THERMODYNAMIC INSTABILITY OF SOLID BODIES

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Summary

The maximum free energy of solid bodies is always higher than the minimum F_i characteristic of the equilibrium state of ideal bodies. This is caused by the maximum free energy surplus F belonging partly to their surface and partly to the crystal errors indispensably present in their volume. The characteristics for a given system are determined by the thermodynamic state. It has been proven that the thermodynamic state of solid bodies of identical maximum free energy surplus is not by all means identical. The metastability F is the sum of different crystal errors of the maximum free energy surplus F_i.

The parameters indicating the characteristics of solid bodies show — even under identical chemical composition — considerable scattering. This causes a special problem in the practice of electrical engineers where the characteristics (electrical resistance, the number of charge carriers etc.) determine the operation of the appliances. The cause of the scattering of the characteristics is that the thermodynamic state of the solid bodies is unstable. While the characteristics of liquids and gases are unambiguously determined by temperature, pressure and chemical composition, the characteristics of solid bodies are greatly scattering. The cause of this is that the mobility of atoms in solid bodies is very low and the maximum free energy of the body is unable to reach and maintain the minimum value determined by a given temperature and pressure. Thus the maximum free energy of every solid body is higher by some value F than the minimum value belonging to the ideal thermodynamic equilibrium. The maximum free energy surplus F is composed of the surpluses F_i belonging to the individual types of crystal errors (dislocation, foreign atoms, crystallite limits etc.). As a result of this, the given value of maximum free energy surplus can be brought about by a number of variations in crystal error and a determined system of characteristics belongs to every variation. That is why different thermodynamic states belong to a given maximum free energy F.

The research of solid bodies always offers new materials, more suitable for certain tasks than known so far. Among these there are materials of chemical compositions identical with the previous ones. A fundamental characteristic of the solid bodies is that their characteristics can be modified easily, in spite of the unchanged chemical composition. This feature originates in the fact that their thermodynamic state — in spite of a given pressure and temperature — differs from the equilibrium, i.e., the minimum free enthalpy because of the crystal errors always present in higher than equilibrium quantity.

As an unequivocally stated aggregation of macro-characteristics belongs to the given state of every thermodynamic system and the thermodynamic state be changed, the characteristics can be changed with it. In the following we prove that the thermodynamic state of the solid bodies not only can be changed but that these states are unstable even if their temperatures T, the concentrations of their components c_k, their pressure P and a characteristic function of their thermodynamic state, the free enthalpy G are identical.

Let the free enthalpy G_i of an ideal solid body be:

$$G_i = U_i - TS_i + PV_i \tag{1}$$

where U is the inside energy, S the entropy and V the specific volume. Subscript i refers to the ideal state to which belongs a minimum value of enthalpy.

$$G_r = U_r - TS_r + PV_r \tag{2}$$

Owing to the already mentioned crystal errors, the free enthalpy of the real bodies is always higher by a value

$$\varDelta G = G_r - G_i \tag{3}$$

The free enthalpy surplus is the measure of metastability.

Let us suppose that a specimen B, corresponding in dimension and composition to the specimen prepared from a material of a given chemical composition A and of free enthalpy G^A, can be prepared with a free enthalpy G^B of identical value. Accordingly, if their temperature is identical, then

$$\begin{aligned} G^A &= U_i + \varDelta U^A - T(S_i + \varDelta S^A) + P(V_i + \varDelta V^A) = \\ &= U_i + \varDelta U^B - T(S_i + \varDelta S^B) + P(V_i + \varDelta V^B) = G^B \end{aligned} \tag{4}$$

and

$$\varDelta G^A = \varDelta U^A - T\varDelta S^A + P\varDelta V^A = \varDelta U^B - T\varDelta S^B + P\varDelta V^B = G^B \tag{5}$$

These equalities can be true if

$$\begin{gathered} \varDelta U^A \neq \varDelta U^B \\ \varDelta S^A \neq \varDelta S^B \\ \varDelta V^A \neq \varDelta V^B \end{gathered} \tag{6}$$

i.e., if crystal errors of n^A and m^B kinds occur in the two specimens in concentrations $\rho_1, \rho_2, \ldots, \rho_k, \ldots, \rho_n$, then the following can be written

$$\begin{aligned} \varDelta U^A &= \varDelta U_1^A + \varDelta U_2^A + \ldots + \varDelta U_K^A + \ldots + \varDelta U_n^A \\ \varDelta S^A &= \varDelta S_1^A + \varDelta S_2^A + \ldots + \varDelta S_K^A + \ldots + \varDelta S_n^A \\ \varDelta V^A &= \varDelta V_1^A + \varDelta V_2^A + \ldots + \varDelta V_K^A + \ldots + \varDelta V_n^A \end{aligned} \tag{7a}$$

and

$$\begin{aligned}\varDelta U^B &= \varDelta U_1^B + \varDelta U_2^B + \ldots + \varDelta U_K^B + \ldots + \varDelta U_m^B \\ \varDelta S^B &= \varDelta S_1^B + \varDelta S_2^B + \ldots + \varDelta S_K^B + \ldots + \varDelta S_m^B \\ \varDelta V^B &= \varDelta V_1^B + \varDelta V_2^B + \ldots + \varDelta V_K^B + \ldots + \varDelta V_m^B\end{aligned} \tag{7b}$$

