



On the size- and shape-dependence of integral and partial molar Gibbs energies, entropies, enthalpies and inner energies of solid and liquid nano-particles

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ABSTRACT

In this paper the size- and shape dependences of 8 different integral and partial molar thermodynamic quantities are derived for solid and liquid nano-phases, starting from the fundamental equation of Gibbs: i) The integral molar Gibbs energies of nano-phases and the partial molar Gibbs energies of components in those nano-phases, ii) The integral molar enthalpies of nano-phases and the partial molar enthalpies of components in those nano-phases, iii) The integral molar entropies of nano-phases and the partial molar entropies of components in those nano-phases, and iv) The integral molar inner energies of nano-phases and the partial molar inner energies of components in those nano-phases. All these 8 functions are found proportional to the specific surface area of the phase, defined as the ratio of its surface area to its volume. The equations for specific surface areas of phases of different shapes are different, but all of them are inversely proportional to the characteristic size of the phase, such as the diameter of a nano-sphere, the side-length of a nano-cube or the thickness of a thin film. Therefore, the deviations of all properties discussed here from their macroscopic values are inversely proportional to their characteristic sizes. The 8 equations derived in this paper follow strict derivations from the fundamental equation of Gibbs. Only the temperature dependent surface energy of solids and surface tension of liquids will be considered as model equations to simplify the final resulting equations. The theoretical equations are validated for the molar Gibbs energy against the experimental values of liquidus temperatures of pure lead. The theoretical equations for the molar enthalpy are validated i) Against the experimental values of dissolution enthalpy differences between nano- and macro cobalt particles in the same liquid alloy and ii) Against the size dependent melting enthalpy of nano-indium particles. In this way, also the theoretical equations for the molar entropy

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and molar inner energy are validated as they are closely related to the validated equations for the molar Gibbs energy and molar enthalpy.

Introduction

Nano-materials contain at least one nano-phase. Nano-phases have at least one of their dimensions below 100 nm. The size- and shape-dependence of various properties of nano-phases and nano-materials is one of the important topics of nano-materials-sciences [1–36]. The theoretical papers usually develop different models to estimate the size dependence of the properties, and so the results are usually model-dependent. Most frequently, the size dependence of complex thermodynamic quantities, such as melting point is discussed.

In this paper a strict thermodynamic derivation is offered for the size- and shape-dependence of eight basic thermodynamic functions: The integral molar properties of nano-phases and the partial molar properties of components in those nano-phases, with the following four properties considered: i) Gibbs energy, ii) entropy, iii) enthalpy, iv) inner energy. First, the size- and shape-dependence of the integral molar Gibbs energies are derived from the fundamental equation of Gibbs, and then these results are extended to other derived integral molar quantities. Further, partial molar quantities of components in nano-phases are derived from the corresponding integral molar quantities of the nano-phases.

From the fundamental equation of Gibbs to the size dependent molar Gibbs energies

Although this subject has been discussed by the author before [13, 18, 37], for completeness of the present paper let me shortly summarize the ideas and the results. The integral form of the fundamental equation of Gibbs is written in its simplified form as [38–40]:

$$G_{\Phi} = H_{\Phi} - T \cdot S_{\Phi} + A_{\Phi} \cdot \sigma_{\Phi/g} \quad (1a)$$

where G_{Φ} (J) is the Gibbs energy of solid or liquid phase Φ , H_{Φ} (J) is the enthalpy of the phase, S_{Φ} (J/K) is the entropy of the phase, $\sigma_{\Phi/g}$ (J/m²) is the surface energy or surface tension of the solid or liquid phase with its surrounding gaseous phase, T (K) is the absolute temperature in the phase, A_{Φ} (m²) is the surface area of the phase. Now, let us define the amount of

matter in that phase (n_{Φ} , mol), and the specific surface area of that phase ($A_{sp,\Phi}$, 1/m) as:

$$n_{\Phi} \equiv \frac{V_{\Phi}}{V_{m,\Phi}} \quad (1b)$$

$$A_{sp,\Phi} \equiv \frac{A_{\Phi}}{V_{\Phi}} \quad (1c)$$

where $V_{m,\Phi}$ (m³/mol-phase) is the integral molar volume of the phase, defined from Eq. (1b) as:

$$V_{m,\Phi} \equiv \frac{V_{\Phi}}{n_{\Phi}} \quad (1d)$$

Other integral molar quantities are defined similarly as:

$$G_{m,\Phi} \equiv \frac{G_{\Phi}}{n_{\Phi}} \quad (1e)$$

$$H_{m,\Phi} \equiv \frac{H_{\Phi}}{n_{\Phi}} \quad (1f)$$

$$S_{m,\Phi} \equiv \frac{S_{\Phi}}{n_{\Phi}} \quad (1g)$$

where $G_{m,\Phi}$ (J/mol-phase) is the integral molar Gibbs energy of phase Φ , $H_{m,\Phi}$ (J/mol-phase) is the integral molar enthalpy of the phase, $S_{m,\Phi}$ (J/mol-phaseK) is the integral molar entropy of the phase. Now, let us divide Eq. (1a) by n_{Φ} , considering Eqs. (1b–g):

$$G_{m,\Phi} = H_{m,\Phi} - T \cdot S_{m,\Phi} + A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \quad (1h)$$

Equation (1h) can be also written as:

$$G_{m,\Phi} = G_{m,\Phi}^o + A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \quad (1i)$$

where $G_{m,\Phi}^o$ (J/mol-phase) is the integral molar Gibbs energy of a large phase with $A_{sp,\Phi} = 0$. The size- and shape-dependence of the molar integral Gibbs energy of a nano-phase is expressed in Eq. (1i) via the specific surface area, being inversely proportional to the characteristic size of the nano-phase (see Table 1). Thus, the size-effect of the integral molar Gibbs energy of a nano-phase is also inversely proportional to the characteristic size of the nano-phase.

