



Pharmaceutical Nanotechnology

On the size and shape dependence of the solubility of nano-particles in solutions

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ABSTRACT

The general equation is derived for the equilibrium of a small solid particle and a large solution, being consistent with the thermodynamics of Gibbs. This equation can be solved in a closed form for solubility if an ideal (or an infinitely diluted) solution is considered, if the interfacial energy is independent of the composition of the solution and if all physical parameters (other than the solubility itself) are taken size independent. The solubility of the particles is found to increase with increasing its specific surface area, i.e. if non-spherical particles are applied. This simplified solution further simplifies if the shape of the solid is supposed to be spherical. This latter equation, however, is found to be in contradiction with the Ostwald–Freundlich equation, widely used in chemistry, biology and materials science to describe the size dependence of solubility of a spherical crystal. The reason for its incorrectness is shown to be due to the incorrect application of the Laplace equation. It is found that the solubility increases with decreasing the size of the dissolving phase not due to the increased curvature of the phase (Kelvin and Freundlich), but rather due to the increased specific surface area of the phase (Gibbs, Ostwald). Equations are also derived for the case, when the size effect of the interfacial energy is taken into account, and when the crystal is surrounded by several planes of different interfacial energies. The role of wettability is discussed on the size dependence of solubility.

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1. Introduction

Probably the first paper on the size dependence of solubility of solid particles in liquid solutions is due to Ostwald (1900). His derivation is based on the thermodynamics of Gibbs (1875–1878) and is applicable to the solubility of a spherical solid particle in a large liquid solution:

$$x_{A(\beta)} = x_{A(\beta)}^0 \cdot \exp\left(\frac{3 \cdot V_{A(\alpha)}^0 \cdot \sigma_{\alpha/\beta}^0}{R \cdot T \cdot r_{\alpha}}\right) \quad (1a)$$

where $x_{A(\beta)}$ is the solubility of component A (mole fraction) in the form of a spherical, pure phase α of radius r_{α} (m) in a given solution β at temperature T (K) and at a fixed pressure p (Pa), $x_{A(\beta)}^0$ is the same of an infinitely large phase α , $\sigma_{\alpha/\beta}^0$ is the interfacial energy (J/m²) between the two phases (supposed to be size independent), $V_{A(\alpha)}^0$ is the molar volume (m³/mol) of the pure phase A(α), and $R = 8.3145$ J/(mol K), the universal gas constant. Using the analogy of

the Kelvin equation (under the name Thomson, 1871), the Ostwald equation was quite soon corrected by Freundlich (1909) as:

$$x_{A(\beta)} = x_{A(\beta)}^0 \cdot \exp\left(\frac{2 \cdot V_{A(\alpha)}^0 \cdot \sigma_{\alpha/\beta}^0}{R \cdot T \cdot r_{\alpha}}\right) \quad (1b)$$

Since then, Eq. (1b) has become widely accepted and is called today as the Ostwald–Freundlich equation. According to Google Scholar, more than 400 papers refer to this equation under this name. Its usage accelerated during the recent years, as follows from Fig. 1. Except the year of 1999, the yearly number of papers mentioning the Ostwald–Freundlich equation was below 10 before 2005, while it started to increase in an unexpected way during the last 5 years. Although the equation is used time to time in chemistry (Wu and Nancollas, 1998; McCoy, 2001; Cherginets et al., 2002, 2010; Godec et al., 2009; Bouzid et al., 2011; Deflorian et al., 2011), physics (Letellier et al., 2007; Shchekin and Rusanov, 2008), materials science (Znaidi, 2010; Chiang and Sankaran, 2012), environmental sciences (Mudunkotuwa and Grassian, 2011; Bian et al., 2011) and nano-sciences (Ravichandran, 2010; Picher et al., 2011; Dodd and Saunders, 2011), the boom of its usage is due to its application in pharmaceutical nanotechnology (Müller et al., 2001; Nagy et al., 2012; Liu et al., 2012). Only in the 2010–2011 issues of this journal 9 papers are published citing the Ostwald–Freundlich equation (Cerdeira et al., 2010; Deng et al., 2010; Pardeike and Müller, 2010; Keck, 2010; Gao et al., 2011; Jiang et al., 2011; Kawabata et al., 2011; Pardeike et al., 2011).

