

To the 300th Anniversary of the founding of St. Petersburg University

Thermodynamic Potentials of Solid-State Systems

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Abstract—By now, the thermodynamics of fluid systems is well developed, but many issues related to solids still require discussion. In this work, six characteristic functions of classical thermodynamics are investigated in application to solid-state systems: energy, free energy, Gibbs energy, enthalpy, grand thermodynamic potential, and a new characteristic function recently discovered by the author, called the *J*-potential. The need to introduce such a potential appears in the thermodynamics of solid-state or mixed systems subjected to complex mechanical impacts, and also in colloidal science. Definitions are given for all six functions, fundamental thermodynamic equations are derived, and the conditions under which this function assumes the status of a thermodynamic potential are established.

Keywords: energy, free energy, Gibbs energy, enthalpy, grand thermodynamic potential, *J*-potential

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INTRODUCTION

The idea of thermodynamics as an outdated science which lost its significance is regrettable. Thermodynamics is of lasting importance, because it formulates the most general laws of nature and forms the foundation on which any physicochemical theory is based. The face of thermodynamics changed in the 19th century owing to the works of Gibbs [1, 2], who introduced thermodynamic potentials, although he did not use this term himself (the term “thermodynamic potentials” belongs to Dugem [3] who proposed it in 1886, when all thermodynamic potentials were already available). Gibbs called them functions, and, using modern terminology, we can say that thermodynamic potentials are characteristic functions, by differentiating which all the basic thermodynamic parameters can be obtained. The initial expressions (differential and integral) for thermodynamic potentials have been called fundamental equations since the time of Gibbs. Thermodynamic potentials have an energy dimension and are associated with work under certain conditions. It follows from this that there should be many

of them, or at least several. The more of them there are, the better thermodynamics is developed.

Gibbs introduced five thermodynamic potentials, but the chemical thermodynamics based on them was developed in detail (in hardware terms as well), mainly for fluid systems. Solid-state thermodynamics is much more complicated and involves more mathematics (primarily tensor calculus), and therefore has been developing (since about the middle of the 20th century) rather slowly. A particular difficulty for chemists is caused by the tensor nature of the chemical potential, the main thermodynamic quantity of chemistry. In such a situation, publishing in a chemical journal even a purely hardware thermodynamic work on solid-state topics, such as this article, is a useful thing. In the end, it will be noted that ten years ago, the author discovered one more thermodynamic potential, called the *J*-potential. This has already been written about in the anniversary review [4], but since the present work is devoted specifically to thermodynamic potentials, it is necessary to mention this again.

In nomenclature and symbols, the author mainly adheres to the recommendations of IUPAC and the

International Organization for Standardization (ISO). They are collected on the Internet [5–8], but not all are fulfilled. A typical example is free energy. The symbol A is recommended for it, but the majority of the thermodynamic community (including the author) writes F . It can also be noted that the author belongs to the St. Petersburg Thermodynamic School (in my opinion, the second in the world after the Van der Waals school in Holland) [9], thanks to which he firmly stands on the Gibbs principles of chemical thermodynamics (this is no longer relevant to symbols).

INTERNAL ENERGY— THE MAIN THERMODYNAMIC POTENTIAL

The internal energy of an open system finds replenishment from three sources: heat δQ coming from the outside, work δW done on the system by external bodies, and energy δU_N of the substances themselves coming from the outside to form the system:

$$\delta U = \delta Q + \delta W + \delta U_N. \quad (1)$$

In the framework of equilibrium thermodynamics, the first contribution is written as $\delta Q = T\delta S$, where T is the absolute temperature and S is the entropy. The second contribution is most often used in the form of the simplest mechanical work $-p\delta V$ for the fluid, where p is the pressure inside the system and V is the volume of the system. As for the general case, including solids, mechanical work can be written as

$$\delta W_M = \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA = \iiint_{(V)} (\hat{E} : \delta \hat{e}) dx_1 dx_2 dx_3, \quad (2)$$

where \mathbf{P} is the external force (stress) per unit surface area of the system as a function of the position on the surface (A), \mathbf{u} is the local displacement vector of the surface, and A is the surface area; integration is performed over the entire surface of the system. The second recording form includes local tensors of stress \hat{E} and strain \hat{e} that occur in the body as a result of external mechanical actions. The colon means the biscalar product of tensors:

