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THERMAL DECOMPOSITION OF BASIC ALUMINIUM POTASSIUM SULPHATE. PART I. STAGES OF DECOMPOSITION

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ABSTRACT

The stages of thermal decomposition of basic aluminium potassium sulphate were studied with the use of differential thermal analysis (DTA), thermogravimetry (TG), mass spectrometry (MS), IR spectroscopy (IR), and X-ray diffraction phase analysis (XRD). The individual stages of the decomposition were determined and both solid and gaseous products of the dissociation were identified. On the basis of spectrometric data and thermodynamic calculations the possibility of the occurrence of the SO in the gaseous reaction products is discussed.

INTRODUCTION

In the final technological processes of aluminium oxide production by the Bretsznajder method the main product — basic aluminium ammonium sulphate (BAAS) — is accompanied by basic aluminium potassium sulphate (BAPS), which is an unwanted admixture.

BAPS is formed in the hydrolysis of aluminium potassium alum according to the following equation

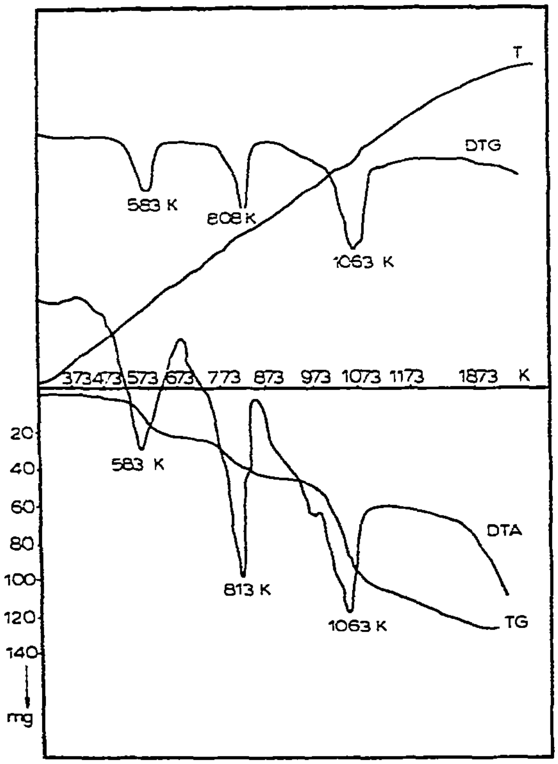
$$3\ K_2Al_2(SO_4)_4 \cdot 24\ H_2O = 2\ K[Al_3(OH)_6][SO_4]_2 + 2\ K_2SO_4 + 6\ H_2SO_4 + 60\ H_2O$$

Aluminium oxide suitable for foundry purposes is produced in the final operation which is the thermal decomposition of BAAS and BAPS admixtures. The thermal dissociation of BAAS — the stages and the kinetics of the reaction — have been recognized and described [1].

The present work is devoted to the study of the stages of the dissociation of BAPS and the determination of all intermediate solid and gaseous reaction products, with special attention to the possibility of the occurrence of SO in the gaseous decomposition products of metal sulphates. The problem has been mentioned in the literature [2—6], but it has not been sufficiently explained.

EXPERIMENTAL

The starting material was obtained under laboratory conditions by hydrolysis of analytical grade aluminium potassium alum. The grain size of the product was 0—60 μm with a characteristic Rosin—Ramler—Stirling distribution. The thermogravimetric studies were performed in an atmosphere of air and under reduced pressure of about 10^{-6} hPa. The samples to be analysed were 0.300 g in air and 0.010 g in vacuum. The analyses made in an atmosphere of air were carried out with a Hungarian derivatograph Paulik, Paulik and Erdey type OM-102. The vacuum measurements were performed with the aid of a Mettler thermoanalyser coupled with a Balzers mass spectrometer type QMG-101. Measurements were taken at 290—1270 K with heating rates of 2, 6 and 10 K min^{-1}. The X-ray diffraction measurements were performed in a high-temperature chamber type GPWT-1500 and X-ray apparatus URS-50 IM with goniometer GUR-4, using CuK_α radiation monochromatised with LiF. Infrared absorption analyses were performed with the use of a Carl Zeiss Specord 71 IR spectrophotometer (700—400 cm^{-1}) and a Perkin-Elmer spectrophotometer (200—4000 cm^{-1}).



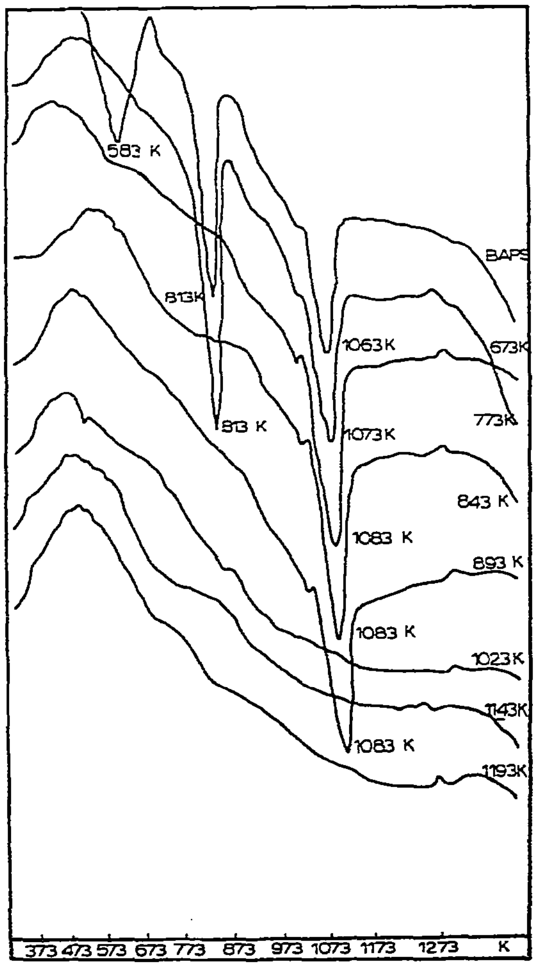


Fig. 1. Thermogravimetric curves of basic aluminium potassium sulphate (BAPS) in an atmosphere of air.