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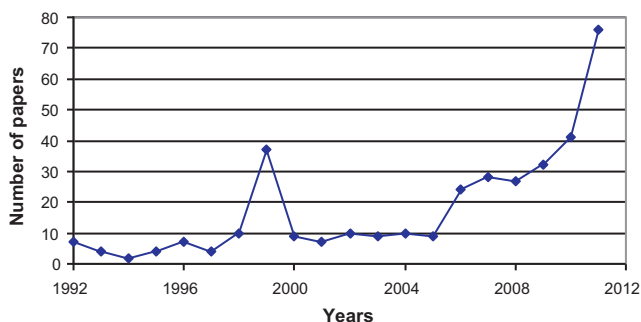


Fig. 1. The number of papers published yearly during the last 20 years, containing the expression “Ostwald–Freundlich” (according to Google Scholar, searched on 26 December, 2011).

One can see that Eqs. (1a) and (1b) differ from each other only by a numerical coefficient. However, behind this small qualitative difference, a quantitative difference between different approaches are hidden, as recently shown by Kaptay (2012a) for the vapor pressure of small droplets. In this paper the equation for the size and shape dependence of the solubility of small solid particles is described, based on the thermodynamics of Gibbs. In this context, the validity of Eqs. (1a) and (1b) will be discussed.

2. Derivation of the general equation

Let us consider component A in the form of a pure, solid phase α of any size and shape in an infinitely large solution β of any nature and number of components (including component A), at fixed temperature and pressure. The task is to derive a general equation to describe the solubility of A in β . Thus, we search for an equation for the equilibrium mole fraction of component A in solution β ($x_{A(\beta)}$), which keeps equilibrium with the solid phase A(α) of the given size and shape at given temperature and pressure.

The size and shape of the pure solid phase α is described by its volume V_α (m^3) and by its total surface area A_α (m^2). In the first approximation we consider that the interfacial energy is identical along the total interfacial area of the phase (for the correction, see below). Thus, the specific surface area of this phase α ($A_{S,\alpha}$, $1/\text{m}$), is defined as:

$$A_{S,\alpha} \equiv \frac{A_\alpha}{V_\alpha} \quad (2)$$

According to Gibbs (1875–1878), the condition of equilibrium between phases α and β is the equality of their partial Gibbs energies. In our particular case, the standard Gibbs energy of pure phase A(α) (denoted as $G_{A(\alpha),S}^\circ$, J/mol, where subscript “S” refers to the given specific surface area $A_{S,\alpha}$) and the partial Gibbs energy of component A in the solution phase β ($G_{A(\beta)}$, J/mol) should equal:

$$G_{A(\alpha),S}^\circ = G_{A(\beta)} \quad (3)$$

According to the theory of solutions (Lewis, 1907; Kaptay, 2004, 2012b; Lukas et al., 2007), the partial Gibbs energy of component A in solution β can be written as:

$$G_{A(\beta)} = G_{A(\beta)}^\circ + R \cdot T \cdot \ln x_{A(\beta)} + \Delta G_{A(\beta)}^E \quad (4)$$

where $G_{A(\beta)}^\circ$ is the standard Gibbs energy of component A in the pure phase β (J/mol) (being the function of only T and p), $\Delta G_{A(\beta)}^E$ is the partial excess Gibbs energy of component A in solution β (J/mol), being a difficult function of $x_{A(\beta)}$, T and p . The (molar) standard Gibbs energy of pure phase A(α) of the given specific

surface area can be written as (for the derivation of this equation, see Appendix A):

$$G_{A(\alpha),S}^\circ = G_{A(\alpha)}^\circ + A_{S,\alpha} \cdot V_{A(\alpha)}^\circ \cdot \sigma_{\alpha/\beta}^\circ \quad (5)$$

where $G_{A(\alpha)}^\circ$ is the standard Gibbs energy of component A in the pure phase α (J/mol) (being the function of only T and p). Substituting Eqs. (4) and (5) into Eq. (3):

$$G_{A(\alpha)}^\circ + A_{S,\alpha} \cdot V_{A(\alpha)}^\circ \cdot \sigma_{\alpha/\beta}^\circ = G_{A(\beta)}^\circ + R \cdot T \cdot \ln x_{A(\beta)} + \Delta G_{A(\beta)}^E \quad (6)$$

