Phase transitions of some sulfur-containing ammonium salts

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A B S T R A C T

For the first time high-temperature polymorphic transition of ammonium sulfate $(NH_4)_2SO_4$ ($T_{pt} \sim 370$ °C) was experimentally recorded and characterized by differential scanning calorimetry. Phase transitions parameters of $(NH_4)_2SO_4$, of ammonium bisulfate NH_4HSO_4, of triammonium hydrogen disulfate $(NH_4)_3H(SO_4)_2$ and of ammonium sulfamate $NH_4SO_3NH_2$ were clarified. Method of determining the phase transitions parameters for thermally unstable substances, in particular for the triammonium hydrogen disulfate $(NH_4)_3H(SO_4)_2$, was developed and tested with the help of differential scanning calorimetry.

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1. Introduction

Sulfur-containing ammonium salts are widely applied in agriculture [1,2], construction [3] and metallurgical industry [4,5]. For the prediction of phase and chemical reactions involving these substances it is necessary to have information about the phase transitions parameters of the individual compounds and the conditions of their thermal stability.

Ammonium sulfate $(NH_4)_2SO_4$ (AS), ammonium bisulfate NH_4HSO_4 (AHS), triammonium hydrogen disulfate $(NH_4)_3H(SO_4)_2$ (A_3HS_2) and ammonium sulfamate $NH_4SO_3NH_2$ (ASM) were investigated in the present work by differential scanning calorimetry (DSC).

Literature data of phase transitions parameters for these substances are listed in Tables 1–5. These values are fragmentary and contradictory. In our opinion this fact is primarily due to incorrect experimental techniques performed in some previous studies.

Experimental technique [6,7] doesn't comply with the requirements for modern standards according to the practice of DSC method (for example, ISO11,357-1); data on the composition and purity of the samples are missing in these articles. In [9] temperature correction of AHS melting point was carried out by the extrapolated calibration curve to the high-temperature range. This inevitably reduced the accuracy of the results. Sample A_3HS_2

studied by the authors [11] probably contained an appreciable amount of AHS impurities. This is evidenced by splitting the peak near 140 °C in the DSC curve corresponding to the polymorphic transition (AHS melting point lies close to the temperature of A_3HS_2 phase transition (Tables 1 and 3). It is impossible to judge about the correctness of measurement techniques in [8,11–15] because experimental details are not described in publications. It is also not mentioned whether calibration of instruments was performed or not. Samples were characterized quantitatively only in [13,14].

In our opinion the results of [10,16–18] are considered reliable for the following reasons: (1) the test sample was sufficiently pure to be regarded as an individual phase; (2) before performing experiments calorimeters [10,17,18] and thermometer [16] were properly calibrated; (3) method of analysis [10,17,18] (adiabatic calorimetry) is one of the most reliable and accurate techniques for determining the phase transition parameters; (4) cooling rate (CR) was low (0.2 °C/min) near the ASM melting point [16]. This in most cases provides sufficient time for the system relaxation when external conditions change. The nature of the AHS melting point is mentioned in [8,19]. In [8] it is found that AHS melts without decomposition, however, in the later publication [19] the authors claim the contrary. According to [15] ASM melts congruently, but the authors haven't provided particular experimental facts confirming this hypothesis.

Polymorphic transition of AS taking place near −50 °C is the first order phase transition according to [18]. Significant difference between the values of the polymorphic transition enthalpy of AS (Table 5) [17,18] cannot be explained with experimental error,

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Table 1
Literature data of AHS melting parameters.

T_m, °C	$\Delta_m H°$, kJ/mol	Source
139, 147	10.9, 12.7	[6]
146	11.93, 12.67, 10.92	[7]
~150	–	[8]
146.9 ± 0.5	–	[9]
144.0 ± 0.5	14.3 ± 0.3	[10]

Table 3
Literature data of A_3HS_2 high-temperature polymorphic transition parameters.

T_{pt}, °C	$\Delta_{pt} H°$, kJ/mol	Source
138	1.84	[7]
130	–	[8]
141	–	[11]
139.8	4.3 ± 0.3	[12]

because the methodology and rigorous analysis of sample impurities allow to expect reliable results. The value of enthalpy of the AS phase transition (2219 cal/mol) adduced in [17] is probably expressed not in cal/mol but in J/mol. It is necessary to conduct additional experiments to eliminate contradictions on this issue.