Table 1 Specific surface areas of nano-phases of selected simple shapes

Shape	Characteristic size (m)	Specific surface area (1/m)
Sphere	Diameter: D	$A_{sp,sphere} = 6/D$
Cube	Side length: a	$A_{sp,cube} = 6/a$
Thin film	Thickness: d	$A_{sp,thin-film} = 2/d$

The integral molar quantities of a nano-phase are connected with the partial molar quantities of components in the same nano-phase as:

$$G_{m,\Phi} = \sum_i x_{i(\Phi)} \cdot G_{m,i(\Phi)} \tag{1j}$$

$$V_{m,\Phi} = \sum_i x_{i(\Phi)} \cdot V_{m,i(\Phi)} \tag{1k}$$

$$H_{m,\Phi} = \sum_i x_{i(\Phi)} \cdot H_{m,i(\Phi)} \tag{1l}$$

$$S_{m,\Phi} = \sum_i x_{i(\Phi)} \cdot S_{m,i(\Phi)} \tag{1m}$$

where $x_{i(\Phi)}$ is the mole fraction of component i in phase Φ , $G_{m,i(\Phi)}$ (J/mol-component) is the partial molar Gibbs energy (= the chemical potential) of component i in phase Φ , $V_{m,i(\Phi)}$ (m³/mol-component) is the partial molar volume of component i in phase Φ , $H_{m,i(\Phi)}$ (J/mol-component) is the partial molar enthalpy of component i in phase Φ , $S_{m,i(\Phi)}$ (J/mol-componentK) is the partial molar entropy of component i in phase Φ . Combining Eq. (1h) with Eqs. (1j–m), the following equation follows for the partial molar Gibbs energy of component i in phase Φ :

$$G_{m,i(\Phi)} = H_{m,i(\Phi)} - T \cdot S_{m,i(\Phi)} + A_{sp,\Phi} \cdot V_{m,i(\Phi)} \cdot \sigma_{\Phi/g} \tag{1n}$$

Equation (1n) can be also written in a shorter form as:

$$G_{m,i(\Phi)} = G_{m,i(\Phi)}^o + A_{sp,\Phi} \cdot V_{m,i(\Phi)} \cdot \sigma_{\Phi/g} \tag{1o}$$

where $G_{m,i(\Phi)}^o$ (J/mol-component) is the partial molar Gibbs energy of a component in a large phase with $A_{sp,\Phi} = 0$. Note, that T and $A_{sp,\Phi}$ are the state parameters, so these quantities are equally present in Eqs. (1h, 1n). Note also, that $\sigma_{\Phi/g}$ in Eq. (1n) is not replaced by its partial quantity $\sigma_{i(\Phi/g)}$, because in equilibrium $\sigma_{\Phi/g} = \sigma_{i(\Phi/g)}$, according to the Butler equation [41–45]. As follows from Eqs. (1n–o), the size- and shape-dependences of the partial molar Gibbs energies of the

components in a nano-phase are expressed via the specific surface area of the nano-phase, equally as the size- and shape-dependence of the integral molar Gibbs energy of the nano-phase is expressed by Eqs. (1h–i).

Simplified forms of Eqs. (1i, 1o) for solid and liquid nano-phases

The size dependence of integral molar Gibbs energy of a nano-phase is due to the last term of Eqs. (1h–i). The problem with this expression is that the specific surface area is a hidden function of molar volume. To show this, let us define the amount of matter in the surface monolayer of the nano-phase ($n_{s,\Phi}$, mole) as:

$$n_{s,\Phi} \equiv \frac{A_{\Phi}}{\omega_{\Phi}} \tag{2a}$$

where ω_{Φ} (m²/mol) is the molar surface area of the phase [46]. The ratio of the surface atoms situated in the outer monolayer of a nano-phase to the total number of atoms in the nano-phase (y_{Φ} , dimensionless) is defined as:

$$y_{\Phi} \equiv \frac{n_{s,\Phi}}{n_{\Phi}} \tag{2b}$$

Substituting Eqs. (1b, 2a–b) into Eq. (1c):

$$A_{sp,\Phi} = y_{\Phi} \cdot \frac{\omega_{\Phi}}{V_{m,\Phi}} \tag{2c}$$

Note that according to Eq. (2c), the state parameter $A_{sp,\Phi}$ is replaced by a new state parameter y_{Φ} . Now, let us substitute Eq. (2c) into Eq. (1i):

$$G_{m,\Phi} - G_{m,\Phi}^o = A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} = y_{\Phi} \cdot \omega_{\Phi} \cdot \sigma_{\Phi/g} \tag{2d}$$

