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Heat capacity and thermodynamic functions of Na_2MoO_4 in the temperature range 0–300 K

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Abstract

The heat capacities of two samples of Na_2MoO_4, prepared by different methods, were measured at low temperatures. Obtained C_p^0 data differ significantly (from 3 to 7% at temperatures 50–300 K) from literature ones. Smoothed values of thermodynamic functions (heat capacity, entropy, change of enthalpy and Gibbs energy) were calculated in the temperature range 0–300 K. At temperature 298.15 K standard values are: $C_p^0(298.15\,\mathrm{K}) = 132.2 \pm 0.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $S^\circ(298.15\,\mathrm{K}) = 149.9 \pm 0.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $H^\circ(298.15\,\mathrm{K}) - H^\circ(0\,\mathrm{K}) = 23.82 \pm 0.02\,\mathrm{kJ\,mol^{-1}}$, $\Phi^0(298.15\,\mathrm{K}) = 69.98 \pm 0.24\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Refined values of sodium molybdate entropy of formation and Gibbs energy of formation are: $\Delta_f S^\circ(Na_2MoO_4, 298.15\,\mathrm{K}) = -391.39 \pm 0.60\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $\Delta_f G^\circ(Na_2MoO_4, 298.15\,\mathrm{K}) = -1351.0 \pm 1.3\,\mathrm{kJ\,mol^{-1}}$, relatively.

Keywords: Sodium molybdate; Calorimetry; Heat capacity; Thermodynamic functions

1. Introduction

Anhydrous sodium molybdate Na_2MoO_4 has four polymorphous modifications: cubic, hexagonal and two orthorhombic. Its lattice parameters are given in [1–4] and presented in Table 1. Structural phase transitions occur, in accordance with [5], at the following temperatures: crIV (cubic) → crIII (hexagonal), $T_{tr} = 724 \pm 7$ K; crIII (hexagonal) → crII (orthorhombic), $T_{tr} = 858 \pm 7$ K; crII (orthorhombic) → crI (orthorhombic), $T_{tr} = 908 \pm 11$ K. The last modification is stable up to melting point $T_m = 961 \pm 3$ K. Studies of sodium molybdate thermodynamic properties at high temperatures were carried out in [6–8]. In works [6,7] the measurements of enthalpy increment were conducted by drop-calorimetry. In [8] authors determined the temperature dependence of heat capacity by less accurate method of semi-quantitative thermal analysis. Heat capacity measurement of cubic Na_2MoO_4 at low temperatures was carried out by adiabatic calorimetry [9].

In the preliminary studies we found the dependence of thermal behavior of anhydrous Na_2MoO_4 at high temperatures on the method of its preparation. The goal of this study is to determine the influence of preparation method on the heat capacity and to obtain reliable thermodynamic functions of Na_2MoO_4.

2. Experimental

2.1. Preparation of samples

Sodium molybdate dihydrate $Na_2MoO_4{\cdot}2H_2O$ (pure for analysis, GOST 10931-74, main sample content >99.5 wt.%) was used as the starting substance. Anhydrous sodium molybdate was prepared by three different methods:

(1) Firing of $Na_2MoO_4{\cdot}2H_2O$ at 200 °C during 12 h (Sample 1),
(2) Firing of sample, prepared by method (1), at 300 °C during 48 h (Sample 2),
(3) Heating of sodium molybdate dihydrate up to melting, holding during 30 min and slow cooling to room temperature (Sample 3).

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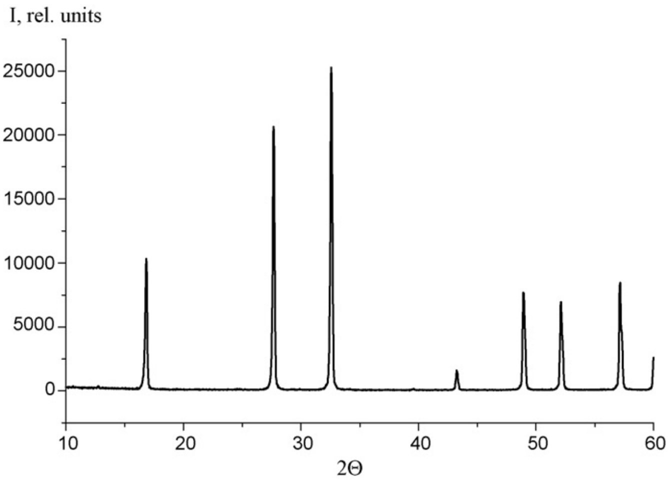

Fig. 1. X-ray pattern for Na_2MoO_4 Sample 1.

