Research Article

The Standard Molar Enthalpies of Formation of Nano-ZnO Particles with Different Morphologies

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The thermodynamic properties of nano-ZnO particles with different morphologies were studied. First, based on the measurements of XRD and SEM, the morphologies of the five nano-ZnO products were determined as sheet, block, sieve, column, and rod, and their particle size was about 40 nm. Then, based on a designed thermodynamic cycle, the standard molar enthalpies of formation ($\Delta_f H_m^\ominus$) of the nano-ZnO particles were determined by the RD496-2000 microcalorimeter, and they are $\Delta_f H_m^\ominus(\text{sheet}) = (-337.43 \pm 0.47) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{block}) = (-336.57 \pm 0.43) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{sieve}) = (-337.04 \pm 0.57) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{column}) = (-343.56 \pm 0.39) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_f H_m^\ominus(\text{rod}) = (-341.43 \pm 0.41) \text{ kJ} \cdot \text{mol}^{-1}$. The results show that the bigger difference of the morphologies of nano-ZnO, the bigger difference of the standard molar enthalpies of formation.

1. Introduction

Along with the development of nanotechnology, nano-ZnO becomes an important new species of material in the nanotechnology field [1–3]. Nano-ZnO is a kind of particles whose size is among 1–100 nm. Compared with conventional ZnO, nano-ZnO shows many special properties, such as surface effect and size effect. Because of the small size and large specific surface area, nano-ZnO exhibits unique properties of light, electricity, heat, and magnetic susceptibility. So it is widely used in many fields, such as ultraviolet absorption materials, piezoelectric materials, magnetic materials, pressure sensitive materials, and medicine [4–6]. It has many morphologies, such as rod, sheet, and needle ones. In present work, the preparation of nano-ZnO with different morphologies has been studied. It is the base to research the different functions of nano-ZnO with different morphologies in different fields. The thermodynamic properties are inherent properties of nano material. To find out the change rule of the thermodynamic properties of nano-ZnO with different morphologies and different sizes is helpful for its application in different fields [7, 8]. The “word” nanothermodynamics appeared formally in 2000 [9]. Then Giebultowicz classified nanothermodynamics to thermodynamics [10]. He thought

nanothermodynamics is a small-system thermodynamics, which created a new branch of thermodynamics. In 2001, Hill published a series of papers about nanothermodynamics in *Nano Letters* [11–13]. The prospects of nanothermodynamics and the contribution of it to the nanosystem were described in those papers. In 2010, a report about the entropy and enthalpy change of nanoparticle with different sizes was published [14]. But the study on the thermodynamic properties of nano-ZnO with different morphologies is absent.

In this work, we determined the standard molar enthalpies of solution of nano-ZnO particles with five different morphologies by RD496-2000 microcalorimeter and calculated the standard molar enthalpies of the nano-ZnO particles.

2. Experimental

2.1. Reagents and Instruments. Reagents: zinc oxide (ZnO) nanoparticles (J&K Scientific Ltd.), potassium bisulfate (AR, Beijing Jingqiu Chemical Co., Ltd.), potassium sulfate (AR, Beijing Beihua Fine Chemicals Co., Ltd.), potassium chloride (AR, Beijing Chemical Works), and zinc sulfate heptahydrate (AR, Beijing Jingqiu Chemical Co., Ltd.).

Instruments: microcalorimeter (RD496-2000, Mianyang Zhongwu Thermal Analysis Instruments Co., Ltd.), X-ray

TABLE 1: The enthalpy of solution of KCl in water at 298.15 K.

Reaction system	Number	m_{KCl} (g)	$V_{\text{H}_2\text{O}}$ (mL)	Q_1 (mJ)	$\Delta_f H_{\text{m}}^\ominus$ ($\text{kJ}\cdot\text{mol}^{-1}$)
$\text{KCl} \rightarrow \text{H}_2\text{O}$	1	0.0112	3.0	2640.34	17.56
	2	0.0112	3.0	2643.35	17.58
	3	0.0112	3.0	2642.60	17.58
	4	0.0112	3.0	2639.89	17.56
	5	0.0112	3.0	2641.10	17.57
	6	0.0112	3.0	2640.80	17.57
Average value				2641.35	17.57 ± 0.02

diffractometer (Beijing Purkinje General Instrument Co., Ltd.), and field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F, USA).