Now, let me write the model equation for the last two terms of Eq. (2d) as [46]:

$$\omega_{\Phi} \cdot \sigma_{\Phi/g} \cong -k \cdot H_{m,c,\Phi} - T \cdot \Delta_s S_{m,\Phi} \tag{2e}$$

where k (dimensionless) is a ratio of broken bonds along the surface, $H_{m,c,\Phi}$ (J/mol) is the integral molar cohesive energy of the phase with a negative value, $\Delta_s S_{m,\Phi}$ (J/molK) is the integral molar excess surface entropy of the phase. It is supposed in this paper that

the surface energy and surface tension are isotropic, for simplicity. Now, let us substitute Eq. (2e) into Eq. (2d):

$$G_{m,\Phi} - G_{m,\Phi}^o \cong -\gamma_\Phi \cdot (k \cdot H_{m,c,\Phi} + T \cdot \Delta_s S_{m,\Phi}) \quad (2f)$$

Equation (2f) is more suitable to our purposes compared to Eq. (2d), as it does not contain any hidden function. Note: for the given size and shape of a nano-phase the value of γ_Φ in Eq. (2f) has a constant value, as it is a state parameter. Similarly to Eq. (2f), the equation for the partial molar Gibbs energy follows from Eq. (1o) as:

$$G_{m,i(\Phi)} - G_{m,i(\Phi)}^o \cong -\gamma_\Phi \cdot (k \cdot H_{m,c,i(\Phi)} + T \cdot \Delta_s S_{m,i(\Phi)}) \quad (2g)$$

where $H_{m,c,i(\Phi)}$ (J/mol) is the partial molar cohesive energy of component i in the phase with a negative value, $\Delta_s S_{m,i(\Phi)}$ (J/molK) is the partial molar excess surface entropy of component i in the phase.

The size- and shape-dependences of molar entropies of nano-phases

The integral molar entropy of a phase follows from the integral molar Gibbs energy of the same phase as [39, 40]:

$$S_{m,\Phi} \equiv - \left(\frac{\partial G_{m,\Phi}}{\partial T} \right)_{p,x_i(\Phi)} \quad (3a)$$

The difference between size-dependent and not size-dependent molar entropies are written by extending Eq. (3a) as:

$$S_{m,\Phi} - S_{m,\Phi}^o = - \left[\frac{\partial (G_{m,\Phi} - G_{m,\Phi}^o)}{dT} \right]_{p,x_i(\Phi)} \quad (3b)$$

where $S_{m,\Phi}^o$ (J/molK) is the integral molar entropy of a large phase with $\gamma_\Phi = A_{sp,\Phi} = 0$. Now, let us take the first derivative of Eq. (2f) by temperature:

$$\left[\frac{\partial (G_{m,\Phi} - G_{m,\Phi}^o)}{dT} \right]_{p,x_i(\Phi)} \cong -\gamma_\Phi \cdot (k \cdot C_{p,m,\Phi} + \Delta_s S_{m,\Phi}) \quad (3c)$$

Applying the model parameters of [46], $\Delta_s S_{m,\Phi} \cong k \cdot C_{p,m,\Phi}$ for solid metals and $\Delta_s S_{m,\Phi} \cong 0$ for liquid metals. Then, Eq. (3c) can be re-written in a simplified form as:

$$\left[\frac{\partial (G_{m,\Phi} - G_{m,\Phi}^o)}{dT} \right]_{p,x_i(\Phi)} \cong -\gamma_\Phi \cdot z_\Phi \cdot k \cdot C_{p,m,\Phi} \quad (3d)$$

where $z_s \cong 2$ for solid nano-particles and $z_l \cong 1$ for liquid nano-particles. As $k \cdot |H_{m,c,\Phi}| \gg T \cdot |\Delta_s S_{m,\Phi}|$, in the first approximation $A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \cong -\gamma_\Phi \cdot k \cdot H_{m,c,\Phi}$ follows from Eqs. (2d–e). Then, Eq. (3d) can be re-written as follows, considering also Eq. (2d):

$$\left[\frac{\partial (G_{m,\Phi} - G_{m,\Phi}^o)}{dT} \right]_{p,x_i(\Phi)} \cong \frac{C_{p,m,\Phi}}{H_{m,c,\Phi}} \cdot z_\Phi \cdot A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \quad (3e)$$

Now, let us substitute Eq. (3e) into Eq. (3b):

$$S_{m,\Phi} \cong S_{m,\Phi}^o - \frac{C_{p,m,\Phi}}{H_{m,c,\Phi}} \cdot z_\Phi \cdot A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \quad (3f)$$

The partial molar entropy of a component in a phase can be obtained in a similar way, considering Eq. (2g):

$$S_{m,i(\Phi)} \cong S_{m,i(\Phi)}^o - \frac{C_{p,m,i(\Phi)}}{H_{m,c,i(\Phi)}} \cdot z_\Phi \cdot A_{sp,\Phi} \cdot V_{m,i(\Phi)} \cdot \sigma_{\Phi/g} \quad (3g)$$

where $S_{m,i(\Phi)}^o$ (J/molK) is the partial molar entropy of component i in a large phase with $\gamma_\Phi = A_{sp,\Phi} = 0$. As follows from Eqs. (3f–g), molar entropies also depend on the size- and shape of the nano-phase via its specific surface area. Note, that because the sign of heat capacity is positive and the sign of cohesive energy is negative, the molar entropies shift towards more positive values by increasing the specific surface area and decreasing the characteristic size of the phase. This is because the local entropy of surface atoms is larger compared to that of the bulk atoms and because the ratio of surface atoms increases with decreasing the size of the phase.