In accordance with the X-ray data all obtained samples have the cubic structure with the same lattice parameter as in reference value [1] (Table 1). In the X-ray patterns of Na_2MoO_4 sample, obtained by the above-described methods, no peaks of impurity phases were observed. As the example X-ray pattern for Sample 1 is plotted in Fig. 1.

2.2. *Heat capacity measurements*

For the study of Na_2MoO_4 heat capacity in the temperature range 12–300 K two similar adiabatic calorimetric setups BKT-3 (AVK), designed and produced in “TERMIS” Joint Stock Company (Mendeleyevo, Moscow region) were used. These setups are applied in the Chemistry Research Institute, Lobachevsky State University of Nizhni Novgorod and Kurnakov Institute of General and Inorganic Chemistry. Heat capacity measurements were carried out at automatic regime using the operating system with PC and unit of analogous control and data acquisition. Samples were loaded in thin-wall cylindrical titanium containers (inner volume 1 cm^3) with indium seals. The 100-Ohm Iron–Rhodium thermometers (ITS-90 scale) were used for temperature measurement. Sensitivity of thermometric circuit is 10^{-3} K, the absolute error of temperature measurement $\pm 10^{-3}$ K. Setups design and operating procedures were described in detail in [10]. The reliability of measuring procedure was tested by the heat capacity measurements of standard substances: special purity copper (OSCh 11-4), synthetic corundum and K-2 benzoic acid from the Metrological Institute of the State Standard Committee of Russian Federation in Nizhni Novgorod Chemistry Research Institute, and metrological K-1 benzoic acid in the Kurnakov Institute. The uncertainties of heat capacity measurements for both setups were ±2% at temperatures below 20 K, ±0.4% in the range 20–50 K and 0.2% in the range 40–350 K.

Containers were filled with helium (0.1 atm) after samples loading. Sample 1 was studied in Nizhni Novgorod Chemistry Research Institute (specimen mass is 1.0034 g) and Sample 2—in the Kurnakov Institute (specimen mass is 1.0306 g). Molecular mass of Na_2MoO_4 is equal to 205.9172 g mol^{-1} was taken from Ref. [11].

Smoothing of experimental heat capacity data and calculation of entropy, change of enthalpy and Gibbs energy was performed by the method described in [12]:

$$C_p^0(T) = a_0 T (C_v)^2 + n\left[\frac{1}{3}\sum_{j=1}^{3} a_j D_j\left(\frac{\theta_j}{T}\right) + a_4 E\left(\frac{\theta_E}{T}\right) + a_5 K\left(\frac{\theta_L}{T}, \frac{\theta_U}{T}\right)\right] \qquad (1)$$

where n is the number of atoms in molecule (for Na_2MoO_4 $n = 7$), θ_1, θ_2, θ_3, θ_E, θ_L, θ_U are characteristic temperatures; D and E are Debye and Einstein functions, K is Kieffer K-function [13] and a_0, a_1, a_2, a_3, a_4, a_5 are coefficients.

3. Results and discussion

Initially obtained low temperature (12.90–299.63 K) heat capacity data for Sample 1 differ significantly from published [9] (from 3 to 7% at temperatures 50–300 K) (Table 2, Fig. 2). That is why we checked the methods of anhydrous sodium molybdate preparation by the firing at different temperatures (Samples 1 and 2). In addition, Sample 3 was prepared by the melting and slow cooling as well as namely this method (earlier described in [14]) was used in [9]. And next we studied the heat capacity of Sample 2 in the range 80–300 K (Table 2). In the main part of studied temperature range results for both Samples differ not more than 0.4%, exceeding this value only in the side parts (to 0.65%) (Fig. 3). Measurements of Sample 3 heat capacity were carried out fragmentary in the range 230–280 K. This series lies moderately below (not more than 0.6%) the data for Samples 1 and 2.

By this means measurements of heat capacities of different samples in different setups allow to obtain the reproducible heat capacity data for sodium molybdate. The reason of discrepancy of our data and literature ones [9] is unclear.

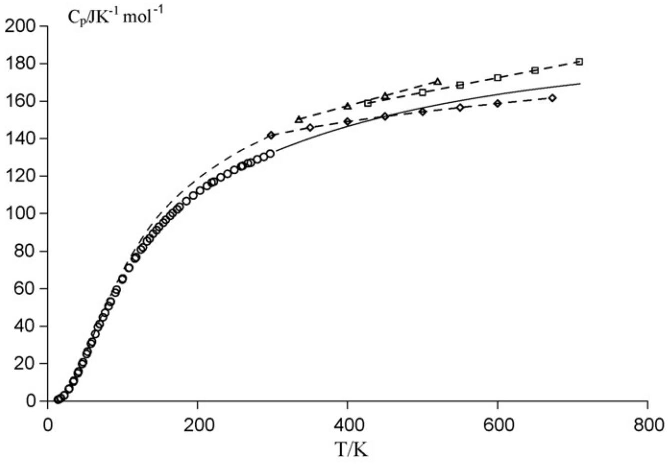

Fig. 2. Heat capacity of Na_2MoO_4: (◯) this work; dashed line [9]; solid line extrapolation of Eq. (1); (□) [6]; (△)[7]; (◊) [8].

