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COMMENT

Comment on the Article "A New Understanding of the Relationship between Solubility and Particle Size" by W. Wu and G.H. Nancollas

Aljaž Godec · Miran Gaberšček · Janez Jamnik

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Abstract In their paper, Wu and Nancollas (WN) (Wu W., Nancollas H. 1998. A New Understanding of the Relationship between Solubility and Particle Size. J. Sol. Chem. 27:521–531) discussed the validity of the Ostwald–Freundlich equation when used for description of the relationship between the size of a particle and its solubility. We show that the reasoning and the main conclusions in the paper by WN are incorrect—regardless of the actual shape of the particle. We present derivations for the case where the particle is spherical as well as for the case of a general polyhedral shape. We show that in either case the Ostwald–Freundlich equation is valid, without any restrictions, for all cases discussed by WN.

Keywords Ostwald–Freundlich equation · Surface tension · Particle size · Solubility · Phase rule

Introduction

In their paper, Wu and Nancollas [1] (WN) discuss the validity of the Ostwald–Freundlich equation when used for description of the relationship between the size of a particle and its solubility. They also discuss the feasibility of extracting interfacial energies from particle solubility data. First they derive equations describing the chemical potential of a small liquid bubble and a small single crystal starting from the Gibbs–Duhem equation. From the latter they derive the Ostwald–Freundlich equation, which relates the solubility of the particle to its size and interfacial energy. Then they list several experimental limitations that may occur if one intends to verify this relation experimentally; they also provide a list previous works that had dealt with this subject. In the last section they attempt to give a thermodynamic justification for the limited validity of the Ostwald–Freundlich equation.

From the paper by WN it remains unclear whether the particle considered is spherical or polyhedral. We show that the reasoning, and thus the main conclusions, in the paper by WN are entirely incorrect—regardless of the actual shape of the particle. Because the particle

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A. Godec · M. Gaberšček (✉) · J. Jamnik
National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
e-mail: miran.gaberscek@ki.si

shape dictates the phase rule to be used, we present derivations for two limiting cases: for the case where the particle is spherical (Sects. 1.1 and 2.1) and for case of a general polyhedral shape (Sects. 1.2 and 2.2). We show that in either case the Ostwald–Freundlich equation is valid, without any restrictions, for all cases discussed by WN.

1 Phase Rule for Capillary Systems

1.1 Systems with Curved Interfaces

We first derive the general case of the modified phase rule for capillary systems with curved interfaces (see, for example, [2]).

Consider a system consisting of s types of surface, ϕ bulk phases, c components, ψ surface phases and in which w independent chemical reactions can occur. Chemical reactions are independent if no one of them is a linear combination of the others [2]. The type of a surface may be characterized by the bulk phases which it separates. If two surface phases, β and β', coexist on the same surface without the interposition of any obstacle, then it has to hold that $\gamma^{\beta} = \gamma^{\beta'}$ for mechanical equilibrium to be maintained.

For the example shown in Fig. 1, we have $\phi = 4$, $\psi = 6$, and $s = 5$. Two surface phases, denoted Ω^5 and Ω^6, coexist on the same type of surface.

In any arbitrary non-equilibrium state the following set of variables must be specified to fix completely the intensive state of the system:

$$T; \quad c_1^1, \ldots, c_c^{\varphi}; \quad \Gamma_1^1, \ldots, \Gamma_c^{\psi}; \quad r^1, \ldots, r^{\psi} \tag{1}$$

where T is the temperature, c_i^j is the concentration of component i in the bulk phase j, Γ_i^{β} is the adsorption of component i (in mol per unit area on the surface phase β) and r^{β} is the mean radius of curvature of the surface phase β defined by

$$\frac{1}{r} = \frac{1}{2}\left(\frac{1}{r_1} + \frac{1}{r_2}\right). \tag{2}$$

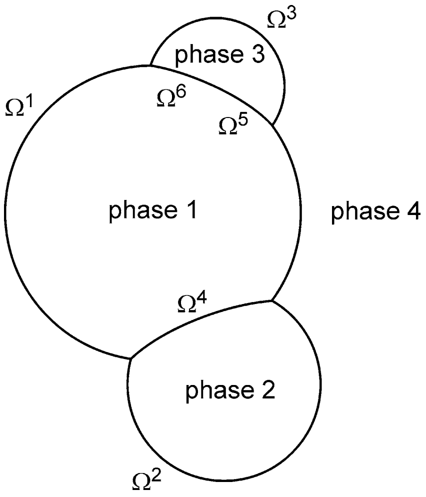

Fig. 1 Scheme of a model capillary system

Here r_1 and r_2 are the principal radii of curvature of the surface at the point considered. For a sphere, the mean radius is equal to its radius. However, when the system is in equilibrium, these variables can no longer be fixed arbitrarily, since there will be relations between them ensuring the following equilibria:

