Effect of Particle Size and Morphology on the Molar Enthalpy and Molar Entropy of Nanomaterials in Different Processes

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Abstract. When the size of the material reaches the nanometer level, due to surface effects and small size effects, the substances would cause great changes in chemical reaction equilibrium, reaction kinetics, phase transition, adsorption, electrochemistry and catalysis, and these changes are attributed to changes in their thermodynamic properties. Particle size and morphology are the main factors affecting the thermodynamic properties of nanomaterials, while molar enthalpy and molar entropy are important thermodynamic properties of nanomaterials. The effects of particle size and morphology on molar entropy and molar enthalpy in phase transitions (including melting and sublimation), electrochemistry and adsorption are described in this paper.

1. Introduction
The concept of nanothermodynamics first appeared in Nature magazine in 2000. That term was used by Chamberlin of the State University in studying the critical behavior of ferromagnets. However, the initial research on nano-thermodynamics based on statistics did not advance to a deeper level. Later, it gradually developed into simulation based on physical models and molecular dynamics. Particle size and morphology are the two main factors affecting the thermodynamic properties of nano-nanomaterials. The effect of particle size on the thermodynamic properties of nano-systems is significant. However, most of the research on the thermodynamic properties of nano-systems is spherical nanoparticles or spheres. Nano-small droplets and other morphological studies are less, and the influence of morphology on nano-thermodynamic properties has not yet formed a systematic theory. Studying the thermodynamic properties of nanomaterials has extremely important scientific significance and application value.

2. Phase change
Phase change thermodynamics plays an important role in the preparation and application of nanomaterials. As nanomaterials have the properties of melting and sublimation, the molar enthalpy and molar entropy of nanomaterials are divided into melting enthalpy, melting entropy and sublimation enthalpy and sublimation entropy.
2.1. Melt.

![Fig. 1. Relationship between melting enthalpy of spherical nanoparticles and inverse particle size](image1)

![Fig. 2. Relationship between Melt Entropy of Spherical Nanoparticles and Inverse Particle Size](image2)

The thermodynamic properties of the melting of nanoparticles depend on morphology and particle size [1, 2], and current on the thermodynamic model of nanoparticle melting. There are three main types: Pawlow model[3, 4], Rie model[5], and Reiss model[6]. The Pawlow melting model does not conform to the equilibrium condition of true melting, which has been proved by some scholars to be wrong[1, 2], recently, the Rie and Reiss models have also been proved to be approximate theoretical models, so that the derived phase-change thermodynamic equations are not accurate[7]. The above several models can not accurately predict the melting temperature of nanoparticles with particle size less than 5 nm, nor can it explain the overheating phenomenon when nanoparticles are melted.

Applying the Gibbs-Helmholtz equation to the melting of nanoparticles, then

$$\left[ \frac{\partial}{\partial T} \left( \frac{\Delta G_{m}}{T} \right) \right]_{p} = -\frac{\Delta H_{m}}{T^2}$$  \hspace{1cm} (1)

When the nanoparticles are melted, the molar Gibbs energy change is

$$\Delta G_{m} = \mu_0 - \mu_i = \Delta G_{m}^s + \sigma \left( \frac{\partial A}{\partial n} \right)_{T,p} - \sigma \left( \frac{\partial A}{\partial n} \right)_{T,p}$$  \hspace{1cm} (2)

The relationship between the two types of nanoparticles melting enthalpy

$$\Delta H_{m} = \Delta H_{m}^s + \sigma \left( \frac{\partial A}{\partial n} \right)_{T,p} - \sigma \left( \frac{\partial A}{\partial n} \right)_{T,p}$$  \hspace{1cm} (3)
Also due to

\[ \frac{\partial \Delta \bar{G}_m}{\partial T} = -\Delta \bar{S}_m \]  

(5)

Binding (1) can give the relationship between the molar melting entropy of nanoparticles.

\[ \Delta \bar{S}_n = \Delta \bar{S}_n^0 - \left( \frac{\partial A_n}{\partial n} \right)_{T, p} \sigma_n + \left( \frac{\partial A_n}{\partial n} \right)_{T, p} \sigma_n \]  