The requested solubility ($x_{A(\alpha)}$) is found by solving Eq. (6). This solution has a mathematically closed form only in simplified cases.

3. A simplified solution to Eq. (6)

Now, let us suppose that solution β is an ideal solution, at least, from the point of view of component A.¹ Thus, its excess partial Gibbs energy will be zero, by definition. Also, let us suppose that the interfacial energy $\sigma_{\alpha/\beta}^\circ$ is independent on the composition of phase β , i.e. can be taken as a constant parameter. Then, the solubility (i.e. the equilibrium mole fraction) of component A in phase β can be expressed from Eq. (6) as:

$$x_{A(\beta)} = \exp \left(\frac{G_{A(\alpha)}^\circ - G_{A(\beta)}^\circ + A_{S,\alpha} \cdot V_{A(\alpha)}^\circ \cdot \sigma_{\alpha/\beta}^\circ}{R \cdot T} \right) \quad (7)$$

Let us express from Eq. (7) the solubility of a large phase, with negligible specific surface area (i.e. large size):

$$x_{A(\beta)}^\circ = \exp \left(\frac{G_{A(\alpha)}^\circ - G_{A(\beta)}^\circ}{R \cdot T} \right) \quad (8)$$

Substituting Eq. (8) into Eq. (7), the final equation for the solubility is obtained as:

$$x_{A(\beta)} = x_{A(\beta)}^\circ \cdot \exp \left(\frac{A_{S,\alpha} \cdot V_{A(\alpha)}^\circ \cdot \sigma_{\alpha/\beta}^\circ}{R \cdot T} \right) \quad (9)$$

Let us mention that Eq. (9) is valid only, if $G_{A(\alpha)}^\circ$, $V_{A(\alpha)}^\circ$ and $\sigma_{\alpha/\beta}^\circ$ are not size dependent. As follows from Eq. (9), the larger is the specific surface area of the particle, the larger is its solubility. Thus, the smaller is the particle, or the more its shape deviates from that of a sphere, the higher is its solubility.

For a spherical particle of radius r_α , the specific surface area equals: $A_{S,\alpha} = 3/r_\alpha$. Substituting this value into Eq. (9), the following particular expression is obtained:

$$x_{A(\beta)} = x_{A(\beta)}^\circ \cdot \exp \left(\frac{3 \cdot V_{A(\alpha)}^\circ \cdot \sigma_{\alpha/\beta}^\circ}{R \cdot T \cdot r_\alpha} \right) \quad (10)$$

Eq. (10) is obtained exactly under the same conditions as the Ostwald equation (1a) or as the Freundlich equation (1b). From the comparison of Eqs. (1a), (1b) and (10) one can see that our solution coincides with that of Ostwald. It is not surprising as both equations are derived using the thermodynamics of Gibbs.

Although the difference between Eqs. (1a), (10) and (1b) is only in a numerical coefficient 2 vs. 3, behind this quantitative difference a qualitative difference is hidden. The present author believes that the derivation of Eqs. (6), (9) and (10), presented in this paper, are free of contradictions. The reason why the Freundlich equation (and the Kelvin equation in its roots) contradicts the thermodynamics of Gibbs is explained in Appendix B. From the comparison of the present derivation with that, presented in Appendix B, the following qualitative difference follows:

¹ The same results of Eqs. (9), (10) and (13) are obtained, when solution β is real, but is infinitely diluted in component A (as in this case the solution is also quasi-ideal from the point of view of component A).

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