1) Mechanical equilibrium between bulk and surface phases: There will be one equation of type $p'' - p' = 2\gamma/r_m$ (where p is the pressure and γ is the interfacial energy) for each surface phase, making it a total of ψ equations.
2) Mechanical equilibrium between surface phases. There is no need to take any account of the equilibrium between different surface phases, either where two surfaces join along a line of contact, or where more than two meet in a point, for it can be shown that the conditions for these equilibria introduce no new relations between the intensive variables [2]. On the other hand, wherever two phases coexist on the same type of surface, an equation of the type $\gamma^{\beta} = \gamma^{\beta'}$ must be satisfied. There will be $(\psi - s)$ such equations.
3) Equilibrium with respect to the transfer of molecules from one phase to another. For each component i there will be $(\phi + \psi - 1)$ equations of type $\mu_i' = \mu_i^{\gamma} = \mu_i''$ where μ_i' is the chemical potential of component i in bulk phase $'$ and μ_i^{γ} is called the ordinary chemical potential of component i adsorbed at the surface between bulk phases $'$ and $''$. For the whole system there will be $c(\phi + \psi - 1)$ such equations.
4) Chemical equilibrium in the w reactions: The affinity of each reaction, $\mathbf{A}$, must be zero, so that equations of the form [see Appendix 1]

$$\mathbf{A}_{\rho} = -\sum_i \sum_a v_{i,\rho}^{a} \overline{\mu}_i = 0 \quad (\rho = 1, \ldots, w) \tag{3}$$

must be satisfied where $v_{i,\rho}^{a}$ is the stoichiometric coefficient of component i of the ρ-th reaction and the suffix a, denoting the phase, runs from 1 to $\phi + \psi$.

Hence, in all there are $\psi + (\psi - s) + c(\phi + \psi - 1) + w$ equations between $1 + c\phi + c\psi + \psi$ variables (Eq. 1). The variance, f, (or the number of degrees of freedom) is equal to the number of intensive variables which remain independent under equilibrium conditions [2] and is given by

$$f = 1 + (c - w) - (\psi - s). \tag{4}$$

The modified phase rule must be used when the system contains curved interfaces.

1.2 Closed Systems with Flat Interfaces

In a closed system, even in the case when only flat surfaces are present, the classical phase rule cannot be applied [2]. We consider here a closed system with plane surfaces which are in contact with one another. Let $m_{i,0}$ be the total mass of component i. The conditions for the enclosure of the system may be written as

$$\sum_{\beta} \underline{\Gamma_i}^{\beta} A^{\beta} + \sum_{\alpha} c_i^{\alpha} V^{\alpha} - \sum_{\rho} v_{i,\rho} M_i \xi_{\rho} = m_{i,0} \tag{5}$$

where $\underline{\Gamma_i}^{\beta}$ represents the adsorption of i on surface β in mass per unit area (specific adsorption), c_i^{α} denotes the concentration of i in bulk phase α in terms of mass per unit volume, and the summation $\sum_{\rho}$ extends over the r' independent chemical reactions, excluding diffusion across phase boundaries. The system has ϕ bulk phases, separated by s kinds of surface and ψ surface phases. We shall say that the state of the system is completely determined if we know:

1. The physico-chemical state of all the phases defined, for example, by intensive variables

$$T, \quad c_1^1, \ldots, c_c^{\varphi}, \quad \underline{\Gamma}_1^1, \ldots, \underline{\Gamma}_c^{\psi}. \tag{6}$$

2. The sizes of all the phases defined, for example, by the extensive variables

$$T, \quad V^1, \ldots, V^{\varphi}, \quad A^1, \ldots, A^{\psi}. \tag{7}$$

In closed systems at equilibrium, the following relations between the $1 + c\phi + c\psi + \phi + \psi$ variables (Eq. 6) and (Eq. 7) exist:

1. The $(\phi - 1) + (\psi - s) + c(\phi + \psi - 1) + r'$ conditions of equilibrium (as is the previous case of systems with curved interfaces with the exception of statements concerning the curvatures).
2. The conditions of enclosure (Eq. 5).

