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DSC STUDIES OF BINARY INORGANIC AMMONIUM COMPOUND SYSTEMS

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The thermal behaviour of the binary systems

HNH_2SO_3–$NH_4NH_2SO_3$ (I), HNH_2SO_3–$(NH_4)_2SO_4$ (II),
HNH_2SO_3–NH_4HSO_4 (III), $NH_4NH_2SO_3$–$(NH_4)_2SO_4$ (IV),
$NH_4NH_2SO_3$–NH_4HSO_4 (V), $(NH_4)_2SO_4$–NH_4HSO_4 (VI)

was investigated with a Du Pont Thermal Analyzer supplied with a DSC module. The corresponding single compounds and freshly prepared $(NH_4)_2S_2O_7$ were examined under the same conditions in preliminary experiments. The ΔH_f values of HNH_2SO_3, $NH_4NH_2SO_3$, $(NH_4)_2S_2O_7$ and $(NH_4)_2SO_4 \cdot NH_4HSO_4$ determined in the absence of air were 11.9, 16.8, 11.7 and 11.7 kJ/mole. Due to the moisture content of the atmosphere, an repeated heating in air the DSC curves showed more endothermic peaks than under air-free conditions. Exothermic additive reactions took place for binary systems (I) and (III), resulting in the formation of $(NH_4SO_3)_2NH$ and $(NH_4)_2S_2O_7$, respectively, and for systems (II) and (VI), producing a new compound on melting.

Thermoanalytical investigations on several inorganic salts containing NH_4^+, S and O have shown that the circumstances of the first thermal treatment (upper limit of temperature, heating rate, atmosphere, etc.) determine the course of decomposition, including the possibility for the salt to react with moisture or with its own decomposition products, etc. [1]. The present paper gives an account of an investigation of binary systems of inorganic ammonium compounds containing S and O. Previously, the corresponding single compounds were examined under the same conditions.

Experiments

Measurements were made with a Du Pont 990 Thermal Analyzer supplied with a DSC module. Analytical grade reagents were used: HNH_2SO_3, $(NH_4)_2SO_4$, $(NH_4)_2S_2O_8$ (Reanal, Hungary); $NH_4NH_2SO_3$ (Fluka AG, Buchs SG, Switzerland), and NH_4HSO_4 prepared from $(NH_4)_2SO_4$ with the calculated amount of H_2SO_4. The samples for the binary systems were weighed so as to correspond roughly to a 1:1 molar ratio.

Table 1 Single compounds and binary systems examined by DSC

Single compounds		HNH_2SO_3	$NH_4NH_2SO_3$	$(NH_4)_2SO_4$	NH_4HSO_4
Double systems*	I	HNH_2SO_3	$NH_4NH_2SO_3$		
	II**	HNH_2SO_3		$(NH_4)_2SO_4$	
	III	HNH_2SO_3			NH_4HSO_4
	IV		$NH_4NH_2SO_3$	$(NH_4)_2SO_4$	
	V		$NH_4NH_2SO_3$		NH_4HSO_4
	VI			$(NH_4)_2SO_4$	NH_4HSO_4
Supplementary experiment		$(NH_4)_2S_2O_8 \longrightarrow (NH_4)_2S_2O_7 + O_2/2$			(1)

*The binary systems contained the single compounds at 1:1 molar ratio

**$HNH_2SO_3 \cdot (NH_4)_2SO_4$ is used as a herbicide

Two series were prepared: (a) one for an open sample holder in static air atmosphere, (b) another for a hermetically sealed holder placed in the DSC cell flushed with argon. The upper limit of temperature was 523 K, the heating rate was 5 deg/min, and the sensitivities were 4.2 and 2.1 (mJ/sec)/in. When the samples had cooled to 373–353 K, the thermal treatment was repeated.

Qualitative differences between the first and the second DSC curves were striking. These were studied by measuring the endothermic heat effects.

The following compounds and systems were examined (Table 1).