2.2. Characterization of Nano-ZnO. XRD and SEM analyses were done to determine the particle size and morphology of nano-ZnO products.

2.3. Determination of Standard Molar Enthalpy. The determination of enthalpy of formation was carried out with the RD496-2000 microcalorimeter [15]. To verify the reliability of the microcalorimeter, the molar enthalpy of solution of KCl in water was measured at 298.15 K, and the experimental data were shown in Table 1. The calculated molar enthalpy of solution of KCl was determined to be $17.57 \pm 0.02 \text{ kJ}\cdot\text{mol}^{-1}$, which was within $\pm 0.5\%$ of literature values ($17.56 \pm 0.21 \text{ kJ}\cdot\text{mol}^{-1}$) [16].

The standard enthalpies of formation of nano-ZnO particles were determined according to a designed chemical cycle shown in Figure 1.

In the experiment of calorimetry, 15 mL steel reservoir with two separable glass sleeves in it is used as sample cells, and the solid and liquid substances were put into the glass sleeves, respectively. Then the cells were put into calorimeter chamber at 298.15 K; when the baseline kept going steadily (the fluctuation is less than $\pm 0.00001 \text{ mV}$) the firing pin was triggered to break the glass sleeve and to make the sample mix with the solution. Then the chamber was kept to be at 298.15 K until the thermodynamic curve kept going parallel to the baseline with very small fluctuation which shows the completion of reaction. In this experiment, the solids were products ($0.0141 \text{ g ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $0.0086 \text{ g K}_2\text{SO}_4$) and reactants (0.0040 g ZnO and 0.0134 g KHSO_4) (there were 5 kinds of reactant systems by choosing different morphologies of nano-ZnO) showed in Figure 1. The liquid was 0.3000 g HCl solution ($0.26 \text{ mol}\cdot\text{L}^{-1}$). The products and reactants were mixed with the HCl solution separately. Then the heat of the reaction (Q_1 and Q_2) in the process was determined.

3. Result Analysis and Discussion

3.1. Particle Size and Morphology of Nano-ZnO. The XRD and SEM results of 5 kinds of nano-ZnO particles with different morphologies were shown in Figures 2 and 3. The sharp XRD peaks suggest that the products are highly crystallized and the morphology of each nanoparticle is uniform, and the

FIGURE 1: Designed thermochemical cycle of ZnO reaction system.

FIGURE 2: XRD spectra of 5 nano-ZnO particles with different morphologies (the serial numbers 1~5 were denoted by the ones of sheet, sieve, block, column, and rod morphology).

morphologies of the nano-ZnO can be seen clearly in the SEM pictures.

3.2. Standard Molar Enthalpy of Formation of Nano-ZnO. Standard molar enthalpy of formation of nano-ZnO can be obtained according to the designed thermodynamic cycle shown in Figure 1 and Hess law, and the detailed calculation was performed as formula (1). The experimental and calculated data were shown in Tables 2, 3, and 4

$$\begin{aligned}
 \Delta_f H_{\text{m}}^\ominus (\text{ZnO}) &= \Delta_f H_{\text{m}}^\ominus (\text{K}_2\text{SO}_4) \\
 &+ \Delta_f H_{\text{m}}^\ominus (\text{ZnSO}_4 \cdot 7\text{H}_2\text{O})
 \end{aligned}$$

FIGURE 3: SEM pictures of 5 nano-ZnO particles.

$$\begin{aligned}
 & + \Delta_r H_{m2}^{\ominus} - \Delta_r H_{m1}^{\ominus} \\
 & - 6\Delta_f H_m^{\ominus}(\text{H}_2\text{O}) - 2\Delta_f H_m^{\ominus}(\text{KHSO}_4) \\
 = & (-1414) \text{ kJ} \cdot \text{mol}^{-1} + (-3077.75) \text{ kJ} \cdot \text{mol}^{-1} \\
 & - 6 \times (-285.83 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1} \\
 & - 2 \times (-285.83 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1} \\
 & + \Delta_r H_{m2}^{\ominus} - \Delta_r H_{m1}^{\ominus} \\
 = & (-455.57 \pm 0.24) \text{ kJ} \cdot \text{mol}^{-1} \\
 & + \Delta_r H_{m2}^{\ominus} - \Delta_r H_{m1}^{\ominus}.
 \end{aligned} \tag{1}$$

According to (1) and the data in Table 2 to Table 4, the standard molar enthalpies of formation of the five kinds of

TABLE 2: Thermochemical data of reactant system of sheet nano-ZnO with particle size of 45 nm.

