

## THERMAL DISSOCIATION OF BASIC ALUMINIUM AMMONIUM SULFATE IN VACUUM

### PART I. STAGES OF DECOMPOSITION

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The course of thermal decomposition of basic aluminium ammonium sulfate was investigated. Temperature ranges were established in which dehydration of the compound and liberation of ammonia and sulfur oxides take place. The presented scheme of thermal dissociation of the basic salt was based on the determination of the solid and gaseous products of the reaction.

The thermal decomposition of basic aluminium ammonium sulfate is the final stage in Bretsznajder's method of producing metallurgical aluminium oxide from Polish clays [1]. Previous studies on calcination of basic aluminium ammonium sulfate [2–4] were concerned with the essential stages and with some intermediates of decomposition of that compound in air. No studies have yet been performed on the decomposition of the basic salt in vacuum.

No account has been given either of the gas-phase changes during the process, and the course of the reaction has been evaluated merely from the composition of the solid phases.

The aim of the present work was to establish precisely the stages of decomposition of basic aluminium ammonium sulfate, and to identify all the solid and gaseous intermediates of the decomposition. In the present part of the work the course of dissociation of the basic salt was studied with the use of thermal analysis, mass-spectrometry, infrared absorption and X-ray phase analysis.

### Experimental

The subject of the studies was commercial basic aluminium ammonium sulfate of the following composition:  $\text{Al}_2\text{O}_3$  34.60–35.75%;  $\text{SO}_3$  42.00–43.50%;  $\text{NH}_3$  3.40–3.60% and  $\text{H}_2\text{O}$  17.15–20.00%. Its approximate formula was  $(\text{NH}_4)_2 \cdot 0.3 \text{Al}_2\text{O}_3 \cdot 4 \text{SO}_3 \cdot (6-8)\text{H}_2\text{O}$ .

Basic aluminium ammonium sulfate was subjected to thermogravimetric analysis coupled with mass-spectrometry, using a Mettler thermoanalyzer connected with a Balzers quadrupole mass-spectrometer. The applied setup enabled simultaneous registration of T, TG, DTG, DTA, P (total pressure of gaseous decomposition