Results and discussion

Single compounds

Sulfamic acid, HNH_2SO_3

(a) According to literature data, sulfamic acid melts at 478 K with decomposition [2, 3]. In moist air it decomposes through $(NH_4)_2S_2O_7$; the process is preceded by the formation of NH_4HSO_4 as follows:

$$HNH_2SO_3 + H_2O \longrightarrow NH_4HSO_4 \qquad (2)$$

$$2\ NH_4HSO_4 \longrightarrow (NH_4)_2S_2O_7 + H_2O \qquad (3)$$

Our DSC curves showed that the melting of HNH_2SO_3 at 479 K *in air* is preceded by an exothermic peak at 443–473 K (Fig. 1a); this presumably indicates reaction (2). This assumption is supported by the fact that the DSC curve for the subsequent

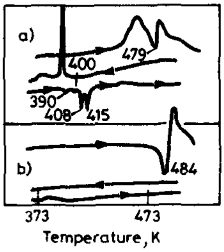

Fig. 1 Cyclic DSC curves of HNH_2SO_3 (a) in air (5.05 mg), (b) in airtight conditions (5.43 mg)

heating of the HNH_2SO_3 sample was very similar to the DSC curve for the second heating of NH_4HSO_4 (cf. Figs 1a and 4a). From the increase in weight of the HNH_2SO_3 sample after the DSC experiment, it may be assumed that the bulk of the HNH_2SO_3 was converted to NH_4HSO_4. The unchanged HNH_2SO_3 underwent immediate exothermic decomposition after melting.

(b) *In a closed system,* sulfamic acid melted at 484 K, and total exothermic decomposition then took place (Fig. 1b). The average value of $\Delta H_{f\,HNH_2SO_3}$ was 11.9 kJ/mole; these data are presumably influenced (decreased) by the immediate decomposition of HNH_2SO_3 after its melting. As there were no literature data on the melting enthalpy of sulfamic acid, and our parallel experiments were in good agreement with one another, this value was used in our further calculations.

Ammonium sulfamate, $NH_4NH_2SO_3$

(a) *In air,* the melting point of $NH_4NH_2SO_3$ is 406 K. $\Delta H_{f\,NH_4NH_2SO_3}$ is 15.2 kJ/mole [1]. From the present investigations it is clear that HNH_2SO_3 is produced during the heating of $NH_4NH_2SO_3$, in accordance with the following equations:

$$2\ NH_4NH_2SO_3 \longrightarrow (NH_4SO_3)_2NH + NH_3 \qquad (4)$$

$$(NH_4SO_3)_2NH + H_2O \longrightarrow HNH_2SO_3 + (NH_4)_2SO_4 \qquad (5)$$

$$2\ NH_4NH_2SO_3 + H_2O \longrightarrow HNH_2SO_3 + (NH_4)_2SO_4 + NH_3 \qquad (6)$$

(*One procedure for the manufacture of HNH_2SO_3 is based on the hydrolysis of* $(NH_4SO_3)_2NH$ with an aqueous solution of H_2SO_4.) The resulting exothermic enthalpy changes indicated that formation of a new compound began. On the next heating, the melting point of HNH_2SO_3 appeared (Fig. 2a). In parallel with the above reactions (when the upper limit of temperature was 523 K), other processes also took place, e.g. the partial degradation of HNH_2SO_3 and $(NH_4)_2SO_4$.

(b) *In an airtight* sample holder, the melting point of $NH_4NH_2SO_3$ was 408 K, and $\Delta H_{f\,NH_4NH_2SO_3}$ was 16.8 kJ/mole (Fig. 2b). In the absence of water there was no exothermic reaction and HNH_2SO_3 was not produced.

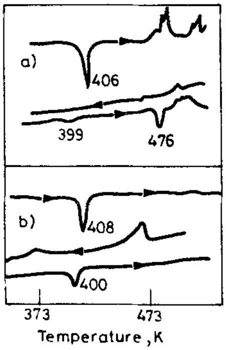

Fig. 2 Cyclic DSC curves of $NH_4NH_2SO_3$ (a) in air (4.49 mg), (b) in airtight conditions (4.73 mg)

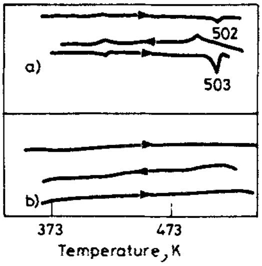

Fig. 3 Cyclic DSC curves of $(NH_4)_2SO_4$ (a) in air (5.43 mg), (b) in airtight conditions (6.87 mg)

Ammonium sulfate, $(NH_4)_2SO_4$

(a) When ammonium sulfate was heated *in static air,* the incongruent melting point of $(NH_4)_2SO_4 \cdot NH_4HSO_4$ (4) appeared at 502 K. On the next heating it was enhanced significantly as a result of further decomposition of $(NH_4)_2SO_4$ (Fig. 3a). The polymorphic transition of $(NH_4)_2SO_4 \cdot NH_4HSO_4$ gave an endothermic peak at 412 K in the DSC curve.

