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Research paper

Thermodynamic paths for calculating energy balance in systems containing nanoparticles

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ABSTRACT

Size-dependent physicochemical properties of nanoparticles led to certain complications in thermodynamic calculations followed by energy balance as the first step in these calculations. This work reviewed recent studies on nanothermodynamic topics in an attempt to find some thermodynamic methods for establishing energy balance in systems containing nanoparticles. Some thermodynamic paths were introduced to establish energy balance for ease of calculation by avoiding unknown functions. Based on the proposed pathway, enthalpy changes for several processes involving nanoparticles, such as formation of nanoparticles and phase transitions, were investigated and formulated.

1. Introduction

Nanoscience has achieved significant progress in recent years, especially in various branches of engineering. Nanotechnology can be used to produce new structures, devices, and materials on a near atomic scale. For example, using nanometals in fluids leads to enhancement of heat transfer coefficients and reduces the size of heat exchangers [1]. Nano-filters help to capture nanoaerosols and prevent their emission into the environment [2–4].

Undoubtedly, the first step to working at the nanoscale level is understanding the thermodynamic behavior of nanoparticles. For the first time, Hill [5] showed that the differential equations of macroscopic thermodynamics can be generalized in such a way that they may also be applied to small (i.e., non-macroscopic) systems. Hill explained that, unlike macroscopic thermodynamics, thermodynamic functions are different for different environments in nonmacroscopic scale. Another important difference noted by Hill was the effect of fluctuations. Fluctuations are negligible in macroscopic thermodynamics; therefore, we can use the mean values of fluctuating extensive variables appearing in thermodynamic equations. Hill and Chamberlin [6] showed how the statistical thermodynamics of small systems could be extended to include metastable supersaturated gaseous states close to the gas-liquid equilibrium transition point. Furthermore, Hill [7] suggested a method to handle a macroscopic system with potential energy (μ), pressure (p), and temperature (T) by starting with the corresponding small system partition function, calculating the thermodynamic properties from this function. Hill [8] also explained two interrelated topics: 1. generalizing macrothermodynamics to nanothermodynamics, starting with Gibbs' generalization of macrothermodynamics and then chemical potential calculations; and 2. finding a new logical path in the derivation of the basic ideas and results of nanothermodynamics. Chamberlin [9] explained that Hill's theory is crucial for treating the heterogeneous distribution of independently relaxing regions which are now known to dominate the primary response of most materials. Umberto Lucia [10], using the Gouy-Stodola theorem to complex systems based on the use of entropy generation, tried to extend classical thermodynamics to nanothermodynamics. Babuk et al. [11], using an optimization procedure, determined the size and structure of nanoparticles. Dixit [12] presented a maximum entropy approach to analyze the state space of a small system. Carrete et al. [13] investigated nonequilibrium nanothermodynamics using entropy production concepts. Hong Qian [14] applied a statistical perspective to investigate Hill's small systems nanothermodynamics theory. In another study, Li and Truhlar [15] examined the nanothermodynamics of metal nanoparticles. Many researchers have studied the subject of nanothermodynamics from different perspectives, for example, thermodynamic behavior of nanoparticles [16], phase separation [17], geometry of quantum [18], statistical thermodynamics [19], mechanical strength, thermal stability, acoustics, photonics, electronics, magnetism, dielectrics, and chemical reactivity [20], phase stability [21], physicochemical properties [22] behavior of nanoparticles in magnetic fields [23] and application of the second law of thermodynamics in nanoparticles [24].

Energy balance is the first step in chemical, thermal, fluid, and energy-environment calculations, and the introduction to

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thermodynamics calculation. Engineers will have a better understanding of the principles of thermodynamics if they have a solid understanding of energy balance, which is the root of integral issues such as design and optimization. As in any other system, energy balance in systems containing nanoparticles is a basic step. However, the specific characteristics of nanoparticles require particular study. The environmental and surface effects of nanoparticles lead to complexity in the calculation of their properties.

