

Short communication

Thermodynamic properties of hydrated sodium L-threonate $\text{Na}(\text{C}_4\text{H}_7\text{O}_5) \cdot \text{H}_2\text{O}(\text{s})$

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Abstract

Low-temperature heat capacities of the compound $\text{Na}(\text{C}_4\text{H}_7\text{O}_5) \cdot \text{H}_2\text{O}(\text{s})$ have been measured with an automated adiabatic calorimeter. A solid–solid phase transition and dehydration occur at 290–318 K and 367–373 K, respectively. The enthalpy and entropy of the solid–solid transition are $\Delta_{\text{trans}}H_{\text{m}} = (5.75 \pm 0.01) \text{ kJ mol}^{-1}$ and $\Delta_{\text{trans}}S_{\text{m}} = (18.47 \pm 0.02) \text{ J K}^{-1} \text{ mol}^{-1}$. The enthalpy and entropy of the dehydration are $\Delta_{\text{d}}H_{\text{m}} = (15.35 \pm 0.03) \text{ kJ mol}^{-1}$ and $\Delta_{\text{d}}S_{\text{m}} = (41.35 \pm 0.08) \text{ J K}^{-1} \text{ mol}^{-1}$. Experimental values of heat capacities for the solids (I and II) and the solid–liquid mixture (III) have been fitted to polynomial equations.

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1. Introduction

Until now, except for the combustion enthalpy of the compound [1], no report about heat capacity and thermodynamic properties of the hydrated sodium L-threonate, $\text{Na}(\text{C}_4\text{H}_7\text{O}_5) \cdot \text{H}_2\text{O}(\text{s})$, is found in the literature. In the present work, thermodynamic properties of the compound have been investigated by adiabatic calorimetry.

2. Experimental

2.1. Synthesis, purification and characterization of the sample

Preparation, purification and characterization of the sample were carried out according to the literature [1–3].

Chemical composition of the compound should be: $\text{Na}(\text{C}_4\text{H}_7\text{O}_5) \cdot \text{H}_2\text{O}(\text{s})$. The dehydration temperature was determined to be 97.60–99.50 °C by TG-DTG. The actual purity of

the sample was measured to be >0.9995 mass fraction, as indicated in literature [1].

2.2. Adiabatic calorimetry

The low-temperature heat capacities were measured with a precision automatic adiabatic calorimeter over the temperature range from 78 K to 390 K. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [4–6].

The mass of the sample used in heat capacity test was 2.4648 g, which was equivalent to 0.013996 mol, based on molar mass of 176.1013 g mol⁻¹.

To confirm the accuracy and reliability of the calorimeter, heat-capacity measurements for $\alpha\text{-Al}_2\text{O}_3$ (a reference standard substance) were made over the same temperature range, $70 \leq (T, \text{K}) \leq 373$, as that of the sample measurements. The sample mass used for the calibration measurements was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, $M(\text{Al}_2\text{O}_3) = 101.9613 \text{ g mol}^{-1}$. The results indicated that deviations of the experimental data from those of the smoothed curve in the same temperature range were within $\pm 0.2\%$, while the inaccuracy was within $\pm 0.3\%$, as compared with those recommended by the National Bureau of Standards [7].

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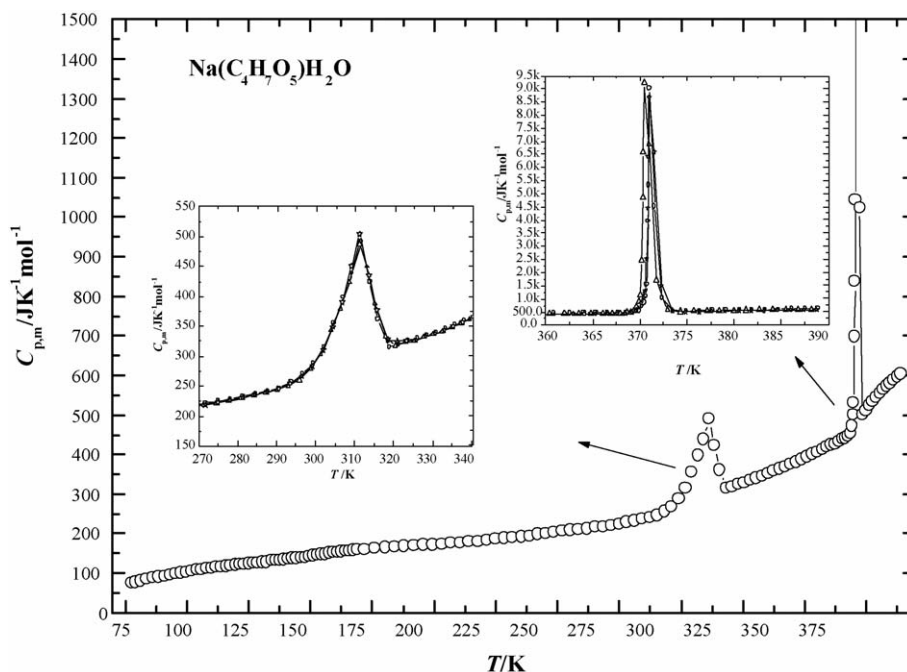


Fig. 1. The experimental molar heat capacity curve of the solid compound $\text{Na}(\text{C}_4\text{H}_7\text{O}_5)\cdot\text{H}_2\text{O}$. “○” represents the first series of measurements; “△” represents the second series of measurements; and “☆” represents the third series of heat capacity measurements.