(b) *In a closed* sample holder, no enthalpy change occurred (Fig. 3b).

Ammonium hydrogen sulfate, NH_4HSO_4

(a) *In air,* the melting point of NH_4HSO_4 is 418 K. $\Delta H_{f NH_4HSO_4}$ is 10.9 kJ/mole [1]. After thermal treatment to 523 K as upper limit and subsequent cooling, frequently more than one small endothermic peak appeared in the DSC curves for the repeated heating cycle (Fig. 4a).

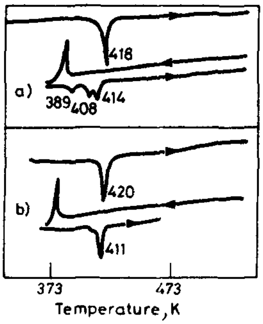

Fig. 4 Cyclic DSC curves of NH_4HSO_4 (a) in air (4.99 mg), (b) in airtight conditions (5.23 mg)

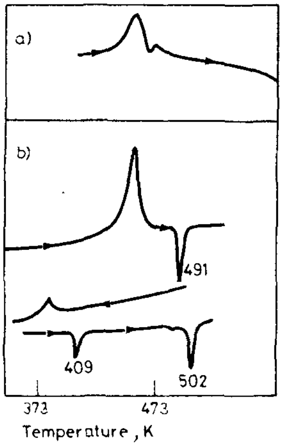

Fig. 5 Cyclic DSC curves of $(NH_4)_2S_2O_8$ (a) in air, (b) in airtight conditions (2.07 mg)

(b) *In an airtight* sample holder, the melting point of NH_4HSO_4 is 420 K. $\Delta H_{f NH_4HSO_4}$ is 12.7 kJ/mole [1]. As long as water is absent, there are fewer anomalies (Fig. 4b).

Ammonium pyrosulfate, $(NH_4)_2S_2O_7$ (supplementary experiments)

During the thermal decomposition of NH_4HSO_4, $(NH_4)_2S_2O_7$ may be formed as an intermediate. To study its thermal behaviour, we prepared $(NH_4)_2S_2O_7$ from $(NH_4)_2S_2O_8$ "in situ nascendi" [5].

(a) *In air,* after an intense exothermic reaction (Fig. 5a) the freshly formed $(NH_4)_2S_2O_7$ decomposed immediately according to Eq. (1) without melting.

(b) *In a closed* system, $(NH_4)_2S_2O_7$ melted at 491 K after its formation (Fig. 5b). $\Delta H_{f(NH_4)_2S_2O_7}$ is 11.7 kJ/mole. When the upper limit of the first heating was 523 K,

$(NH_4)_2S_2O_7$ decomposed with $(NH_4)_2SO_4$ formation [6]; however, the latter partly disintegrated to NH_4HSO_4. This is proved by the fact that, on subsequent heating, the characteristic thermal signs of $(NH_4)_2SO_4 \cdot NH_4HSO_4$ appeared, viz. its polymorphic transformation at 409 K and the incongruent melting point at 502 K.

Binary systems

HNH_2SO_3–$NH_4NH_2SO_3$ (I)

(a) The melting point of $NH_4NH_2SO_3$ *in air* (Fig. 6a$_1$ and 6a$_2$) is decreased in the presence of a large amount of HNH_2SO_3. In the melt of $NH_4NH_2SO_3$ an exothermic additive reaction occurs at 413–423 K [7]:

$$HNH_2SO_3 + NH_4NH_2SO_3 \longrightarrow (NH_4SO_3)_2NH \qquad (7)$$

The by-product is $(NH_4)_2SO_4$ (see Eq. (5)), which does not take part in the above reaction. The second heating curve shows NH_4HSO_4 formation (see Eq. (2)), as evidenced partly by the endothermic peaks at 390–412 K, and partly by $(NH_4)_2SO_4 \cdot NH_4HSO_4$ formation during thermal treatment. It was striking that, in the presence of $NH_4NH_2SO_3$, HNH_2SO_3 did not decompose quantitatively, in contrast with when it was heated alone in air. The repeated DSC curve led to a calculated amount of HNH_2SO_3 of about 50% of the original HNH_2SO_3 sample when sulfamic acid was in excess (Fig. 6a$_1$).

