

On the formulation of the material equilibrium condition for a dissolving solid nanoparticle

A. I. Rusanov^{a)} and A. K. Shchekin

Mendeleev Center, St. Petersburg State University, St. Petersburg 199034, Russia

(Received 30 August 2007; accepted 5 November 2007; published online 21 November 2007)

Widely known Gibbs' relationship predicting a difference of chemical potentials in a small solid particle and in a surrounding fluid phase at equilibrium is shown to refer to a real or imaginary bulk phase inside the particle. A similar relationship derived for the real surface monolayer of a nanoparticle exhibits the equality of chemical potentials at equilibrium, which allows for experimental measurement of the surface chemical potential of a dissolving solid nanoparticle.

© 2007 American Institute of Physics. [DOI: 10.1063/1.2818049]

Since the time when the concept of chemical potential was introduced by Gibbs¹ to create chemical thermodynamics, the chemical potential has become a powerful tool for solving various problems of physics and chemistry. This is due to two universal properties of the chemical potential: (a) the uniformity of chemical potential in a state of equilibrium and (b) spontaneous transition of matter from places with a larger chemical potential to places with a smaller chemical potential in the absence of equilibrium. On the other hand, Gibbs came to a contradictive conclusion that the chemical potentials of the matter of a solid particle inside the particle and in its surrounding solution cannot be equal even in a true state of equilibrium. On the face of it, this conclusion looks shocking and disproving the above universal properties of chemical potential, and the situation has remained a source of misunderstandings and misinterpretations for a long time. The goal of this communication is to address the apparent contradiction and to reformulate the condition of equilibrium for a dissolving solid nanoparticle in such a form as to be compatible with the general properties of chemical potential. For the sake of simplicity, we confine ourselves with the case of an isotropic particle, which is of no principal importance.

Considering a solid, we will follow Gibbs' model of an ideally elastic solid. The model implies the presence of at least one immobile component forming a regular (as a result of crystallization) or irregular (as a result of glass transition) solid matrix, i.e., a stable distribution of molecules (or ions) in space. The molecules of an immobile species are incapable of migration (diffusion) and can change their location in space only as a result of strain (returning to their initial positions after ceasing strain). For this reason, the composition with respect to immobile species (if they are several) cannot be changed, and any combination of immobile species can be formally regarded as a single component. In addition, a solid can contain mobile components (Gibbs called them "fluid components") which can move freely over the whole interior of the solid matrix. The behavior of mobile components in no way differs from that of a free fluid, so that their thermodynamics description is the same as for liq-

uid solutions. The presence of mobile components is unnecessary for a solid, but, for the sake of generality, we will take them into account. In view of the above discussion, we will consider a solid particle consisting of a single immobile component and an arbitrary number of mobile components.

Surface tension is known to play a significant role in the formulation of the equilibrium conditions for small liquid or solid bodies, but for solids, the situation is complicated by an ambiguous definition of surface tension. Gibbs¹ was first to distinguish between the mechanical (defined via force) surface tension γ and the thermodynamic (defined via energy) surface tension σ as the work of formation of the unit area of a new surface. $\gamma = \sigma$ for liquids, but γ is generally different from σ for solids. Both for liquid drops and isotropic solid particles, γ participates in the mechanical equilibrium condition that is widely known for a spherical case as

$$p^\alpha - p^\beta = \frac{2\gamma}{R} + \frac{d\gamma}{dR}, \quad (1)$$

where p is pressure (superscripts α and β refer to the inner and outer phases, respectively) and R is the dividing surface radius. Gibbs¹ interpreted the derivative in Eq. (1) as a physical change and Kondo² as an imaginary shift of the dividing surface, both the approaches being adequate. More generally, Eq. (1) can be written in the form³

$$p^\alpha - p^\beta = 2\gamma c + \frac{d\gamma}{dN}, \quad (2)$$

where c is the mean surface curvature and N is the normal to the surface.

On the contrary, the thermodynamic surface tension σ is used when formulating the dissolution equilibrium condition (since the detachment of molecules from a particle means the creation of a new surface). Gibbs' Eq. (661) can be written as

$$\mu_j^\beta = \frac{f^\alpha + p^\beta + 2c\sigma}{c_j^\alpha}, \quad (3)$$

where μ_j^β is the chemical potential of a solid matter in a dissolved state and f^α and c_j^α are the free energy and the matter density in the solid phase, respectively. Gibbs' Eq. (3)

