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Entropy as a Free Parameter in Thermodynamics[1]

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ABSTRACT

The method of the variation of the entropy in thermodynamics is presented. It allows to formulate a simple phenomenological approach for the metastable states, which allows one to calculate the explicit dependence of the Gibbs Free Energy on temperature, to calculate the heat capacity and the thermodynamic barrier, dividing metastable and unstable states, and the thermal expansion coefficient. Thermodynamic stability under conditions of mechanical loading is considered. The influence of the heating (cooling) rate on the measured dynamic heat capacity is investigated. A general description of the metastable phase equilibrium is proposed. Mechanisms of the transition from the diffusional mechanism of the supercritical nucleus growth to the martensitic one as the rate of the heating is raised are discussed. The Ostwald's stage rule is derived.

KEY WORDS: metastable states; stability; thermodynamic properties; high-rate heating and cooling; diffusional and martensitic transformation; Ostwald's stage rule.

1. INTRODUCTION

The method of the entropy variation in thermodynamics was proposed by the author in [1]. Let us consider it in detail here.

Let us consider the Gibbs free energy (GFE) per one atom, divided by Boltzmann's constant, k, as a function of entropy (per atom and divided by k), s, temperature, T, and pressure, P:

$$\varphi = h(P,s) - Ts, \tag{1}$$

where h is the enthalpy per atom and divided by k.

Let us derive this formula. Each equilibrium state of the system at given T and P corresponds to certain values of the enthalpy, $h = h(P,T)$, and the entropy, $s = s(P,T)$. Eliminating T from the last two formulas we obtain: $h = h(P,s)$ and $\varphi = h(P,s) - Ts$. The entropy itself depends on P and T in an equilibrium state.

Let us regard s as a free variational parameter. Then introduced GFE has a remarkable property: in a state of equilibrium it has a minimum on s. To show this let us differentiate the last equation for φ with respect to s: $(\partial\varphi/\partial s)_p = (\partial h/\partial s)_p - T$. In a state of the equilibrium the right-hand part of this equation is zero: $(\partial h/\partial s)_p - T = 0$. So the first condition of a minimum, $(\partial\varphi/\partial s)_p = 0$, is fulfilled. Now let us differentiate the expression, $(\partial h/\partial s)_p = T$, with respect to T, taking into consideration that h is a composite function of T (h depends on s which is a function of T): $(\partial^2 h/\partial s^2)_p(\partial s/\partial T)_p = 1$. Taking into account that when s is a free parameter, $(\partial^2 h/\partial s^2)_p \equiv (\partial^2\varphi/\partial s^2)_p$,and that in an equilibrium $(\partial s/\partial T)_p = c_p/T$ (c_p is the heat capacity per atom at constant pressure in the units of the Boltzmann's constant), we obtain:$(\partial^2\varphi/\partial s^2)_p = T/c_p > 0$ (the second condition of a minimum).

When $h(P,T)$ is expressed as $h(P, s(P,T))$ and then s is regarded as a free variational parameter, so that $h = h(P,s)$, a minimum of the GFE on s corresponds to a state of equilibrium and an equation of equilibrium, $(\partial h/\partial s)_p = T$, determines an explicit dependence of s on T. The described approach allows us to calculate explicit dependencies of the GFE, c_p and other thermodynamic quantities on T and to formulate a

model for metastable states which shows that a thermodynamic barrier, dividing metastable and unstable states is proportional to $(T_i - T)^{3/2}$ (T_i is the temperature of the absolute instability). Thermodynamic instability under mechanical loading is also considered.

2. APPROXIMATION

Dependence of h on s is different for various systems. This problem is discussed in detail in [2]. Here let us restrict ourselves with the case when $h = h(P, s)$ can be expanded in power series in $(s - s_0)$. The first three terms of the series are,

$$h(P,s) = h(P,s_0) + (T_0/2)(s - s_0)^2 - (T_0^2/12T_i)(s - s_0)^3 , \quad (2)$$

where s_0 is the entropy at $T = 0$ ($s_0 = 0$ for the stable systems), T_0 and T_i are some parameters, depending on P.

Such an approach is applicable for metastable systems, including disordered (e.g., amorphous) ones and for systems which include electrons of conductivity or disordered subsystems, e.g., disordered grain boundaries in polycrystals, randomly distributed dislocations or quenched vacancies in a crystal, solid solutions, etc.

3. THERMODYNAMIC STABILITY

Using Eq. (2) one can see that φ as a function of $(s - s_0)$ has a minimum at

$$s_{min} = s_0 + (2T_i/T_0)\{1 - [1 - (T/T_i)]^{1/2}\} \quad (3)$$

and a maximum at

$$s_{max} = s_0 + (2T_i/T_0)\{1 + [1 - (T/T_i)]^{1/2}\} . \quad (4)$$

The thermodynamic barrier (per atom and in k units), dividing metastable and stable areas is described as

$$\Delta\varphi(T) = \varphi(s_{max}) - \varphi(s_{min}) = (8/3)(T_i^{1/2}/T_0)(T_i - T)^{3/2} , \quad (5)$$

and $s_{max} - s_{min} = (4T_i/T_0)[1 - (T/T_i)]^{1/2}$.