Therefore, recent studies have tried to link nano- and macro-thermodynamics with a more practical approach for engineering purposes. Xiong et al. [25,26] introduced some equations for calculating the size-dependent properties of nanoparticles based on the relations between macro- and nano-dimensions of materials. In their method, some properties of nanoparticles could be obtained as a function of the same properties in macro scale, size of the atom and size of the nanoparticle. The thermodynamic properties of materials in macro dimensions are well known. However, changing the size of nanoparticles during thermodynamic processes is another challenge. For example, specific heat capacity of solids in macro systems is a function of temperature, and this functionality is well known. Yet in nanoparticles, specific heat capacity is a function of nanoparticle diameter and the heat capacity of that substance in the macro state. In other words, while the specific heat capacity of nanoparticles at a fixed diameter is known, the functionality of the diameter of a nanoparticle with respect to temperature is unknown. Therefore, the changes of heat capacity are unknown during most thermodynamic processes. Establishing energy balance requires the calculation of enthalpy changes, and the calculation of these changes also requires an awareness of heat capacity changes during the thermodynamic process.

In the present work, to fill this knowledge gap identified by an overview of past works, simple thermodynamic pathways were proposed to obtain the enthalpy change of nanoparticle systems and solve the energy balance equations. Following the publication of a new book on the subject of mass and energy balances by the author and his colleague in January, 2018, [27] which included a preliminary study of the mass and energy balances for nanoparticles in its last chapter, the author decided to investigate the subject more deeply to provide an introduction to other researchers who may be interested in the topic.

2. Thermodynamic properties of nanoparticles

Nanoparticles can be considered a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant intensive physical properties regardless of its size; however, at the nano-scale, size-dependent properties are often observed. These differences mainly depend on the surface thermodynamic properties of nanoparticles that have a large influence on reactions [28], phase transitions [29], adsorptions [30], electrochemical [31], and dissolutions [32] processes. An important influential parameter on the properties of nanoparticles is the number of atoms at their surface or surface area to volume (S/V) ratios compared to bulk materials [33].

Different thermodynamic behaviors of bulk and nano-scale materials led to the creation and growth of a new branch of thermodynamics called nanothermodynamics.

Classical thermodynamics is applied for macro-systems. However, small (micro-nano) systems involve two important issues: (1) environmental effects on the thermodynamic functions; and (2) thermal fluctuations that are random deviations of a system from its average state, which occur in a system at equilibrium [34]. In 1962, Hill introduced the theory of small-system thermodynamics [9] which he gradually developed by 2013 [34].

Fig. 1 shows a system that gradually becomes smaller. The system continues diving into smaller sub-systems as long as the effect of the surface free energy is negligible. Finally, in stage (e), the system is divided into $\mathcal{N}$ number sub-systems (nanoparticles).

Before stage (e), the surface free energy is negligible and classical thermodynamics' relations can be applied.

The complexity of the surface effects on the calculation of nanoparticles' properties has led some researchers to consider creating a link between thermodynamic properties in nanoparticles and macrosystems (bulk systems). Many studies have shown a close relation between the Gibbs free energy of a particle and its thermodynamic properties. The Gibbs free energy can be calculated by Eq. (1) for a bulk system [35–37]:

$$\Delta G_b = \Delta H_b - T\Delta S_b \tag{1}$$

where ΔG = the Gibbs free energy change, ΔH = enthalpy change, ΔS = entropy change, and subtitle b refers to the bulk. In bulk materials, surface atoms have a minuscule role in the Gibbs free energy. However, in nanoscale materials, the effect of surface free energy is much higher than that of core free energy.