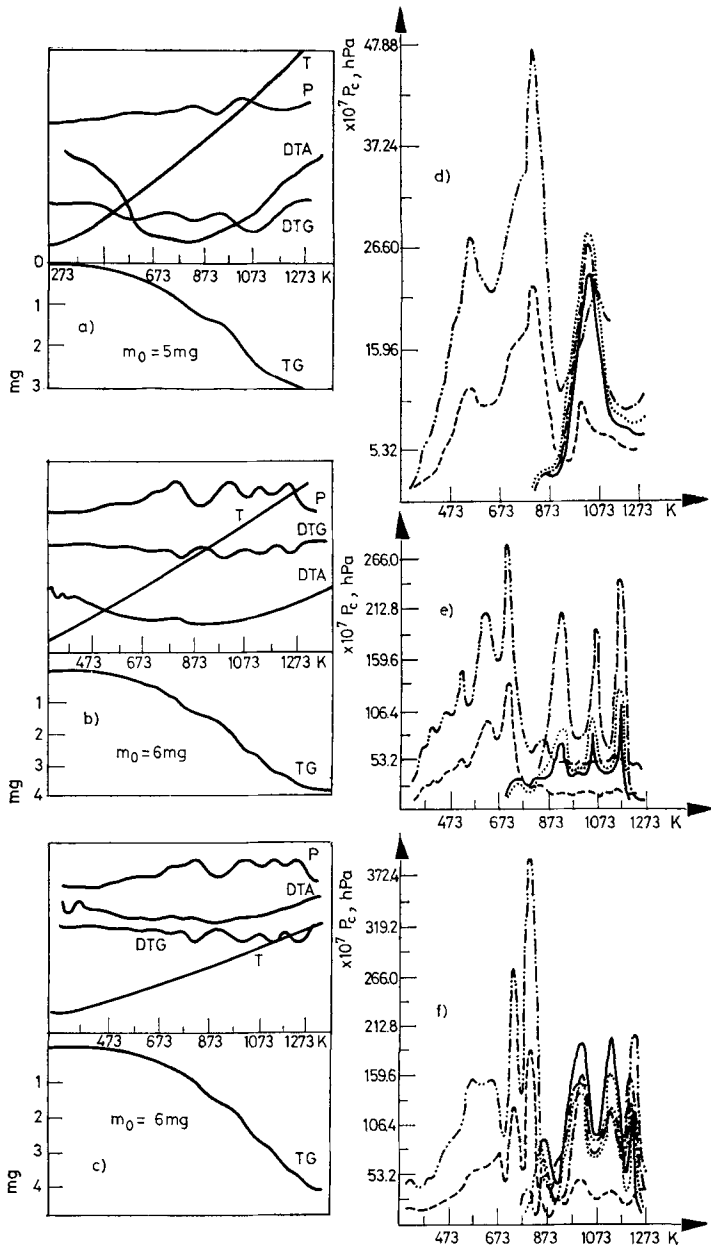


Fig. 1. Thermogravimetric and mass-spectrometric analyses of basic aluminium ammonium sulfate at different heating rates: a, d — 2 degree/min; b, e — 6 degree/min; c, f — 10 degree/min; d, e, f —  $\text{--xx--xx--}$   $\text{H}_2\text{O}$ ;  $\text{-----}$   $\text{OH}^-(\text{NH}_3)$ ;  $\text{.....}$   $\text{SO}$ ;  $\text{-----}$   $\text{SO}_2$ ;  $\text{--.-.-}$   $\text{O}_2$

products) and MTA curves, the latter being the result of almost continuous analysis of the composition of the gaseous products by means of a mass-spectrometer. The measurements were performed on roughly 5 mg samples at pressures of the order of  $10^{-6}$  hPa in the temperature range 298–1273 K. The MTA curves were recorded in the mass interval 0–100 with a rate of 1 s/mass.

Measurements were made with three rates of temperature increase: 2, 6 and 10 degree/min. The capacity of the Pt sample holder was  $0.33 \text{ cm}^3$ , and the reference substance in DTA was  $\alpha\text{-Al}_2\text{O}_3$ .

Samples of the starting aluminium ammonium sulfate and products of its partial decomposition were also analyzed by infrared absorption. Partly decomposed samples were obtained by roasting the basic salt to 823, 843, 923, 973, 1023, 1123 and 1273 K under conditions similar to those existing in the Mettler thermoanalyzer, with a heating rate of 10 degree/min. The infrared spectra were recorded with a Specord 71-IR spectrophotometer (Carl Zeiss, Jena) (within the wavenumber interval  $400\text{--}4000 \text{ cm}^{-1}$ ), and with a Perkin-Elmer spectrophotometer ( $200\text{--}4000 \text{ cm}^{-1}$ ). The samples were pressed into tablets containing 2.65 mg of the material and 150 mg KBr for analyses with the Specord 71-IR, and 1.4 mg material and 300 mg KBr with the Perkin-Elmer spectrophotometer.

X-ray phase analysis of aluminium ammonium sulfate samples was carried out in vacuum under continuous heating at a rate of 2 degree/min. The rate of heating was controlled semiautomatically according to the accepted program.

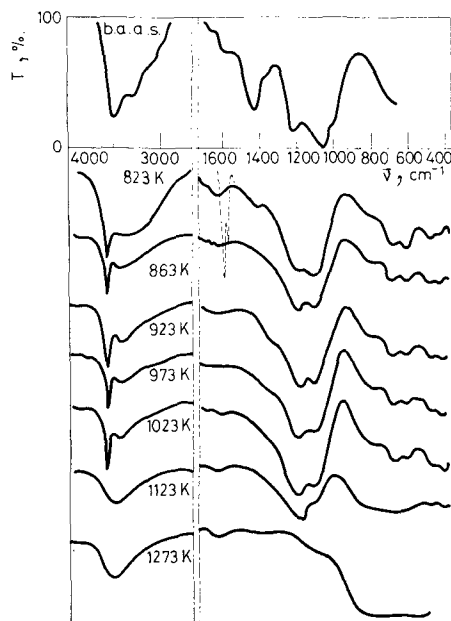


Fig. 2. Infrared spectra of starting material and of partly and completely decomposed samples

Table 1  
X-ray diffraction analyses of basic aluminium ammonium sulfate and its products