However, the conditions of enclosure bring in additional r' variables, $\xi_1, \ldots, \xi_{r'}$, so that altogether there are $1 + c\phi + c\psi + \phi + \psi + r'$ variables and $(\phi - 1) + (\psi - s) + c(\phi + \psi - 1) + r' + c$ equations. Therefore, there are $(2 + s)$ independent variables:

$$f = 2 + s. \tag{8}$$

The theorem therefore states: *The equilibrium state of a closed capillary system, with plane surfaces and contiguous surface phases, is in general completely determined by* $2 + s$ *independent variables.*

2 Solid Particle in Equilibrium with Solution of Its Own Molecular Species

In continuation we use the following notation: superscript $('')$ denotes the particle and superscript $(')$ stand for the solution phase. Following the derivations in Sect. 1, the solid particle is either a sphere of radius r or a polyhedral particle, whose shape is described with parameters h^{β}, which are chosen in the following manner. From some point O in the interior of a crystalline lattice we draw the lines normal to all possible orientations of crystal faces. On each line we choose a point P^{β} situated at a distance $h^{\beta} = OP^{\beta}$ from O. At P^{β} we construct the surface normal to OP^{β}; this will be called face β. This face is limited by its intersections with other faces constructed in a similar manner. A surface of this kind, which does not intersect any other of the planes so constructed, cannot be a face of the crystal under consideration. We include only those variables h^{β} which relate to actual faces. Suppose that we have constructed N faces which form a closed polyhedral surface. The heights $h^1, \ldots, h^N$ and the directions of the lines along which they are measured define completely the form of the crystal, its volume V'' and the areas A^{β} of its faces. The only equilibrium shape of a crystal is the Wulff shape which is given by the Wulff relations (see Appendix 2):

$$\frac{\gamma^{(1)}}{h^{(1)}} = \frac{\gamma^{(2)}}{h^{(2)}} = \cdots = \frac{\gamma^{(N)}}{h^{(N)}} = \frac{\lambda}{2} \tag{9}$$

where $\gamma^{(i)}$ is the surface energy of face i and λ is given by Eq. A19 in Appendix 2. The crystalline particle is in its stable crystalline shape (i.e. no polymorphic transformations occur). By this the crystal shape is fixed, regardless of size.

The solid phase consists solely of component 1 while the liquid phase consists of c components ($c \geq 2$) including component 1. The number of independent chemical reactions, w, is zero, since transfer of a component from one bulk phase to the other can be regarded as compounded from an adsorption from one phase and desorption from the interface to the second phase. This reaction can be obtained by a linear combination of adsorption reactions (Eq. A1), *therefore it is not an independent reaction*. Because it is also the only reaction in the system, $w=0$. The number of surface phases is 1, so is the number of types of surfaces. Now we can determine the variance for given type of particle shape:

A) For a spherical particle the variance is $f=c+1$. The number of components is $c\geq 2$, thus $f\geq 3$ (it is >3, if the molecule dissociates in solution to form ions). We can therefore always give arbitrary values to the three variables T, p' and r. Thus we can vary r while maintaining T and p' constant.

B) In the case of polyhedral particles with flat surfaces, the generalization of Duhem's theorem (also known as the extension of Duhem's theorem to capillary systems-as derived in 1.2) ($f=2+s=3$) must be used [2], since we are dealing with a closed capillary system.

In both cases (spherical or polyhedral) we must specify three independent variables to completely determine the equilibrium state of the system. In neither case, however, it is allowed to use the classical Gibbs phase rule as it is not valid for closed capillary systems!

Thus, the system does not have zero variance at constant T and p (regardless of particle shape), as wrongly concluded by WN.

2.1 Ostwald–Freundlich Equation for a Spherical Particle Derived from Mechanical and Physico-chemical Equilibrium Conditions

The conditions for mechanical and physico-chemical equilibrium are

$$p''-p'=\left(\frac{2\gamma_{s/l}}{r}\right),\qquad \mu_i'=\mu_i''=\mu_i^{\gamma}\quad (i=1,\dots,c). \tag{10}$$

Upon an equilibrium displacement (going from one equilibrium state to a neighboring equilibrium state) it must hold that

$$\delta p''-\delta p'=\delta\left(\frac{2\gamma_{s/l}}{r}\right),\qquad \delta\mu_i'=\delta\mu_i''\quad (i=1,\dots,c). \tag{11}$$