Reaction system	Number	m_{ZnO} (g)	m_{KHSO_4} (g)	Q_1 (mJ)	$\Delta_r H_{\text{ml}}^\ominus$ (kJ·mol ⁻¹)
ZnO + KHSO ₄ + HCl	1	0.0040	0.0134	-1720.67	-35.01
	2	0.0040	0.0134	-1734.42	-35.29
	3	0.0040	0.0134	-1739.00	-35.38
	4	0.0040	0.0134	-1766.67	-35.94
	5	0.0040	0.0134	-1722.82	-35.05
	6	0.0040	0.0134	-1745.87	-35.52
Average value				-1738.24	-35.37 ± 0.34

TABLE 3: The $\Delta_r H_{\text{ml}}^\ominus$ of reactants system of nano-ZnO with the morphology of sieve, block, column, and rod.

Reaction system	Number	Sieve (45 nm)	Block (45 nm)	Column (37 nm)	Rod (36 nm)
ZnO + KHSO ₄ + HCl $\Delta_r H_{\text{ml}}^\ominus$ (kJ·mol ⁻¹)	1	-35.69	-36.05	-29.66	-31.45
	2	-35.01	-36.44	-29.36	-31.03
	3	-35.90	-36.05	-29.12	-31.59
	4	-36.39	-36.12	-29.11	-31.18
	5	-35.52	-36.74	-29.02	-31.25
	6	-36.04	-36.01	-29.17	-31.70
Average value $\Delta_r H_{\text{ml}}^\ominus$ (kJ·mol ⁻¹)		-35.76 ± 0.47	-36.23 ± 0.29	-29.24 ± 0.24	-31.37 ± 0.26

TABLE 4: Thermochemical data of system products.

Reaction system	Number	$m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}}$ (g)	$m_{\text{K}_2\text{SO}_4}$ (g)	Q_2 (mJ)	$\Delta_r H_{\text{m}2}^\ominus$ (kJ·mol ⁻¹)
ZnSO ₄ ·7H ₂ O + K ₂ SO ₄ + HCl	1	0.0141	0.0086	4044.12	82.48
	2	0.0141	0.0086	4065.86	82.93
	3	0.0141	0.0086	4060.14	82.81
	4	0.0141	0.0086	4068.27	82.98
	5	0.0141	0.0086	4064.98	82.91
	6	0.0141	0.0086	4046.63	82.53
Average value				4058.33	82.77 ± 0.21

nano-ZnO with different morphologies were calculated as follows:

$$\Delta_f H_{\text{m}}^\ominus (\text{ZnO}) = (-455.57 \pm 0.24) \text{ kJ} \cdot \text{mol}^{-1}$$

$$+ \Delta_r H_{\text{m}2}^\ominus - \Delta_r H_{\text{m}1}^\ominus$$

$$= (-455.57 \pm 0.24) \text{ kJ} \cdot \text{mol}^{-1}$$

$$+ (88.77 \pm 0.21) \text{ kJ} \cdot \text{mol}^{-1} - \Delta_r H_{\text{m}1}^\ominus$$

$$= (-372.80 \pm 0.32) \text{ kJ} \cdot \text{mol}^{-1} - \Delta_r H_{\text{m}1}^\ominus$$

$$\Delta_f H_{\text{m}}^\ominus (\text{Sheet}) = (-372.80 \pm 0.32) \text{ kJ} \cdot \text{mol}^{-1}$$