$$\hat{E} : d\hat{e} \equiv \sum_{s,t} E_{s,t} de_{s,t}, \quad (3)$$

and integration is performed throughout the entire volume of the system. For a homogeneous body in the form of a rectangular parallelepiped with sides parallel to the basic directions x_s ($s = 1, 2, 3$), equation (2) can be written as

$$dW_M \equiv \sum_{s=1}^3 A_s \mathbf{E}_s \cdot d\mathbf{u}_s = \sum_{s=1}^3 \mathbf{E}_s \cdot d\mathbf{V}_s = V \sum_{s=1}^3 \mathbf{E}_s \cdot d\mathbf{e}_s, \quad (4)$$

where A_s is the area of the face normal to the s direction, $\mathbf{V}_s = A_s \mathbf{u}_s$ is the volume displacement vector, and $\mathbf{e}_s = \mathbf{u}_s/L_s$ is the dimensionless strain vector (L_s is the linear size of the body in the s direction). The vector tripods at the sites of the basic directions form a volumetric displacement tensor [4–6]

$$\hat{V} \equiv \sum_{s=1}^3 \mathbf{i}_s \mathbf{V}_s = \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix} \quad (5)$$

and the strain tensor \hat{e} inherent in mechanics.

The third term in equation (1) was revealed by Gibbs only for fluid systems in the form

$$dU_N = \sum_i \mu_i dN_i, \quad (6)$$

where μ_i is the chemical potential of component i , which has become the most important quantity in chemistry, and N_i is the number of component i molecules. After Gibbs introduced the chemical potential and the associated law of mass action, the term “chemical thermodynamics” appeared. The chemical potential looks like a scalar in equation (6), and Gibbs himself did not interpret it differently, but it was he who first revealed the tensor nature of the chemical potential. Gibbs showed that a solid body can be in equilibrium simultaneously with three liquids at different pressures in different directions. This fact proves that the chemical potential is a tensor, if we consider the homogeneity of the chemical potential in direction as a sign of equilibrium.

The entire right side of equation (6) is work and therefore scalar, but if μ_i is a tensor ($\hat{\mu}_i$), then the second multiplier on the right side of equation (6) must be a tensor. For a quantity of substance N_j (we assume that j is

an immobile component of a solid forming a lattice), this is impossible, but for its change – yes. It is known that crystals grow unevenly in different directions. To reflect this, a mass displacement tensor \hat{N}_j is introduced [4–6]. Displacement vectors \mathbf{N}_j are introduced first, and then tensor (7) by analogy with equations (4) and (5)

$$\hat{N}_j \equiv \sum_{s=1}^3 \mathbf{i}_s \mathbf{N}_{j(s)} = \begin{pmatrix} N_{j(11)} & N_{j(12)} & N_{j(13)} \\ N_{j(21)} & N_{j(22)} & N_{j(23)} \\ N_{j(31)} & N_{j(32)} & N_{j(33)} \end{pmatrix} \quad (7)$$

There is also an easier way to introduce a mass displacement tensor by multiplying the volume displacement tensor by the concentration c_j :

$$\hat{N}_j = c_j \hat{V}. \quad (8)$$

Now we can write equation (6) in general form (considering the body homogeneous for simplicity), including the case of a solid body, as

$$dE_N = \sum_i \hat{\mu}_i : d\hat{N}_i. \quad (9)$$

The reason for the tensor nature of the chemical potential is the possible mechanical anisotropy of a solid, and therefore the symmetry of the stress tensor entails the symmetry of the chemical potential tensor. But then the chemical potential tensor can be reduced to a diagonal form by choosing a coordinate system

$$\hat{\mu}_j = \begin{pmatrix} \mu_{j(1)} & 0 & 0 \\ 0 & \mu_{j(2)} & 0 \\ 0 & 0 & \mu_{j(3)} \end{pmatrix}, \quad (10)$$

where $\mu_{j(s)}$ ($s = 1, 2, 3$) are the principle values of the tensor. For a fluid system, all the principle values are the same (μ_j), and equation (10) takes the form

$$\hat{\mu}_j = \mu_j \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \mu_j \hat{1}, \quad (11)$$

where $\hat{1}$ is the unit tensor, which makes it possible to treat the chemical potential tensor as a scalar.