For each phase there is a Gibbs–Duhem type equation. If so, it follows immediately:

$$\delta\left(\frac{2\gamma_{s/l}}{r}\right)=\sum_i (c_i''-c_i')\delta\mu_i\quad (i=1,\dots,c). \tag{12}$$

$c_2'',\dots,c_c''$ are all zero, because the particle consists solely of component 1. If $\delta p'=0$ (note that we required before that T and p' be constant), Eq. 12 reduces to

$$\delta\left(\frac{2\gamma_{s/l}}{r}\right)=c_1''\delta\mu_1. \tag{13}$$

The chemical potential of component 1 in solution is given by

$$\mu_1=\mu_1^{\theta}(T,p')+RT\ln\gamma_1'x_1' \tag{14}$$

where μ_1^θ is the standard chemical potential of component 1, x_1' is the mole fraction of 1 in the fluid phase ($'$) and γ_1' is the activity coefficient of 1 in phase $'$. At constant T and p' Eq. 13 can be rewritten as

$$\delta\left(\frac{2\gamma_{s/l}}{r}\right) = c_i'' RT\delta\ln\gamma_i' x_i'. \tag{15}$$

Note that $c_1'' = 1/v'' = 1/v_1^0$, where v_1^0 is the molar volume of the solid phase, thus Eq. 15 becomes

$$\delta\left(\frac{2\gamma_{s/l}}{r}\right) = \frac{RT}{v_1^0}\delta\ln\gamma_1' x_1'. \tag{16}$$

Integrating Eq. 16 from $1/r = 0$ (plane surface-large particle) to $1/r$ and assuming that v_1^0 stays constant we arrive at

$$\frac{2\gamma_{s/l}}{r} = \frac{RT}{v_1^0}\ln\frac{\gamma_1' x_1'}{(\gamma_1')_0(x_1')_0} \tag{17}$$

where $(x_1')_0$ is the mole fraction of the solution which, at constant T and p', is in equilibrium with a large particle (infinite radius of curvature—flat surface) of component 1. Equation 17 is essentially a more precise version of the Ostwald–Freundlich equation (more precise because activity coefficients were introduced).

2.2 Ostwald–Freundlich Equation for a Polyhedral Particle

In the case of a polyhedral particle, the bulk crystalline phase is separated from the solution phase by flat surfaces, whose areas (i.e. ratio of areas) are fixed by Wulff relations. Even in this case the variance, according to the generalization of Duhem's theorem [2], is $2 + s = 3$. We have to consider the system to be at constant T and V, thus choosing T, V, A (or T, V, h since the relation between A and h is fixed by Wulff relations) in order to stay consistent with using the Gibbs definition of the dividing surface and surface tension of the crystal face. Alternatively, the sets T, p, A and T, p, γ can be used (which are obtained by appropriate change of variables). In the case of set T, p, γ all variables are intensive but it is well known that the Duhem theorem fails when we attempt to determine the state of the system completely by specifying $(2 + s)$ intensive variables [2]! Of course, the theorem is valid (even for bulk and surface indifferent systems) if we choose at least one extensive variable [2]! Thus only sets T, V, A and T, p, A are allowed (since A is an extensive variable). If we wish to be absolutely consistent, we will select the set T, V, A. Therefore, one has to be extremely careful, since the equilibrium state of a closed system can generally be determined by $(2 + s)$ properly chosen variables. Note that by selecting the set T, V, A we do not affect the message of the Ostwald–Freundlich equation in any respect.

By substituting Eq. A19 (see Appendix 2) into Eq. 9 or (Eq. A21, Appendix 2) we obtain

$$\frac{2\gamma^{(\alpha)}}{h^{(\alpha)}} = \left(\sum_i \mu_i' c_i'' - \overline{f}''\right) - \left(\sum_i \mu_i' c_i' - \overline{f}'\right). \tag{18}$$

For the fluid (solution) phase we can write

$$F' = \sum_i \mu_i' n_i' - p'V' \quad \text{or} \quad p' = \sum_i \mu_i' c_i' - f'. \tag{19}$$

We consider a crystal consisting of a single component 1, Eq. 18 thus reduces to

$$\frac{2\gamma^{(\alpha)}}{h^{(\alpha)}} = \mu_1' c_1'' - \overline{f}'' - p' \tag{20}$$

so that the chemical potential of the solution phase as a function of the size of the solid particle is given by

$$\mu_1' = v_1^0\left(\frac{2\gamma^{(\alpha)}}{h^{(\alpha)}} + \overline{f}'' + p'\right). \tag{21}$$