The size- and shape-dependences of molar enthalpies of nano-phases

The integral molar enthalpy of a phase follows from the integral molar Gibbs energy of the same phase as [39, 40]:

$$H_{m,\Phi} \equiv G_{m,\Phi} - T \cdot \left(\frac{\partial G_{m,\Phi}}{\partial T} \right)_{p,x_i(\Phi)} \quad (4a)$$

The difference between size-dependent and not size-dependent molar enthalpies are written by extending Eq. (4a) as:

$$H_{m,\Phi} - H_{m,\Phi}^o = G_{m,\Phi} - G_{m,\Phi}^o - T \cdot \left[\frac{\partial(G_{m,\Phi} - G_{m,\Phi}^o)}{\partial T} \right]_{p,x_i(\Phi)} \quad (4b)$$

where $H_{m,\Phi}^o$ (J/molK) is the integral molar enthalpy of a large phase with $y_\Phi = A_{sp,\Phi} = 0$. Now, let us substitute Eqs. (2f, 3e) into Eq. (4b):

$$H_{m,\Phi} \cong H_{m,\Phi}^o + \left(1 - T \cdot z_\Phi \cdot \frac{C_{p,m,\Phi}}{H_{m,c,\Phi}} \right) \cdot A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \quad (4c)$$

The partial molar enthalpy of a component in a phase can be obtained in a similar way, considering Eq. (2g):

$$H_{m,i(\Phi)} \cong H_{m,i(\Phi)}^o + \left(1 - T \cdot z_\Phi \cdot \frac{C_{p,m,i(\Phi)}}{H_{m,c,i(\Phi)}} \right) \cdot A_{sp,\Phi} \cdot V_{m,i(\Phi)} \cdot \sigma_{\Phi/g} \quad (4d)$$

dependence of molar enthalpies is the same as that of the molar Gibbs energies. However, with increasing temperature, the size- and shape-dependence of molar enthalpies will become somewhat stronger compared to that of the molar Gibbs energy. It also follows from Eqs. (4c–d) that with increasing the specific surface area of the phase or reducing its size, molar enthalpies shift towards positive values, i.e. the cohesive energy weakens within the nano-phase. This is because the coordination number of surface atoms is smaller compared to the bulk atoms and with reducing the size of the phase, the ratio of those surface atoms (y_Φ) increases.

Let me note that both molar entropies and molar enthalpies shift similarly towards more positive values with decreasing size, in accordance with the Clausius equation. It is also worth to note that Eqs. (1i, 3f, 4c) obey the following equation: $G_{m,\Phi} = H_{m,\Phi} - T \cdot S_{m,\Phi}$, while Eqs. (1n, 3g, 4d) obey the following equation: $G_{m,i(\Phi)} = H_{m,i(\Phi)} - T \cdot S_{m,i(\Phi)}$. This further proves the validity of all these Eqs. (1i, n, 3f–g, 4c–d).

The size- and shape-dependences of molar inner energies of nano-phases

The integral molar inner energy of a phase follows from the integral molar Gibbs energy of the same phase as [39, 40]:

$$U_{m,\Phi} \equiv G_{m,\Phi} - T \cdot \left(\frac{\partial G_{m,\Phi}}{\partial T} \right)_{p,x_i(\Phi)} - p \cdot \left(\frac{\partial G_{m,\Phi}}{\partial p} \right)_{T,x_i(\Phi)} \quad (5a)$$

The difference between size-dependent and not size-dependent molar inner energies are written by extending Eq. (5a) as:

$$U_{m,\Phi} - U_{m,\Phi}^o = G_{m,\Phi} - G_{m,\Phi}^o - T \cdot \left[\frac{\partial(G_{m,\Phi} - G_{m,\Phi}^o)}{\partial T} \right]_{p,x_i(\Phi)} - p \cdot \left[\frac{\partial(G_{m,\Phi} - G_{m,\Phi}^o)}{\partial p} \right]_{T,x_i(\Phi)} \quad (5b)$$

where $H_{m,i(\Phi)}^o$ (J/molK) is the partial molar enthalpy of component i in a large phase with $y_\Phi = A_{sp,\Phi} = 0$. As follows from Eqs. (4c–d), molar enthalpies also depend on the size- and shape of the nano-phase via its specific surface area. Note, that at T = 0 K the size

where $U_{m,\Phi}^o$ (J/molK) is the integral molar inner energy of a large phase with $y_\Phi = A_{sp,\Phi} = 0$.