Let us return to equation (1) and, using all the results obtained, write down (for simplicity, we consider the body homogeneous) the most general fundamental equation for energy

$$\delta U = T\delta S + \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA + \sum_j \hat{\mu}_j : \delta \hat{N}_j + \delta W \quad (12)$$

or, taking into account (2)

$$dU = TdS + \hat{E} : d\hat{V} + \sum_j \hat{\mu}_j : d\hat{N}_j + dW, \quad (13)$$

where dW presents all other types of work, except mechanical. The components of the system are traditionally divided into immobile (forming a lattice of a solid body) and mobile, which freely move inside the entire volume of the system and behave like fluids. For simplicity, we assume that there is only one fixed component (let us denote it as j ; this is not too serious a limitation, since any combination of fixed substances can often be considered a single component). The numbers of the mobile components are indicated by the symbol i . There may be as many of them as you like, or there may not be at all, and then we are dealing only with a solid body. If, on the contrary, component j is missing, we are dealing with a fluid system. For the general case when both types of components are present, equation (13) takes the form

$$dU = TdS + \hat{E} : d\hat{V} + \hat{\mu}_j : d\hat{N}_j + \sum_i \mu_i dN_i + dW \quad (14)$$

or

$$dU = TdS + V\hat{E} : d\hat{e} + V\hat{\mu}_j : d\hat{c}_j + \sum_i \mu_i dN_i + dW, \quad (15)$$

where $c_j \equiv N_j/V$ is the concentration of the immobile component, and the tensor $d\hat{c}_j$ is introduced in the same way as the tensor $d\hat{N}_j$. As already noted, both equations relate to homogeneous systems, but the second form of writing the fundamental equation for energy is more

convenient for unhomogeneous systems. In this case, equations (14) and (15) are understood as local relations, and to proceed to the equation for the entire system in the second and third terms of equation (15), it is necessary to take integrals over the entire volume of the system from the expressions $\hat{E} : d\hat{e}$ and $\hat{\mu}_j : d\hat{c}_j$. However for chemists, the form of writing (14) is perceived easier, since it corresponds more to the usual chemical thermodynamics of fluids. From equation (14), we see that in the general case, energy is a thermodynamic potential with constant entropy, volume, mass displacement tensors (which means that the boundaries of the system and the number of non-moving components remain unchanged), and the number of mobile components.

Equation (14) can serve as the basis for the derivation of all thermodynamic relations. First, we bring it to an integral form. Let us take any of the basic directions r and mentally add substance along it with a fixed physical condition and absence of work:

$$dU = TdS + E_{rr}dV_{rr} + \mu_{j(rr)}dN_{j(rr)} + \sum_i \mu_i dN_i \quad (16)$$

(the other components of the tensors \hat{V} and \hat{N}_j are equal to zero). Integrating equation (16) gives

$$U = TS + E_{rr}V + \mu_{j(rr)}N_j + \sum_i \mu_i N_i. \quad (17)$$

The expression for energy should not depend on the direction of integration, and therefore the combination $E_{rr}V_{rr} + \mu_{j(rr)}N_j$ is invariant with respect to direction. For a fluid system, equation (17) takes the form

$$U = TS - pV + \sum_i \mu_i N_i, \quad (18)$$

where $p = -E_{rr}$ is pressure in the system.

OTHER CLASSICAL THERMODYNAMIC POTENTIALS

Let us now recall other standard thermodynamic potentials. The most popular free energy is F (Helmholtz free energy or Helmholtz energy) defined as

$$F \equiv U - TS, \quad (19)$$

which, in conjunction with equation (17), gives for a homogeneous solid-state system

$$F = E_{rr}V + \mu_{j(rr)}N_j + \sum_i \mu_i N_i, \quad (20)$$

and for the fluid system

$$F = -pV + \sum_i \mu_i N_i. \quad (21)$$

The corresponding differential fundamental equations have the form

$$\delta F = -S\delta T + \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA + \hat{\mu}_j : \delta \hat{N}_j + \sum_i \mu_i \delta N_i + \delta W \quad (22)$$

or

$$dF = -SdT + \hat{E} : \hat{e} + \hat{\mu}_j : d\hat{N}_j + \sum_i \mu_i dN_i + dW, \quad (23)$$

and for the fluid system

$$dF = -SdT - pdV + \sum_i \mu_i dN_i + dW, \quad (24)$$

which shows that the main advantage of free energy is the replacement of the variable “entropy” with the variable “temperature” (it is much easier for the experimenter to control temperature than entropy). Equation (22) shows that the free energy is a thermodynamic potential at constant temperature, system boundaries (for fluid systems, this condition is replaced by a less stringent condition of constant volume), and the mass of all components.