All faces must have the same chemical potential, which is ensured by Wulff relations. For a large crystal $h^{(\alpha)} \to \infty$ and $1/h^{(\alpha)} \to 0$ so the corresponding chemical potential of such a crystal is

$$\mu_{1\,0}' = v_1^0(\overline{f}_0'' + p_0') \tag{22}$$

where v_1'' has the same value (because the solid is considered to be incompressible) and f_0'' does not differ appreciably from f''. Hence

$$\mu_1' - \mu_{1\,0}' = \frac{2\gamma^{(\alpha)}}{h^{(\alpha)}} v_1^0 + v_1^0(p' - p_0'). \tag{23}$$

We obtain exactly the same result (namely Eq. 23), if we consider first the variation of Eq. 21 ($\delta\mu_1' = v_1^0\delta(\frac{2\gamma^{(\alpha)}}{h^{(\alpha)}} + \overline{f}'' + p')$) and then integrate from $h^{(\alpha)} \to \infty$ to $h^{(\alpha)}$ (and the potential from a large to a small particle). The second term on the right of Eq. 23 is generally negligible in comparison to the first one (especially for particle sizes where the Ostwald–Freundlich effect becomes important), so that we can write with sufficient accuracy

$$\mu_1' - \mu_{1\,0}' = \frac{2\gamma^{(\alpha)}}{h^{(\alpha)}} v_1^0. \tag{24}$$

By insertion of Eq. 14 for a large and small crystal we obtain the most general form of the Ostwald–Freundlich equation for a polyhedral particle

$$\frac{2\gamma^{(\alpha)}}{h^{(\alpha)}} = \frac{RT}{v_1^0} \ln \frac{\gamma_1' x_1'}{(\gamma_1')_0 (x_1')_0}. \tag{25}$$

3 Discussion

In the following, we comment on the selected most critical statements appearing in the paper by WN.

Statement: "It is generally accepted that neither the amount of excess solid nor the size of the particles present will change the position of the equilibrium" is incorrect. Equation 17 (or the analogous Eq. 25) is derived for one particle only. It cannot be used for many particle problems. In the case of a single particle one cannot alter the amount of excess solid at fixed particle radius. WN, however, discuss multiparticle systems and find it paradoxal that the one-particle model is not valid in such cases.

Statement: "How to reconcile these statements? The problem has a solution that can be drawn from the papers by Ibl and Dodge (61) and by Good". This statement is incorrect because it references papers that have nothing to do with the solid–liquid system. Rather than that, references (61) and (62) consider a liquid–vapor system for which the variance is in fact 2. But in the case of the present interest (solid–solution system) the variance is 3, either for a spherical or a polyhedral particle, as shown above. So, WN are comparing two inequivalent (and thus uncomparable) systems.

The same confusion results in an incorrect interpretation of Eq. 15 shown in the paper by WN. This equation is not pathological as claimed. It is not true that under constant T and p the system has a zero variance. For the spherical particle, this would only be true if the system had exactly one component. For the polyhedral case this is never valid (here the variance is always 3). But WN consider solutions which by definition have at least two components. So, the correct statement would be that under constant T and p the system has at least one free parameter—the particle radius (or h for a polyhedral particle). So, Eq. 15 in the paper by WN is not in any way pathological and can be derived normally as shown in Sects. 1 and 2 above.

Statement around Eq. 16 "…is not valid when $d\mu_i$ is not identically zero" is incorrect from the same reason as above. For the spherical particle already in the case of two components the variance is 3. For the polyhedral case the variance is fixed at 3.

Statement: "If we assume that the constraints for the constant temperature-constant pressure two-phase system are valid, the number of components must be greater than two" is incorrect. Same reason as above.

Statement: "For solid–liquid systems the Ostwald–Freuendlich has not been justified." This statement has no grounds whatsoever. WN themselves derive such an equation. We also show the same here. Reference [2] given below dedicates a large portion to show the deepest thermodynamic justification for a capillary solid-liquid system, regardless of shape.

Equation 19 in the paper by WN is irrelevant in the frame of their discussion. This equation considers bulk systems. WN and this Comment consider a closed system (which in the case of spherical particle has a curved interface). The modified phase rule (for example, Eq. 4 above) or the generalized Duhem theorem (Eq. 8) has to be applied whenever in a system phases are separated by curved surfaces (in this case the modified phase rule is applicable), or we are dealing with a closed system with flat interfaces (in this case the generalized Duhem theorem is applicable) [2]. Because WN use the wrong equation, the conclusions that follow are also completely wrong. So, there is not a slightest doubt about the validity of the Ostwald–Freundlich equation.

