum_j \nu_j\bar{s}_j dT - \Delta\sum_i \nu_i\bar{s}_i dT + \Delta\sum_j \nu_j v_j\Big[\sum_{l,m=1}^{3}(E_{lm} - \delta_{lm}E_{rr})de_{lm} - dE_{rr}\Big] + \Delta\sum_i \nu_i\Big\{\sum_{l,m=1}^{3}\Big[\bar{v}_i(E_{lm} - \delta_{lm}E_{rr}) + V\frac{\partial E_{lm}}{\partial N_i}\Big]de_{lm} - \bar{v}_i dE_{rr}\Big\}. \quad (3.7)$$

For processes involving no matter movement in space (chemical reactions, polymorphous transitions, etc.), the initial and final states are usually compared at the same temperature. Then the perfect differential of chemical affinity (3.6) may be written in a more compact form as

$$(dA_{rr})_{\hat{N}_j,N_i} = -\Delta\Big(\sum_j \nu_j\Big(\frac{\partial S}{\partial N_{j(rr)}}\,dT + \sum_{l,m=1}^{3} \nu_i\,\frac{\partial S}{\partial N_i}\Big)dT$$

$$-\sum_{l,m=1}^{3}\Delta\Big[\Big(\sum_j \nu_j v_j \lambda_{lmrr} - \sum \nu_i\,\frac{\partial E_{lm}}{\partial c_i}\Big)\,de_{lm}\Big]. \qquad (3.8)$$

If not only temperature, but also stress E_{rr} is equal for the initial and final states, the representation of the perfect differential of chemical affinity (3.7) is simplified:

$$(dA_{rr})_{\hat{N}_j,N_i} = -\Delta\bar{S}dT - \Delta\bar{V}dE_{rr}$$

$$+\sum_{l,m=1}^{3}\Delta\Big\{\Big[\bar{V}(E_{lm} - \delta_{lm}E_{rr}) + V\sum_i \nu_i\,\frac{\partial E_{lm}}{\partial N_i}\Big]\,de_{lm}\Big\}. \qquad (3.9)$$

Here $\bar{S}$ and $\bar{V}$ are the entropy and volume of a stoichiometric mixture of substances:

$$\bar{S} \equiv \sum_j \nu_j \bar{s}_j + \sum_i \nu_i \bar{s}_i, \qquad (3.10)$$

$$\bar{V} \equiv \sum_j \nu_j v_j + \sum_i \nu_i \bar{v}_i, \qquad (3.11)$$

so that $-\Delta\bar{S}$ and $-\Delta\bar{V}$ are the entropy and volume effects of the physicochemical process under consideration, respectively.

The value of chemical affinity determines the rate of a physicochemical process, while the sign of the chemical affinity determines the direction of the process (“plus” corresponds to the direct, a “minus” to the reverse process). When the affinity is zero, the process ceases, and the equilibrium involves the substances in the initial and final states. Generally, the chemical affinity and the rate of a physicochemical process are related by a coefficient whose value depends on the temperature and the mechanical state of the system. Therefore, one cannot ensure that, in the course of the process, the constancy of chemical affinity implies a stationary process. This is true only in the case of equilibrium, since the process rate will be always zero if the chemical affinity remains equal to zero. For this reason, equations for stationary affinity (which are valid at any its value) turn to be the most important in practice for equilibrium states and are most frequently used for studying just these states.

At given amounts of substances in the initial and final states of a physicochemical process, the differential equation of the stationarity of chemical affinity can be obtained from Eqs. (3.8) and (3.9) by setting $dA_{rr} = 0$:

$$\Delta\Big(\sum_j \nu_j\,\frac{\partial S}{\partial N_{j(rr)}} + \sum_i \nu_i\,\frac{\partial S}{\partial N_i}\Big)dT$$

$$-\sum_{l,m=1}^{3}\Delta\Big[\Big(\sum_j \nu_j v_j \lambda_{lmrr} - \sum_i \nu_i\,\frac{\partial E_{lm}}{\partial c_i}\Big]\,de_{lm}\Big], \qquad (3.12)$$

$$\Delta\bar{S}dT = -\,\Delta\bar{V}dE_{rr}$$

$$+\sum_{l,m=1}^{3}\Delta\Big\{\Big[\bar{V}(E_{lm} - \delta_{lm}E_{rr}) + V\sum_i \nu_i\,\frac{\partial E_{lm}}{\partial N_i}\Big]\,de_{lm}\Big\}. \qquad (3.13)$$

Equation (3.12) gives temperature as a function of the components of the strain tensor in the initial and final states of a process. Equation (3.13) gives temperature as a function of the normal component of the stress tensor in the r direction and the complementary components of the strain tensor for the initial and final states. If a process is carried out, as it often occurs, at a constant stress, all the components of the strain tensor can be expressed through (common for the initial and final states) six components of the stress tensor. Using these variables, the dimensionality of the state diagram is 7, and the temperature of stationary affinity makes a six-dimensional hypersurface in a seven-dimensional space. Note that the second term on the right-hand side of Eq. (3.13) reflects the specificity of the mechanical anisotropy of a system. This term disappears on passing to a mechanically isotropic state (we remind that the derivative standing there is taken at constant E_{rr} and, therefore, becomes zero at $E_{lm} = E_{rr}$).