Some researchers, by using surface free energy as a link between classical thermodynamics and nanothermodynamics, have obtained thermodynamic properties of nanoparticles [38,39]. Surface energy is defined as the energy required to produce a new surface by breaking the bonds of a nanoparticle core. Some of these researchers have achieved the thermodynamic properties of nanoparticles in terms of surface tension [39]. However, surface tension calculation can be a serious challenge which has been looked into by other researchers with a more practical approach to engineering purposes. For example, Xiong et al. [25,26] obtained an equation for size-dependent surface free energy of nanoparticles expressed as Eq. (2):

$$\gamma = \gamma_0\left(1 - \frac{1.45d}{D}\right) \tag{2}$$

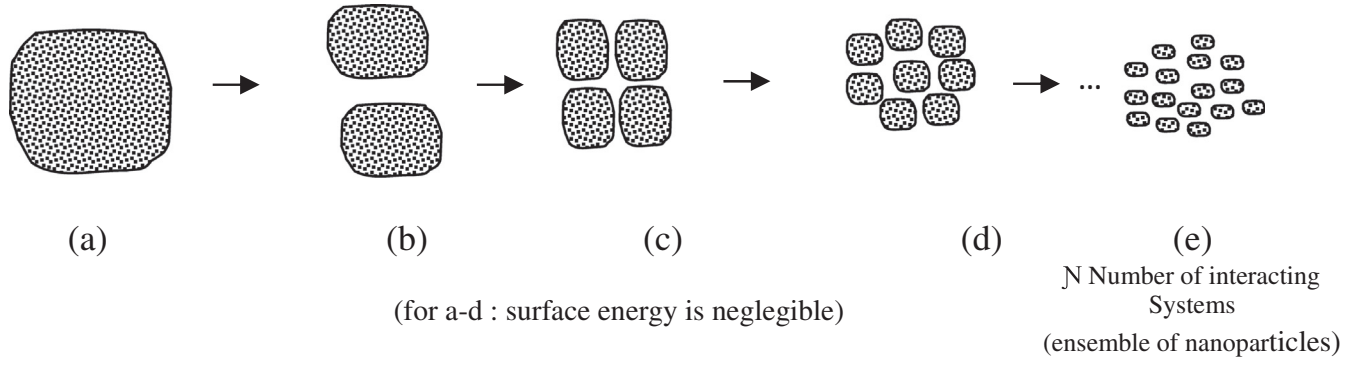

Fig. 1. Macro-system converts to surface free energy significant level (e state).

where γ_0 = bulk-free energy, d = atom diameter, and D = nanoparticle diameter. Moreover, γ, which is a function of temperature, changes linearly with respect to temperature. Eq. (3) shows this relation [33]:

$$\gamma_{(T)} = \gamma_0 + bT \tag{3}$$

where b is a negative constant for each material. The Gibbs free energy of nanomaterials can be obtained by summing the Gibbs free energy of bulk and surface free energy of nanomaterials, as shown by Eq. (4) [29]:

$$G_n = G_b + \frac{\gamma V_s N_A}{N} \tag{4}$$

where G_n and G_b are mole Gibbs free energy of nanomaterials and bulk, respectively; N_A is Avogadro constant; and $V_s = Ad = \pi D^2 d$ and $N = (D/d)^3$ denote the volume of the first layer of atoms and the total number of atoms in a nanoparticle, respectively.

Nanoparticles may contain a greater density of the unpaired electrons (broken bonds) than bulk particles; thus, their surface energy is more than that of bulk materials. Now a parameter is needed so that we can associate the thermodynamic properties and surface properties. Here we use cohesive energy.

Cohesive energy is defined as the energy required to divide materials into individual atoms. The relation between the cohesive energy of bulk and nanomaterials is given by Eq. (5) [26].

$$\frac{E_n}{E_b} = 1 - \frac{d}{D} \tag{5}$$

where E_b = bulk cohesive energy, E_n = nanoparticle cohesive energy, and D and d are the diameters of nanoparticle and atom, respectively. Most thermodynamic properties are functions of bonding atoms and thus cohesive energy. Therefore, researchers have sought to connect the thermodynamic properties of bulk and nano-scale materials like that of cohesive energy: $\frac{M_n}{M_b} = 1 - \frac{f(d)}{f(D)}$, where M_n and M_b are the same thermodynamic properties for nano-scale and bulk materials, respectively. Moreover, f(d) and f (D) are functions of atom diameter and nanoparticle diameter, respectively.