When $NH_4NH_2SO_3$ was in excess, the experimental amount of HNH_2SO_3 was about 80% of the weighed one (Fig. 6a$_2$).

(b) *In* a hermetically *closed* sample holder, the first heating curve was very similar to the DSC curves of the HNH_2SO_3–$NH_4NH_2SO_3$ system in air, but on subsequent thermal treatment there was no change of enthalpy (Fig. 6b). Obviously, in the absence of air (and hence in the absence of moisture) the following reaction took place:

$$(NH_4SO_3)_2NH \longrightarrow 2\ HNH_2SO_3 + NH_3 \qquad (8)$$

with subsequent decomposition of sulfamic acid.

HNH_2SO_3–$(NH_4)_2SO_4$ (II)

(a) *In air,* the melting point of the HNH_2SO_3–$(NH_4)_2SO_4$ system (with a molar ratio of about 1:1) is 438 K (Fig. 7a). This is in good agreement with the literature data on the melting point of the double salt $HNH_2SO_3 \cdot (NH_4)_2SO_4$ [8, 9]. After melting, an exothermic reaction took place. However, the present findings indicate that the components reacted with one another, and the reverse reaction of that described in Eq. (5) took place. This conclusion is supported by the fact that the enthalpy of melting of $HNH_2SO_3 \cdot (NH_4)_2SO_4$ was not reproducible (probably due to a reaction during the melting process), and by the finding that the determined amount of HNH_2SO_3 was far below the real one. Further, the reaction of sulfamic

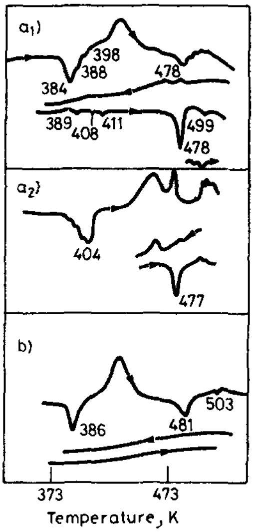

Fig. 6 Cyclic DSC curves of the systems: (a_1) in air HNH_2SO_3 (5.77 mg) $NH_4NH_2SO_3$ (5.17 mg) molar ratio 1.31 : 1.00, (a_2) in air HNH_2SO_3 (4.69 mg) $NH_4NH_2SO_3$ (6.18 mg) molar ratio 1.00 : 1.12, (b) in airtight conditions HNH_2SO_3 (5.63 mg) $NH_4NH_2SO_3$ (6.49 mg) molar ratio 1.02 : 1.00

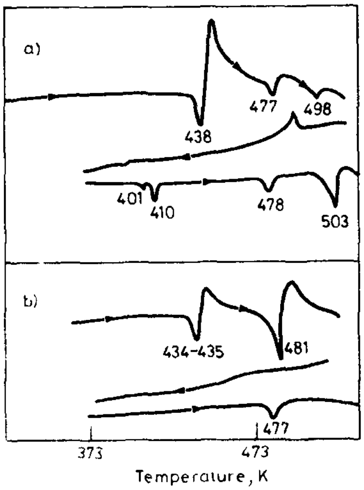

Fig. 7 Cyclic DSC curves of the systems (a) in air HNH_2SO_3 (4.86 mg) $(NH_4)_2SO_4$ (5.91 mg) molar ratio 1.12 : 1.00, (b_1) in airtight conditions HNH_2SO_3 (5.26 mg) $(NH_4)_2SO_4$ (6.50 mg) molar ratio 1.10 : 1.00, (b_2) in airtight conditions HNH_2SO_3 (5.31 mg) $(NH_4)_2SO_4$ (6.86 mg) molar ratio 1.05 : 1.00

acid with moisture from the air resulted in NH_4HSO_4. The endothermic peak at 498 K relates to the incongruent melting point of $(NH_4)_2SO_4 \cdot NH_4HSO_4$ formed during the process. In the next heating curve, the endotherm of the polymorphic transition of the double salt also appeared and the melting endotherm increased.