(6)

After melting equilibrium, the difference in density between solid and liquid is small, so it can be simplified.

\[ \Delta \bar{H}_m = \Delta \bar{H}_m^0 - \frac{2M}{\rho \sigma_i} \left( \sigma_{sl} - T \left( \frac{\partial \sigma_{sl}}{\partial T} \right)_{p} \right) - \frac{2T \sigma_i \alpha_i}{3} \]  

\[ \Delta \bar{S}_m = \Delta \bar{S}_m^0 + \frac{2M}{\rho \sigma_i} \left( \frac{\partial \sigma_{sl}}{\partial T} \right)_{p} + \frac{2 \sigma_i \alpha_i}{3} \]  

(7)

(8)

It can be seen that the molar melting enthalpy of spherical nanoparticles is mainly determined by \(-2M \sigma_{sl}/(\rho \sigma)\). When the radius of the nanoparticles is approximately 10 nm or more, the melting enthalpy of the spherical nanoparticles is linearly related to the reciprocal of the particle size. Similarly, the molar melting entropy of nanoparticles is mainly determined by \(-2M \left( \sigma_{sl}/\rho \sigma \right) / \rho \). Similarly, when the radius of the nanoparticles is approximately 10 nm or more, the molar melting entropy of the spherical nanoparticles is linear with the reciprocal of the particle size.

2.2. Sublimation.

![Fig. 3. Relationship between Sublimation Enthalpy of Spherical Nanoparticles and Reciprocal Particle Size](image)
The study of metamorphism and entropy change in the sublimation process is less than the melting process. Melchor et al. measured the sublimed enthalpy of C60, C70, C76, C78, and C84 at a temperature range of 810-1170 K [8]. It was found that the sublimation of fullerenes increased with the number of atoms.

Under equal pressure conditions, according to the Gibbs-Helmholtz equation

$$\left( \frac{\partial \left( \Delta_v^i G_m / T \right)}{\partial T} \right)_p = - \frac{\Delta_v^i H_m}{T^2}$$  \hspace{1cm} (9)

with

$$\Delta_v^i G_m = \mu_v^a - \mu_v^b = \sigma_v \left( \frac{\partial A}{\partial n} \right)_{\mu_p}$$  \hspace{1cm} (10)

Accurate nanoparticle molar sublimation relationship

$$\Delta_v^i H_m = \frac{\partial \Delta_v^i G_m}{\partial T} \left[ \sigma_v - T \left( \frac{\partial \mu_v^a}{\partial T} \right)_p \right] + \sigma_v \left( \frac{\partial \Delta_v^i G_m}{\partial T} \right)_p T \sigma_v$$  \hspace{1cm} (11)

Also due to

$$\left( \frac{\partial \Delta_v^i G_m}{\partial T} \right)_p = - \Delta_v^i S_m$$  \hspace{1cm} (12)

Combining (9) and (12) can obtain accurate nanoparticle molar sublimation entropy

$$\Delta_v^i S_m = \Delta_v^i S_n + \left( \left( \frac{\partial A}{\partial n} \right)_{\mu_p} \left( \frac{\partial \mu_v^a}{\partial T} \right)_p \right) + \sigma_v \left( \frac{\partial \Delta_v^i G_m}{\partial T} \right)_p$$  \hspace{1cm} (13)

Simplified

$$\Delta_v^i H_m = \Delta_v^i H_n - \frac{2M}{\rho r} \left[ \sigma_v - T \left( \frac{\partial \mu_v^a}{\partial T} \right)_p + \frac{2}{3} \sigma_v \alpha_v \right]$$  \hspace{1cm} (14)

$$\Delta_v^i S_m = \Delta_v^i S_n + \frac{2M}{\rho r} \left[ \left( \frac{\partial \mu_v^a}{\partial T} \right)_p + \frac{2}{3} \sigma_v \alpha_v \right]$$  \hspace{1cm} (15)

It can be seen from the formulas (14) and (15) that the smaller the particle size of the nanoparticles, the smaller the molar sublimation enthalpy and the molar sublimation entropy. When the particle size of the nanoparticles is larger than 10 nm, the surface tension is approximated. As a constant, its molar
sublimation and molar sublimation entropy vary linearly with the reciprocal of its radius.

