Electronic Supplement to the paper

A New Paradigm on the Chemical Potentials of Components in Multi-component Nano-Phases within Multi-phase Systems

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Supplement A. Some simple examples of nano-equilibria

First let us suppose that the nano-phase is a liquid ($\alpha = l$), which is surrounded by a large vapor phase ($\beta = v$). The chemical potential of component *i* in this vapor phase ($\mu_{i(v)}$, J/mol) is written as:

$$\mu_{i(v)} = \mu_{i(v)}^{o} + R \cdot T \cdot ln\left(\frac{p_i}{p^o}\right) \tag{A1a}$$

where $\mu_{i(v)}^{o}$ (J/mol) is the standard chemical potential of component *i* in the vapor phase, corresponding to the standard pressure of p^o = 10^5 Pa, *R* = 8.3145 J/molK is the universal gas constant, *T* (K) is the absolute temperature, p_i (Pa) is the partial pressure of component *i* in equilibrium with the liquid nano-droplet. The latter can be obtained by substituting Eq-s (2) of the main text) and the above Eq.(A1a) into Eq.(1) of the main text:

$$p_i = p_i^{\infty} \cdot exp\left[\frac{z \cdot V_{m,i(l)} \cdot \sigma_{l/v}}{R \cdot T}\right] \tag{A1b}$$

$$p_i^{\infty} = p^o \cdot exp\left[\frac{\mu_{i(l)}^{b} - \mu_{i(v)}^{o}}{R \cdot T}\right] \tag{A1c}$$

where p_i^{∞} (Pa) is the equilibrium vapor pressure of component *i* above a large liquid phase with $r = \infty$, *r* (m) is the radius of the liquid droplet. Eq.(A1b) is a generalized Kelvin equation. If $z = 2/r$ is substituted into Eq.(A1b), the classical Kelvin equation is obtained in accordance with the Kelvin paradigm. If $z = A_{sp,\alpha}$ from Eq.(8g) and parameters of Table 1 are substituted into Eq.(A1b), the new equations according to the new paradigm are obtained (see Table 2). Please, note: Eq.(A1b) can be applied also to calculate the equilibrium vapor pressure around a solid nano-phase, if $\mu_{i(l)}^{b}$ is replaced by $\mu_{i(s)}^{b}$ in Eq.(A1c) and if subscripts "*l*" are replaced by subscripts "*s*" in Eq.(A1b).

Now, suppose that the nano-phase is a pure solid phase ($\alpha = s$), which is surrounded by a large liquid phase ($\beta = l$). The chemical potential of a diluted component *i* in this large liquid phase ($\mu_{i(l)}$, J/mol) is written as:

$$\mu_{i(l)} = \mu_{i(l)}^{o} + R \cdot T \cdot lnx_{i(l)} + L_o \tag{A2a}$$

where $x_{i(l)}$ (dimensionless) is the mole fraction of component *i* in the diluted liquid solution, L_o (J/mol) is the interaction energy between components *i* and *j* in the liquid solution. The bulk chemical potential of component *i* in a one-component solid nano-phase is written as the standard chemical potential of a pure solid phase:

$$\mu_{i(s)}^{b} = \mu_{i(s)}^{o} \tag{A2b}$$

Substituting Eq-s (A2a-b, 2) into Eq.(1), the equilibrium solubility of the pure solid component *i* in the liquid *i-j* solution is expressed as:

$$x_{i(l)} = x_{i(l)}^{\infty} \cdot exp\left[\frac{z \cdot V_{m,i(s)} \cdot \sigma_{s/l}}{R \cdot T}\right] \tag{A2c}$$

$$x_{i(l)}^{\infty} = exp\left[\frac{\mu_{i(s)}^{o} - \mu_{i(l)}^{o} - L_o}{R \cdot T}\right] \tag{A2d}$$

where $x_{i(l)}^{\infty}$ (dimensionless) is the equilibrium solubility of a large pure solid phase *i* in the liquid solution. Eq.(A2c) is a generalized Ostwald-Freundlich equation. If $z = 2/r$ is substituted into Eq.(A2c), the classical Freundlich equation is obtained, in accordance with the Kelvin paradigm. If $z = A_{sp,\alpha}$ from Eq.(8g) and parameters of Table 1 are substituted into Eq.(A2c), the new equations according to the new paradigm are obtained, which are also in agreement with the Ostwald equation (see Table 2).