The above relationships are of general character and apply to any processes in time and space: chemical and physical and directed and undirected. This makes these relationships valuable. However, the above reasoning may seem to be too abstract. To understand them better, a representative example is needed, involving both directed and undirected processes and illustrative of the role of mechanical anisotropy. Evidently, a solid should be considered, and we choose polymorphous transformations for such an example.

4. POLYMORPHOUS TRANSFORMATIONS

The gist of polymorphism is that, depending on external conditions (thermal and mechanical action, external fields, etc.), spatial structures of various types can arise in a system of a given chemical composition. In other words, the lattice formed by an immobile component can change its type (symmetry) depending on external conditions. As was already noted, the concept of lattice is applicable not only to crystals, but also to amorphous solids (in the latter case, the lattice is characterized by random location of its sites in space). Therefore, amorphization of solids can also be classified conditionally as a polymorphous transformation. From the thermodynamic standpoint, polymorphous transformations are phase transitions of the first or second order. Let us consider these two cases separately. For the sake of simplicity, the system is implied to contain only one immobile component and no mobile components.

4.1. First-Order Phase Transitions

If a phase α transforms to a phase β through the mechanism of a first-order phase transition, the phases contact each other and have a common interface. The r direction of matter transfer from phase α to phase β can be then defined as the direction of an external, with respect to phase α, normal to the interface. Correspondingly, the transition will be governed by chemical affinity

$$A_{rr} \equiv \mu^{\alpha}_{j(rr)} - \mu^{\beta}_{j(rr)}, \tag{4.1.1}$$

where $\mu^{\alpha}_{j(rr)}$ and $\mu^{\beta}_{j(rr)}$ are the components in the r direction of the chemical potential tensor for the only immobile component in phases α and β, respectively. At phase equilibrium, we have

$$A_{rr} = 0, \quad \mu^{\alpha}_{j(rr)} = \mu^{\beta}_{j(rr)}. \tag{4.1.2}$$

The range of state parameters, where maintenance of the phase equilibrium is possible, is determined, depending on the choice of variables, by Eqs. (3.12) and (3.13) which in the case in hand ($v_j = 1$, $v_i = 0$, $\bar{S} = s_j$, $\bar{V} = v_j$), take the form

$$\Delta \frac{\partial S}{\partial N_{j(rr)}} dT = -\sum_{l,m=1}^{3} \Delta(v_j \lambda_{lmrr} de_{lm}), \tag{4.1.3}$$

$$\Delta s_j dT = -\Delta v_j dE_{rr} + \sum_{l,m=1}^{3} \Delta[v_j(E_{lm} - \delta_{lm}E_{rr})de_{lm}], \tag{4.1.4}$$

where Δ now symbolizes the difference in a quantity for phases α and β. In particular, Δs_j and Δv_j are the molar entropy and molar volume effects for the reverse phase transition $\beta \to \alpha$:

$$\Delta s_j \equiv s^{\alpha}_j - s^{\beta}_j, \tag{4.1.5}$$

$$\Delta v_j \equiv v^{\alpha}_j - v^{\beta}_j \tag{4.1.6}$$

(molar and partial molar quantities coincide for one-component phases). Equation (4.1.3) is convenient when polymorphous modifications are compared at the same state of strain. If, however, polymorphous modifications are compared at given stresses, Eq. (4.1.4) turns to be more convenient. In the equilibrium state diagram, both the equations specify a hypersurface separating the regions of existence of phases α and β (coexistence of the two phases is possible on the hypersurface itself).

Equation (4.1.4) can be obtained directly from the equilibrium condition derived by Gibbs (who, as is known, never used the notion of the chemical potential of a solid) for a stressed solid contacting with a liquid along a certain direction [5]. Under conditions of isotropic deformation produced by hydrostatic pressure p ($E_{lm} = \delta_{lm}E_{rr} = -\delta_{lm}p$), Eq. (4.1.4) is reduced to the known Clapeyron–Clausius equation

$$\frac{dT}{dp} = \frac{\Delta v_j}{\Delta s_j}. \tag{4.1.7}$$

The equation of the same simple form is obtained from Eq. (4.1.4) in the case of one-sided compression (in the theory of elasticity, this term designates longitudinal compression of a column under the condition that its transverse dimensions cannot change)

$$\left(\frac{\partial T}{\partial E_{rr}}\right)_{e_{lm\neq rr}} = -\frac{\Delta v_j}{\Delta s_j}. \tag{4.1.8}$$

As correctly noted in [5], the same equation is also obtained for any small strain, provided the initial state of a solid is isotropic, i.e. $E_{lm} = \delta_{lm}E_{rr}$ (Kumazava has derived a similar equation for one-sided compression of a specimen under the condition of a uniform hydrostatic pressure [6, 7]). As for Eq. (4.1.8), it is not related to the vicinity of an isotropic state.