Eq. (6) gives the relation between the specific heat capacity of nanoparticles and bulk materials [33]:

$$\frac{C_{np}}{C_{bp}} = 1 - K\frac{d}{D} \tag{6}$$

where K = −0.5, D = nanoparticle diameter, and C_{np} and C_{bp} are specific heat capacities for nanoparticles and bulk, respectively.

These equations reveal that if D increases, then 1-(d/D) will increase; thus, E_n will increase because E_b is constant. The cohesive energy of materials reveals the strength of the chemical bonds; therefore, an increase in the cohesive energy is associated with an increase in the strength of the corresponding bond, which leads to an increase in most thermodynamic properties of nanoparticles.

3. Energy balance for nanoparticles

The general expression of the first law of thermodynamics (energy balance) at steady state- steady flow is shown as Eq. (7):

$$Q - W_s = \sum_{j=1}^{n} m_{e_j}\left(h_{e_j} + g z_{e_j} + \frac{1}{2} v_{e_j}^2\right) - \sum_{j=1}^{m} m_{i_j}\left(h_{i_j} + g z_{i_j} + \frac{1}{2} v_{i_j}^2\right) \tag{7}$$

where Q = heat, w_s = shaft work, m = mass, h = enthalpy, z = height, v = velocity, and subscripts i and e denote input and output, respectively. In most cases where kinetic and potential energy changes are negligible, Eq. (8) can be summarized by the following equation:

$$Q - W_S = \sum_j m_{ej} h_{e_j} - \sum_j m_{ij} h_{i_j} \tag{8}$$

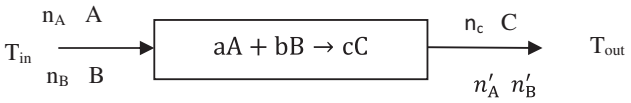

Fig. 2. A system with chemical reaction.

If there is no chemical reaction, the equation can be easily applied. Surely, the enthalpy of materials is needed to use this equation. Even if chemical reactions occur, the equation should apply so that its general form is preserved. For example, consider the system shown in Fig. 2:

Enthalpy change should now be written in such a way that the overall form of the first law does not change. For this purpose, enthalpy changes of the system are written as follows:

$$\Delta H = \Delta H_e - \Delta H_i \tag{9}$$

where ΔH_e and ΔH_i are the enthalpy differences between exit and input state with the reference state respectively that can be obtained using Eqs. (10) and (11).

$$\Delta H_i = \left(n_A h^\circ_{fA} + n_A \int_{T_0}^{T_{in}} c_{pA} dT\right) + \left(n_B h^\circ_{fB} + n_B \int_{T_0}^{T_{in}} c_{pB} dT\right) \tag{10}$$

$$\Delta H_e = \left(n'_A h^\circ_{fA} + n'_A \int_{T_0}^{T_{out}} c_{pA} dT\right) + \left(n'_B h^\circ_{fB} + n'_B \int_{T_0}^{T_{out}} c_{pB} dT\right) + \left(n_C h^\circ_{fC} + n_C \int_{T_0}^{T_{out}} c_{pC} dT\right) \tag{11}$$

where n' indicates the mole numbers of reactants in outlets. By substituting Eqs. (10) and (11) in Eq. (9), we will have:

$$\Rightarrow \Delta H = \left(n'_A h^\circ_{fA} + n'_B h^\circ_{fB} + n_C h^\circ_{fC} - n_A h^\circ_{fA} - n_B h^\circ_{fB}\right) + \int_{T_0}^{T_{out}} \left(n'_A c_{pA} + n'_B c_{pB} + n_C c_{pC}\right) dT - \int_{T_0}^{T_{in}} \left(n_A c_{pA} + n_B c_{pB}\right) dT \tag{12}$$

where h°_{fi} and c_{pi} are the standard enthalpy of formation and specific heat capacity for each component. Then, we will need information about enthalpy of formation and specific heat capacity of nanoparticles, both of which are challenging topics in nanothermodynamics.

