CHEM. RES. CHINESE U.
2007, 23(5), 574—578
Article ID 1005-9040(2007)-05-574-05

Low-temperature Heat Capacities and Thermodynamic Properties of Hydrated Sodium Cupric Arsenate [$NaCuAsO_4 \cdot 1.5H_2O(s)$] *

CHEN Jing-tao[1,2], DI You-ying[1]**, TAN Zhi-cheng[3] and SUN Li-xian[3]

1. *College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng* 252059, *P. R. China*;
2. *Department of Chemistry, Shaanxi Educational College, Xi'an* 710061, *P. R. China*;
3. *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian* 116023, *P. R. China*

Received Mar. 19, 2007

Low-temperature heat capacities of the solid compound $NaCuAsO_4 \cdot 1.5H_2O(s)$ were measured using a precision automated adiabatic calorimeter over a temperature range of $T = 78$ K to $T = 390$ K. A dehydration process occurred in the temperature range of $T = 368$—374 K. The peak temperature of the dehydration was observed to be $T_D = (371.828 \pm 0.146)$ K by means of the heat-capacity measurement. The molar enthalpy and entropy of the dehydration were $\Delta_D H_m = (18.571 \pm 0.142)$ kJ/mol and $\Delta_D S_m = (49.946 \pm 0.415)$ J/(K · mol), respectively. The experimental values of heat capacities for the solid(Ⅰ) and the solid-liquid mixture(Ⅱ) were respectively fitted to two polynomial equations by the least square method. The smoothed values of the molar heat capacities and the fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K were tabulated at an interval of 5 K.

Keywords $NaCuAsO_4 \cdot 1.5H_2O(s)$; Adiabatic calorimetry; Heat capacity; Thermodynamic function; Dehydration process

Introduction

Previously, arsenates were used only as insecticides and antiseptics, which were mainly based on their toxicities. In the past several decades, it was found that the sort of compounds has excellent electric and optical properties and has been applied to the fields of semiconductor, laser, transparent ceramics techniques, and so on. With the development of modern material science, the importance of the arsenates will be greatly enhanced.

In 1963, Bhadraver[1] investigated the reactions of $CuSO_4(s)$ with $Na_3AsO_4(s)$ in aqueous solutions with different concentrations by means of the methods of temperature titration and conductivity titration, which yielded a blue-green precipitate, in which the molar ratio of Cu to AsO_4 [$n(Cu)/n(AsO_4)$] was 1∶1, and its composition was determined to be $NaCuAsO_4$ by chemical analysis. For the purpose of the thermochemical study of the sort of the compound, we have synthesized a new compound($NaCuAsO_4 \cdot 1.5H_2O$). The composition of the compound was determined by ignition loss-in-weight method and chemical analysis. Low-temperature heat capacities of the solid compound $NaCuAsO_4 \cdot 1.5H_2O(s)$ were measured using a precision automated adiabatic calorimeter over a temperature range of $T = 78$ K to $T = 390$ K.

Materials and Methods

1 Materials

All chemicals($CuSO_4 \cdot 5H_2O$, $Na_3AsO_4 \cdot 12H_2O$) used in these experiments were of analytical grade (Shanghai Reagent Factory), and were purified by means of recrystallization prior to use.

2 Methods

2.1 Preparation and Characterization of $NaCuAsO_4 \cdot 1.5H_2O$

The hydrated sodium cupric arsenate[$NaCuAsO_4 \cdot 1.5H_2O(s)$] was prepared in aqueous solution according to the method given in literature [1]. The precipitate of $NaCuAsO_4$ from aqueous solution was left for 48 h at ambient temperature so as to age-harden it, and then it was filtered, and washed for three times with twice distilled water. It was baked in an oven at about 318 K, and then dried in a vacuum oven with anhydrous calcium chloride used as the drying-agent at ambient temperature for two days up to a constant mass. The composition of the sample prepared was determined

* Supported by the National Natural Science Foundation of China(No. 20673050).

** To whom correspondence should be addressed. E-mail: yydi@lcu.edu.cn; diyouying@126.com

by chemical analysis and the ignition loss-in-weight method, respectively.

2.2 Ignition Loss-in-weight Method

The tested sample dried to a constant weight was put in a platinum pan, which was set in a pipe electric stove. The ignition was carried out under the atmosphere of the drying-up oxygen for more than 60 min at 973.15 K. The mole number of H_2O in 1 mole of $NaCuAsO_4$ sample can be derived according to the differences between the weights before and after the ignition, as shown in Table 1:

$$M(xH_2O) : M(NaCuAsO_4 \cdot xH_2O) = 10.72\% : 100\%$$

where, x is the mole number of H_2O in 1 mole of $NaCuAsO_4 \cdot xH_2O$, and M is the molecular weight. Thus, $x = 1.509 \approx 1.5$.