It is seen from a comparison of Eqs. (4.1.7) and (4.1.8) that the dependence of the temperature of a polymorphous transformation on stress is the same at all-sided and one-sided compression. The sign of theentropy effect Δs_j is the same for all substances, since the molar entropy of a high-temperature phase is always larger than the molar entropy of a low-temperature phase. However, the volume effect Δv_j can have any sing. Most typically, the molar volume of the high-temperature phase is also larger than the molar volume of the low-temperature phase. Then the signs of the volume and entropy effects of phase transition and the temperature of polymorphous transformation decreases with increasing stress, as shown in Fig. 2 (the character of the dependence will be opposite when stress is replaced by pressure). However, there exist abnormal cases of polymorphous transformations (we can point out red and yellow modifications of PbO or monoclinic and tetragonal forms of ZrO_2 as examples) when the high-temperature phase turns to be denser than the low-temperature phase, so that the derivative dT/dE_{rr} becomes positive (and the pressure derivative negative).

Equation (4.1.4) can also describe the case of the simple tension (or compression) of a column when lateral stresses (but not strain) are constant, as it happens, for example, at the tension of a column in open air. The matter is that any diagonal summand of the sum standing in Eq. (4.1.4) disappears not only at constant strain, but also at constant stress if it is equal to E_{rr}. We first consider the case when tension is carried out along a certain direction (direction 1) parallel to the interface, whereas the stress on the interface E_{rr} is kept constant. If the column consists of two phases, both phases will be subjected to a variable stress E_{11} and constant stresses $E_{22} = E_{33} \equiv E_{rr}$ (herewith, $E_{l \neq m} = 0$). Then Eq. (4.1.4) takes the form

$$\Delta s_j dT = (E_{11} - E_{rr})\Delta(v_j de_{11}) \tag{4.1.9}$$

and describes the behavior of the phase-transtion temperature in a mechanically anisotropic system (it is impossible to pass to an isotropic system in Eq. (4.1.9) which then simply loses its sense). Passing to the independent variable E_{11} and dividing both parts of Eq. (4.1.9) by dE_{11}, we arrive at the relationship

$$\left(\frac{dT}{dE_{11}}\right)_{E_{lm \neq 11}} = \frac{E_{11} - E_{rr}}{\Delta s_j} \Delta \left(v_j \frac{de_{11}}{dE_{11}}\right). \tag{4.1.10}$$

The derivative de_{11}/dE_{11} can be represented as

$$\frac{de_{11}}{dE_{11}} = \left(\frac{de_{11}}{dE_{11}}\right)_{T, E_{lm} \neq E_{11}} + \left(\frac{de_{11}}{dT}\right)_{\hat{E}} \frac{dT}{dE_{11}}$$

$$\equiv \frac{1}{\lambda_{1111}} + \theta_{11} \frac{dT}{dE_{11}}, \tag{4.1.11}$$

where λ_{1111} and θ_{11} are Young’s modulus and the thermal strain coefficient (the component of tensor (1.9) in direction 1), respectively. Substitution of Eq. (4.1.11) transforms Eq. (4.1.10) to the form

$$\left(\frac{dT}{dE_{11}}\right)_{E_{lm \neq 11}} = \frac{(E_{11} - E_{rr})}{\Delta s_j} \Delta \left(\frac{v_j}{\lambda_{1111}}\right) /$$

$$\left[1 - \frac{E_{11} - E_{rr}}{\Delta s_j} \Delta(v_j \theta_{11})\right]. \tag{4.1.12}$$

Equation (4.1.12) describes the dependence of the phase-transition temperature on the excess stress $E_{11} - E_{rr}$ applied parallel to the interface. In the initial isotropic state, the derivative dT/dE_{11} is zero, but it becomes more and more appreciable with increasing excess stress.

Until the excess stress is small, the denominator of Eq. (4.1.12) is close to unity. Thus one may set

$$\left(\frac{dT}{dE_{11}}\right)_{E_{lm \neq 11}} \approx \frac{(E_{11} - E_{rr})}{\Delta s_j} \Delta \left(\frac{v_j}{\lambda_{1111}}\right), \tag{4.1.13}$$

from which it follows that the phase-transition temperature increases or decreases proportionally the square of the stress applied. If, however, the stress is so large that, inversely, one may neglect unity in the denominator of Eq. (4.1.12), then Eq. (4.1.12) changes to

$$\left(\frac{dT}{dE_{11}}\right)_{E_{lm \neq 11}} \approx \frac{\Delta(v_j/\lambda_{1111})}{\Delta(v_j \theta_{11})}. \tag{4.1.14}$$

The dependence of T on E_{11}, given by Eq. (4.1.14), is practically rectilinear. Especially illustrative is the case when the difference in the molar volumes of polymorphous modifications is negligible. Then Eq. (4.1.14) becomes

$$\left(\frac{dT}{dE_{11}}\right)_{E_{lm \neq 11}} \approx \frac{\Delta(1/\lambda_{1111})}{\Delta\theta_{11}}. \tag{4.1.15}$$

This case is hardly rare, since polymorphous transformation is a structural one and involves primarily changes in the shape of the body than in its volume (which is usually rather small). When it comes to anisotropic solids, we can easily imagine the case of a first-order phase transition, when the molar volumes are strictly the same, whereas some components of the strain tensor have a break, let alone such structural characteristics as Young’s modulus and the thermal strain coefficient.