(b) *In the absence of air,* the double salt $HNH_2SO_3 \cdot (NH_4)_2SO_4$ melted at 434–435 K; this was followed by an exothermic peak less than in air, then by the melting endotherm of HNH_2SO_3 at 481 K, and finally by decomposition (Fig. 7b). It was interesting that on subsequent heating the melting point of sulfamic acid appeared, in spite of the fact that during the thermal treatment in the hermetically sealed sample holder HNH_2SO_3 decomposed quantitatively. This means that different reactions take place in the presence of $(NH_4)_2SO_4$.

HNH_2SO_3–NH_4HSO_4 (III)

(a) The melting point of NH_4HSO_4 *in air* decreased to 410 K in the presence of a large amount of HNH_2SO_3. In the melt the two compounds reacted with each other with the release of heat (Fig. 8a). The first heating curve indicated that some $(NH_4)_2S_2O_7$ was produced (cf. Figs 5a and 8a):

$$HNH_2SO_3 + NH_4HSO_4 \longrightarrow (NH_4)_2S_2O_7 \qquad (9)$$

The presence of unreacted HNH_2SO_3 was indicated only by a slight endothermic slope. The consecutive heating curve was very similar to the second heating curve of HNH_2SO_3 and NH_4HSO_4 (cf. Figs 1a, 4a and 8a).

(b) The first curve for the two salts heated together was similar to that obtained in air of *under air-free conditions:* only the melting endotherm of sulfamic acid was more marked (Fig. 8b). In the absence of water, $(NH_4)_2S_2O_7$ decomposed with $(NH_4)_2SO_4$ production. On the next heating, the melting endotherm at 497 K involved the melting of both $(NH_4)_2S_2O_7$ and $(NH_4)_2SO_4 \cdot NH_4HSO_4$. The curve for the third heating cycle of this series had a similar appearance to the curve for $(NH_4)_2S_2O_7$ heated under air-free conditions (Figs 5b and 8b).

$NH_4NH_2SO_3$–$(NH_4)_2SO_4$ (IV)

(a) The thermal behaviour of $NH_4NH_2SO_3$ determined the behaviour of this system *in air;* the curves were very similar to the curves for $NH_4NH_2SO_3$ (cf. Figs 2a and 9a).

(b) When the investigations were made in a closed sample holder, the courses of the cycles were roughly the same as in the case of $NH_4NH_2SO_3$ under *air-free* circumstances (Fig. 9b).

$NH_4NH_2SO_3$–NH_4HSO_4 (V)

(a) When the components were present in a 1:1 molar ratio *in air,* their melting points did not appear separately (Fig. 10a). The melting was followed by a rapid

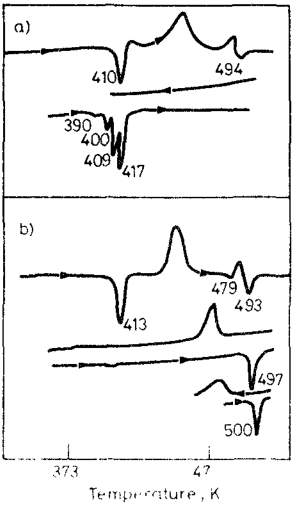

Fig. 8 Cyclic DSC curves of the systems (a) in air HNH_2SO_3 (5.32 mg) NH_4HSO_4 (5.62 mg) molar ratio 1.12:1.00, (b) in airtight conditions HNH_2SO_3 (4.62 mg) NH_4HSO_4 (5.17 mg) molar ratio 1.06:1.00