2.3. Electrochemistry.

![Fig. 5. Relationship between molar surface enthalpy of spherical nanoparticles and inverse particle size](image1)

![Fig. 6. Relationship between molar surface enthalpy of spherical nanoparticles and inverse particle size](image2)

Electrochemical thermodynamic properties and phases of nanoelectrodes composed of nanoparticles due to their unique nano-effects. There are significant differences in the block electrodes that should be used. Many studies have shown that the particle size of nanoparticles is composed of nanometers. The electrode potential of the electrode has a significant effect on the electrochemical thermodynamic properties [9-11]. Kai et. al prepared LixFePO4 with different particle sizes, and determined the electrode reaction entropy by electrochemical calorimetry[12]. It was found that the electrode reaction entropy increased with the increase of particle size.

The molar Gibbs energy of the nanoelectrode reaction can be expressed as

$$\Delta_i G_m = \Delta_r G_m^b + \Delta_r G_m^s$$

(16)

The electrode potential of the nanoelectrode can be expressed as

$$E = - \frac{\Delta_i G_m}{zF} = E^b + E^s$$

(17)

Among them,

$$E^b = - \frac{\Delta_r G_m^b}{zF}, \quad E^s = - \frac{\Delta_r G_m^s}{zF}$$
When nano-electrodes composed of different morphological nanoparticles as a dispersed phase, the molar Gibbs energy of the surface phase of the nano-electrode reaction can be expressed as

$$\Delta_r G_m^i = \sum_n V_B \mu_B^n = \sum_n \frac{\gamma \nu_x \sigma_B^x M_x}{\rho_B l_B}$$

(18)

Combining the electrode potentials of (17) and (18) nanoelectrodes with the particle size of component B in the electrode reaction system can be expressed as

$$E = E^h + E' = E^h - \frac{1}{zF} \sum_n \frac{\gamma \nu_x \sigma_B^x M_x}{\rho_B l_B}$$

(19)

The T-differentiation on both sides can obtain the relationship between the temperature coefficient of the nano-electrode and the particle size.

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E^h}{\partial T}\right)_p - \frac{1}{zF} \sum_n \frac{\gamma \nu_x \sigma_B^x M_x}{\rho_B l_B} \left[\frac{\partial \sigma_B^x}{\partial T}\right]_p \frac{2 \sigma_B^x}{3}$$

(20)

The molar reaction entropy of the nanoelectrode is

$$\Delta_r S_m = -\left(\frac{\partial \Delta_r G_m^i}{\partial T}\right)_p = \Delta_r S_m^h + \Delta_r S_m'$$

(21)

$$\Delta_r S_m' = zF \left(\frac{\partial E'}{\partial T}\right)_p$$

(22)

The molar reaction entropy of the nanoelectrode can be obtained by combining (20), (21), (22).

$$\Delta_r S_m = \Delta_r S_m^h - \sum_n \frac{\gamma \nu_x M_x}{\rho_n l_n} \left[\frac{\partial \sigma_B^x}{\partial T}\right]_p + \frac{2 \sigma_B^x}{3}$$

(23)

According to (22), the particle size of the nanoparticles constituting the electrode is greater than 20 nm, the surface tension can be approximated as a constant. If the dispersed phase B constituting the nanoelectrode is a reactant, the particle size is reduced, and the molar reaction entropy of the nanoelectrode is decreased. Conversely, as the particle size of the nanoparticle decreases, the molar reaction entropy of the nanoelectrode increases. There is a linear relationship with the reciprocal of the nanoparticles.