Now, let us take the first derivative of $G_{m,\Phi} - G_{m,\Phi}^o$ by pressure after $H_{m,c,\Phi}$ in Eq. (2f) is replaced by $U_{m,c,\Phi} + p \cdot V_{m,\Phi}$:

$$\left[\frac{\partial(G_{m,\Phi} - G_{m,\Phi}^o)}{\partial p} \right]_{T, x_i(\Phi)} \cong -y_\Phi \cdot k \cdot V_{m,\Phi} \tag{5c}$$

As $k \cdot |H_{m,c,\Phi}| \gg T \cdot |\Delta_s S_{m,\Phi}|$, in the first approximation $A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \cong -y_\Phi \cdot k \cdot H_{m,c,\Phi}$ follows from Eqs. (2d–e). Multiplying and dividing Eq. (5c) by $H_{m,c,\Phi}$, this latter equation can be re-written as:

$$\left[\frac{\partial(G_{m,\Phi} - G_{m,\Phi}^o)}{\partial p} \right]_{T, x_i(\Phi)} \cong \frac{V_{m,\Phi}}{H_{m,c,\Phi}} \cdot A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \tag{5d}$$

Now, let us substitute Eqs. (2f, 3e, 5d) into Eq. (5b):

$$U_{m,\Phi} \cong U_{m,\Phi}^o + \left(1 - T \cdot z_\Phi \cdot \frac{C_{p,m,\Phi}}{H_{m,c,\Phi}} - p \cdot \frac{V_{m,\Phi}}{H_{m,c,\Phi}} \right) \cdot A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/g} \tag{5e}$$

The partial molar inner energy of a component in a phase can be obtained in a similar way, considering Eq. (2g):

$$U_{m,i(\Phi)} \cong U_{m,i(\Phi)}^o + \left(1 - T \cdot z_\Phi \cdot \frac{C_{p,m,i(\Phi)}}{H_{m,c,i(\Phi)}} - p \cdot \frac{V_{m,i(\Phi)}}{H_{m,c,i(\Phi)}} \right) \cdot A_{sp,\Phi} \cdot V_{m,i(\Phi)} \cdot \sigma_{\Phi/g} \tag{5f}$$

where $U_{m,i(\Phi)}^o$ (J/molK) is the partial molar inner energy of component i in a large phase with $y_\Phi = A_{sp,\Phi} = 0$. As follows from Eqs. (5e–f), molar inner energies also depend on the size- and shape of the nano-phase via its specific surface area. Note, that at $T = 0$ K and $p = 0$ bar the size- and shape-dependence of molar inner energies is the same as that of the molar Gibbs energies, while at $p = 0$ bar it is the same as that of the molar enthalpy. However, with increasing temperature, the size- and shape-dependence of molar inner energies will become somewhat stronger compared to that for the molar Gibbs energy. Also, with increasing pressure, the size- and shape-dependence of molar inner energies will become somewhat stronger compared to that for the molar enthalpy. However, this effect will have at least a 0.1% role only if pressure is above 100 bar = 10 MPa. It also follows from Eqs. (5e–f) that with increasing the specific surface area of the phase or reducing its size, molar inner energies shift towards positive values, similarly to the molar enthalpy.

Experimental validation of the theoretical equations

Experimental validation of Eq. (1i)

Eqs. (1i, 3f, 4c, 5e) are used here to predict the maximum size effect of different integral molar properties, valid for 1 nm radius solid and liquid nano-particles (see Table 2). Characteristic values are given in Table 2 for pure solid and liquid lead (Pb) at its melting point, as an example. As follows from Table 2, the size effects are quite large.

The condition of equilibrium between solid and liquid Pb nano-particles is written as:

Table 2 Characteristic values for solid and liquid pure lead (Pb) at its melting point

Quantity	Unit	Value	Remark	Source	Eqs
p	Pa	10 ⁵	Average	–	–
T, T _m	K	600.6	Melting point	[47]	–
A _{sp}	1/m	3 · 10 ⁹	Maximum*	–	(1c)
V _{m,s}	m ³ /mol	1.88 · 10 ⁻⁵	Measured	[48]	–
σ _{s/g}	J/m ²	0.533	Estimated	[17]	–
C _{p,m,s}	J/molK	29.4	Measured	[47]	–
H _{m,c,s}	kJ/mol	-180.5**	Estimated	[49]	–
z _s	–	2	Estimated	[46]	–
G _{m,s} - G _{m,s} ^o	kJ/mol	+30.1	Maximum*	–	(1i)
H _{m,s} - H _{m,s} ^o	kJ/mol	+36.0	Maximum*	–	(4c)
U _{m,s} - U _{m,s} ^o	kJ/mol	+36.0	Maximum*	–	(5e)
S _{m,s} - S _{m,s} ^o	J/molK	+9.81	Maximum*	–	(3f)
V _{m,l}	m ³ /mol	1.94 · 10 ⁻⁵	Measured	[48]	–
σ _{l/g}	J/m ²	0.458	Measured	[50, 51]	–
C _{p,m,l}	J/molK	30.7	Measured	[47]	–
H _{m,c,l}	kJ/mol	-175.7***	Estimated	[49]	–
z _l	–	1	Estimated	[46]	–
G _{m,l} - G _{m,l} ^o	kJ/mol	+26.7	Maximum*	–	(1i)
H _{m,l} - H _{m,l} ^o	kJ/mol	+29.5	Maximum*	–	(4c)
U _{m,l} - U _{m,l} ^o	kJ/mol	+29.5	Maximum*	–	(5e)
S _{m,l} - S _{m,l} ^o	J/molK	+4.67	Maximum*	–	(3f)