Equation (4.1.10) can be represented in one more very compact form. Since Eq. (4.1.10) actually describes the dependence of the phase-transition temperature on the excess stress $E_{11} - E_{rr}$, the isotropic state at $E_{11} = E_{22} = E_{33}$ may be conditionally taken for the initial state of zero strain. Although the derivative de_{11}/dE_{11} is here not isothermal, one can assume (because of the smallness of strain) a linear dependence between the quantities e_{11} and $E_{11} - E_{rr}$. Then, by putting the difference $E_{11} - E_{rr}$ under the symbol Δ, we can write Eq. (4.1.10) as

$$\left(\frac{dT}{dE_{11}}\right)_{E_{lm \neq 11}} = \frac{\Delta(v_j e_{11})}{\Delta s_j}. \tag{4.1.16}$$

where the deformation e_{11}, remember, is produced not only by mechanical, but also by thermal effects.

We now consider the case when the interface is perpendicular to the direction of uniaxial dilatation.

Then $E_{33} \equiv E_{rr}$ is the variable stress applied to both phases simultaneously at the constancy of all other stresses ($E_{11} = E_{22} \equiv E_{ll}$, $E_{l \neq m} = 0$). From Eq. (4.1.4) we have

$$\left(\frac{dT}{dE_{rr}}\right)_{E_{lm \neq rr}} = \frac{\Delta v_j}{\Delta s_j} - \frac{E_{rr} - E_{ll}}{\Delta s_j} \sum_{l=1}^{2} \Delta\left(v_j \frac{de_{ll}}{dE_{rr}}\right). \qquad (4.1.17)$$

By analogy with Eq. (4.1.11), one may use the representation

$$\frac{de_{ll}}{dE_{rr}} = \left(\frac{\partial e_{ll}}{\partial E_{rr}}\right)_{T, E_{lm \neq E_{rr}}} + \left(\frac{\partial e_{ll}}{\partial T}\right)_{\hat{E}} \frac{dT}{dE_{rr}}$$

$$= -\frac{\kappa_{lr}}{\lambda_{rrrr}} + \theta_{ll} \frac{dT}{dE_{rr}}, \qquad (4.1.18)$$

where κ_{lr} is a usual (three-dimensional) Poisson's ratio, λ_{rrrr} is Young's modulus for the r direction, and θ_{ll} is the thermal strain coefficient (the component of the tensor shown in Eq. (1.9)) in the l direction. Substitution of Eq. (4.1.18) in Eq. (4.1.17) leads to the relationship

$$\left(\frac{dT}{dE_{rr}}\right)_{E_{lm \neq rr}} = \left[-\frac{\Delta v_j}{\Delta s_j} + \frac{E_{rr} - E_{ll}}{\Delta s_j} \Delta\left(\frac{v_j}{\lambda_{rrrr}} \sum_{l=1}^{2} \kappa_{lr}\right)\right] /$$

$$\left[1 + \frac{E_{rr} - E_{ll}}{\Delta s_j} \Delta\left(v_j \sum_{l=1}^{2} \theta_{ll}\right)\right], \qquad (4.1.19)$$

which show how the excess uniaxial dilatation in a direction perpendicular to the interface, affects the phase-transition temperature. In the initial isotropic state, the value of the derivative dT/dE_{rr} exactly corresponds to the Clapeyron–Clausius equation (and can be small if the molar volumes of the polymorphous modifications are close). In the region of small excess stresses, Eq. (4.1.19) can be written as

$$\left(\frac{dT}{dE_{rr}}\right)_{E_{lm \neq rr}} \approx -\frac{\Delta v_j}{\Delta s_j} + \frac{E_{rr} - E_{ll}}{\Delta s_j} \Delta\left(\frac{v_j}{\lambda_{rrrr}} \sum_{l=1}^{2} \kappa_{lr}\right), \qquad (4.1.20)$$

from where it is seen that the dependence is still practically linear (unless the volume effect of the polymorphous transformation is too small). In the limit of large excess stresses, Eq. (4.1.19) is reduced to

$$\left(\frac{dT}{dE_{rr}}\right)_{E_{lm \neq rr}} \approx \Delta\left(\frac{v_j}{\lambda_{rrrr}} \sum_{l=1}^{2} \kappa_{lr}\right) / \Delta\left(v_j \sum_{l=1}^{2} \theta_{ll}\right), \qquad (4.1.21)$$

and becomes still simpler when the molar volumes of the polymorphous modifications are close to each other:

$$\left(\frac{dT}{dE_{rr}}\right)_{E_{lm \neq rr}} \approx \Delta\left(\frac{1}{\lambda_{rrrr}} \sum_{l=1}^{2} \kappa_{lr}\right) / \Delta\left(\sum_{l=1}^{2} \theta_{ll}\right), \qquad (4.1.22)$$