2.4. Adsorption.

Fig. 7. Relationship between Standard Molar Adsorption Enthalpy and Inverse Particle Size of Nanoparticles with Different Particle Sizes
Nanomaterials have strong adsorption properties due to their large specific surface area, high specific surface energy, special crystal face structure, a large number of high reaction edges and corner defect sites, and are widely used in many fields. For example, the use of nanoparticle adsorption to separate and enrich precious metals in the field of hydrometallurgy [13], the adsorption of harmful substances in water in the field of environmental protection and toxic and harmful gases in the gas. Because for solid nanoparticles, the effect of temperature on its volume is negligible, and the following formula is used to indicate the adsorption of nanoparticles in solution.

\[ B(l) + N(s) \rightarrow A(s) \quad (24) \]

According to the adsorption formula (24) the molar Gibbs function of the adsorption process can be expressed as

\[ \Delta_{\text{ads}} G_m = \mu_A - \mu_B - \mu_N \quad (25) \]

Among them

\[ \Delta_{\text{ads}} G^{\text{bo}}_m = \Delta_{\text{ads}} G^b_m + \Delta_{\text{ads}} G^{\text{so}}_m \quad (26) \]

\[ \Delta_{\text{ads}} G^{\text{bo}}_m = (\mu^b_A + \mu^b_B) - \mu^b_N - \mu^b_n \quad (27) \]

\[ \Delta_{\text{ads}} G^{\text{bo}}_m = \mu^b - \mu^b_N = (\sigma_N - \sigma^*_N) \frac{3V_t}{r} \quad (28) \]

\[ J = \frac{\Gamma_B}{\alpha_n} \quad (29) \]

For the adsorption of the same component block material, there is

\[ \Delta_{\text{ads}} G^{\text{bo}}_m = \Delta_{\text{ads}} G^{\text{bo}}_m + RT \ln J \quad (30) \]

Among them (16) turned into

\[ \Delta_{\text{ads}} G_m = \Delta_{\text{ads}} G^b_n + \Delta_{\text{ads}} G^b_r - \Delta_{\text{ads}} G^b_m + (\sigma_N - \sigma^*_N) \frac{3V_t}{r} \quad (31) \]

Bringing in the basic equation of thermodynamics

\[ \Delta S = -\left( \frac{\partial \Delta G}{\partial T} \right)_P \quad (32) \]

The thermodynamic relationship between the molar adsorption entropy of the nanoparticles and the
particle size can be obtained as follows:

\[
\Delta_{ads}S_r = \left( \frac{\partial G}{\partial T} \right)_r - \left( \frac{\partial G}{\partial T} \right)_{r'} = \Delta_{ads}S_r^{3V_n / r} - \left( \frac{\partial G}{\partial T} \right)_r - \left( \frac{\partial G}{\partial T} \right)_{r'}
\] (33)

From equation (32), the influence of particle size on the molar adsorption entropy \((3V_n / r)\) is determined by the difference between the value of the difference between the surface tension temperature coefficient before and after adsorption and the adsorption system studied. When the particle size decreases, the molar adsorption entropy of the nanoparticles decreases.

Substituting (33) into the Gibbs-Helmholz equation

\[
\Delta H = -T^2 \left[ \partial \left( \frac{\Delta G}{T} \right)/\partial T \right]
\]

Thermodynamic relationship between nanoparticle molar adsorption enthalpy and particle size

\[
\Delta_{ads}H_r = -T \left[ \frac{\partial (\Delta G/T)}{\partial T} \right] = \Delta_{ads}H_r^{3V_n / r} - \left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_r - \left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_{r'}
\] (34)

From the formula (35), the effect of particle size on the molar adsorption of nanoparticles is determined by the sign of \((3V_n / r)\) and \(\left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_r - \left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_{r'}\), which is determined by the sign of the value in the brace on the right side of the equal sign. If \(\left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_r - \left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_{r'} > 0\), when the particle size is reduced, the molar adsorption enthalpy of the nanoparticles is reduced. If \(\left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_r - \left( \frac{\partial \sigma_n^{3}}{\partial T} \right)_{r'} < 0\), then the particle size pair. The direction of influence of the molar adsorption enthalpy is determined by the absolute value of the value and the value of \(\sigma_n^{3} - \sigma_n^{3}\). The more the number of faces of the nanoparticles, that is, the closer the shape is to the spherical shape, the closer the adsorption entropy and the adsorption enthalpy are to the spherical nanoparticles.