Alunite $K_2O \cdot 3 Al_2O_3 \cdot 4SO_3 \cdot 6 H_2O$		$3 Al_2O_3 \cdot 4 SO_3(0-2)H_2O$				$Al_2O_3$					
standard <sup>6</sup> Mirkin's		starting -sample	standard <sup>7</sup> (ASTM)		sample 893 K	standard <sup>8</sup> Mirkin's $\gamma - Al_2O_3$		standard <sup>8</sup> Mirkin's $\alpha - Al_2O_3$		sample 1173 K	sample 1373 K
<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>d</i> , Å
5.70	25	5.80	4.53	10	4.65	2.39	19	3.479	72	2.43	2.40
4.94	50	4.95	3.49	30	3.50	1.975	72	2.552	92	2.07	2.15
3.49	41	3.50	3.09	100	3.10	1.396	100	2.379	41	1.97	1.99
2.98	100	3.00	2.47	15	—			2.085	103	1.40	1.40
2.29	50	2.32	2.20	10	—			1.740	83		
								1.601	42		

The X-ray diffraction analyses were performed with the use of a URS-50 IM device supplied with a GUR-4 goniometer (made in the USSR), using  $CuK_{\alpha}$  radiation monochromatized by LiF.

The sample was located in a GWPT-1500 high-temperature cell. The investigation was carried out in two manners: Either complete X-ray diffraction analysis was performed after a definite temperature had been attained, or changes of some selected (known) reflexions were observed and new ones were noted in order to determine the temperatures of crystallographic transformations.

## Results

Selected results of investigations on the stages of aluminium ammonium sulfate decomposition are presented in Figs 1 and 2 and in Table 1. TG and DTG curves, and changes in the pressure of gaseous products of basic aluminium ammonium sulfate decomposition (P) at heating rates of 2, 6 and 10 degree/min are presented in Fig. 1a, b, c. Figure 1d, e, f presents the results of analysis of the gas phase in the form of the relations between the partial pressure of the gaseous reaction products and the temperature for three heating rates: 2, 6 and 10 degree min. Table 1 contains the results of X-ray diffraction analysis of basic aluminium ammonium sulfate and of products of its partial and complete decomposition. The infrared absorption spectra of the basic salt and of the products of its partial and complete decomposition are presented in Fig. 2.

## Discussion

The courses of the thermogravimetric curves and the MTA of basic aluminium ammonium sulfate (see Fig. 1) show that the thermal dissociation of this compound depends strongly on the experimental conditions; variations are observed, for instance, when the heating rate is changed.

Comparison of the curve obtained on heating the sample in vacuum at a rate of 2 degree/min (Fig. 1a) with the mass-spectrum MTA (Fig. 1d) indicates that the thermal dissociation of basic aluminium ammonium sulfate proceeds essentially in three stages.

In the first stage, at 293–623 K, a characteristic feature is a peak at about 573 K in the P, DTG and MTA curves. The shape of the TG curve and mass-spectrometric analysis of the gaseous reaction products show that in this stage the compound loses 4 H<sub>2</sub>O molecules. However, the solid product retains its initial alunite structure, as shown by the X-ray diffractogram.

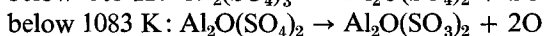
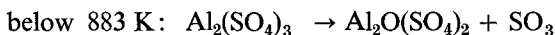
In the second stage of dissociation (623–873 K) one can observe a peak at 823 K in the DTG, P (Fig. 1a) and MTA (Fig. 1d) curves, corresponding to an endothermic effect in the DTA curve (Fig. 1a). As can be seen from the TG curve, the loss in weight in the second stage of decomposition is about 18%. Analysis of the MTA spectrum indicates that the loss corresponds to the simultaneous evolution of ammonia and water with the exception of one mole. In this stage one can also observe the first signs of desulfuration of the basic salt. The loss of sulfur may be due to removal of H<sub>2</sub>SO<sub>4</sub> formed from (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> produced in the earlier stage, according to hypotheses put forward by Johnson and Gallagher [9] and Pizzolato and Papazian [10]. The beginning of desulfuration in this temperature range has also been observed by other authors dealing with the decomposition of compounds of the alunite type.

Increase of the heating rate to 6 and 10 degree/min results in separation of the peaks in the DTG, P, DTA (Fig. 1a, b, c) and MTA (Fig. 1d, e, f) curves. The stepwise evolution of water from the compound confirms the views of Hendricks and Krogius [14, 15] on the possibility of the existence of more than one kind of water binding in alunite type compounds.