From Eq. (5) one can see that the thermodynamic barrier vanishes at $T \to T_i$. So T_i has a meaning of the temperature of the absolute instability. But the system can not exist up to $T = T_i$ as the thermodynamic barrier is too small at $T \geq T_c$; T_c , which has a meaning of a real critical temperature, could be approximated as

$$T_c = 2.67T_i^2/T_0 . \quad (6)$$

The system goes from the metastable state at $T \geq T_c$, and accordingly to the kinetics [3] the higher the heating rate the higher the temperature of the going from the metastable state.

4. THERMODYNAMIC STABILITY UNDER CONDITIONS OF MECHANICAL LOADING

At $T \ll T_i$ the thermodynamic barrier does not depend on T, but it depends on mechanical stresses. Expansion of the barrier in power series in the tensor of stresses, σ_{ik}, yields

$$k\Delta\varphi = k\Delta\varphi(0) - (v/3)\sigma_{ii} - u_{el} , \quad (7)$$

where $\Delta\varphi(0) = gT_c$ is $\Delta\varphi$ at $\sigma_{ik} = 0$, g is a coefficient of the order of unity, exact value of which depends on the rate of change in thermodynamic conditions, e.g., T_t/T (T_t is the rate of change of the temperature), and on the temperature at which the instability occurs; v has a meaning of the activation volume, σ_{ii} is a spur of σ_{ik} and u_{el} is the elastic energy per one atom. When $\Delta\varphi \approx gT$ the system goes from the metastable state. According to the given considerations critical shear stress may be estimated as

$$P_c = [2kgG(T_c - T)/v_a]^{1/2} , \quad (8)$$

where G is the shear modulus and v_a is the volume per one atom.

To estimate P_c using Eq. (8) let us take $g = 1$, $v_a = 2\cdot10^{-23}$ cm^3, $G = 12\cdot10^9$ Pa, $T_c - T = 370$ K. At such values of the parameters Eq. (8) yields $P_c = 2.48\cdot10^9$ Pa.

Instability under compression and elongation is described in [2].

Thermodynamic instability under loading may often result in a fracture because of the extreme brittleness or low strength of a more stable phase. This refers to the majority of the amorphous metallic alloys and other metastable phases, e.g., diamond (the stable phase - graphite is of a very low strength).

5. THERMAL PROPERTIES

Heat capacity at constant pressure (in k units and per one atom)

$$c_p = T(\partial s/\partial T)_p = (T/T_0)[1 - (T/T_i)]^{-1/2} . \quad (9)$$

This formula is derived for the metastable phase, so it is applicable when the phase is still stable, i.e. for $T \leq T_c$ only.

The thermal expansion coefficient was considered in [2]. The results are applicable for $T \leq T_c$ only, like in the previous case.

6. LIMITS OF VALIDITY OF THE THEORY

It is clear that the theory is valid when $4T_i \ll T_0$. Both parameters, T_i and T_0, ought to be taken from the comparison with the experimental results. To determine T_0 one ought to use low T heat capacity data, and to estimate T_i - the data on the temperature of the instability at low heating rates.

As an appropriate example one may take $T_0 = 5 \cdot 10^4$ K and $T_i = 3000$ K. Then we have $T_c = 475$ K, $s_{min} - s_0 \leq 0.12$ and $s_{max} - s_0 \leq 0.24$. In a general case the presented theory is valid when $T \ll T_i$ at any rate.

7. HEAT CAPACITY AT FINITE HEATING RATE

Heat capacity, c, is usually measured in finite heating (cooling) rate experiments. For the sake of simplicity let us consider a model of one relaxation time. The relaxation time, τ, may be considerable at low T due to barriers, dividing different states of the system. These barriers may be got through with the aid of tunneling. The rate of the relaxation of the enthalpy, h, depends on the deviation of h from it's equilibrium value at a given T, $h_e(T)$. Let us consider small deviations, when it is possible to use the linear approximation. In this case the kinetic equation is

$$(dh/dt) + (h - h_e)/\tau = 0 , \quad (10)$$

where c_e is the equilibrium value of c. At low T $c_e = T/T_0$, $h_e = T^2/2T_0$ and Eq. (10) yields:

$$(dh/dT) + h/T_t\tau = T^2/2T_0T_t\tau . \quad (11)$$

Eq. (11) describes the evolution of $h = h(T)$ from the initial value, $h_0 = h(T_{in})$, at the beginning of the experiment. This equation is applicable only for low T. In this case τ usually does not depend on T.