Suppose that the nano-phase is a pure solid phase ($\alpha = s$), which is surrounded by a large pure liquid phase ($\beta = l$). The chemical potential of component *i* in this large liquid phase ($\mu_{i(l)}$, J/mol) is written as:

$$\mu_{i(l)}^{b} = H_{i(l)}^{o} - T \cdot S_{i(l)}^{o} \tag{A3a}$$

where $H_{i(l)}^{o}$ (J/mol) is the standard enthalpy of pure liquid phase *i*, $S_{i(l)}^{o}$ (J/molK) is the standard entropy of pure liquid phase *i*. The bulk chemical potential of component *i* in a solid nano-phase is written as:

$$\mu_{i(s)}^{b} = H_{i(s)}^{o} - T \cdot S_{i(s)}^{o} \tag{A3b}$$

Substituting Eq-s (A3a-b, 2) into Eq.(1), the equilibrium melting point of the solid nano-phase ($T_{m,i}$, K) can be expressed as:

$$T_{m,i} \cong T_{m,i}^{\infty} - \frac{z \cdot V_{m,i(s)} \cdot \sigma_{s/l}}{\Delta_m S_i^o} \tag{A3c}$$

where $T_{m,i}^{\infty}$ is the standard melting point of the large solid phase, $\Delta_m S_i^o \equiv S_{i(l)}^o - S_{i(s)}^o$ (J/molK) is the standard melting entropy of pure phase *i*. When Eq.(A3c) is derived, the chemical potential difference between pure liquid and solid phases is written approximately as: $\mu_{i(l)}^b - \mu_{i(s)}^b \cong \Delta_m S_i^o \cdot \left(T_{m,i}^{\infty} - T\right)$. Eq.(A3c) is a generalized Gibbs-Thomson equation. If $z = 2/r$ is substituted into Eq.(A3c), the classical Gibbs-Thomson equation is obtained, in accordance with the Kelvin paradigm. If $z = A_{sp,\alpha}$ from Eq.(8g) and parameters of Table 1 are substituted into Eq.(A3c), the new equations according to the new paradigm are obtained (see Table 2). Let us mention that the solid/liquid equilibrium can also take place in other morphologies, leading to different equations, among which Eq.(A3c) is only the simplest one (for details see [25, 31]).

Supplement B. On the ratio of surface atoms / molecules in nano-phases

Let us denote the mole fraction of surface atoms /molecules to all atoms / molecules within a nano-phase by x_s (dimensionless), defined as:

$$x_s \equiv \frac{N_s}{N} \tag{B1}$$

where *N* (dimensionless) is the number of all atoms /molecules within the nano-phase, N_s (dimensionless) is the number of atoms / molecules in the surface monolayer of the nano-phase. These quantities can be written as:

$$N = \frac{V_\alpha}{V_{m,\alpha}} \cdot N_{Av} \tag{B2}$$

$$N_s = \frac{A_\alpha}{\omega_\alpha} \cdot N_{Av} \tag{B3}$$

where $N_{Av} = 6.023 \cdot 10^{23}$ 1/mol is the Avogador number, ω_α (m^2/mol) is the molar surface area of phase α. Substituting Eq-s (B2-3) into Eq.(B1) and taking into account the definition written by Eq.(4f), the final equation is obtained as:

$$x_s = A_{sp,\alpha} \cdot \frac{V_{m,\alpha}}{\omega_\alpha} \tag{B4}$$

As follows from Eq.(B4), the ratio of surface atoms / molecules in a nano-phase is proportional to the specific surface area of the nano-phase. Eq.(B4) is the same as Eq.(9) of the main text.