^{a)}Electronic mail: rusanov@ar1047.spb.edu

implies a solid to be an ideally elastic one-component body (with no mobile components) surrounded by a liquid. Cahn⁴ generalized Eq. (3) for arbitrary numbers of immobile (substitutional) and mobile (interstitial) components. In addition, Cahn and Larche⁵ considered the case when a solid particle is embedded in a solid matrix. As for the main restriction, accepted by Gibbs, that the properties of a particle are independent of the particle size, it has been overcome only recently to give³

$$\mu_j^\beta = \mu_j^\alpha + \frac{1}{c_j^\alpha} \left[2c\sigma - (p^\alpha - p^\beta) + \frac{d\sigma}{dN} \right]. \quad (4)$$

It is easy to show that the only difference between Eqs. (3) and (4) is an additional derivative, $d\sigma/dN$, whose presence in Eq. (4) allows extending Gibbs' formula to nanoparticles. With the aid of Eq. (2), Eq. (4) can be written as³

$$\mu_j^\beta = \mu_j^\alpha + \frac{1}{c_j^\alpha} \left[2c(\sigma - \gamma) + \frac{d(\sigma - \gamma)}{dN} \right]. \quad (5)$$

Equation (5) exhibits, indeed, that the equality of chemical potentials of species j in coexisting phases is possible in two cases: (a) when α and β are fluids (then $\sigma = \gamma$) and (b) when α is a solid, but the interface is plane [then $c=0$ and $d(\sigma - \gamma)/dN=0$]. This is exactly what was claimed by Gibbs.

To understand the chemical potential difference in Eq. (5), we have to remember that σ is an excess surface quantity (per unit area) with respect to a hybrid thermodynamic potential^{6,7}

$$\tilde{\Omega} \equiv F - \sum_i \mu_i N_i, \quad (6)$$

where F is free energy and N_i is the number of molecules of sort i in a system. In Eq. (6), subscript i refers only to mobile species so that potential $\tilde{\Omega}$ (that can be termed as the semi-grand thermodynamic potential) possesses the properties of grand thermodynamic potential with respect to mobile components and of free energy with respect to the immobile component j . The fundamental equation for the $\tilde{\Omega}$ potential of an isotropic bulk phase is

$$d\tilde{\Omega} = -SdT - pdV + \mu_j dN_j - \sum_i N_i d\mu_i, \quad (7)$$

where S is entropy, T is temperature, and V is volume, a summation on j being not performed since, as was already mentioned above, every combination of immobile species may be treated as a single component. For an equilibrium phase, the local values of temperature and chemical potentials of mobile species are uniform not only in the bulk but also in the surface region. However, this is not the case with the chemical potential of an immobile species forming the solid lattice. This component is incapable of migration (which is the main mechanism of leveling chemical potential) and, as a consequence, there is always a certain gradient of its chemical potential in the surface layer. Just this gradient is the cause of a difference between γ and σ .^{6,7}

Considering Eq. (7) as a local relationship and proceeding to surface excesses, we have no problems with every term, except $\mu_j dN_j$, since only one of two conjugated prop-

erties varies in the surface layer: S produces excess entropy \bar{S} , p produces the mechanical surface tension γ , and N_i produces the surface excess of the i th species $\bar{N}_i = \Gamma_i A$ (Γ is adsorption and A is surface area), not mentioning that $\tilde{\Omega}$ produces $\bar{\Omega}$. However, the product $\mu_j dN_j$ contains a complication that both μ_j and N_j change in the surface layer. To avoid this complication, we eliminate the term $\mu_j dN_j$ by setting the amount of the immobile component constant and writing the fundamental equation for the surface potential $\bar{\Omega}$, which in this case is written as

$$d\bar{\Omega} = -\bar{S}dT + \gamma dA - \sum_i \bar{N}_i d\mu_i \quad (8)$$

for a flat interface and (with an additional curvature term)

$$d\bar{\Omega} = -\bar{S}dT + \gamma dA - \sum_i \bar{N}_i d\mu_i + A \frac{d\gamma}{dc} dc \quad (9)$$

for a curved interface (with neglecting, after Gibbs, the deviatoric curvature, i.e., assuming a relatively slight deviation from the spherical shape). On the other side, we can use the definition $\sigma \equiv \bar{\Omega}/A$ to write

$$d\bar{\Omega} = \sigma dA + A d\sigma. \quad (10)$$

Equations (8) and (10) are well compatible with Shuttleworth's classical relationship⁸

$$\gamma = \sigma + d\sigma/d \ln A \quad (11)$$

with the specification of necessary conditions as constancy of temperature and the chemical potentials of mobile species.