Appendix 1: Fundamental Equations for Closed Systems

In a closed system the number of moles of each component in all phases $n'_1, \dots, n^{\gamma}_c$ at any instant can be expressed in terms of initial compositions $n'^{,0}_1, \dots, n^{\gamma,0}_c$ together with the extents of change in the various chemical reactions and phase transfers which can occur.

If component i is adsorbed at the surface at the expense of the n'_i moles of this component in the bulk phase $'$, this component is said to be adsorbed from the first phase by passage of molecules from this phase to the surface. More generally the component i can be adsorbed at the interface $^{\gamma}$ from both bulk phases $'$ and $''$. The extent of adsorption of i from phase $'$ will be denoted by ξ'_i. It this case we can write the adsorption reactions

$$n^{\gamma}_i - n^{\gamma,0}_i = \xi'_i + \xi''_i, \qquad n'_i - n'^{,0}_i = -\xi'_i, \qquad n''_i - n''^{,0}_i = -\xi''_i. \tag{A1}$$

The affinities of reactions are defined as

$$-\mathbf{A}'_i = \frac{\partial F}{\partial \xi'_i}; \qquad -\mathbf{A}''_i = \frac{\partial F}{\partial \xi''_i}; \qquad -\mathbf{A}_\rho = \frac{\partial F}{\partial \xi_\rho} \tag{A2}$$

where F is the free energy. $\mathbf{A}'_i$ denotes the affinity of adsorption of component i from the first phase, $\mathbf{A}''_i$ denotes the affinity of adsorption of i from the second phase and $\mathbf{A}_\rho$ is the affinity of the ρ-th chemical reaction.

Appendix 2: The Equilibrium Form of a Crystal—Wulff's Relations

If one of the heights h^β is varied by $\mathrm{d}h^\beta$, the change of volume is, to the first order of small quantities, equal to

$$\mathrm{d}V'' = A^\beta\,\mathrm{d}h^\beta \quad \text{thus} \quad \frac{\partial V''}{\partial h^\beta} = A^\beta. \tag{A3}$$

If we consider the second-order cross differentials of V'' (combination of Eq. A3 for two different faces) we can write

$$\frac{\partial A^\beta}{\partial h^\alpha} = \frac{\partial A^\alpha}{\partial h^\beta}. \tag{A4}$$

Furthermore if we multiply all the $h^1, \dots, h^N$ by the same number, the areas $A^1, \dots, A^N$ will be multiplied by the square of the number. Each area A^β is thus a homogeneous function of second order in $h^1, \dots, h^N$. According to Euler's theorem concerning homogeneous functions we have

$$A^\beta = \frac{1}{2}\sum_\alpha h_\alpha \frac{\partial A^\beta}{\partial h^\alpha} = \frac{1}{2}\sum_\alpha h_\alpha \frac{\partial A^\alpha}{\partial h^\beta} \tag{A5}$$

where the second equality follows from (Eq. A4). If a straight line is drawn form each corner of the crystal to O, the crystal will be divided into pyramids. Each pyramid will have a crystal face as its base and O as its apex. The volume of the crystal is therefore

$$V'' = \sum_\beta \frac{1}{3} h^\beta A^\beta \tag{A6}$$

thus

$$\mathrm{d}V'' = \frac{1}{3}\sum_\beta h^\beta\,\mathrm{d}A^\beta + \frac{1}{3}\sum_\beta A^\beta\,\mathrm{d}h^\beta. \tag{A7}$$

However from Eq. A3 we have

$$\mathrm{d}V'' = \sum_\beta A^\beta\,\mathrm{d}h^\beta \tag{A8}$$

and by comparing Eq. A8 and Eq. A7 we can write

$$\sum_\beta A^\beta\,\mathrm{d}h^\beta = \frac{1}{2}\sum_\beta h^\beta\,\mathrm{d}A^\beta \quad \text{and consequently also} \quad \mathrm{d}V'' = \frac{1}{2}\sum_\beta A^\beta\,\mathrm{d}h^\beta. \tag{A9}$$