The third place is occupied by the Gibbs energy G (Gibbs free energy or Gibbs thermodynamic potential). For fluid systems, it is defined as

$$G \equiv U - TS + pV = \sum_i \mu_i N_i \quad (25)$$

and is no less popular than free energy. It can be seen from the fundamental equation

$$dG = -SdT + Vdp + \sum_i \mu_i dN_i \quad (26)$$

that here the pressure becomes a variable which can be controlled and, in particular, fixed. For a solid, which can be studied in a state of arbitrary stress, it is necessary to have a wide range of stresses as variables. In particular, directed Gibbs energy was proposed for uniaxial stress (in the r direction) [11]

$$G_r = F - E_{rr}V \quad (27)$$

(the directed Gibbs energy itself, of course, remains a scalar; by direction we mean only the direction in which the force is applied). The thermodynamics of uniaxial stress is developed in [11]. In particular, it is shown that the normal component of the tensor of the chemical potential of a stationary component in the direction r is a partial molar (molecular) value from G_r :

$$\mu_{j(rr)} = \left(\frac{\partial G_r}{\partial N_{j(rr)}} \right)_{T, e_{\text{stress}}, E_{rr}, N_{j(\text{stress})}, N_i}, \quad (28)$$

and the directed Gibbs energy itself (like the usual Gibbs energy) is made up of chemical potentials:

$$G_r = \mu_{j(rr)}N_j + \sum_i \mu_i N_i. \quad (29)$$

A more general definition was proposed in [12]

$$G \equiv F - \int_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA. \quad (30)$$

It can be seen from the fundamental equation for a homogeneous system

$$\delta G = -S\delta T - \int_{(A)} (\delta \mathbf{P} \cdot \mathbf{u}) dA + \hat{\mu}_j : \delta N_j + \sum_i \mu_i \delta N_i + \delta W \quad (31)$$

that the Gibbs energy (29) is a thermodynamic potential provided that the temperature, the external stress, and the number of all components are fixed.

Let us move on to enthalpy. It is known as a thermal function with a definition for a fluid system

$$H \equiv U + pV = TS + \sum_i \mu_i N_i. \quad (32)$$

By analogy with (30), the enthalpy of an arbitrarily loaded solid can be defined as [13]

$$H \equiv U - \int_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA \quad (33)$$

with the fundamental equation for a homogeneous system

$$\delta H = T\delta S - \int_{(A)} (\delta \mathbf{P} \cdot \mathbf{u}) dA + \hat{\mu}_j : \delta N_j + \sum_i \mu_i \delta N_i + \delta W. \quad (34)$$

It follows from equation (34) that the thermal function can still be a thermodynamic potential (i.e., give work). To do this, it is necessary to fix the entropy, the mechanical stress acting on the system, and the number of all components.

The fifth of the classical thermodynamic potentials is the grand potential Ω (grand thermodynamic potential or Landau potential). Its name echoes the grand canonical distribution of Gibbs statistical mechanics, but the main thing is its special status. If all four previous thermodynamic functions had the potential status only for closed systems, a grand thermodynamic potential is intended for open systems that freely exchange matter with the environment. In this case, chemical potentials become the control variables.

For a fluid system, the definition of a grand thermodynamic potential has a well-known form

$$\Omega \equiv U - TS - \sum_i \mu_i N_i = -pV. \quad (35)$$

The fundamental equation corresponds to definition (35)

$$d\Omega = -SdT - pdV - \sum_i N_i d\mu_i, \quad (36)$$

from which it can be seen that chemical potentials take on the character of natural variables. In the transition to a solid, the formulation of such equations encounters difficulties related to the tensor properties of the chemical potentials of stationary components. The fact is that the formulas do not contain the chemical potentials themselves, but their components. Which of them to take and what to subtract—the situation is ambiguous. To date,

two solutions have been proposed. The first is based on the fact that in the relation of type (35), the chemical potentials of not all, but only the mobile components are subtracted. Then a hybrid thermodynamic potential is obtained (marked with a tilde at the top)

$$\tilde{\Omega} \equiv U - TS - \sum_i \mu_i N_i = \hat{E} : \hat{V} + \hat{\mu}_j : \hat{N}_j, \quad (37)$$

which acts as a large potential in relation to mobile components and as a free energy in relation to an immobile component (hybridization of thermodynamic potentials was introduced into science quite a long time ago [16]).