Where $\varDelta U_i$ is the internal energy surplus originating from the i-th crystal error, $\varDelta S_i$ and $\varDelta V_i$ are the pertinent entropies and specific volumes, respectively. Thus

$$\begin{aligned}\varDelta G^A &= \sum_{K=1}^{n} \varDelta U_K^A - T \sum_{k=1}^{n} \varDelta S_K^A + P \sum_{k=1}^{n} \varDelta V_K^A = \\ &= \varDelta G^B = \sum_{k=1}^{n} \varDelta U_K^B - T \sum_{k=1}^{n} \varDelta S_K^B + P \sum_{k=1}^{n} \varDelta V_K^B\end{aligned} \tag{8}$$

In accordance with the facts mentioned above $3n$ data are necessary to determine the free enthalpy surplus of the given solid body at a given temperature and pressure. These $3n$ data are not independent from each other, only the equality has to be fulfilled. Taking into account that the following functions can be written for concentration ρk of k-th type:

$$\varDelta U_K = f_K(\rho_K); \;\; \varDelta S_K = g_K(\rho_K)$$

$$\varDelta U_K = f_K(\rho_K) \;\; \varDelta S_K = g_K(\rho_K)$$

and

$$\varDelta V_K = h_K(\rho_K) \tag{9}$$

i.e., every increment originating in the k-th type of crystal error changing free enthalpy, is only the function of concentration. *(Correlations among crystal errors were neglected in the calculation. This does not modify the correctness of the consideration.)* This decreases variable $3n$ to n. Thus, e.g., a solid body that contains m_v surplus empty lattice stations above the equilibrium value n_v

$$\varDelta U_v = m_v Q = f_v(m_v) \tag{10}$$

causes an inside energy surplus if Q is the energy of formation of one empty lattice station. The entropy surplus is

$$S_v = K \ln \frac{(N - n_v)!\, n_v!}{(N - m_v - n_v)!\, (n_v + m_v)!} = g_k(m_v) \tag{11}$$

Here N is the total number of lattice stations. The number of equilibrium empty lattice stations

$$n_v = N e^{-\frac{Q}{KT}} \tag{12}$$

K is the Boltzmann constant. At last the specific volume increment is

$$\Delta V_v = m\frac{V_0}{z} = h_v(m_v) \tag{13}$$

Here V_0 is the volume of the elementary cell belonging to the crystal structure of the material, z is the number of atoms in it (e.g. in the interval cube 2, on the surface of centre 4 etc.).

According to the above, equation 8 can be written as

$$\Delta G^A = \sum_{k=1}^{n} f_K(\rho_k^A) - T\sum_{k=1}^{n} g_k(\rho_k^A) + P\sum_{k=1}^{n} h_k(\rho_k^A)$$

or

$$\Delta G^B = \sum_{k=1}^{n} f_k(\rho_k^B) - T\sum_{k=1}^{n} g_k(\rho_k^B) + P\sum_{k=1}^{n} h_k(\rho_k^B) \tag{14}$$

From the above two equations it follows that identical chemical composition and free enthalpy are only necessary but not sufficient preconditions of the identical thermodynamic state. The two latter equalities can be fulfilled if

$$\rho_k^A \neq \rho_k^B \tag{15}$$

In this case a great number of specimens of a chemical composition corresponding to substance A and of identical free enthalpy can be prepared with different characteristics and consequently, different thermodynamic states. I.e., the free enthalpy surplus ΔG^B can be ensured also by the free choice of $n-1$ kinds of crystal error types out of the n types, but the sum of their free enthalpy surplus, $[\Delta G^B]_{n-1}$ should be smaller than ΔG^A. The concentration of the last one, the n-th type has to be chosen, so that

$$\Delta G_n^B = \Delta G^A - [\Delta G^B]_{n-1} = \Delta G^A - \sum_{i=1}^{n-1} \Delta G^B \tag{16}$$

$[\Delta G^B]_{n-1}$ is the free enthalpy increment caused by freely chosen crystal errors. Thus one of the fulfilments of (14) was ensured, however, specimens of different characteristics, of different thermodynamic states were obtained.

The above said shall be illustrated by an example. Let one of our metal specimens selected with all its characteristics (dimension, shape, composition etc.) be identical with the other one.

Let one of them be an acicular crystal (Whisker) without dislocations, the other one a wire of identical chemical composition, of the same width. Owing to crystallite limits and dislocations, the latter one shall have in the soft state a free enthalpy, higher by some ΔG_j. The free enthalpy of the acicular crystal ΔG_h can be increased if the temperature is increased so that the concentration of the empty lattice stations should be as much that on freezing after quick cooling, the free enthalpy surplus ΔG of the two pieces should be equal. This can be ensured without special difficulty. Thus two specimens of identical free enthalpy have been prepared. However, the characteristics of the two materials greatly differ from each other. The solidity of the acicular crystal approximates the theoretical value, that of the wire is lower by several order of magnitude.

Identical chemical composition and free enthalpy increment of identical value are not sufficient for the identity of thermodynamical states, the condition

$$\rho_k^A = \rho_k^B \tag{18}$$

has to be fulfilled, too. Identical solid body characteristics can be expected only — at least in principle — if the concentration of every kind of crystal error is identical.

The instability of the thermodynamic solid bodies originates in this, hence, according to present knowledge, two or more specimens that fulfill equation (18) cannot be produced.

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