Consider now a crystal surrounded by a liquid with which it can undergo exchange by solution. Let the total volume of the system (solid + fluid) be V. The only mechanical work that can be done on the system is the work $-p'\,\mathrm{d}V$ done by the piston (Fig. 2-left). The first and the second law of thermodynamics are then written as

$$\mathrm{d}U = \mathrm{d}Q - p'\,\mathrm{d}V \quad \text{and} \quad \mathrm{d}S = \frac{\mathrm{d}Q}{T} + \frac{\mathrm{d}Q'}{T} \quad \text{with } \mathrm{d}Q' \geq 0 \tag{A10}$$

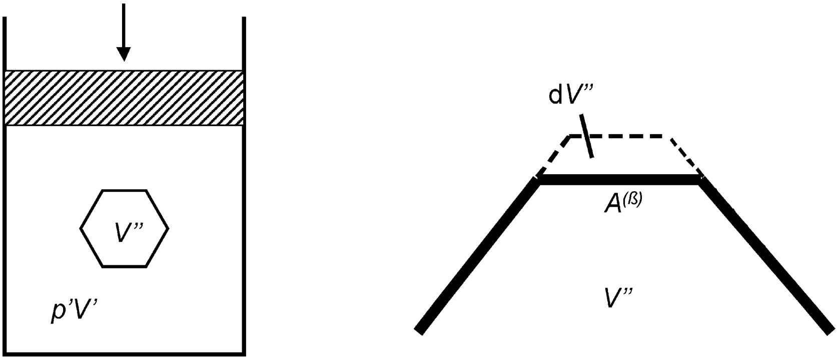

Fig. 2 Equilibrium of a crystal immersed in solution (*left*) and growth of a crystal by deposition on one face only

where $\mathrm{d}Q'$ is the uncompensated heat. The total differential of the free energy is thus

$$\mathrm{d}F = -S\,\mathrm{d}T - p'\,\mathrm{d}V - \mathrm{d}Q'. \tag{A11}$$

All real transformations at constant T and V are such that

$$(\mathrm{d}F)_{T,V} = -\mathrm{d}Q' < 0 \tag{A12}$$

while for equilibrium transformations it holds

$$(\mathrm{d}F)_{T,V} = 0. \tag{A12}$$

Equation A12 is also valid for the initial stage of any transformation starting from a state of true equilibrium (for such a state the affinity of transformation, **A**, is zero). Consider now a crystal in true equilibrium with the fluid which surrounds it. Equation A12 is satisfied for any infinitesimal transformation starting from this equilibrium state. Now let us consider a transformation which consists of the growth of the crystal by deposition on face β-only (Fig. 2-right). We suppose that this happens at constant adsorption as well as constant T and $V = V' + V''$. We define each face of the crystal by the surface which makes the adsorption Γ_1 of the main component of the crystal zero (this definition is equivalent to Gibbs' indirect definition of the surface tension of a crystal face, i.e. the definition of the dividing surface [2]). The total volume V can be thought to be made up of three undeformable components: the volume $V''^{,b}$, which is the volume V'' before the transformation, the volume $\mathrm{d}V'' = A^{(\beta)}\mathrm{d}h^{(\beta)}$ which becomes filled with the solid during the transformation, and the volume $V'^{,f}$, which is the final volume of the fluid phase. Since the solid is virtually incompressible the amount of material (in moles) $\sum_i c_i'' V''$ contained in the volume $V''^{,b}$ remains constant during the transformation. The amount of material in the volume $\mathrm{d}V''$ changes by $\sum_i (c_i'' - c_i')V''$, where c_i' denotes the concentration before and after the transformation (these two concentrations differ infinitesimally and the difference when multiplied by $\mathrm{d}V''$ is an infinitesimal quantity of second order, therefore c_i' is used for both concentrations). The amount of material in the fixed volume, $V'^{,f}$ has varied during the transformation because the solid has grown at the expense of the fluid phase (i.e. the solution phase). Let the change in the number of moles in $V'^{,f}$ be $\mathrm{d}n_i'^{,f}$. For component 1 (for which the adsorption is zero by definition) the conservation of mass requires that

$$(c_i'' - c_i')\mathrm{d}V'' + \mathrm{d}n_1'^{,f} = 0 \quad \text{or} \quad (c_i'' - c_i')A^{(\beta)}\mathrm{d}h^{(\beta)} + \mathrm{d}n_1'^{,f} = 0. \tag{A13}$$

We must also take into account for the amount of matter of other components which has been adsorbed or desorbed following the change of the area of the face β and the adjacent faces:

$$\mathrm{d}A^{(\alpha)} = \frac{\partial A^{(\alpha)}}{\partial h^{(\beta)}} \cdot \mathrm{d}h^{\beta}. \tag{A14}$$