Differentiating the identity in (36) and taking into account fundamental equations (12) and (14) for energy, we find the fundamental equations for the hybrid grand thermodynamic potential

$$d\tilde{\Omega} = -SdT + \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA + \hat{\mu}_j : d\hat{N}_j - \sum_i N_i d\mu_i + dW, \quad (38)$$

$$d\tilde{\Omega} = -SdT + \hat{E} : d\hat{V} + \hat{\mu}_j : d\hat{N}_j - \sum_i N_i d\mu_i + dW. \quad (39)$$

From equations (37) and (38) it can be seen that $\tilde{\Omega}$ acquires the properties of the thermodynamic potential in the case of fixed temperature, boundaries of the system, mass displacement tensor of the immobile component (which means the immutability of the amount of the stationary component j), and chemical potentials of the mobile components.

The second approach to determining the grand thermodynamic potential of a solid [17] still uses the chemical potential of an immobile component, but in general, as a scalar chemical potential of an immobile component dissolved in a neighboring fluid. Imagine that a macroscopic solid (phase α) is in contact with its flat surface with the fluid phase β , in which the immobile component j is to some extent soluble and in equilibrium with the solid. For a flat interphase boundary, the equilibrium condition was established by Gibbs and in modern interpretation is written as

$$\mu_{j(m)}^\alpha = \mu_j^\beta, \quad (40)$$

where $\mu_{j(m)}^\alpha$ is the normal component of the tensor of the chemical potential of an immobile component of a solid.

Taking into account (40), the definition of a large potential can be written in two equivalent forms:

$$\Omega \equiv F - \sum_i \mu_i N_i - \mu_j^\beta N_j = F - \sum_i \mu_i N_i - \mu_{j(m)}^\alpha N_j. \quad (41)$$

The solubility and chemical potential of the immobile component in solution are determined by the state of stress of the solid. Therefore, although both definitions (37) are completely equivalent, the value $\mu_{j(m)}^\alpha$ is still primary, and we will use the second form of the definition.

To obtain the fundamental equation of such a grand thermodynamic potential, it is necessary to differentiate equation (41) and substitute equation (22) or (23):

$$d\Omega \equiv -SdT + \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA + \hat{\mu}_j : d\hat{N}_j - \sum_i N_i d\mu_i - N_j d\mu_{j(m)}^\alpha - \mu_{j(m)}^\alpha dN_j + dW, \quad (42)$$

$$d\Omega \equiv -SdT + \hat{E} : d\hat{V} + \hat{\mu}_j : d\hat{N}_j - \sum_i N_i d\mu_i - N_j d\mu_{j(m)}^\alpha - \mu_{j(m)}^\alpha dN_j + dW. \quad (43)$$

Note that the full differential includes a change in the mass of component j in all directions, including the normal direction. Therefore, the term $-\mu_{j(m)}^\alpha dN_{j(m)}$ is contained in the penultimate term of expressions (42) and (43). The same term, but with a plus sign, is present in the third term of the right-hand side of (42) and (43), so that these terms are mutually eliminated. If the solid is in real contact and equilibrium with its solution, so that the normal is the only direction in which the mass of the immobile component can change (as a result of dissolution), then the third and penultimate terms are mutually eliminated entirely. Then fundamental equations (41)–(42) are simplified to the form

$$d\Omega \equiv -SdT + \oint_{(A)} (\mathbf{P} \cdot \delta \mathbf{u}) dA - \sum_i N_i d\mu_i - N_j d\mu_{j(m)}^\alpha + dW, \quad (44)$$

$$d\Omega \equiv -SdT + \hat{E} : d\hat{V} - \sum_i N_i d\mu_i - N_j d\mu_{j(m)}^\alpha + dW. \quad (45)$$

According to these equations, the characteristic function Ω becomes a thermodynamic potential when the temperature, the boundaries of the system, the chemical

potentials of the mobile components, and the normal component of the immobile component are fixed.