*values are calculated for a sphere of 1 nm in radius

195.9 kJ/mol (the sublimation energy at T=0 K)+6.9 kJ/mol (enthalpy change from 0 K till 298.15 K)+8.5 (enthalpy change from 298.15 K till melting point) *+4.8 kJ/mol (heat of melting)

$$\Delta_m G_m = G_{m,l} - G_{m,s} = 0 \tag{6a}$$

where $\Delta_m G_m$ (J/mol) is the molar Gibbs energy change accompanying melting of Pb nano-crystals. Equation (6a) can be re-written as:

$$G_{m,l} - G_{m,s} = (G_{m,l} - G_{m,l}^o) - (G_{m,s} - G_{m,s}^o) + (G_{m,l}^o - G_{m,s}^o) = 0 \tag{6b}$$

Substituting the values of $(G_{m,l} - G_{m,l}^o) = 26.7$ kJ/mol and $(G_{m,s} - G_{m,s}^o) = 30.1$ kJ/mol from Table 2 and the simplified expression for $(G_{m,l}^o - G_{m,s}^o)$ from [47] into Eq. (6b):

$$-3400 + 7.942 \cdot (600.6 - T) \cong 0 \tag{6c}$$

The solution of Eq. (6c): $T_m = 172$ K, which is the estimated melting point of pure Pb of 1 nm in radius. Replacing $(G_{m,l} - G_{m,l}^o) - (G_{m,s} - G_{m,s}^o)$ in Eq. (6b) by Eq. (1i), the general equation is obtained instead of Eq. (6c) for pure Pb:

$$\frac{3}{r} \cdot (V_{m,s} \cdot \sigma_{s/g} - V_{m,l} \cdot \sigma_{s/l}) \cong 7.942 \cdot (600.6 - T) \tag{6d}$$

where r (m) is the radius of the spherical nano-particle, $3/r$ is its specific surface area. In the first approximation $(V_{m,s} \cdot \sigma_{s/g} - V_{m,l} \cdot \sigma_{s/l}) \cong 1.14 \cdot 10^{-6}$ J/mol from Table 2 has a constant value. Substituting this value into Eq. (6d), the size dependent melting point of pure Pb is obtained as:

$$T_m \cong 600.6 - \frac{4.29 \cdot 10^{-7}}{r} \tag{6e}$$

The values calculated by Eq. (6e) are shown in Fig. 1 together with experimental liquidus data measured by

Kofman et al. [52]. As follows from Fig. 1, our theoretical Eq. (6e) reproduces well the measured liquidus data. This proves the validity of our Eq. (1i) on the size dependence of the molar Gibbs energy. Note that due to the extended phase rule of Gibbs valid for nano-phases [53], also a solidus line exists for nano-Pb [52]. This can be estimated by taking into account the solid/liquid interface neglected above, as shown in details in [17, 54]. There are two further interesting details visible in Fig. 1:

- The melting point (= liquidus line) of the nano-crystal approaches that of the macro-crystal (600.6 K) when the size of the nano-crystal approaches 100 nm, in agreement with the general definition of nano-materials [15].
- The melting point of the nano-crystal approaches zero as its radius approaches $r = 0.71$ nm, being about 4 times larger than the atomic radius of lead (= 0.18 nm). It means, that a nano-particle with about 4 atoms along its diameter is the smallest nano-particle that can be considered as a solid

Figure 1 The size dependence of melting point of pure lead (Pb). The continuous line is calculated by Eq. (6e). The dots are experimental liquidus points measured by [52]. The size of the dots corresponds to the experimental error.