The stepwise dehydration of basic aluminium ammonium sulfate has also been observed by other authors concerned with the decomposition of this compound [6, 11–13]. The shape of the infrared absorption spectrum may be accounted for by existence of at least 2 kinds of water binding in the compound (see Fig. 2).

In the temperature region 873–1273 K (third stage of decomposition) a peak appears at a temperature of about 923 K in the P and DTG curves, with a simultaneous endothermic effect in the DTA curve. In this stage the sample loses about 37% of its weight (the TG curve), which means complete desulfuration and removal of all the remaining water. From the thermal curves recorded in vacuum at heating rates of 6 and 10 degree/min (see Fig. 1b, c) and from the curves corresponding to the partial pressures of the gaseous decomposition products (see Fig. 1e, f), it emerges that desulfuration of the basic salt proceeds in three stages. Characteristic temperatures in the P, DTG and DTA curves are 1008, 1133 and 1233 K at a heating rate of 6 degree/min, and 1013, 1138 and 1238 K at a rate of 10 degree/min. These effects correspond to the evolution of 2 moles of SO<sub>3</sub>, the third mole of SO<sub>3</sub>, and the last mole of SO<sub>3</sub>, respectively. The courses of the DTA curves (Fig. 1b, c) seem to suggest that the thermal effects of desulfuration may overlap the exothermic effect, due to a crystal lattice transformation, as postulated by other authors [4, 5]. A pre-

cise interpretation of the DTA curves in the high-temperature region is difficult, however, because of some distortions resulting from the small thermal conductance of the sample material under high vacuum. The X-ray diffraction data (see Table 1) made it possible to identify a solid intermediate in the decomposition of basic aluminium ammonium sulfate. This compound is  $\text{AlH}(\text{SO}_4)_2$ , formed as a consequence of the destruction of the alunite structure. The decomposition of  $\text{AlH}(\text{SO}_4)_2$  leads to the formation of a compound with a sulfate structure. The existence of  $\text{AlH}(\text{SO}_4)_2$  is also confirmed by the presence of water in the mass-spectrograms above 873 K (see Fig. 1d, e, f) and by the characteristic absorption band at  $3500 \text{ cm}^{-1}$  in the infrared spectrum (Fig. 2). The X-ray diffraction patterns did not permit identification of the crystalline structures (probably not sufficiently developed) of basic aluminium ammonium sulfate samples partly decomposed at temperatures in the range 993–1173 K. It was thus impossible to confirm the Lorant hypothesis [16], which postulates the following scheme of thermal decomposition of aluminium sulfate:

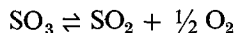


Lorant's scheme assumes the existence of the alumoxane cation ( $\text{Al}_2\text{O}^{4+}$ ) in the alumoxane sulfate and sulfite claimed to exist as intermediates of thermal decomposition. In our work the alumoxane cation has been identified by means of infrared absorption spectrophotometry, based on the known absorption maximum [17–19] characteristic for the  $=\text{Al}-\text{O}-\text{Al}=\text{}$  group in the wave number range  $700-800 \text{ cm}^{-1}$ .

The infrared spectra of basic aluminium ammonium sulfate samples heated at 823–1273 K exhibited a characteristic absorption band at  $700-800 \text{ cm}^{-1}$  (see Fig. 2) which may be accounted for by vibrations of the  $=\text{Al}-\text{O}-\text{Al}=\text{}$  group. The presence of the alumoxane cation in products of basic aluminium ammonium sulfate decomposition seems to confirm Lorant's hypothesis.

The reactions in the solid phase also determine the composition of the gas phase. Mass-spectrometric analysis of the latter in the stage of desulfuration demonstrated the presence of  $\text{SO}_2$ ,  $\text{SO}$  and  $\text{O}_2$  in the gaseous decomposition products (see Fig. 1d, e, f).

The absence of  $\text{SO}_3$  in the gas phase is also confirmed by calculation of the equilibrium transformation degree (see Table 2) of the reaction



The degree of  $\text{SO}_3$  dissociation approaches unity at the temperatures of the third stage of decomposition.