Table 1 Results of hydrated sodium cupric arsenate [$NaCuAsO_4 \cdot 1.5H_2O(s)$] obtained from the ignition loss-in-weight method

No.	m^* (Pre-ignition)/g	m(Post-ignition)/g	m(Loss-in-weight)/g	Percent of dehydration(%)
1	0.03227	0.02879	0.00348	10.78
2	0.04766	0.04260	0.00506	10.62
3	0.03270	0.02915	0.00355	10.75

* The mass of the sample. Mean: percent of dehydration = (10.72 ± 0.05)%.

2.3 Chemical Analysis

Since the given and matured synthetic method was used to prepare the compound, the key to determine its composition was to calculate the number of H_2O molecules in a molecule of the substance in accordance with the experimental result. The tested sample dried to a constant weight was dissolved in a 1.5 mol/L HCl solution. The content of arsenic in the sample molecule was measured by chemical titration and the number of H_2O molecules in a molecule of the substance can be derived in terms of the following equation:

$$M(xH_2O) : M(NaCuAsO_4 \cdot xH_2O) = 0.0024 : 0.0224$$

$x = 1.503 \approx 1.5$ can be calculated, as shown in Table 2.

Table 2 Results of hydrated sodium cupric arsenate [$NaCuAsO_4 \cdot 1.5H_2O(s)$] from chemical analysis

No.	$m^a(NaCuAsO_4 \cdot xH_2O)$/g]	$m^b(NaCuAsO_4)$/g	$m^c(H_2O)$/g
1	0.0224	0.0203	0.0021
2	0.0224	0.0196	0.0028
3	0.0224	0.0201	0.0023

a. The mass of the sample; *b*. the left mass after the ignition; *c*. the mass occupied by H_2O in the sample. Mean: $m(H_2O)$ = (0.0024 ± 0.0002) g.

In addition, the purity of the prepared sample was confirmed to be greater than 0.9990 (molar fraction) by chemical analysis.

2.4 Adiabatic Calorimetry

The low-temperature heat capacities were measured using a precision automatic adiabatic calorimeter over a temperature range of 78—390 K. The principle and structure of the adiabatic calorimeter are described in detail elsewhere[2,3]. It mainly consists of a sample cell, an inner adiabatic shield, an outer adiabatic shield, a platinum resistance thermometer, an electric heater, differential thermocouples, and a high vacuum Dewar can.

The mass of the sample, $NaCuAsO_4 \cdot 1.5H_2O(s)$, used in the heat capacity test was 2.1323 g, which was equivalent to 0.00845 mol, based on the molar mass of 252.4778 g/mol.

To confirm the accuracy and reliability of the calorimeter, the heat-capacity measurement for α-Al_2O_3 (a reference standard substance) was carried out over the same temperature range, 70 K ≤ T ≤ 390 K, as that of the sample measurement. The sample mass used for the calibration measurements was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, $M(Al_2O_3)$ = 101.9613 g/mol. The results indicate that the deviations of the experimental data from those of the smoothed curve in the same temperature range were within ±0.2%, while the inaccuracy was within ±0.3% as compared with those recommended from the former National Bureau of Standards[4].

Results and Discussion

1 Low-temperature Heat Capacities

All heat-capacity experimental results, plotted in Fig. 1 and listed in Table 3, show that two stable phases, solid I (T = 77—368 K) and solid-liquid mixture

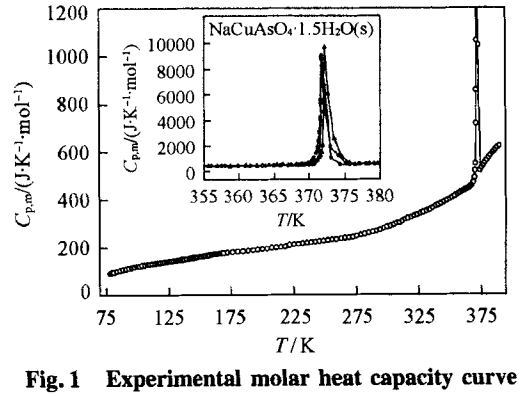

Fig. 1 Experimental molar heat capacity curve of solid compound $NaCuAsO_4 \cdot 1.5H_2O(s)$ *vs.* temperature

○ The first series of heat capacity measurements;
△ the second series of heat capacity measurements;
☆ the third series of heat capacity measurements.