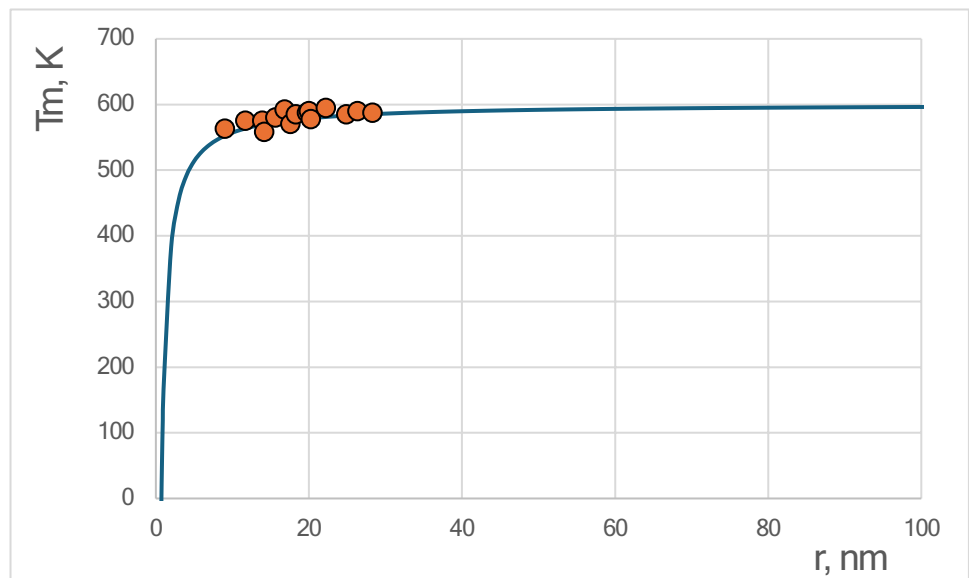
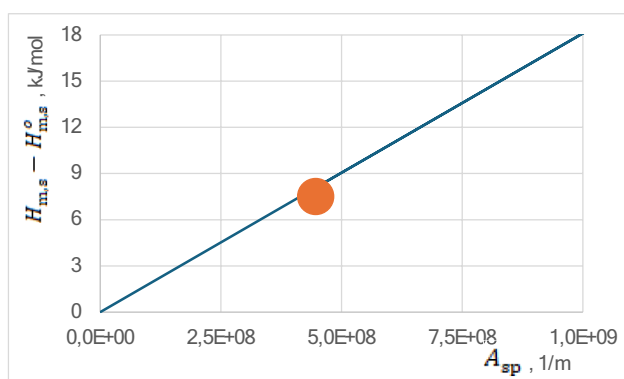


Table 3 Characteristic values for solid cobalt (Co)

Quantity	Unit	Value	Source	Eqs
T	K	1040		–
A_{sp}	1/m	$(4.45 \pm 0.89) 10^8$	[7]	
$V_{m,s}$	m ³ /mol	$6.63 10^{-6}$	[7]	–
$\sigma_{s/g}$	J/m ²	2.3 ± 0.1	[55]	–
$C_{p,m,s}$	J/molK	36.9	[47]	–
$H_{m,c,s}$	kJ/mol	– 401	[49]	–
z_s	–	2	[46]	–
$G_{m,s} - G_{m,s}^o$	kJ/mol	6.8 ± 1.7	–	(1i)
$H_{m,s} - H_{m,s}^o$	kJ/mol	8.1 ± 2.0	–	(4c)

**Figure 2** The molar enthalpy difference between nano-Co and macro-Co crystals as function of their specific surface area. The line is calculated by the data of Table 3 and by Eq. (4c). The dot was measured by dissolution calorimetry in [7]. Its size means the experimental error.

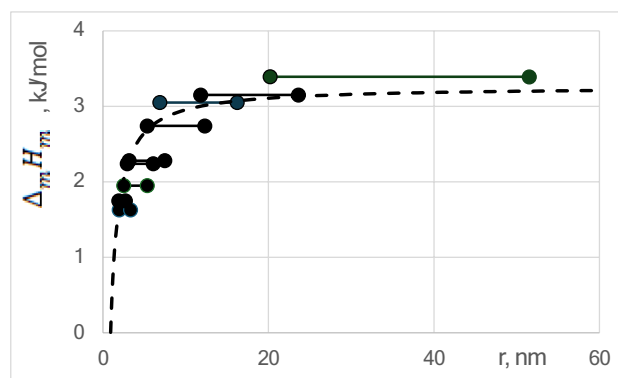
phase. It also means that nano-thermodynamics is not valid for phases with radii below 1 nm.

Experimental validation of Eq. (4c)

The size dependence of the molar enthalpy of cobalt (Co) nano-crystals is measured as the difference in enthalpies of dissolution between nano-Co and macro-Co in the same liquid alloy at same temperature, resulting into identical liquid alloys. The measured molar enthalpy difference between nano-sized and macro-sized Co crystals was found 7.5 ± 1.0 kJ/mol-Co at the average temperature of $T = 1040$ K for Co nano-particles with their measured BET surface area of $(50 \pm 10) 10^3$ m²/kg [7]. Multiplying this value by the density of Co (8,890 kg/m³), the specific surface area applied in this paper is obtained as: $A_{sp} = (4.45 \pm 0.89) 10^8$ 1/m. As

Table 4 Properties of solid and liquid indium (In) around its melting point

Quantity	Unit	Value	Source	Eqs
T_m	K	430	[47]	–
$C_{p,m,l}$	J/molK	29.4	[47]	–
$H_{m,c,l}$	kJ/mol	– 236	[47]	–
$V_{m,l}$	m ³ /mol	$1.64 10^{-5}$	[56]	–
$\sigma_{l/g}$	J/m ²	0.560	[56]	–
$C_{p,m,s}$	J/molK	30.3	[47]	–
$H_{m,c,s}$	kJ/mol	– 239	[47]	–
$V_{m,s}$	m ³ /mol	$1.57 10^{-5}$	[56]	–
$\sigma_{s/g}$	J/m ²	0.618	[56]	–
$\Delta_m H_m^o$	kJ/mol	3.26	[47]	–
$3 \cdot []$	kJ/molm	$-3.06 10^{-9}$	–	(7b)

**Figure 3** The molar enthalpy of melting of nano-In as function of the radius of its particles. The dotted line is calculated by the data of Table 4 and by Eq. (7b). The experimental intervals were measured by ultrasensitive scanning calorimetry and by transmission electron microscopy in [56].

follows from the last row of Table 3, the experimental value of 7.5 ± 1.0 kJ/mol-Co and the theoretical value of 8.1 ± 2.0 kJ/mol-Co overlap (see also Fig. 2). Thus, we can conclude that the equation for the size dependence of the molar enthalpy written by Eq. (4c) is also validated experimentally.

