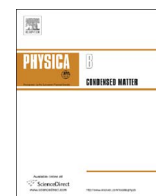




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Size dependence of surface thermodynamic properties of nanoparticles and its determination method by reaction rate constant



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ABSTRACT

Surface thermodynamic properties are the fundamental properties of nanomaterials, and these properties depend on the size of nanoparticles. In this paper, relations of molar surface thermodynamic properties and surface heat capacity at constant pressure of nanoparticles with particle size were derived theoretically, and the method of obtaining the surface thermodynamic properties by reaction rate constant was put forward. The reaction of nano-MgO with sodium bisulfate solution was taken as a research system. The influence regularities of the particle size on the surface thermodynamic properties were discussed theoretically and experimentally, which show that the experimental regularities are in accordance with the corresponding theoretical relations. With the decreasing of nanoparticle size, the molar surface thermodynamic properties increase, while the surface heat capacity decreases (the absolute value increases). In addition, the surface thermodynamic properties are linearly related to the reciprocal of nanoparticle diameter, respectively.

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1. Introduction

Chemical processes of nanoparticles are related to its thermodynamic properties, such as the processes of the thermal decomposition [1–3], the catalysis [4], the adsorption [5] etc., while the thermodynamic properties are greatly different from those of the corresponding bulk materials.

Nanothermodynamics [6–8], developed from the thermodynamics of small systems proposed by Hill in the early 1960s [9], has become the focus of the field of nanoscience. Currently, Hill's theory has been widely acknowledged as the foundation of the nanothermodynamics. However, several abstract variables (such as numbers of small systems and subdivision potential) were introduced by statistical thermodynamics method [10], which are hard to be characterized, measured and connected with the physical characteristics of nanoparticles (such as particle size, morphology, specific surface area and surface tension). As a result, it is difficult to apply the theory to actual nanosystems.

Nowadays, it is generally believed that the nanothermodynamic properties can be divided into two parts both the bulk phase and the surface phase [11–13], of which, the surface phase is the crucial part for the great differences of thermodynamic properties between nanoparticles and the corresponding macroscopic counterparts. Some researches related to surface

thermodynamic properties of nanoparticles have been reported. Piloyan et al. [14] put forward a method to get the surface thermodynamic properties of nanoparticles by thermal analysis (DTA or DSC), and successfully got those properties (surface enthalpy, surface entropy and surface energy) of nanoparticles (boehmite, magnetite and γ -Al₂O₃). Huang et al. [15,16] determined the surface thermodynamic properties of nano-octahedral cadmium molybdate and peanut-like nano-CaMoO₄ by microcalorimetry, the results showed that molar surface enthalpy, molar surface Gibbs energy and molar surface entropy of the two nanoparticles are much larger than those of the corresponding bulk ones. Zhang et al. [17] reported the morphology dependence of the surface enthalpy of nanophase ZnO by a direct calorimetric measurement; the result showed that the surface enthalpies of hydrated surfaces for nanoparticles, nanoporous composites, nanorods, and nanotetrapods are different from each other. Park et al. [18] reported the direct determination of surface enthalpies for nanophase TiO₂ anatase with different morphologies by drop solution calorimetry, which showed the enthalpies of hydration appear to be similar for all morphologies. It is clear that the surface thermodynamic properties depend on the particle size. Unfortunately, the influence regularity of particle size on surface thermodynamic properties of nanoparticles remains unclear.

Besides, research on the influence regularity is possible only based on an accurate determination of the surface thermodynamic properties. Currently, the surface thermodynamic properties of nanoparticles were obtained only by calorimetric methods [14–19], which could cause a larger relative error because the loss of

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heat in experimental procedure is inevitable. It is necessary to establish a new method of accurately determining the surface thermodynamic properties of nanoparticles.

In this paper, the reactions of surface thermodynamic properties with particle size were derived, and the method of determining those properties by reaction rate constant was established. Using this method, the reaction rate constants of nano-MgO with different particle sizes were determined, and then the surface thermodynamic properties were obtained and the effects of particle size of nanoparticles on surface thermodynamic properties were got, which were then compared with the thermodynamic reactions.

2. Theoretical relations of surface thermodynamic properties of nanoparticles

The molar Gibbs energy of a nanoparticle can be divided into two parts both the bulk phase and the surface phase:

$$G_m = G_m^b + G_m^s \quad (1)$$

where superscript b denote the bulk quantities and s the surface quantities.

For a spherical nanoparticle without inner hole, the molar surface Gibbs energy (G_m^s) can be expressed as follows:

$$G_m^s = A_m \times \sigma = \frac{6\sigma M}{\rho d} \quad (2)$$

where A_m , σ , M , ρ and d denote the molar interfacial area, the surface tension, the molar mass, the density and the diameter of the particle, respectively.

From Eq. (2), it can be seen that the effect of particle size on the surface Gibbs energy depends on the surface tension and the particle size, and the surface tension is also related to the particle size. Only if the radius of the nanoparticles approaches or reaches the order of 10^{-9} m does the effect of particle size on the surface tension become significant [20,21]. If the radius of the nanoparticles is greater than 10 nm, the effect of particle size on the surface tension can be neglected. So for a larger nanoparticle, the surface Gibbs energy increases with the decrease of particle size, and exhibits a linear relationship with the reciprocal of particle diameter.