Considering now a solid particle (with bulk phase α) in contact with bulk phase β , we can derive the material equilibrium condition from the terms of a minimum of $\Omega^\alpha + \Omega^\beta + \bar{\Omega}$ at constant temperature, the whole system volume, the total amount of an immobile species, and the chemical potentials of mobile species. Using Eq. (10), this procedure leads to the condition (4) where mechanical quantities turn to be in combination with material ones, and chemical potential μ_j^α refers to the bulk phase either inside a particle or pure imaginary if the particle is entirely nonuniform. Since a solid dissolves and reacts mainly with its surface and the state of the solid bulk is of less practical significance, we suggest a modified approach to the derivation of the material equilibrium condition for a dissolving nanoparticle. We now consider α not as the bulk phase inside a solid particle but as the solid particle as a whole with volume V^α . It is worthy to note that the particle can be nonuniform in all its parts, especially if it is a nanoparticle. Indeed, bulk phases are uniform and surface layers are nonuniform, but a nanoparticle containing no bulk phase looks as if it consists of a surface layer only, which makes it completely nonuniform. Inferring the subsequent application of the equilibrium principle for $\tilde{\Omega}$ in this case, let us write all expressions at fixed temperature and chemical potentials of mobile species. Then a change in $\tilde{\Omega}^\alpha$ can be written as

$$d\tilde{\Omega}^\alpha = -p_N^\alpha dV^\alpha + \mu_j^{\alpha(\sigma)} dN_j^\alpha, \quad (12)$$

where p_N^α is the real normal pressure at the boundary surface of the solid particle and $\mu_j^{\alpha(\sigma)}$ is the chemical potential of molecules in the surface monolayer (superscript σ) of the particle. Although Eq. (12) refers to a solid particle, it implies that the amount of the immobile component can be varied. However, this variation can be only of two kinds: increasing the solid matrix by crystallization or decreasing by dissolution. In the last case, the solid matrix is destructed, and the immobile component acquires mobility when passing to the solution.

Considering the boundary surface of the particle as a dividing surface, we now take excess only on the side of phase β . Then, again we formally have Eqs. (9) and (10) but with the interpretation that they refer to the fluid part of the surface layer on the side of phase β . In such interpretation, γ and σ coincide, and we can jointly write Eqs. (9) and (10) at constant T and μ_i in the form

$$d\tilde{\Omega} = \gamma dA + Ad\gamma = \sigma dA + Ad\sigma. \quad (13)$$

The ordinary fundamental equation for fluid phase β at constant temperature and the chemical potentials of mobile species is

$$d\tilde{\Omega}^\beta = -p^\beta dV^\beta + \mu_j^\beta dN_j^\beta. \quad (14)$$

The equilibrium principle is formulated as

$$(d\tilde{\Omega}^\alpha + d\tilde{\Omega}^\beta + d\tilde{\Omega})_{T,V,N_j,\mu_i} = 0 \quad (15)$$

with $dV^\beta = -dV^\alpha = -AdN$ and $dN_j^\beta = -dN_j^\alpha$. We first consider the mechanical equilibrium condition by assuming a displacement of a certain part of the boundary surface of area A and curvature c along the normal N in the absence of material exchange between the particle and phase β ($dN_j^\alpha = 0$). Placing then Eqs. (12) and (14) and Eq. (13) in the first form in Eq. (15), we have

$$p_N^\alpha - p^\beta = \gamma \frac{dA}{dV^\alpha} + A \frac{d\gamma}{dV^\alpha}, \quad (16)$$

or, after applying $dA/dV^\alpha = 2c$ and $dV^\alpha = AdN$,

$$p_N^\alpha - p^\beta = 2\gamma c + \frac{d\gamma}{dN}. \quad (17)$$

Equation (17) expresses that the mechanical equilibrium condition looks similar with Eq. (2) but differs from it in two respects: (a) p_N^α is a real pressure at the particle boundary surface and not pressure inside the bulk phase of the particle; (b) γ is not the total surface tension but only its part referring to the fluid zone of the interface.

Proceeding now to the derivation of the material equilibrium condition, we set total Eqs. (12)–(14) in Eq. (15), Eq. (13) being taken in the second form, to obtain

$$p_N^\alpha - p^\beta = (\mu_j^{\alpha(\sigma)} - \mu_j^\beta) \frac{dN_j^\alpha}{dV^\alpha} + \sigma \frac{dA}{dV^\alpha} + A \frac{d\sigma}{dV^\alpha}. \quad (18)$$