AS high-temperature phase transition was originally predicted by Savada et al. [20]. There are a lot of studies investigating the AS properties in situation of elevated temperatures. The authors [21–23] detected anomalies on DC electrical conductivity curves and dielectric permittivity curves in the range by 130–150 °C. They decided that the reason of these anomalies was the AS phase transition. But later other scientists [24–26] showed that these anomalies were connected with the beginning of the AS thermal decomposition at the crystal surface and the sharp increase of electrical conductivity beyond 130–150 °C was caused by proton migration. According to [25] the AS high-temperature polymorphic transition occurs at significantly higher temperatures (~312 °C). This transition was not detected experimentally because the AS had a significant rate of decomposition above 235 °C at atmospheric pressure [6–8,27].

AHS melting parameters and ASM melting point can be considered reliable by the results of only one work [10,16] for each compound respectively. Therefore it is necessary to clarify values by independent methods. None of the values of the A_3HS_2 melting and high-temperature phase transition parameters (Tables 2, 3) as well as the heat of ASM fusion (Table 4) is reliable.

In this paper in order to prevent common methodological errors in determining the phase transitions parameters of the substances, we have adopted the following measures: (1) studied samples have been characterized for purity; (2) according to [6–31] AHS, A_3HS_2 and ASM decompose at the temperature close to their melting point, therefore an integral part of the work has to prove that the decomposition of compounds with the formation of gaseous products in the temperature range of melting point under the experimental conditions has not occurred. In this regard additional research of samples was conducted by thermogravimetric method (TGA) or by weighing samples before and after DSC measurements.

2. Experimental

2.1. Reagents

2.1.1. Ammonium sulfate AS
Dried commercial reagent AS (chemically pure) was used in the present study. The sample did not contain significant amounts of impurities; this fact was confirmed by consistency of the results of

measurements of polymorphic transition heat in the present study with the literature data (Table 5).

2.1.2. Ammonium bisulfate AHS
AHS was obtained by the method described in [32]. The elemental composition was determined by capillary electrophoresis. Quantity of ions in the analyzed solution was 10.6 ± 0.5 mg/L (theoretical value 10.6 mg/L), 57 ± 3 mg/L (theoretical value 56 mg/L) for the NH_4^+ and SO_4^{2-} respectively.

2.1.3. Triammonium hydrogen disulfate A_3HS_2
A_3HS_2 was obtained by annealing equimolar mixture AHS and AS at 150 °C in a dry inert atmosphere [28]. Optimal annealing time was chosen empirically. Firstly, the peaks corresponding to the phase transitions of the reagents (AS – 50 °C [17,18] and AHS – 10 °C [33]) were lacking on the DSC curve of annealed mixture. Secondly, forms of DSC curves were reproduced for samples with different annealing time (Fig. 1). The DSC curves of samples obtained by annealing for 45 and 60 min are identical. This fact indicated that the system had reached an equilibrium state and a single phase of A_3HS_2 was obtained.

2.1.4. Ammonium sulfamate ASM
Dried commercial reagent ASM (chemically pure) was used in the present study. Amount of ASM in the sample calculated according to the method ASTM E-928 by melting peak in the DSC curve was equal to 99.5 ± 0.2%.

2.2. Methods

Samples were weighed on an analytical balance A&D GH-202 with an accuracy of 10^{-2} mg.

Phase composition of the substances was determined on a diffractometer *STOE STADI-P* (Ge-monochromator, radiation $CuK_{\alpha 1}, \lambda = 1.54056$ Å, linear PSD) in transmission geometry. Angle 2θ was varied in the range from 10° to 100° in steps of 0.01°; the exposure time was 10 s per point. Samples were identified by comparing theoretical and experimental roentgenograms, by means of complex computer programs WinXPOW [34].

Capillary electrophoresis was performed on a device Capel-105M. The concentrations of solutions were selected on basis of the instrument sensitivity (10 mg/L–100 mg/L).

Experimental and computational procedures for DSC and TGA were performed according to standards ISO 11,357-1, ISO 11,358, ASTM E-928.

Specimens ($m = 1$–3 mg) were tested in aluminum crucibles ($V = 56$ mm³, $d = 6$ mm) with pierced lid (ratio of the orifice area to

Table 2
Literature data of A_3HS_2 melting parameters.

T_m, °C	$\Delta_m H°$, kJ/mol	Source
234	11.7	[6]
225	–	[7]
–	–	[8]
232	–	[11]

Table 4
Literature data of ASM melting parameters.

T_m, °C	$\Delta_m H°$, kJ/mol	Source
135	16.8	[6]
134	15.23	[7]
131	–	[13]
131	–	[14]
125	–	[15]
132.9 ± 0.2	–	[16]