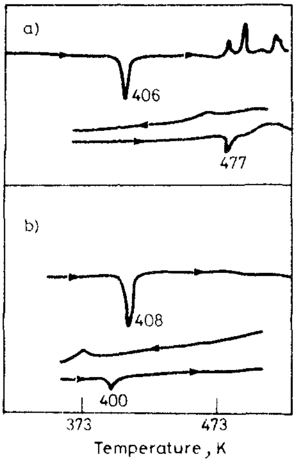

Fig. 9 Cyclic DSC curves of the systems (a) in air $NH_4NH_2SO_3$ (4.52 mg) $(NH_4)_2SO_4$ (5.19 mg) molar ratio 1.00:1.00, (b) in airtight conditions $NH_4NH_2SO_3$ (5.91 mg) $(NH_4)_2SO_4$ (7.68 mg) molar ratio 1.00:1.12

exothermic deflection, which quickly decreased at 453 K, and at 477 an endothermic peak represented the formation of HNH_2SO_3. The two salts reacted in the melt with heat liberation, in accordance with the following equation:

$$NH_4NH_2SO_3 + NH_4HSO_4 \longrightarrow HNH_2SO_3 + (NH_4)_2SO_4 \qquad (10)$$

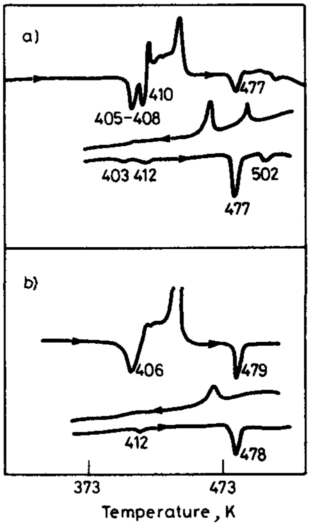

Fig. 10 Cyclic DSC curves of the systems (a) in air $NH_4NH_2SO_3$ (5.06 mg) NH_4HSO_4 (5.20 mg) molar ratio 1.00:1.02, (b) in airtight conditions $NH_4NH_2SO_3$ (5.61 mg) NH_4HSO_4 (5.73 mg) molar ratio 1.00:1.01

$(NH_4)_2SO_4$ reacted immediately with NH_4HSO_4 to give a small amount of $(NH_4)_2SO_4 \cdot NH_4HSO_4$. The DSC curve for the second cycle proved that the above equation is correct. The calculated amount of HNH_2SO_3 was about 92% of the theoretical value on the basis of this equation.

(b) *Under closed* conditions, the exothermic peak (which followed the melting endotherm) was larger and more HNH_2SO_3 was formed on the first thermal treatment than in air (Fig. 10b).

$(NH_4)_2SO_4$–NH_4HSO_4 (VI)

(a) On the first heating *in air,* NH_4HSO_4 melted at 412 K, and the double salt $(NH_4)_2SO_4 \cdot NH_4HSO_4$ at 504 K (Fig. 11a). On subsequent heating, the characteristic endothermic peak of thermally treated NH_4HSO_4 appeared at 390–412 K, and the size of the peak of the incongruent melting endotherm of $(NH_4)_2SO_4 \cdot$ $\cdot NH_4HSO_4$ increased by about 45%.

(b) *Under air-free* circumstances, the heating curve was quantitatively similar to the DSC curve for the $(NH_4)_2SO_4$–NH_4HSO_4 sample (1:1 molar ratio) recorded in air (Fig. 11b). On the second thermal treatment, the melting enthalpy of the double salt $(NH_4)_2SO_4 \cdot NH_4HSO_4$ increased by about 62%.

In the absence of literature data, we made attempts to determine the ΔH_f of the double salt $(NH_4)_2SO_4 \cdot NH_4HSO_4$. We used the enthalpy values of the DSC curves obtained under air-free conditions for $(NH_4)_2SO_4$–NH_4HSO_4 (1:1 molar ratio). It

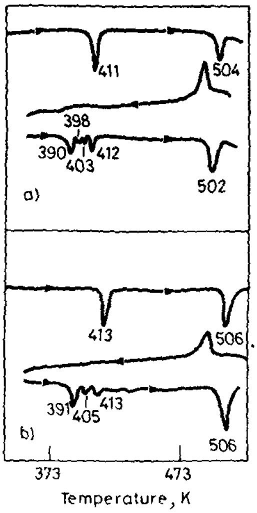

Fig. 11 Cyclic DSC curves of the system (a) *in air* $(NH_4)_2SO_4$ (5.04 *mg*) NH_4HSO_4 (4.64 mg) *molar ratio* 1.00:1.06, (b) *in airtight conditions* $(NH_4)_2SO_4$ (6.10 *mg*) NH_4HSO_4 (5.31 mg) *molar ratio* 1.00:1.00