At low heating rates, when $T_t\tau \ll T$, $h = h_e$ and $c = c_e$. At high heating rates $T \ll T_t\tau$, relaxation is slow, $h \ll h_e$ and as follows from Eq. (11), $(dh/dT) = c = h_e/T_t\tau$. As an example let us consider the case when at $t = 0$ $T = 0$. In this case we have:

$$h = (T^2/2T_0) - (T_t\tau/T_0)T + (T_t\tau)^2[1 - \exp(-T/T_t\tau)]/T_0 . \quad (12)$$

Measured dynamic heat capacity is given by the formula:

$$c = (T/T_0) - (T_t\tau/T_0)[1 - \exp(-T/T_t\tau)] . \quad (13)$$

Eq. (13) shows that the dynamic heat capacity, $c \leq c_e$. At low heating rates, $T_t\tau \ll T$ and $c = T/T_0$. At high heating rates $T \ll T_t\tau$ and $c = T^2/2T_0T_t\tau$. Using this expression it is possible to evaluate the relaxation time, τ, and to use it to calculate the static heat capacity, T/T_0, with the aid of measured heat capacity, c, and Eq. (13).

8. METASTABLE HOMOGENEOUS-PHASE EQUILIBRIUM

First-order phase transitions occur at temperatures different from the equilibrium of the phases temperatures, T_e, for the phases with fixed compositions. The transition to the higher-temperature phase requires overheating and that to the lower-temperature one, overcooling. The transition may involve various mechanisms dependent on the temperature variation rate. At low heating (cooling) rates the diffusional mechanism prevails, while the martensitic one does so at high rates. The scope for these is governed by the thermodynamic conditions in the superheated (supercooled) phase and is governed by the height of the barrier, separating the state of an atom in equilibrium with the metastable phase from the other states, as well as by the kinetic conditions: temperature variation rate, diffusion coefficients, etc.

Let us consider a superheated metastable phase. Let us expand the enthalpy in a a power series in the deviation of s from it's equilibrium value, s_e at T_e. The first four terms of the series are:

$$h(P,s) = h(P,s_e) + T_e(s - s_e) + (T_0/2)(s - s_e)^2 - [T_0^2/12(T_i - T_e)](s - s_e)^3 . \quad (14)$$

This expansion is valid for $s - s_e \ll 1$; in other cases it can be considered as a model representation for h describing the system in the metastable state for

$$s = s_{min} = s_e + 2[(T_i - T_e)/T_0]\{1 - [(T_i - T)/(T_i - T_e)]^{1/2}\} \quad (15)$$

and in unstable equilibrium for

$$s = s_{max} = s_e + 2[(T_i - T_e)/T_0]\{1 + [(T_i - T)/(T_i - T_e)]^{1/2}\} . \quad (16)$$

It is noteworthy that $s_{min} - s_e \leq 2(T_i - T_e)/T_0$ and $s_{max} - s_e \leq 4(T_i - T_e)/T_0$. So Eq. (14) is valid for $4(T_i - T_e) \ll T_0$.

The first-order transition occurs by the more stable phase nucleating and the nuclei larger than the critical ones growing by atoms in equilibria with the metastable phase passing to a state of the equilibrium with the atoms in the nuclei. An atom in equilibrium with the metastable phase is in a potential well, whose bottom is defined by $\varphi(s_{min})$ and the crest by $\varphi(s_{max})$, so the barrier height is described by

$$\Delta\varphi(T) = \varphi(s_{max}) - \varphi(s_{min}) = (8/3)(T_i - T_e)^{1/2}(T_i^{3/2}/T_0)[1 - (T/T_i)]^{3/2} . \quad (17)$$

Eq. (17) shows that the height of the barrier tends to zero as T approaches T_i in accordance with the 3/2 law.

Under the isothermal conditions the transformation can occur for $T \geq \Delta\varphi(T)$ because the individual atoms overcome the barrier and attach to the nuclei by diffusion if the kinetic conditions allow it. At high heating (cooling) rates there may be a substantial superheating (supercooling). As the rate increases, $T \to T_i$, and the barrier height decreases. At sufficiently high rates, the height is reduced so much as to become unimportant and the diffusion-limited growth is replaced by the martensitic one.

9. METASTABLE-PHASE THERMAL PARAMETERS

The specific heat at constant pressure,

$$c_p = T(\partial s/\partial T)_p = (T/T_0)[(T_i - T_e)/(T_i - T)]^{1/2} , \quad (18)$$

has a square root singularity at T_i, which should become more prominent as the rate increases and thus the actual transition temperature approaches T_i.

The thermal expansion coefficient is discussed in [4].

10. DISCUSSION

The entropy as a free parameter gives explicit T relationships for the barrier separating the states, the specific heat and the thermal-expansion coefficient; the approach may be useful in other cases, e.g., if there is a set of the intermediate

metastable phases between the two major ones, which correspond to minima in φ with respect to s , in which case slow uniform heating with constant entropy increase causes the sample to enter the corresponding minima in order of increasing entropy (and in the reverse order during cooling), i.e. in a sequence corresponding to the Ostwald's stage rule.

The approach may be useful in other cases also. In [4] the metastable states in AB_3 alloys are considered and the same approach is applied to the second-order transformations.

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