The presence of  $\text{SO}$  in the gaseous decomposition products may possibly be due to the following facts:

- $\text{SO}$  is a product of dissociation of  $\text{SO}_3$  or  $\text{SO}_2$  (impossible in view of the thermodynamic data – see Table 2);

Table 2

Equilibrium transformation degree of thermal dissociation of sulfur oxides

Temperature, K	Pressure hPa	Equilibrium transformation of reaction		
		$\text{SO}_3 = \text{SO}_2 + \frac{1}{2} \text{O}_2$	$\text{SO}_3 = \text{SO} + \text{O}_2$	$\text{SO}_2 = \text{SO} + \frac{1}{2} \text{O}_2$
298	$1.33 \cdot 10^{-6}$	$0.13 \cdot 10^{-6}$	$\sim 10^{-51}$	$\sim 10^{-86}$
	$1.33 \cdot 10^{-3}$	$0.14 \cdot 10^{-6}$	$\sim 10^{-54}$	$\sim 10^{-89}$
	$1.33 \cdot 10^{-2}$	$0.14 \cdot 10^{-6}$	$\sim 10^{-55}$	$\sim 10^{-90}$
	1013.25	0.0	$\sim 10^{-59}$	$\sim 10^{-94}$
600	$1.33 \cdot 10^{-6}$	0.9148	$\sim 10^{-16}$	$\sim 10^{-33}$
	$1.33 \cdot 10^{-3}$	0.3345	$\sim 10^{-18}$	$\sim 10^{-36}$
	$1.33 \cdot 10^{-2}$	0.1750	$\sim 10^{-20}$	$\sim 10^{-37}$
	1013.25	$0.4557 \cdot 10^{-2}$	$\sim 10^{-24}$	$\sim 10^{-41}$
800	$1.33 \cdot 10^{-6}$	0.9993	$0.6143 \cdot 10^{-4}$	$\sim 10^{-19}$
	$1.33 \cdot 10^{-3}$	0.9780	$\sim 10^{-10}$	$\sim 10^{-22}$
	$1.33 \cdot 10^{-2}$	0.9346	$\sim 10^{-10}$	$\sim 10^{-23}$
	1013.25	0.1124	$\sim 10^{-10}$	$\sim 10^{-25}$
1000	$1.33 \cdot 10^{-6}$	1.0000	$0.2581 \cdot 10^{-1}$	$\sim 10^{-11}$
	$1.33 \cdot 10^{-3}$	0.9988	$0.8164 \cdot 10^{-3}$	$\sim 10^{-14}$
	$1.33 \cdot 10^{-2}$	0.9961	$0.2582 \cdot 10^{-3}$	$\sim 10^{-15}$
	1013.25	0.5393	$\sim 10^{-6}$	$\sim 10^{-15}$
1100	$1.33 \cdot 10^{-6}$		0.2250	$\sim 10^{-8}$
	$1.33 \cdot 10^{-3}$		$0.7301 \cdot 10^{-2}$	$\sim 10^{-11}$
	$1.33 \cdot 10^{-2}$		$0.2309 \cdot 10^{-2}$	$\sim 10^{-11}$
	1013.25		$0.8375 \cdot 10^{-5}$	$\sim 10^{-11}$
1200	$1.33 \cdot 10^{-6}$	1.0000		
	$1.33 \cdot 10^{-3}$	0.9998		
	$1.33 \cdot 10^{-2}$	0.9994		
	1013.25	0.8705		

- it is a product of sulfur oxide splitting in the mass-spectrometer during analysis of the gaseous products in the third stage of decomposition;
- it is a primary product of desulfuration of basic aluminium ammonium sulfate.

In the case of  $\text{SO}_2$  fragmentation in the mass-spectrometer the molecular ratio  $\text{SO}/\text{SO}_2$  should be 0.49 [20], whereas the actual ratio found by analysis of the gas phase is near 1 at a heating rate of 2 degree/min (see Fig. 3). One may assume, therefore, that both  $\text{SO}_3$  and  $\text{SO}$  are primary products of the reaction under investigation.