Along with the detailed representation of Eq. (4.1.17) in the form of Eq. (4.1.19), we can [using the same arguments as in passing from Eq. (4.1.10) to Eq. (4.1.16)] reduce Eq. (4.1.17) to the compact form

$$\left(\frac{dT}{dE_{rr}}\right)_{E_{lm \neq rr}} = -\frac{\Delta v_j}{\Delta s_j} - \frac{1}{\Delta s_j} \Delta\left[v_j \sum_{l=1}^{2} e_{ll}\right], \qquad (4.1.23)$$

where the strain tensor components e_{ll} include not only the (negative) deformations of transverse compression reckoned from a mechanically isotropic state, but also thermal effects. The first term on the right-hand side of Eq. (4.1.23) corresponds to the Clapeyron–Clausius equation. The second term plays the role of a correction whose value depends on the elastic and thermal properties of coexisting phases, as well as on the degree of deviation from the mechanically isotropic state (for the isotropic state itself, $e_{ll} = 0$, and Eq. (4.1.23) strictly changes to the Clapeyron–Clausius equation).

From Eq. (4.1.4) also follows the relationship

$$\left(\frac{\partial T}{\partial e_{lm}}\right)_{\substack{E_{rr}, e_{st \neq rr} \\ st \neq lm}} = -\frac{2 v_j \Delta E_{lm}}{\Delta s_j} \quad (l \neq m). \qquad (4.1.24)$$

that describes the effect of the shear strain on the phase-transition temperature. Here the coefficient 2 appears because of the symmetry of the strain and stress tensors ($e_{lm} = e_{ml}$ and $E_{lm} = E_{ml}$). In addition, the shear strain does not affect the molar volume v_j, so that v_j may be factored outside the difference sign.

It should be said that phase transitions in nonisotropically stressed solids have been well documented. We show here how it should be done on the basis of the chemical potential tensor and with accounting for interface orientation. The notion of chemical potential was never used earlier, and the problem was solved in terms of the truncated thermodynamics of deformation (for example, as it has been formulated in [8]). Instead of the equality of the normal-to-interface components of chemical potential, the equality of molar Gibbs energy or the function $\Phi \equiv F - V_0 \sum_{l,m} E_{lm} e_{lm}$, where V_0 is a certain constant volume in the strainless state usually introduced when using the Piola stress tensor, was postulated. In this way, Coe and Paterson [9] derived the equation (in our notation)

$$\left(\frac{dT}{dE_{lm}}\right)_{E_{st \neq rr}} = -\frac{v_{j0} \Delta e_{lm}}{\Delta s_j}. \qquad (4.1.25)$$

where v_{j0} is the molar volume for a standard state (from which strain is reckoned), assumed to be the same for both polymorphous modifications. This means that, at least for one of the phases, the standard state possesses appreciable stresses which, in addition, are not given uniquely (the same volume can result from various combinations of stresses). Therefore, the final strains present in Eq. (4.1.25) are, at $l = m$, of another (and less clear) meaning than the strains in Eqs. (4.1.16) and (4.1.23). Coe and Paterson [9] passed from their Eq. (4.1.25) to the Clapeyron–Clausius equation by setting $l = m$ and summing up the right-hand side over all directions. Therewith, Eq. (1.16) is needed, but this standard relationship of the theory of elasticity evidently implies that all e_{ll} relate to the same state of strain, i.e. all e_{ll} are simultaneously obtained from the same (single) experiment. However, the right-hand sides of Eq. (4.1.25) refer to simple dilatations in different directions (i.e. to different experiments), and the strains standing there do not coincide generally with their values at all-sided dilatation of the same specimen.

4.2. Second-Order Phase Transitions

Polymorphous modifications cannot coexist simultaneously if the polymorphous transformation $\alpha \to \beta$ is a second-order phase transition. There is no interface in this case and no direction selected in space. However, the interface between phases α and β in the above-mentioned state diagram does still exist as a six-dimensional hypersurface. The difference is that this hypersurface corresponds to the phase equilibrium α–β in the case of a first-order phase transition, but now simply separates two monophase regions. In the case of a first-order phase transition, thermodynamic potentials and their first derivatives do not change at the transition point and belong to both phases simultaneously. Therefore, one can say that Eqs. (4.1.2) (for an arbitrary direction) are still valid, but now as identities.