3. Results and discussion

3.1. Low-temperature heat capacities

Heat-capacity results are listed in Table 1 (see supplementary data) and plotted in Fig. 1. Three stable phases, solid I ($T=77\text{--}290\text{ K}$), solid II ($T=318\text{--}367\text{ K}$) and solid–liquid mixture III ($T=373\text{--}390\text{ K}$), occurred in the heat capacity curve. The phase transition from solid I to solid II and the dehydration from the solid II to the solid–liquid mixture III were $290\text{--}318\text{ K}$ and $367\text{--}373\text{ K}$, respectively. The experimental values of the heat capacities for the three phases have been fitted to polynomial equations of the heat capacities against the reduced temperature by means of the least square method.

(1). For the solid I,

$$C_{p,m} (\text{J K}^{-1} \text{mol}^{-1}) = 165.9583 + 58.8162X - 36.4145X^2 + 20.9812X^3 + 73.1643X^4 + 4.2131X^5 - 45.8559X^6$$

where X is the reduced temperature, $X = (T(\text{K}) - 183.5)/106.5$. The above equation is valid from $T=77\text{ K}$ to 290 K , with an uncertainty of $\pm 0.30\%$.

(2). For the solid II,

$$C_{p,m} (\text{J K}^{-1} \text{mol}^{-1}) = 370.3304 + 65.5072X + 4.3099X^2 - 1.2155X^3 + 9.6006X^4 + 1.0958X^5 - 5.9555X^6$$

where $X = (T(\text{K}) - 342.5)/24.5$. The above equation is suitable from $T=318\text{ K}$ to 367 K , with an uncertainty of $\pm 0.20\%$.

(3). For the solid–liquid mixture III,

$$C_{p,m} (\text{J K}^{-1} \text{mol}^{-1}) = 561.41667 + 57.30077X - 12.48184X^2 - 1.36064X^3 + 4.22467X^4$$

where $X = (T(\text{K}) - 381.5)/8.5$. The above equation is useful from $T=373\text{ K}$ to 390 K , with an uncertainty of $\pm 0.20\%$.

Three series of heat-capacity experiments at $T=250\text{--}340\text{ K}$ were made to confirm the reversibility and repeatability of the transition from the solid I to solid II. Before each series of measurements, the sample was cooled from $T=340\text{ K}$ to 250 K by means of liquid nitrogen and introducing helium gas to the vacuum can of the calorimeter. The results of three series of repeated experiments are plotted in the inset of Fig. 1: introduced to the sample and cell when heating up from T_i to T_f ; \bar{H}_0 is the average heat capacity of empty cell between T_i and T_f ; $C_p(\text{s, I})$ is the heat capacity at T_i ; $C_p(\text{s, II})$ is the heat capacity at T_f ; n is the molar number of the sample.

The values of T_{trans} , $\Delta_{\text{trans}}H_m$ and $\Delta_{\text{trans}}S_m$ obtained from the three series of repeated heat-capacity measurements are $311.4 \pm 0.2\text{ K}$, $5.75 \pm 0.01\text{ kJ mol}^{-1}$ and $18.47 \pm 0.02\text{ J K}^{-1} \text{mol}^{-1}$.

Three series of heat-capacity experiments in the thermal decomposition region of the compound were carried out so that the reversibility and repeatability of the thermal decomposition were verified.

The peritectic point T_d of the sample was determined to be $371.27 \pm 0.08\text{ K}$ from the peak temperature of thermal decomposition based on the heat-capacity data. The different results in TG/DTG and heat capacity measurement arise from the differ-

ent environment in which the sample is placed: in TG/DTG it is in a stream of nitrogen gas and in the heat capacity measurement it is sealed in a vacuum-tight sample cell. The enthalpy of dehydration, $\Delta_d H_m$, was determined following the method described in the literature [6]. The entropy of dehydration was calculated by $\Delta_d S_m = \Delta_d H_m / T_d$.

The values of T_d , $\Delta_d H_m$ and $\Delta_d S_m$ obtained from the three series of repeated heat-capacity measurements are 371.27 ± 0.08 K, 15.35 ± 0.03 kJ mol⁻¹ and 41.35 ± 0.08 J K⁻¹ mol⁻¹.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.05.016.

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