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Thermodynamic properties of ammonium magnesium sulfate hexahydrate $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$

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ABSTRACT

Heat capacity of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ (CAS: 7785-18-4) was measured by low-temperature vacuum adiabatic calorimetry (AC) in the temperature range from 8 to 320 K. A linear combination of Einstein functions was applied to approximate obtained data on the heat capacity. Heat content and entropy of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ in the temperature range from 0 to 320 K were calculated from these data. The molar enthalpy of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ dissolution in water was measured at 298.15 K by solution calorimetry (SC). Standard entropy, enthalpy of formation and Gibbs energy formation of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ at 298.15 K were calculated from these results and literature data. Melting point of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ was evaluated at external pressure 10^4 kPa by differential scanning calorimetry (DSC). The reversible phase transition of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ crystal aggregates was recorded using three independent methods: DSC, AC and dielectric permittivity measurements. It was shown that this transition is absent for $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ having smaller crystal size obtained by grinding of the crystal aggregates in an agate mortar.

1. Introduction

Investigation of the thermodynamic properties of ammonium magnesium sulfate hexahydrate $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ can be of economic and environmental interest. $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ exists as a mineral boussingaultite in the Earth's crust [1]. $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ is the main intermediate that is formed during the process of serpentinite ores autopsy ($Mg_3Si_2O_5(OH)_4$) by ammonium sulfate as magnesium extractant [2].This process is used in the metallurgical industry [3]. Highfield et al. [2] showed that this process can also be applied in the cycle of carbon dioxide capture and storage in the form of magnesite. $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ and its anhydrous salt (efremovite $(NH_4)_2Mg_2(SO_4)_3$) also may find application in agriculture because they contain macro- and meso-elements (N, S, Mg) required for the normal plants growth. It should be noted that potassium-containing analogous of efremovite – langbeinite $(K)_2Mg_2(SO_4)_3$ is applied as a complex fertilizer in agriculture [4].

It is advisable to apply the methods of chemical thermodynamics and thermodynamic modeling for the determination of the optimal conditions of the various technological processes (temperature, external pressure, the amount of the reagents) having the highest yield of the target product and the lowest energy consumption. It is necessary to possess information on the thermodynamic functions of all compounds involved into the reaction, including intermediates, to calculate the equilibrium composition of the system at each stage of the process.

Data on the thermodynamic properties of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ is presented in the literature fragmentary. There is only information about the temperature and enthalpy of $(NH_4)_2Mg(SO_4)_2{\cdot}6.29H_2O$ melting determined by DSC at atmospheric pressure [5]. Voight et al. observed two peaks on the DSC curve and they related their to the incongruent melting of the compound. Both the peaks were characterized: $T^{I}_{m} = 397.2$ K, $\Delta H^{I}_{m}(T^{I}_{m}) = 41$ kJ·mol^{-1} and $T^{II}_{m} = 426.2$ K, $\Delta H^{II}_{m}(T^{II}_{m}) = 48$ kJ·mol^{-1}. The total c uncertainty of the enthalpy determination was 10%, but the uncertainty of the temperature determination wasn't specified in the text of the article. Moreover, it is not clear how the characteristic temperatures of the melting were determined, by the onset or by the extremum of the DSC peaks. In the literature there is information about theoretically predicted standard enthalpy of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ formation $\Delta_f H^0_{m,298.15} = -4270.3 \pm 26.0\ \mathrm{kJ \cdot mol^{-1}}$ [6]. On account of the above mentioned the aim of the present study was to obtain data on the thermodynamic properties of $(NH_4)_2Mg(SO_4)_2(H_2O)_6$: (1) measurements of the heat capacity $C_{p,m}(T)$ in a wide temperature range; (2) determination of the salt

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dissolution enthalpy in water; (3) calculation of the entropy $S^0_m(T)$ and heat content $(H^0_m(T) - H^0_m(0))$; (4) calculation of the standard enthalpy $\Delta_f H^0_m$, entropy $\Delta_f S^0_m$ and Gibbs energy of formation at 298.15 K; (5) estimation of the phase transition parameters.

2. Materials

2.1. Synthesis of samples

Commercial reagents without additional purification (characterization of the compounds is given in Table 1) and distilled water were used in the synthesis of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$.