To derive the phase-interface equation, let us use the following procedure. We select points *a* and *b* infinitesimally close to each other on the phase interface hypersurface in the state diagram (as an example, the points are depicted in Fig. 2 as their projections on the E_{rr}–T coordinate plane) and consider change in a certain property when moving from one point to the other. As such a property, we first choose the component for an arbitrary direction $\mu_{j(rr)}$ of the chemical potential tensor. Its change $d\mu_{j(rr)}$ on passing from point *a* to point *b* can be calculated in various ways by alternately changing state parameters. As seen from Fig. 2, the path from *a* to *b* goes through the region of phase α if we first reduce temperature and then increase stress E_{rr}, or, vice versa, through the region of phase β if we first increase stress and then reduce temperature. Invoking also the rest variables, we may say that there are always two paths from point *a* to point *b*: one through the region of phase α and the other through the region of phase β. We designate the quantity $d\mu_{j(rr)}$ calculated by using the first and second paths as $d\mu^{\alpha}_{j(rr)}$ and $d\mu^{\beta}_{j(rr)}$, respectively. Since the result of calculation must be independent of the path, we, evidently, have

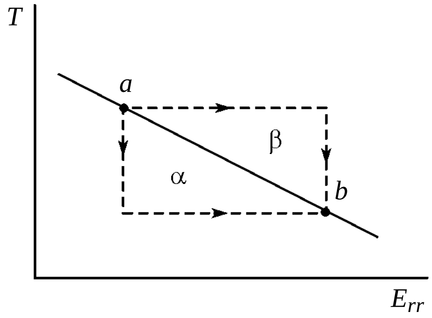

Fig. 2. Fragment of the phase interface *ab* in the E_{rr}–T coordinate plane.

$$d\mu^{\alpha}_{j(rr)} = d\mu^{\beta}_{j(rr)}. \tag{4.2.1}$$

If we now put the expression for the chemical potential of an immobile component, given by Eq. (2.12) or Eq. (2.26) into Eq. (4.2.1), we formally obtain again Eq. (4.1.3) or Eq. (4.1.4), respectively (for a one-component system). However, the first derivatives of the molar Gibbs energy (here chemical potential) exhibit no jump on passing from one phase to the other in the case of a second-order phase transition ($\Delta S = 0$, $\Delta V = 0$, etc.). Therefore, the resultant equations degenerate into identities unusable for calculations.

Second-order phase transitions differ from first-order phase transitions in that not the first, but the second derivatives of thermodynamic potentials undergo a jump at changing from one phase to the other. Therefore, if we wish to derive an equation for the α–β interface in the state diagram for a second-order phase transition, we have, turning to Fig. 2, to consider the variation, along the interface of a certain property which itself is the first derivative of thermodynamic potential (here free or Gibbs energy). The standard procedure for isotropic systems makes use of entropy and volume. Let us see what this gives for anisotropic bodies.

Taking the molar entropy of an immobile component s_j for the property required and repeating all the above reasoning related to Fig. 2, we arrive at the condition

$$ds^{\alpha}_{j} = ds^{\beta}_{j}, \tag{4.2.2}$$

which is evidently true at any choice of variables. Choosing first temperature and the strain tensor components as variables, we have the expression for the perfect differential of molar entropy in a closed system

$$ds_j = \frac{\partial s_j}{\partial T}\,dT + \sum_{l,m=1}^{3} \frac{\partial s_j}{\partial e_{lm}}\,de_{lm} = \frac{c_{\hat{e}}}{T}\,dT - v_j \sum_{l,m=1}^{3} \eta_{lm} de_{lm}, \tag{4.2.3}$$

In the second form of Eq. (4.2.3), we used Eq. (1.7) and introduced two quantities: heat capacity at constant configuration of the system $c_{\hat{e}}$ (analog of specific heat at constant volume in isotropic systems) and thermal stress coefficient η_{lm} (showing what additional stress in a direction chosen arises at changing temperature by one degree in a closed system of fixed configuration). Putting Eq. (4.2.3) in Eq. (4.2.2) leads to the equation

$$\Delta \frac{c_{\hat{e}}}{T}\,dT = \sum_{l,m=1}^{3} \Delta(v_j \eta_{lm}) de_{lm}, \tag{4.2.4}$$

where Δ symbolizes the difference of values of a quantity in phases α and β. Equation (4.2.4) in other terms describes the same hypersurface as that described by Eq. (4.1.3), but now for the case of a second-order phase transition.

Choosing now temperature, the normal stress in the *r* direction, and the strain tensor components in the rest directions as variables, we write the expression for the perfect differential of molar entropy in a closed system as

$$\begin{aligned} ds_j &= \frac{\partial s_j}{\partial T}\,dT + \frac{\partial s_j}{\partial E_{rr}}\,dE_{rr} + \sum_{\substack{l,m=1\\(l,m\neq rr)}}^{3} \frac{\partial s_j}{\partial e_{lm}}\,de_{lm} \\ &= \frac{c_{E_{rr},e_{lm\neq rr}}}{T}\,dT + v_j\theta_{rr} dE_{rr} \\ &\quad - v_j \sum_{\substack{l,m=1\\(l,m\neq rr)}}^{3} [\theta_{rr}(E_{lm} - \delta_{lm}E_{rr}) + \eta_{lm(rr)}] de_{lm}, \end{aligned} \tag{4.2.5}$$