For materials in macroscale, the enthalpy of formation is available. Fig. 3 introduces the standard formation enthalpy of nanoparticles.

Eq. (13) can be used for calculating enthalpy changes of nanoparticles.

$$\Delta h^\circ_{A_{bn}} = h^\circ_{fA_n} - h^\circ_{fA_b} \tag{13}$$

where $\Delta h^\circ_{A_{bn}}$ = enthalpy changes for formation of nanoparticles of A at standard conditions (T_0 & P_0), $h^\circ_{fA_b}$ = enthalpy of formation of A in bulk (macroscale) state, and $h^\circ_{fA_{bn}}$ = enthalpy of formation of nanoparticles of A which can be calculated by using the information about the process production of nanoparticles. Due to the method of

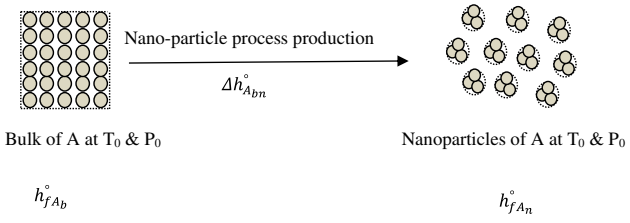

Fig. 3. Enthalpy change of formation of nanoparticles.

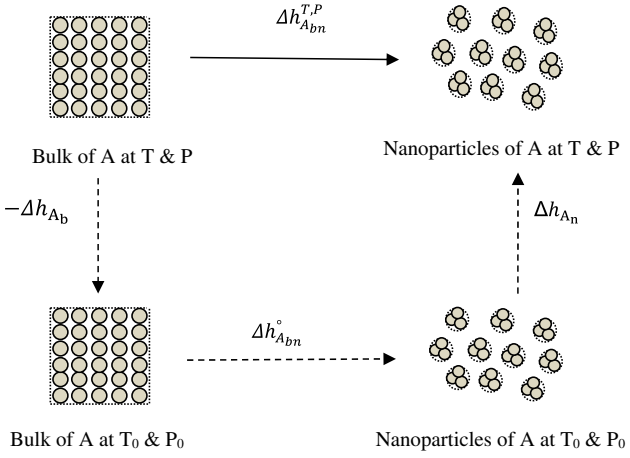

Fig. 4. Hypothetical thermodynamic path to calculate Δh_{Abn} at T & p.

production, if nanoparticles are produced at a different condition from the reference state ($T \neq T_0$ and $P \neq P_0$), then, the hypothetical thermodynamic path (dotted lines) shown in Fig. 4 can be used to calculate the enthalpy changes for formation of nanoparticles of A:

Since enthalpy is a state function, it can be written:

$$\Delta h^{T,P}_{A_{bn}} = -\Delta h_{A_b} + \Delta h^{\circ}_{A_{bn}} + \Delta h_{A_n} \tag{14}$$

where Δh_{A_b} and Δh_{A_n} are the enthalpy changes for bulk and nanoparticles of A, respectively, that can be calculated according to the production conditions of nanoparticles. For example, if pressure changes are not considerable and there is no phase change, then, $\Delta h_{A_b} = \int_{T_0}^{T} c_{p_{bA}} dT = c_{pm_{bA}}(T - T_0)$ and $\Delta h_{A_n} = \int_{T_0}^{T} c_{p_{nA}} dT = c_{pm_{nA}}(T - T_0)$. Moreover, $c_{pm_{bA}}$ and $c_{pm_{nA}}$ are average specific heat capacity of bulk and nanoparticles of A, respectively, between T and T_0.

4. Results and discussion

Now consider nanoparticles heated from T_1 to T_2, as shown in Fig. 5.