Conservation of mass of component i requires that

$$(c_i'' - c_i')A^{(\beta)}\mathrm{d}h^{(\beta)} + \sum_{\alpha} \Gamma_{i,1}^{\alpha}\,\mathrm{d}A^{(\alpha)} + \mathrm{d}n_i^{\prime,f} = 0; \quad (i = 2, \dots, c). \tag{A15}$$

We now write the condition that the variation of total free energy shall be zero (Eq. A12). First we take as zero the variation of free energy in the fixed volume $V^{\prime\prime,f}$, $\overline{f}^{\prime\prime} V^{\prime\prime,f}$, since this change is negligible even though large changes may have occurred in the pressures within the crystal [2]. We now use essentially the same arguments as those employed above in discussion the conservation of mass and obtain

$$(\overline{f}^{\prime\prime} - \overline{f}^{\prime})A^{(\beta)}\,\mathrm{d}h^{(\beta)} + \sum_{\alpha} \overline{f}_1^{\gamma,\alpha}\,\mathrm{d}A^{(\alpha)} + \mathrm{d}F^{\prime,f} = 0 \tag{A16}$$

where $\overline{f}^{\prime\prime}$ and $\overline{f}^{\prime}$ are the free energy densities of phases $''$ and $'$, $\overline{f}_1^{\gamma,\alpha}$ is the free energy per unit surface area of surface α relative to component 1 (for more details see Reference [2]) and $\mathrm{d}F^{\prime,f}$ is the change in free energy in the volume $V^{\prime,f}$. In this volume at constant T the variation is

$$\mathrm{d}F^{\prime,f} = \sum_{i} \mu_i'\,\mathrm{d}n_i^{\prime,f}. \tag{A17}$$

We now substitute into (Eq. A17) the values for $\mathrm{d}n_i^{\prime,f}$ obtained from (Eq. A13) and (Eq. A15) and use (Eq. A14) to obtain

$$\left[\left(\overline{f}^{\prime\prime} - \sum_{i} \mu_i' c_i''\right) - \left(\overline{f}^{\prime} - \sum_{i} \mu_i' c_i'\right)\right] A^{(\beta)} + \sum_{\alpha} \left[\overline{f}_1^{\gamma,\alpha} - \sum_{i=2}^{c} \Gamma_{i,1}^{\alpha} \mu_i'\right] \frac{\partial A^{(\alpha)}}{\partial h^{(\beta)}} = 0. \tag{A18}$$

The algebra can be simplified by writing

$$\left(\sum_{i} \mu_i' c_i'' - \overline{f}^{\prime\prime}\right) - \left(\sum_{i} \mu_i' c_i' - \overline{f}^{\prime}\right) = \lambda \tag{A19}$$

and by replacing A^{β} by the value given in (Eq. A5). By using Gibbs's definition of the surface tension of a crystal face $\gamma = \overline{f}_1^{\gamma} - \sum_{i=2}^{c} \Gamma_{i,1}\mu_i'$ we arrive at

$$\sum_{\alpha} \left[\gamma^{(\alpha)} - \frac{\lambda}{2} h^{(\alpha)}\right] \frac{\partial A^{(\alpha)}}{\partial h^{(\beta)}} = 0; \quad (\beta = 1, \dots, N). \tag{A20}$$

The same reasoning may be applied to each face ($\beta = 1, \dots, N$) so there are N equations of the form (Eq. A20). They can be regarded as N homogeneous equations in the N unknowns $x_{\alpha} \equiv \gamma^{(\alpha)} - (\lambda/2)h^{(\alpha)}$. One possible set of solutions is $x_1 = x_2 = \cdots = x_N = 0$, so that one possible equilibrium shape of the crystal is

$$\frac{\gamma^{(1)}}{h^{(1)}} = \frac{\gamma^{(2)}}{h^{(2)}} = \cdots = \frac{\gamma^{(\alpha)}}{h^{(\alpha)}} = \cdots = \frac{\gamma^{(N)}}{h^{(N)}} = \frac{\lambda}{2}. \tag{A21}$$

The form in which the distance of each face from O is proportional to the surface tension of that face is called the Wulff shape and the set of relations (Eq. A21) are called Wulff's relations. It can be easily shown (Reference [2], page 296) that relations (Eq. A21) are sufficient and also necessary, so that in every crystal which is in its equilibrium form there exists a point such than the Wulff's relations are satisfied. The Wulff shape is therefore the only equilibrium form.

References

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