In the second form of Eq. (4.2.5), we used Eqs. (1.37) and (1.38) containing the quantities $\eta_{lm(rr)}$ (thermal stress coefficient under the condition that the normal stress in the *r* direction is kept constant) and θ_{rr} (thermal linear dilatation coefficient in the *r* direction under the condition that all other directions are blocked). Besides, we introduced the specific heat $c_{E_{rr},e_{lm\neq rr}}$ at constant pressure in one direction and constant system boundaries in all other directions. Substitution of Eq. (4.2.5) in Eq. (4.2.2) leads to the equation

$$\begin{aligned} \Delta \frac{c_{E_{rr},e_{lm\neq rr}}}{T}\,dT &= -\Delta(v_j\theta_{rr}) dE_{rr} \\ &+ \sum_{\substack{l,m=1\\(l,m\neq rr)}}^{3} \Delta[v_j\theta_{rr}(E_{lm} - \delta_{lm}E_{rr}) + v_j\eta_{lm(rr)}] de_{lm}, \end{aligned} \tag{4.2.6}$$

that describes the interface as a hypersurface in the state diagram in the case of a second-order phase transition.

An interesting result is obtained when molar entropy is replaced by molar volume which is also the first derivative with respect to free energy and Gibbs energy. Then, instead of Eq. (4.2.2), we have the initial equality

$$dv_j^{\alpha} = dv_j^{\beta}. \tag{4.2.7}$$

Choosing temperature and the strain tensor components as the variables of the phase state, as in Eq. (4.2.3), is of no interest in this case. The matter is that variation of molar volume with temperature becomes impossible at the constancy of the configuration of a closed system ($e_{lm} = 0$), so that the expression for the perfect differential of molar volume in the closed system will not contain the temperature differential needed. Therefore, we use the set of variables standing in Eq. (4.2.5) and implying presence of a free direction. We write the expression for the perfect differential of molar volume in a closed system as

$$dv_j = \frac{\partial v_j}{\partial T}\,dT + \frac{\partial v_j}{\partial E_{rr}}\,dE_{rr} + \sum_{\substack{l,m=1\\(lm\neq rr)}}^{3} \frac{\partial v_j}{\partial e_{lm}}\,de_{lm}. \tag{4.2.8}$$

Using Eq. (1.34), we express the first derivative on the right-hand side of Eq. (4.2.8) through the thermal linear dilatation coefficient in the *r* direction θ_{rr}. We express the next derivative through the one-sided isothermal compressibility χ_{rr} in the same direction, given by Eq. (1.36). The last term in Eq. (4.2.8) is transformed with accounting for Eq. (1.40) that introduces a two-dimensional Poisson's ratio κ_{rl} in the *rl* plane (dilatation in the *r* direction is accompanied by lateral compression in the *l* direction at the constancy of all other components of the strain tensor). The resultant form of Eq. (4.2.8) is

$$dv_j = v_j\theta_{rr} dT + v_j\chi_{rr} dE_{rr} + v_j \sum_{l\neq r} (1 - \kappa_{rl}) de_{ll} \tag{4.2.9}$$

or

$$d\ln v_j = \theta_{rr} dT + \chi_{rr} dE_{rr} + \sum_{l\neq r} (1 - \kappa_{rl}) de_{ll}. \tag{4.2.10}$$

We now may substitute Eq. (4.2.9) in Eq. (4.2.7). However, it will be simpler if, instead of considering the variation of molar volume, we now consider the variation of the logarithm of molar volume along the phase interface in the state diagram. Instead of Eq. (4.2.7), we write

$$d\ln v_j^{\alpha} = d\ln v_j^{\beta} \tag{4.2.11}$$

and substitute Eq. (4.2.10) in Eq. (4.2.11). This yields the phase-interface equation for a second-order phase transition

$$\Delta\theta_{rr}dT = -\Delta\chi_{rr}dE_{rr} - \sum_{l\neq r}\Delta\kappa_{rl}de_{ll}, \tag{4.2.12}$$

Equation (4.2.12) is essentially simpler and, simultaneously, poorer than Eq. (4.2.5), since Eq. (4.2.12) contains only diagonal components of the strain tensor and only for two directions (different from *r*).

As already noted in the preceding section for the case of anisotropic bodies, the volume change can be continuous even for a first-order phase transition. More generally, observation of only volume behavior in phase transitions is quite insufficient for anisotropic bodies: It is necessary to control the whole strain tensor. In the case of a second-order phase transition, the strain tensor itself is continuous at intersecting the phase interface in the state diagram (this means that all its components e_{lm} are continuous), but some of its derivatives undergo discontinuity. In place of Eq. (4.2.7), we now write

$$de_{lm}^{\alpha} = de_{lm}^{\beta} \quad (l,\ m = 1,\ 2,\ 3), \tag{4.2.13}$$

and choose temperature *T* and the stress tensor components E_{st} as independent variables:

$$de_{lm} = \left(\frac{\partial e_{lm}}{\partial T}\right)_{\hat{E}} dT + \sum_{l,m=1}^{3}\left(\frac{\partial e_{lm}}{\partial E_{st}}\right)_{T,E_{lm\neq st}} dE_{st}$$

$$\equiv \theta_{lm}dT + \sum_{l,m=1}^{3} dE_{st}/\lambda_{stlm}, \tag{4.2.14}$$

(here θ_{lm} is the thermal strain coefficient and λ_{stlm} is the elasticity modulus at given stresses). Substitution of Eq. (4.2.14) in Eq. (4.2.13) leads to the relationship

$$\Delta\theta_{lm}dT + \sum_{l,m=1}^{3}\Delta(1/\lambda_{stlm})dE_{st} = 0 \quad (l, m = 1, 2, 3), \tag{4.2.15}$$

which describes the effect of stresses on the phase-transition temperature.