Specific heat capacity of nanoparticles, which is a function of temperature, size, and other previously mentioned variables, has its own complexity and can lead to an increase in computational

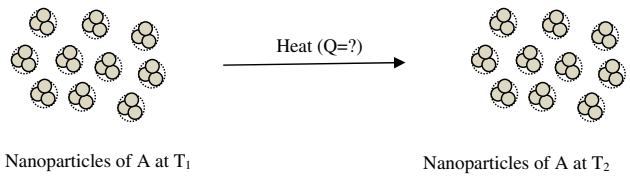

Fig. 5. Heating nanoparticles from T_1 to T_2.

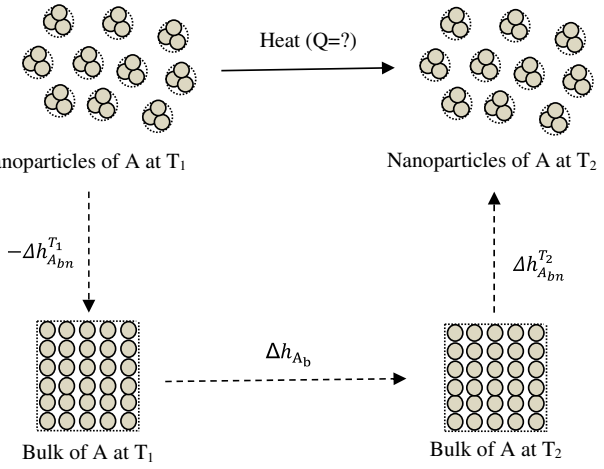

Fig. 6. Hypothetical thermodynamic path to calculate enthalpy changes for heating nanoparticles from T_1 to T_2.

error. Fig. 6 shows a hypothetical thermodynamic path to calculate the enthalpy changes for heating nanoparticles from T_1 to T_2.

Using Eq. (15), the heat can be calculated.

$$Q = \Delta H^{T_1 \to T_2}_{A_n} = -\Delta h^{T_1}_{A_{bn}} + \Delta h_{A_b} + \Delta h^{T_2}_{A_{bn}} \tag{15}$$

$\Delta h^{T_1}_{A_{bn}}$ and $\Delta h^{T_2}_{A_{bn}}$ are enthalpy changes for formation of nanoparticles of A at T_1 and T_2, respectively, that can be calculated using Eq. (14).

This method can be applied to any process, for example, the melting process shown in Fig. 7:

Then:

$$\Delta h^{m}_{A_n} = -\Delta h^{T_m}_{A_{bn}} + \Delta h^{m}_{A_b} \tag{16}$$

where $\Delta h^{m}_{A_n}$ = latent heat of melting of nanoparticles, $\Delta h^{T_m}_{A_{bn}}$ = enthalpy change to produce nanoparticles of A at T_m, and $\Delta h^{m}_{A_b}$ = latent heat of melting of bulk A.

Now consider that nanoparticles of A and B are introduced into a reactor and after a chemical reaction, produce substance C. Then:

$$Q_{Reaction} = -\left(\Delta h^{T}_{A_{bn}} + \Delta h^{T}_{B_{bn}}\right) + \Delta h^{T}_{Reaction} + \Delta h^{T}_{C_{bn}} \tag{17}$$

where $\Delta h^{T}_{A_{bn}}$, $\Delta h^{T}_{B_{bn}}$, and $\Delta h^{T}_{C_{bn}}$ = enthalpy changes for formation of A, B, and C nanoparticles, and $\Delta h^{T}_{Reaction}$ = enthalpy (heat) of reaction at

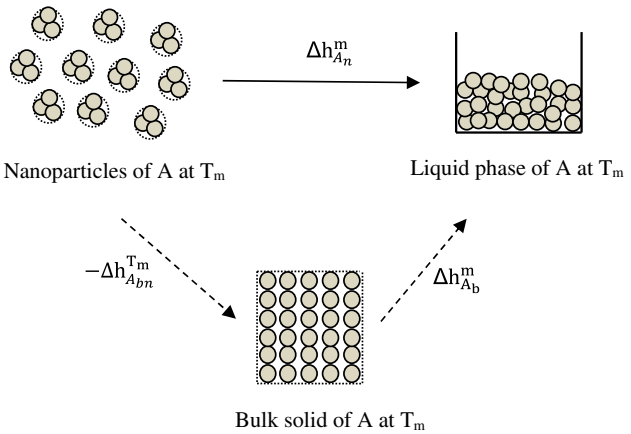

Fig. 7. Hypothetical thermodynamic path to calculate the latent heat of melting.