$$- (-35.37 \pm 0.34) \text{ kJ} \cdot \text{mol}^{-1}$$

$$= (-337.43 \pm 0.47) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_{\text{m}}^\ominus (\text{Block}) = (-372.80 \pm 0.32) \text{ kJ} \cdot \text{mol}^{-1}$$

$$- (-36.23 \pm 0.29) \text{ kJ} \cdot \text{mol}^{-1}$$

$$= (-336.57 \pm 0.43) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_{\text{m}}^\ominus (\text{Sieve}) = (-372.80 \pm 0.32) \text{ kJ} \cdot \text{mol}^{-1}$$

$$- (-35.76 \pm 0.47) \text{ kJ} \cdot \text{mol}^{-1}$$

$$= (-337.04 \pm 0.57) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_{\text{m}}^\ominus (\text{Cloumn}) = (-372.80 \pm 0.32) \text{ kJ} \cdot \text{mol}^{-1}$$

$$- (-29.24 \pm 0.24) \text{ kJ} \cdot \text{mol}^{-1}$$

$$= (-343.56 \pm 0.39) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_{\text{m}}^\ominus (\text{Rob}) = (-372.80 \pm 0.32) \text{ kJ} \cdot \text{mol}^{-1}$$

$$- (-31.37 \pm 0.26) \text{ kJ} \cdot \text{mol}^{-1}$$

$$= (-341.43 \pm 0.41) \text{ kJ} \cdot \text{mol}^{-1}.$$

(2)