The surface enthalpy of nanoparticle can be derived by Gibbs–Helmholtz equation:

$$H_m^s = -T^2 \left[\frac{\partial(G_m^s/T)}{\partial T} \right]_p = \frac{6M}{d\rho} \left\{ \sigma - T \left[\left(\frac{\partial\sigma}{\partial T} \right)_p + \frac{2\alpha\sigma}{3} \right] \right\} \quad (3)$$

where T and α denote the absolute temperature and the volume expansion coefficient respectively. If the effect of temperature on the molar volume of nanoparticle can be ignored, then α equals to zero.

As observed from Eq. (3), the value of $(\partial\sigma/\partial T)_p$ is usually negative for common substance, and the order of volume expansion coefficient α for nanocrystals usually is 10^{-5} [22], so the value of $(\partial\sigma/\partial T)_p + 2\alpha\sigma/3$ is negative. Therefore, the surface enthalpy increases with the particle size decrease. In addition, the surface enthalpy is linearly related to the reciprocal of particle size.

Similarly, the surface entropy can also be obtained from Eq. (4), that is

$$S_m^s = - \left(\frac{\partial G_m^s}{\partial T} \right)_p = - \frac{6M}{d\rho} \left[\left(\frac{\partial\sigma}{\partial T} \right)_p + \frac{2\alpha\sigma}{3} \right] \quad (4)$$

It can be concluded that for the particle size greater than

10 nm, the larger surface entropy being associated with the smaller particle size. In addition, there is a linear relationship between the surface entropy and the reciprocal of particle size.

Taking the partial differential of Eq. (3), then surface heat capacity can be obtained:

$$\begin{aligned} C_p^s &= \left(\frac{\partial H_m^s}{\partial T} \right)_p \\ &= - \frac{6TM}{d\rho} \left[\frac{4\alpha}{3} \left(\frac{\partial\sigma}{\partial T} \right)_p + \frac{4\alpha^2\sigma}{9} + \left(\frac{\partial^2\sigma}{\partial T^2} \right)_p + \frac{2\sigma}{3} \left(\frac{\partial\alpha}{\partial T} \right)_p \right] \end{aligned} \quad (5)$$

From Eq. (5), it can be seen that C_p^s is the function of temperature and particle size. According to the expression of surface tension σ [23], the value of $(\partial^2\sigma/\partial T^2)_p$ is positive. The second and fourth terms can be ignored because the order of α for nanocrystals is usually 10^{-5} . According to the sign of sum of the first and the third terms in the square bracket, the influence regularities of the particle size on C_p^s can be divided into the following two situations. When the sum is a positive value, the smaller the particle size, the bigger absolute value of surface heat capacity, thus leading to the decrease of heat capacity of nanoparticle, which is consistent with that in these literatures [24–26]. On the contrary, the surface heat capacity increases with the decrease of particle size, thus leading to the increase of heat capacity of nanoparticle, which agrees to that in these literatures [11,27,28]. These influencing regularities of the particle size on C_p^s can better explain the divergence of heat capacity of nanoparticle. In addition, C_p^s is linearly related to the reciprocal of particle diameter for a larger nanoparticle.

3. A determination method of the surface thermodynamic properties of nanoparticles by reaction rate constant

According to the transition state theory proposed by Eyring [29], for a reaction between A and nanoparticle (NP) through the formation of an activated complex C^\ddagger , the relation between the reaction rate constant and the activation Gibbs energy is as follows:

$$k = C_1 \exp \left(\frac{\Delta_r G^\ddagger}{RT} \right) \quad (6)$$

where k , C_1 , R , $\Delta_r G^\ddagger$ are reaction rate constant, a constant, gas constant and activation Gibbs energy (superscript \ddagger denotes the transition state), respectively.

Apply Eq. (6) into the nanosystem and the bulk system, the following can be got:

$$\ln \frac{k}{k^b} = \frac{\Delta_r G^{\ddagger b} - \Delta_r G^\ddagger}{RT} \quad (7)$$

The activation Gibbs energy ($\Delta_r G_+^\ddagger$) for nanosystem equals to the partial molar Gibbs energy of activated complex minus those of nanoparticle (NP) and the reactant A,

$$\Delta_r G^\ddagger = G_{C^\ddagger} - G_{NP} - G_A \quad (8)$$

Similarly, the expression of the Gibbs activation energy ($\Delta_r G^{\ddagger b}$) for the bulk system is as follows:

$$\Delta_r G^{\ddagger b} = G_{C^\ddagger}^b - G_{NP}^b - G_A \quad (9)$$

As the particle size of the reactant has no effect on the transition state, the partial molar Gibbs energy of activation of nanoparticle is equal to that of the corresponding bulk substance:

$$G_{C^\ddagger} = G_{C^\ddagger}^b \quad (10)$$

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