T in bulk system. Overall, for multi-reaction systems, the heat of the whole system can be calculated using Eq. (18):

$$Q_{\text{Reaction}} = -\sum_{\text{Reactants}} \Delta h_{bn}^{T_R} + \sum_{\text{Reactions}} \Delta h_R^T + \sum_{\text{Products}} \Delta h_{bn}^T \quad (18)$$

Now, the results of the model can be compared with the data reported by Xiong et al. [26] for silver nanoparticles with a diameter of 5 nm. The latent heat of melting and melting point of the nanoparticles are reported 7 $\frac{kJ}{mol}$ and 530 °C respectively. These two parameters for silver in bulk scale are 11.3 $\frac{kJ}{mol}$and 960 °C respectively. Using the difference in the heat of melting between these two states, the enthalpy changes for formation of silver nanoparticles with a diameter of 5 nm can be estimated at −2.8 $\frac{kJ}{mol}$. Average specific heat capacity of silver in solid and liquid state are 0.0264 *and* 0.0334 $\frac{kJ}{mol.K}$ respectively. Using Eq. (6), this parameter will be 0.0268 $\frac{kJ}{mol.K}$ for nanoparticles (d = 160 pm and D = 5 nm). Using these data, a mole of silver nanoparticles with a diameter of 5 nm and an initial temperature of 25 °C can be melted with 20.53 kJ of heat energy. Using the hypothetical thermodynamic path (the proposed model), this parameter can be estimated at 20.13 kJ. As can be seen, the difference is about 1.9% which indicates the high accuracy of the model.

Here, another application of the model is proposed. Rupp and Birringer [40] showed that to produce nanoparticles of SnO_2, mechnanochemical-thermal milling process can be carried out with a temperature of 600 °C. SnO_2 is produced by the given reaction which is shown in Eq. (19). Average size (diameter) of the produced nanoparticles is 28 nm. Using the energy balance around the reactor and the thermodynamic data of the reactants and products, standard enthalpy formation of the SnO_2 nanoparticles is estimated as $-560\frac{kJ}{mol}$ and the heat needed to melt the SnO_2 nanoparticles is calculated as $112\frac{kJ}{mol}$ using the model shown in Fig. 7.

$$SnCl_2 + Na_2CO_3 + 6NaCl + \frac{1}{2}O_2 \overset{600\,^{\circ}C}{\rightarrow} SnO_{2NP} + CO_2 \uparrow + 8NaCl \quad (19)$$

5. Conclusions

Rapid growth and increasing applications of nanoparticles technology require the performance of thermodynamic analysis with acceptable accuracy at nanoscales, which can be very useful in resolving design and optimization problems. The first step in thermodynamic calculations is to build energy balance. Classical thermodynamics relations are not applicable because of the size-dependent properties of nanoparticles. As a result, concepts of nanothermodynamics should be applied. However, functions of nanothermodynamics are more complex than those of macro-thermodynamics. A link between the thermodynamic properties in nanoparticles and macrosystems is needed to be created so as to establish energy balance available at a fixed diameter of nanoparticles. Since nanoparticle diameter changes are not known during the thermodynamic process, some simple thermodynamic paths have been established for systems containing nanoparticles for any process such as heating, cooling, phase-changing, and chemical reaction. Standard formation enthalpy of nanoparticles and standard enthalpy changes of nanoparticle formation have been defined and used for calculating the energy balance of nanoparticle systems.

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