Table 2 Characteristic thermoanalytical data of $(NH_4)_2SO_4 \cdot NH_4HSO_4$

Phase transition II ⟶ I		Melting point		Reference
T_{tr}, K	ΔH_{tr}, kJ/mole	T_f, K	ΔH_f, kJ/mole	
413.0	1.84	507	11.70	This work
407.4	1.77	–	–	[10]
411.0	–	498	–	[4]

Similar calculations were made on the basis of the DSC curves obtained in air, but they were not consistent.

may be assumed that (*i*) *a quantitative amount of double salt* $(NH_4)_2SO_4 \cdot NH_4HSO_4$ is produced from these two salts when neither of them is in excess and the experiments are made under air-free circumstances, and (ii) the formation of this compound becomes complete during the second heating.

From the enthalpy values for the second thermal treatment, the results presented in Table 2 were obtained.

We made an attempt to calculate also the enthalpy of phase transition of $NH_4HSO_4 \cdot (NH_4)_2SO_4$, for comparison with literature data (Table 2). The endothermic peaks proceeding the phase transformation of $NH_4HSO_4 \cdot (NH_4)_2SO_4$ (Fig. 11b), may be assigned to different combinations of NH_4HSO_4 and $(NH_4)_2SO_4$ [1].

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Zusammenfassung — Das thermische Verhalten von binären Systemen

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HNH_2SO_3–NH_4HSO_4 (III), $NH_4NH_2SO_3$–$(NH_4)_2SO_4$ (IV),
$NH_4NH_2SO_3$–NH_4HSO_4 (V), $(NH_4)_2SO_4$–NH_4HSO_4 (VI)

wurde mit einem thermischen Analysator Du Pont, versehen mit einem DSC-Modul, untersucht. Die entsprechenden einzelnen Verbindungen, und das neugebildete $(NH_4)_2S_2O_7$ wurden im Laufe früherer Untersuchungen unter denselben Umständen untersucht. Die ΔH_f-Werte von HNH_2SO_3, $NH_4NH_2SO_3$, $(NH_4)_2S_2O_7$ und $(NH_4)_2SO_4 \cdot NH_4HSO_4$ die in Abwesenheit von Luft bestimmt wurden, waren 11.9, 16.8, 11.7 und 11.7 kJ/mol. Infolge des Feuchtigkeitsgehaltes der Atmosphäre und der wiederholten Erwärmung in Luft zeigten die DSC-Kurven mehr endothermische Peaks, als unter luftfreien Bedingungen. Exothermische, additive Reaktionen fanden bei den binären Systemen (I) und (III) statt, die eine Bildung von $(NH_4SO_3)_2NH$ beziehungsweise $(NH_4)_2S_2O_7$ resultieren, und bei den Systemen (II) und (VI), wo eine neue Verbindung durch Schmelzen entstand.

Резюме — С помощью Дюпон термического анализатора, совмещенного с ДСК-модулем, было исследовано термическое поведение двойных систем

HNH_2SO_3–$NH_4NH_2SO_3$ (I), HNH_2SO_3–$(NH_4)_2SO_4$ (II),
HNH_2SO_3–NH_4HSO_4 (III), $NH_4NH_2SO_3$–$(NH_4)_2SO_4$ (IV),
$NH_4NH_2SO_3$–NH_4HSO_4 (V), $(NH_4)_2SO_4$–NH_4HSO_4 (VI)

Предварительно, в тех же самых условиях были изучены каждая из компонент, а также свежеприготовленное соединение $(NH_4)_2S_2O_7$. Значения ΔH_f, определенные в отсутствии воздуха, для соединений HNH_2SO_3, $NH_4NH_2SO_3$, $(NH_4)_2S_2O_7$ и $(NH_4)_2SO_4 \cdot NH_4HSO_4$ составляли соответственно: 11.9; 16.8; 11.7; и 11.7 кдж/моль. При повторном нагреве в атмосфере воздуха, кривые ДСК показали больше эндотермических пиков по сравнению с безвоздушной атмосферой, что обусловлено присутствием влаги в воздухе. Для двойных систем I и III, установлены экзотермические реакции, приводящие к образованию, соответственно, соединений $(NH_4SO_3)_2NH$ и $(NH_4)_2S_2O_7$. При плавлении систем II и VI наблюдалось образование нового соединения.