On the basis of the data about solid–liquid phase equilibria in the system $MgSO_4$ – $(NH_4)_2SO_4$ – H_2O [7–10] the following conditions of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ synthesis were applied. Mixtures of 4.164 g $(NH_4)_2SO_4$, 7.780 g $MgSO_4{\cdot}7H_2O$ and 18.056 g H_2O were maintained under stirring at 338 ÷ 343 K until complete dissolution of salts. Reagents were weighted on an AXIS AG300 balance with an expanded uncertainty ($k = 2$) of the mass determination U = 0.001 g. Vessel with a solution was tightly closed and was kept at a room temperature for night. Crystals began to grow immediately during the cooling of the solution. Obtained crystals having the average dimensions about 1 cm (Fig. 1) were decanted from the mother liquor and were dried on air.

In the present study crystals of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ with the different morphology were investigated, namely, the crystal aggregates formed during the synthesis (Fig. 1) without additional preparation and these crystals milled into an agate mortar under a minimal mechanical influence (powdered crystals). Crushing of the crystal aggregates was carried out each time just before the experiment.

Table 1
Purities and sources of chemicals.

Chemical name	CAS number	Source	Purity/mass fraction
$(NH_4)_2SO_4$	7783-20-2	«Irea2000»	≥0.99
$MgSO_4{\cdot}7H_2O$	10034-99-8	«Merck»	≥0.995
$(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$	7785-18-4	Synthesis	≥0.998

Fig. 1. Crystal aggregates of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ obtained during the synthesis.

2.2. Characterization of sample

Crystals of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ obtained in the present study were subjected to chemical, DSC and XRD (X-ray diffraction) analysis. It was revealed that the crystals consist of a boussingaultite $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ single phase by comparison of theoretical [11] and experimental diffraction patterns (Fig. 2). It was shown that the crystals do not contain free ammonium sulfate, because the DSC peak corresponding to the phase transition of ammonium sulfate at 223 K [12] is absent on the experimental curve (Fig. 3). Magnesium Mg^{2+} in the sample was determined by the complexometric titration with EDTA. Ammonium NH_4^+ group quantity was evaluated by Sorensen formol titration. Sulfate SO_4^{2-} group quantity was determined as barium sulfate using gravimetry. Water content in the salt was evaluated by weighting of the substance before and after annealing in a furnace to constant weight of the sample at 373 K. Results of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ chemical analysis are summarized in Table 2.

3. Experimental methods

3.1. Low-temperature vacuum adiabatic calorimetry (AC)

The heat capacity of the $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ was measured with the help of a automated vacuum adiabatic calorimeter in

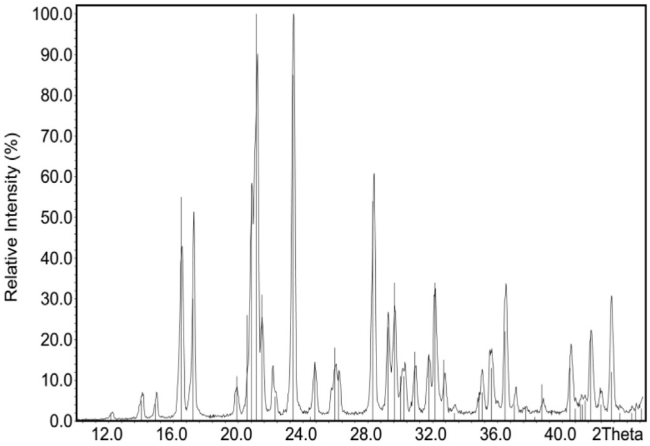

Fig. 2. Diffraction pattern of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ powdered crystals. Solid line – experimental data; strong peaks (vertical lines) – literature data (ICDD 35–771) [11].

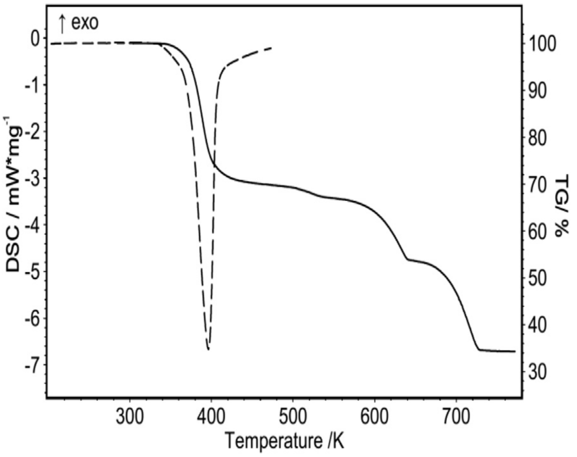

Fig. 3. TGA (solid line) and DSC (dashed line) curves of $(NH_4)_2Mg(SO_4)_2{\cdot}6H_2O$ powdered crystals. Heating rate is 10 K·min^{-1}.