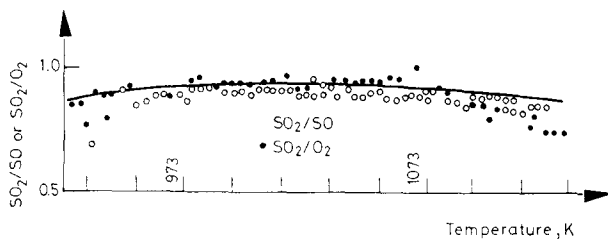


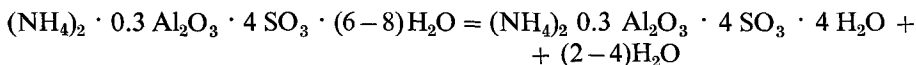
Fig. 3. Effect of temperature on the ratio of partial pressures of gaseous decomposition products

It seems reasonable to expect the confirmation of this conclusion during thermogravimetric analysis of basic aluminium ammonium sulfate with simultaneous chromatographic analysis of the gaseous dissociation products.

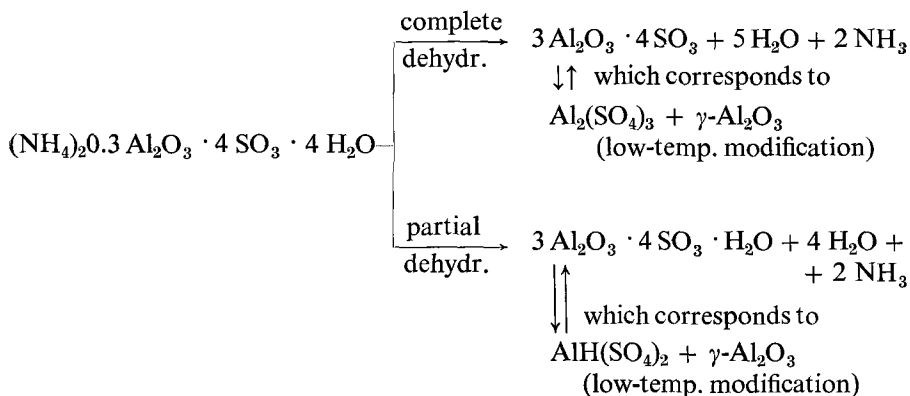
### Conclusion

Joint interpretation of the results of thermogravimetric, X-ray diffraction, mass-spectrometry and infrared absorption studies makes it possible to propose the following scheme for the thermal dissociation of basic aluminium ammonium sulfate:

1st stage: partial dehydration of the compound (below 623 K):



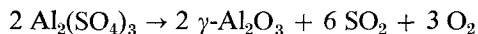
2nd stage: further dehydration and removal of ammonia (within the range 623–873 K):



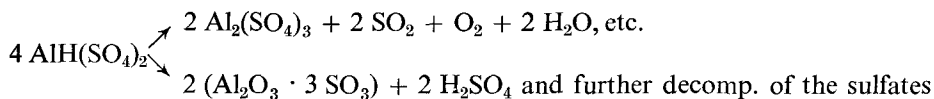


3rd stage: decomposition of sulfate and hydrogen sulfate (above 873 K):

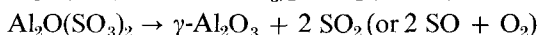
a) decomposition of aluminium sulfate:



b) decomposition of aluminium hydrogen sulfate:



c) decomposition of sulfate with formation of intermediates containing  $\text{Al}_2\text{O}^{4+}$  (alumoxane cation):



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RÉSUMÉ — Les étapes de la décomposition du sulfate basique d'aluminium et d'ammonium ont été étudiées.

On a déterminé les intervalles de température où la déshydratation de ce composé et le dégagement d'ammoniac et des oxydes de soufre ont lieu. Le schéma de la dissociation du sel basique est présenté en tenant compte des produits intermédiaires connus, solides et gazeux, de la dissociation.

ZUSAMMENFASSUNG — Es wurde der Verlauf der thermischen Zersetzung von basischem Ammonium — aluminiumsulfat untersucht. Es wurden Temperaturbereiche festgelegt, bei denen die Dehydratation der Verbindung sowie die Abspaltung von Ammoniak und Schwefeloxiden erfolgen.

Das gezeigte Schema für die Dissoziation vom basischen Salz resultiert aus der Berücksichtigung von erschlossenen gasförmigen und festen Mittelprodukten der Dissoziation.

Резюме — Исследовано термическое разложение основного сульфата алюминия — аммония. Установлены диапазоны температур, в которых происходит обезвоживание, удаление аммиака и окислов серы.

Представлена схема диссоциации основной соли с учетом определенных твердых и газовых промежуточных продуктов.