3.3. Discussions. The experimental data show that the value of standard molar enthalpy of formation of nano-ZnO is

larger than that of bulk ZnO [$(-350.46 \pm 0.27) \text{ kJ}\cdot\text{mol}^{-1}$] [17]. The morphologies of the sheet, sieve, and block nanoparticles are similar to each other by the observation of SEM figure and their particle sizes are all 45 nm. Their enthalpy values are $(-337.43 \pm 0.47) \text{ kJ}\cdot\text{mol}^{-1}$ (sheet), $(-336.56 \pm 0.43) \text{ kJ}\cdot\text{mol}^{-1}$ (block), and $(-337.04 \pm 0.57) \text{ kJ}\cdot\text{mol}^{-1}$ (sieve), which are close to each other. So the influence of the morphology and particle size on the standard molar enthalpy of formation is smaller for the three particles. According to literature 17 and literature 18, the standard molar enthalpy of formation of the same morphology of nano-ZnO decreases with the increase of the particle size. The particle sizes of nano-ZnO with morphologies of column and rod are 37 nm and 36 nm, which are smaller than the sheet, sieve, and block (45 nm) ones, so without considering the influence of the morphology of zinc oxide, the molar enthalpy values of nano-ZnO with morphology of column and rod should be bigger than the ones with morphologies of sheet, sieve, and block. But the experimental results are opposite [$\Delta_f H_m^\ominus(\text{column}) = (-343.56 \pm 0.39) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus(\text{rod}) = (-341.43 \pm 0.41) \text{ kJ}\cdot\text{mol}^{-1}$]. The reason is that their particle sizes are smaller than the sheet, sieve, and block nano-ZnO particles; the surface area of the nanoparticles with morphologies of column and rod is bigger, so they are more instable than the other ones. The more instable the nano-ZnO is, the bigger the Gibbs free energy is. According to the thermodynamic formula, $\Delta_f H_m^\ominus = \Delta_f G_m^\ominus + T\Delta_f S_m^\ominus$, the entropy of nano-ZnO must be considered. The irregularity of nano-ZnO with morphologies of column and rod is smaller, which determines its smaller entropy. So their entropy change (ΔS) becomes smaller in the generative process of nano-ZnO. In conclusion, the standard molar enthalpy of formation is associated with Gibbs free energy and entropy [18, 19]. This agrees well with the experimental results. According to the discussions above, it is concluded that the enthalpy values are influenced by the morphology and particle size. More experiments must be taken to obtain more influencing factors about the standard molar formation enthalpy of nano-ZnO.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] G. C. Fan, L. Sun, Z. Y. Huang, J. Y. Jiang, and Y. F. Li, "Thermodynamic functions of the grain-like ZnO nanostructures," *Materials Letters*, vol. 65, no. 17-18, pp. 2783–2785, 2011.
- [2] Z. L. Wang, "ZnO nanowire and nanobelt platform for nanotechnology," *Materials Science and Engineering R: Reports*, vol. 64, no. 3-4, pp. 33–71, 2009.
- [3] J. B. Tian, L. Liu, J. H. Qian, J. J. Xing, and J. L. Qin, "Research progress on preparing techniques and application of nano zinc oxide," *Journal of Chemical Industry & Engineering*, vol. 2, pp. 46–49, 2008.
- [4] C. Mejía-García, E. Díaz-Valdés, M. A. Ayala-Torres, J. Romero-Ibarra, and M. López-López, "Influence of the hydrothermal method growth parameters on the zinc oxide nanowires deposited on several substrates," *Journal of Nanomaterials*, vol. 2014, Article ID 609262, 9 pages, 2014.
- [5] Q. Xu, S. Zhou, and H. Schmidt, "Magnetic properties of ZnO nanopowders," *Journal of Alloys and Compounds*, vol. 487, no. 1-2, pp. 665–667, 2009.
- [6] D. G. Gao, Z. Chen, and J. Z. Ma, "Progress in preparation and application of nano ZnO in textile industry," *Printing*, vol. 24, pp. 43–49, 2012.
- [7] U. Pal and P. Santiago, "Controlling the morphology of ZnO nanostructures in a low-temperature hydrothermal process," *The Journal of Physical Chemistry B*, vol. 109, no. 32, pp. 15317–15321, 2005.
- [8] M.-P. Lu, J. Song, M.-Y. Lu et al., "Piezoelectric nanogenerator using p-type ZnO nanowire arrays," *Nano Letters*, vol. 9, no. 3, pp. 1223–1227, 2009.
- [9] R. V. Chamberlin, "Mean-field cluster model for the critical behaviour of ferromagnets," *Nature*, vol. 408, no. 6810, pp. 337–339, 2000.
- [10] T. Giebultowicz, "Breathing life into an old model," *Nature*, vol. 408, no. 6810, pp. 299–301, 2000.
- [11] T. L. Hill, "Perspective: nanothermodynamics," *Nano Letters*, vol. 1, no. 3, pp. 111–112, 2001.
- [12] T. L. Hill, "Extension of nanothermodynamics to include a one-dimensional surface excess," *Nano Letters*, vol. 1, no. 3, pp. 159–160, 2001.
- [13] T. L. Hill, "A different approach to nanothermodynamics," *Nano Letters*, vol. 1, no. 5, pp. 273–275, 2001.
- [14] G. Fan, Z. Huang, J. Chen, and Y. Ma, "Impact of size effects on the thermodynamic properties of zinc oxide micro/nano system," *Acta Chimica Sinica*, vol. 70, no. 7, pp. 938–942, 2012.
- [15] X. M. Wu, J. X. Huang, H. Y. Li, and W. Li, "Standard enthalpies of formation of rare earth l-proline chloride complexes $[\text{RE}(\text{l-pro})_2(\text{H}_2\text{O})_5]\text{Cl}_3$ (RE = Ho, Er)," *Journal of Chemical and Engineering Data*, vol. 56, no. 5, pp. 1991–1994, 2011.
- [16] R. Rychlý and V. Pekárek, "The use of potassium chloride and tris(hydroxymethyl)aminomethane as standard substances for solution calorimetry," *The Journal of Chemical Thermodynamics*, vol. 9, no. 4, pp. 391–396, 1977.
- [17] J. A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, NY, USA, 15th edition, 1998.
- [18] B. Marongiu, A. Piras, S. Porcedda, and E. Tuveri, "Excess enthalpies of chloroalkylbenzene + alkylbenzene mixtures," *Journal of Chemical and Engineering Data*, vol. 52, no. 5, pp. 1941–1945, 2007.
- [19] A. Gutterman, N. Rath, and J. Chickos, "Validation of the vaporization enthalpies of some simple aliphatic amides and their use in the evaluation of the vaporization enthalpy of valpromide and valnoctamide," *Journal of Chemical and Engineering Data*, vol. 58, no. 3, pp. 749–757, 2013.