Another way to validate experimentally Eq. (4c) is to compare the experimental size dependence of molar melting enthalpy to our theoretical equation derived from Eq. (4c). The size dependent molar melting enthalpy ($\Delta_m H_m$, J/mol) is defined as:

$$\Delta_m H_m \equiv H_{m,l} - H_{m,s} \quad (7a)$$

where $H_{m,l}$ (J/mol) is the size dependent molar enthalpy of the liquid phase and $H_{m,s}$ (J/mol) is the size dependent molar enthalpy of the solid phase. Now, let us use Eq. (4c) to replace both terms in the right-hand side of Eq. (7a), neglecting the difference between the specific surface areas of solid and liquid phases and writing it through the radius (r , m) of a spherical nanoparticle:

$$\Delta_m H_m \equiv \Delta_m H_m^o + \frac{3}{r} \cdot \left[\left(1 - T \cdot \frac{C_{p,m,l}}{H_{m,c,l}} \right) \cdot V_{m,l} \cdot \sigma_{l/g} - \left(1 - T \cdot 2 \cdot \frac{C_{p,m,s}}{H_{m,c,s}} \right) \cdot V_{m,s} \cdot \sigma_{s/g} \right] \quad (7b)$$

where $\Delta_m H_m^o$ (J/mol) is the molar enthalpy of melting of the macro-crystal with $A_{sp,l} = A_{sp,s} = 0$. The physical properties of In around its melting point are collected in Table 4. Calculated data by Eq. (7b) are compared to experimental data in Fig. 3. One can see that the line calculated by the theoretical Eqs. (7b, 4c) is confirmed by the experimental data, confirming further the validity of Eq. (4c).

The validation of Eqs. (3f, 5e)

As the new Eqs. (1i, 4c) for the size- and shape dependencies of integral molar Gibbs energy and molar enthalpy of nano-phases are validated using experimental results (see the above two sub-sections), also the new equation for integral molar entropy of nano-phases Eq. (3f) can be considered as validated. Although this latter quantity is not measurable, but it obeys the well-known equation $S_{m,\phi} = (H_{m,\phi} - G_{m,\phi})/T$. Similarly, the integral molar inner energy of condensed phases is known to have the same value as the integral molar enthalpy of the same condensed phases below 100 bar of pressure. Thus, the experimental validation of the integral molar enthalpy Eq. (4c) also validates the integral molar inner energy Eq. (5e), at least below 100 bar of pressure. Moreover, as partial molar quantities of components dissolved in nano-phases are closely related to integral molar quantities of the same nano-phases, the validation of new Eqs. (1i, 3f, 4c, 5e) for integral molar quantities also validates the new Eqs. (1o, 3g, 4d, 5f) for partial molar quantities of components in nano-phases.

Conclusions

1. In this paper, the size- and shape dependences of 8 different integral and partial molar thermodynamic quantities are derived for solid and liquid nano-phases, starting from the fundamental equation of Gibbs: i) The integral molar Gibbs energies of nano-phases and the partial molar Gibbs ener-

gies of components in those nano-phases, ii) The integral molar enthalpies of nano-phases and the partial molar enthalpies of components in those nano-phases, iii) The integral molar entropies of nano-phases and the partial molar entropies of components in those nano-phases, and iv). The integral molar inner energies of nano-phases and the partial molar inner energies of components in those nano-phases. All these 8 functions have been found proportional to the specific surface area of the phase, defined as the ratio of its surface area to its volume. The equations for specific surface areas of phases of different shapes are different, but all of them are inversely proportional to the characteristic size of the phase, such as the diameter of a nano-sphere, the side-length of a nano-cube or the thickness of a thin film. Therefore, the deviations of all properties of nano-phases discussed here from their macroscopic values are inversely proportional to their characteristic size.

2. The 8 equations derived in this paper follow strict derivations from the fundamental equation of Gibbs. Only the temperature dependent surface energy of solids and surface tension of liquids are considered as model equations to simplify the final resulting equations.
3. The theoretical equation for the integral molar Gibbs energy is validated against the experimental values of liquidus temperatures of pure lead. The theoretical equation for the integral molar enthalpy is validated against the experimental values obtained for a). The dissolution enthalpy differences between nano- and macro cobalt particles in the same liquid alloy and ii). The size dependent enthalpy of melting of indium nanoparticles. This also leads to the validation of the integral molar entropy and the integral molar inner energy (the

latter at least below 100 bar). Further, as partial and integral molar quantities are closely related, the above also validate the new equations obtained for the partial molar quantities of components in nano-phases.

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Declarations

Conflict of interest The author declares no competing interest.

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