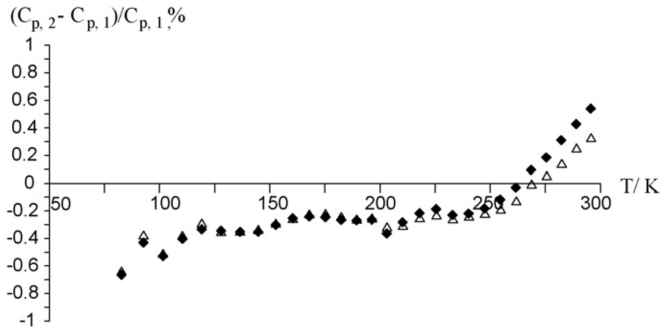

Fig. 3. Deviation of heat capacity for Sample 2 ($C_{p,2}$) from values for Sample 1 ($C_{p,1}$): (△) Sample 2, series 1; (⧫) Sample 2, series 2.

Heat capacity data for Sample 1, studied in the widest temperature region, were used to calculate thermodynamic functions of Na_2MoO_4. Experimental data were smoothed using Eq. (1). Values of $a_0, \ldots, a_5, \theta_1, \ldots, \theta_U$ are given in Table 3. Thermodynamic functions for the range 0–300 K are presented in Table 4. Values below 12.90 K were estimated using Eq. (1). At 298.15 K these values are: $C_p^0(298.15\,\text{K}) = 132.2 \pm 0.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, $S^\circ(298.15\,\text{K}) = 149.9 \pm 0.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, $H^\circ(298.15\,\text{K}) - H^\circ(0\,\text{K}) = 23.82 \pm 0.02\,\text{kJ}\,\text{mol}^{-1}$, $\Phi^\circ(298.15\,\text{K}) = 69.98 \pm 0.24\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. Errors of heat capacity, entropy, change of enthalpy and derived Gibbs energy were estimated by the procedure described in [15].

Comparison of our $C_p(T)$ data, extrapolated to high temperatures using Eq. (1), with literature ones (Fig. 2) shows that our heat capacity curve is parallel with curves from [6,7] and intersects curve [8] at 450 K.

Inasmuch our value of Na_2MoO_4 entropy $S^\circ(298.15\,\text{K})$ differ significantly from reference data [5] $(159.4 \pm 1.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})$ we recalculate the Gibbs energy of sodium molybdate formation. In the literature we found the following values of enthalpy of formation $\Delta_f H^\circ(Na_2MoO_4,\ 298.15\,\text{K})$: $1467.7 \pm 1.3\,\text{kJ}\,\text{mol}^{-1}$ [14] and $-1466.1\,\text{kJ}\,\text{mol}^{-1}$ [16]. In the next calculation we used data from [14] as well as the assessment of experimental errors was made in this work. Standard entropies for sodium, molybdenum and oxygen were taken from [5]: $S^\circ(\text{Na},\ 298.15\,\text{K}) = 51.30 \pm 0.21$; $S^\circ(\text{Mo},\ 298.15\,\text{K}) = 28.62 \pm 0.21$ and $S^\circ(O_2,\ 298.15\,\text{K}) = 205.036 \pm 0.33\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. From these data and our value of sodium molybdate entropy the standard formation entropy $\Delta_f S^\circ(Na_2MoO_4,\ 298.15\,\text{K}) = -391.39 \pm 0.60\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ were calculated. The standard Gibbs energy of formation from elements is equal to $\Delta_f G^\circ(Na_2MoO_4,\ 298.15\,\text{K}) = -1351.0 \pm 1.3\,\text{kJ}\,\text{mol}^{-1}$ $(-1355.1\,\text{kJ}\,\text{mol}^{-1}$ in [5]).

4. Conclusions

Corrected values of thermodynamic functions $C_p^0(298.15\,\text{K})$, $S^\circ(298.15\,\text{K})$, $H^\circ(298.15\,\text{K}) - H^\circ(0\,\text{K})$, $\Delta_f S^\circ(298.15\,\text{K})$, $\Delta_f G^\circ(298.15\,\text{K})$ of sodium molybdate at standard conditions were calculated based on the detail study of low temperature heat capacity.

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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.2007.07.005.

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