3. Outlook

Nanomaterials have a very broad potential application prospect, but the practical application of nanomaterials is also strongly dependent on the development and improvement of preparation technology. The preparation and processing of materials must be inseparable from the thermodynamic properties of materials (hot melt, enthalpy, entropy, Gibbs free energy, etc.), composition phase, phase structure, stability, phase transition characteristics, etc., which requires people to continue to deepen understanding the structure, performance stability, size effect and its influencing factors of the material. The research on the thermodynamics of nanomaterials has made great progress both in theory and in experimental methods. Of course, there are still many scientific problems that need to be solved. For example, the thermodynamic function of conventional materials, in which the specified entropy of solid matter is based on the third law of thermodynamics, using the low-temperature calorimetry technique, firstly determines the change of heat capacity with temperature, and then obtains the experimental temperature range by graphical integration through the second law of thermodynamics. The entropy change, the entropy change near 0K is extrapolated or theoretically calculated, and the entropy of 0K is specified as the reference to obtain the specified entropy of the substance. Whether the thermodynamic function such as the specified entropy of the nanomaterial can be obtained by low-temperature experiment is a value.

4. Conclusion

In this paper, the author analyzes the changes in molar entropy and molar enthalpy of the nanomaterials during the phase transition, electrochemical process and adsorption process. The influence mechanism of morphology and particle size is obtained initially. During the phase transition, the molar enthalpy and molar entropy of spherical nanoparticles are linearly related to the particle radius. There is a linear relationship between the molar reaction entropy of the nanoelectrode and the reciprocal of the particle diameter during the electrochemical process. In addition, the molar adsorption enthalpy and molar adsorption entropy are positively related to the particle diameter within a certain range during the adsorption process.
References

[1] Dick K., Dhanasekaran T., Zhang Z., et al. Size-dependent melting of silica-encapsulated gold nanoparticles[J]. Journal of the American Chemical Society, 2002, 124(10):2312-7.

[2] Barybin A., Shapovalov V. Modification of Pawlow’s thermodynamical model for the melting of small single-component particles[J]. Journal of Applied Physics, 2011, 109(3):034303-034303-9.

[3] Pawlow P. Melting point dependence on the surface energy of a solid body[J]. Zeitschrift fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics, 1909, 65:1-35.

[4] Pawlow P. Relation between melting point and surface energy[J]. Zeitschrift fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics, 1909, 65:545-548.

[5] Rie E. Influence of surface tension on melting and freezing[J]. Zeitschrift fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics, 1923, 104:354-362.

[6] Reiss H., Wilson I. B. The effect of surface on melting point[J]. Journal of Colloid Science, 1948, 3(6):551-561.

[7] Xue Y. Q., Cui Z. X. Nanophysical Chemistry [M]Beijing: Science Press, 2017.

[8] Martinez-Herrera M., Campos M., Torres L. A., et al. Enthalpies of Sublimation of Fullerenes by Thermogravimetry[J]. Thermostochimica Acta, 2015, 622:72-81.

[9] Komaba S., Mikumo T., Ogata A. Electrochemical activity of nanocrystalline Fe3O4 in aprotic Li and Na salt electrolytes[J]. Electrochemistry Communications, 2008, 10(9): 1276-1279.

[10] Zhang Z., Sun D. Effects of particle size on the electrochemical properties of Mm(NiCoMnAl)5 alloy[J]. Journal of Alloys and Compounds, 1998, 270(1): L7-L9.

[11] Yi T., Wang D., Gao K., et al. Powder electrochemical properties with different particle sizes of spinel LiAl0.05Mn1.95O4 synthesized by sol-gel method [J]. Rare Metals, 2007, 26(4): 330-334.

[12] Kai K., Kobayashi Y., Miyashiro H., et al. Particle-Size Effects on the Entropy Behavior of a LixFePO4 Electrode[J]. ChemPhysChem, 2014, 15(10): 2156-2161.

[13] Zhang L., Zhu Y., Li H M., et al. Kinetic and thermodynamic studies of adsorption of gallium(III) on nano-TiO2[J]. Rare Metals, 2010, 29(1): 16-20.