DISCOVERY OF THE SIXTH THERMODYNAMIC POTENTIAL

It took place 10 years ago [18] and, thus, the new thermodynamic potential, called the J -potential, is centuries younger than its counterparts. Such a huge break (as already mentioned, all five classical thermodynamic potentials were proposed by Gibbs) can be explained as follows. If we compare the formula for the energy of the fluid system (18) with the subsequent definitions of thermodynamic potentials (21), (24), (31), and (34), it is easy to see that with each creation of a new potential, some component part of the original formula is taken away. When we reach the grand thermodynamic potential $\Omega = -pV$, it seems that the game ends there, and the illusion of a complete construction of the entire park of thermodynamic potentials is created. Indeed, in the expression for a grand thermodynamic potential, the only component of energy remains $-pV$, and if we take away this part, we get zero. This is true, but is it always true? This is true if the system is fluid and homogeneous, i.e. single-phase. If the system, even if fluid, is heterogeneous, i.e. if it is multiphase (with interphase surfaces and lines), then zero will not work, and by taking away $-pV$ (here we will have to clarify for which phase), a new thermodynamic potential can be introduced.

Initially, it was assumed that the J -potential would serve solid-state topics with very complex cases of stress acting on the solid, which corresponds to the definition [19]

$$J \equiv \Omega - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA, \quad (46)$$

where the designations are the same as in formula (2). Taking into account (43), the differential fundamental equation for the J -potential can be written as

$$\delta J = -S\delta T - \oint_{(A)} (\mathbf{u} \cdot \delta \mathbf{P}) dA - \sum_i N_i \delta \mu_i - N_j d\mu_{j(m)}^\alpha + \delta W. \quad (47)$$

It can be seen from equation (47) that the J -potential is a thermodynamic potential under the condition of constant temperature, external stress acting on a solid,

chemical potentials of mobile components, and the normal component of the tensor of the chemical potential of an immobile component.

The hybrid J -potential is defined similarly through the hybrid grand thermodynamic potential:

$$\tilde{J} \equiv \tilde{\Omega} - \oint_{(A)} (\mathbf{P} \cdot \mathbf{u}) dA, \quad (48)$$

and the differential fundamental equation for \tilde{J} is constructed in accordance with equation (38):

$$\delta \tilde{J} = -S\delta T - \oint_{(A)} (\mathbf{u} \cdot \delta \mathbf{P}) dA + \hat{\mu}_j : \delta \hat{N}_j - \sum_i N_i \delta \mu_i + \delta W. \quad (49)$$

It follows from equation (49) that the hybrid J -potential becomes a thermodynamic potential at constant temperature, external stress, mass of the immobile component, and chemical potentials of the mobile components. With a certain reservation about the determination of thermodynamic potentials up to a constant, it can be said that a special case of definition (48) is the formula [20]

$$J \equiv \Omega + p'V, \quad (50)$$

where p' is some pressure, chosen for convenience reasons. This may be a real external pressure (the classic case), pressure in one of the phases of a heterogeneous system, or something else. The J -potential with definition (50) has found wide application in the thermodynamics of capillary systems and the theory of thin films [20], in colloidal science in general. Such basic relations as the Neumann, Gibbs, and Young equations are easily proved using the J -potential. As for the definition, it was used in the calculations of the tensile strength of brittle materials [18, 21]. Unfortunately, all these works belong to the author, and there are no other options in the literature yet. But if we recall how many years have passed since classical thermodynamic potentials became an everyday help for people engaged in thermodynamics, we can express a timid hope that the adaptation period will be shorter for the J -potential.

CONCLUDING REMARKS

We have described six characteristic functions at approximately the same level in order to establish

under what conditions they become thermodynamic potentials. For this purpose, non-mechanical work was used, which is usually neglected (except, of course, in those cases when it itself becomes the subject of consideration). At the same time, we have encountered a situation where some characteristic functions are already called thermodynamic potentials, regardless of external conditions. There are two examples: the thermodynamic Gibbs potential G (the old name for Gibbs energy) and the grand thermodynamic potential Ω . It is necessary to distinguish between “thermodynamic potential” as a proper name, and “thermodynamic potential” as a functional characteristic. We emphasize that, while not being thermodynamic potentials in a certain situation, G and Ω always remain useful thermodynamic functions.

And one more thing to note: from a thermodynamic point of view, all thermodynamic potentials (each in its own conditions) are equivalent. The same problem can be solved using different conditions and thermodynamic potentials and get the right result. The only question is which way is easier and more convenient. Gibbs once wrote: “One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity” [22]. Thermodynamic potentials serve this purpose.

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CONFLICT OF INTEREST

The author declares no conflict of interest.

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