Considering the crystallization process when the mass and

volume of a solid matrix increase simultaneously, we may interpret the derivative dN_j^α/dV^α as the local surface concentration of the immobile component. Introducing the notation $c_j^{\alpha(\sigma)} \equiv dN_j^\alpha/dV^\alpha$ and using the above expressions for dA/dV^α and dV^α , Eq. (18) becomes

$$p_N^\alpha - p^\beta = (\mu_j^{\alpha(\sigma)} - \mu_j^\beta) c_j^{\alpha(\sigma)} + 2\sigma c + \frac{d\sigma}{dN}. \quad (19)$$

Equation (19) expresses the condition of material equilibrium and is analogous to Eq. (4) for a dissolving nanoparticle. However, Eq. (19) differs from Eq. (4) in those respects that p_N^α and $\mu_j^{\alpha(\sigma)}$ are real quantities for the surface of a nanoparticle and σ refers to the fluid part of the interface. This property gives σ ability to coincide with the mechanical tension γ for the same part of the interface. Then replacing σ by γ in Eq. (19) and applying the mechanical equilibrium condition expressed in Eq. (17) that eliminates all mechanical terms from Eq. (19), we arrive at the relationship

$$\mu_j^{\alpha(\sigma)} = \mu_j^\beta. \quad (20)$$

Equation (20), the main result of this work, is of fundamental importance. First, it shows that, in spite of the difference of chemical potentials in the bulk phase of a nanoparticle and in the surrounding equilibrium solution according to Gibbs' result and Eq. (5), the equality of chemical potentials does take place if one considers the surface monolayer of the nanoparticle. This confirms the generality of leveling chemical potentials at equilibrium even for nanoparticles. Second, Eq. (20) is of a wide practical significance since it opens a simple way for the direct experimental determination of the chemical potential of a solid matter at the particle surface by measuring the chemical potential of a dissolved matter. As for theory, the next challenge is the elaboration of methods for the estimation of $\mu_j^{\alpha(\sigma)}$ as the most practically important characteristics of a solid typically exhibiting its activity in many respects through its surface. It is worthy to note that the most known Ostwald-Freundlich equation for solubility of small solid particles, as an analog of the Gibbs-Kelvin equation for the vapor pressure of a small drop, was derived by extending the condition of equality of chemical potential in bulk phases to the case of a solid particle. Equation (20) makes the basis for an alternative approach in deriving similar relationships.

As another example of application of Eq. (20), one may consider the problem of thermodynamic description of a droplet condensing out the vapor-gas environment around partially dissolving solid nanoparticle (the so-called "deliquescence" problem) recently roused a considerable interest in view of new experimental technique for studying ultrafine aerosols.⁹ The droplet consists of a solid core (the remainder of the deliquesced particle) and a spherical liquid film of saturated solution of the core matter in condensate. According to Eq. (20), the solute chemical potential in the film is equal to the chemical potential of the core matter at the core surface. On the other hand, the solute chemical potential in the film should be equal to the chemical potential of the

solute in the mother phase of the film. These conditions of solute chemical equilibrium jointly with the conditions of solvent chemical equilibrium and conditions of the film mechanical equilibrium lead to the generalized Ostwald-Freundlich and the Gibbs-Kelvin-Kohler equations for liquid spherical nanodroplets with a soluble solid core. Simultaneous solution of the equations at a specified initial (i.e., without a solution film) size of the core allows one to find a relation between the droplet and core radii and establish the limits for these radii at stable and unstable equilibrium. In addition, one may derive a link between the pressure of condensate vapor saturated above the nanodroplet on a partially dissolved solid core and the droplet radius. Such a

link is observed in direct experiment with soluble solid nanoparticles in the solvent gas environment.^{9,10} The work on the problem with detailed calculations is now in progress.

¹J. W. Gibbs, *The Scientific Papers* (Longmans, New York, 1906).

²S. Kondo, *J. Chem. Phys.* **25**, 662 (1956).

³A. I. Rusanov, *Nanotechnology* **17**, 575 (2006).

⁴J. W. Cahn, *Acta Metall.* **28**, 1333 (1980).

⁵J. W. Cahn and F. Larche, *Acta Metall.* **30**, 51 (1982).

⁶A. I. Rusanov, *J. Colloid Interface Sci.* **63**, 330 (1978).

⁷A. I. Rusanov, *Surf. Sci. Rep.* **23**, 173 (1996).

⁸R. Shuttleworth, *Proc. Phys. Soc., London, Sect. A* **63**, 444 (1950).

⁹K. Hameri, A. Laaksonen, M. Vakeva, and T. Suni, *J. Geophys. Res.* **106**, 20749 (2001).

¹⁰G. Biskos, D. Paulsen, L. M. Russell, P. R. Buseck, S. T. Martin, *Atmos. Chem. Phys.* **6**, 4633 (2006).