We now apply the equations obtained to the examples considered in the preceding section for first-order phase transitions. In the case of one-sided tension (in the *r* direction), according to Eqs. (4.2.6) and (4.2.12), the variation of the polymorphous transformation temperature is given by the relationship

$$\left(\frac{\partial T}{\partial E_{rr}}\right)_{e_{lm\neq st}} = -\frac{\Delta(v_j\theta_{rr})}{\Delta\dfrac{c_{E_{rr},e_{lm\neq rr}}}{T}} = -\frac{\Delta\chi_{rr}}{\Delta\theta_{rr}}\cdot \tag{4.2.16}$$

If, however, the substance is placed inside a tube with open ends at constant external pressure (E_{rr} = const), the equations obtained yield

$$\left(\frac{\partial T}{\partial e_{ll}}\right)_{E_{rr},e_{st\neq rr}} = \frac{\Delta[v_j\theta_{rr}(E_{ll} - E_{rr}) + v_j\eta_{ll(rr)}]}{\Delta\dfrac{c_{E_{rr},e_{lm\neq rr}}}{T}}$$

$$= -\frac{\Delta\kappa_{rl}}{\Delta\theta_{rr}}. \tag{4.2.17}$$

for the one-sided transverse compression. If the substance is subjected to shear strain, the corresponding equation can be obtained from Eq. (4.2.6):

$$\left(\frac{\partial T}{\partial e_{lm}}\right)_{\substack{E_{rr},e_{st\neq rr}\\ st\neq lm}} = \frac{\Delta[v_j\theta_{rr}(E_{lm} - \delta_{lm}E_{rr}) + v_j\eta_{lm(rr)}]}{\Delta\dfrac{c_{E_{rr},e_{lm\neq rr}}}{T}}. \tag{4.2.18}$$

We now turn to the case of simple tension. Equation (4.2.12) that originates from the continuity of volume logarithm yields

$$\left(\frac{\partial T}{\partial E_{rr}}\right)_{E_{lm\neq rr}} = -\frac{\Delta\chi_{rr}}{\Delta\theta_{rr}} - \frac{1}{\Delta\theta_{rr}}\sum_{l\neq r}\Delta\kappa_{rl}\frac{de_{ll}}{dE_{rr}}. \tag{4.2.19}$$

Equation (4.2.15) produces an even simpler result. Writing Eq. (4.2.15) for the condition of the continuity of the strain tensor component e_{rr} at fixing all stress tensor components but E_{rr}, we have

$$\left(\frac{\partial T}{\partial E_{rr}}\right)_{E_{lm\neq rr}} = -\frac{\Delta(1/\lambda_{rrrr})}{\Delta\theta_{rr}}, \tag{4.2.20}$$

where λ_{rrrr} is Young's modulus in the *r* direction. Equation (4.2.20) gives evidence showing, first, that the phase-transition temperature is linearly dependent on the value of one-sided stress and, second, that for an anisotropic body the slope of the line depicting this dependence can be different for different directions. In the case of a second-order phase transition, the problem of mutual orientation of the physical phase interface and the direction of the stress applied is cancelled. Therefore, the phase-transition temperature can be assumed to be a function of only the principal stresses E_1, E_2, and E_3:

$$dT = \frac{\partial T}{\partial E_1}dE_1 + \frac{\partial T}{\partial E_2}dE_2 + \frac{\partial T}{\partial E_3}dE_3. \tag{4.2.21}$$

Passing in Eq. (4.2.21) to the isotropic case $dE_1 = dE_2 = dE_3 \equiv dE$, we obtain the relationship

$$\frac{\partial T}{\partial E} = \frac{\partial T}{\partial E_1} + \frac{\partial T}{\partial E_2} + \frac{\partial T}{\partial E_3}, \qquad (4.2.22)$$

that was confirmed experimentally by Coe and Paterson [9], who studied the effect of one-sided stress on the temperature of the transformation of α-quartz to β-quartz (all the four derivatives in Eq. (4.2.22) were determined independently). They obtained a purely linear dependence of the transition temperature on stress. One can say more. Since, according to their data, α-quartz possesses a higher linear compressibility and a higher linear thermal dilatation coefficient as compared with β-quartz, Eq. (4.2.20) also correctly predicts the sign of the slope of the linear dependence (in that experiment, the phase-transition temperature increased under one-sided compression). The above facts incline us to the known interpretation of the α–β transformation as a secon-dorder phase transition, although Coe and Paterson eventually adopted the variant of a coherent first-order phase transition.

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