Fig. 2. DTA curves of the starting material and partially dissociated samples at specified temperatures.

RESULTS AND DISCUSSION

The results of the thermogravimetric studies are presented in Figs. 1—3, and those of the simultaneous analysis of the gas phase composition are given in Fig. 4. Figure 5 shows the IR spectra of the starting material and the intermediate products of the reaction under study.

Analysis of the thermograms of BAPS made in air and in vacuum leads to the conclusion that the thermal dissociation of this compound proceeds essentially in three stages. The DTA and DTG curves exhibit three peaks corresponding to endothermic transformations.

The first effect is accompanied by a 7.5% loss of sample mass corresponding to the evolution of three molecules of water with no change in the alunite structure of the compound.

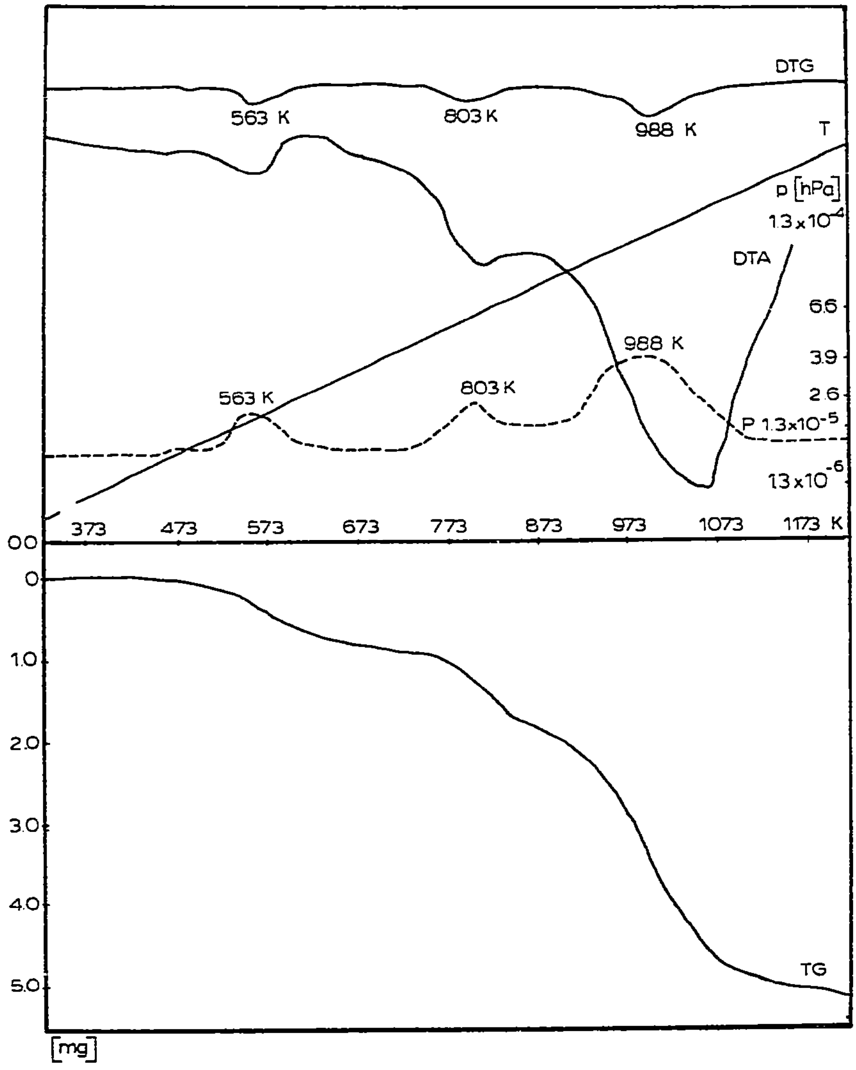


Fig. 3. Thermogravimetric curve of BAPS in vacuum ($p = 10^{-6}$ hPA) at a constant heating rate of 2 K min^{-1}.

The second endothermic effect is accompanied by evolution of more water molecules, and in this step the alunite structure of the starting compound is destroyed. The third peak observed in the 870—1200 K range is connected with desulphuration of the compound. The 29% loss of sample weight observed in this stage corresponds to the evolution of three molecules of SO_3; the fourth SO_3 molecule remains in the potassium sulphate formed. A comparison of the results of the thermogravimetric and spectrophotometric studies has confirmed the three-stage course of thermal decomposition of BAPS.

X-Ray diffraction studies of the dehydration products revealed the presence of aluminium potassium sulphate, aluminium sulphate, and aluminium oxide (γ-Al_2O_3). The desulphuration products are probably alumoxane sulphate and sulphite [7]. This probability has been confirmed by IR spectra of

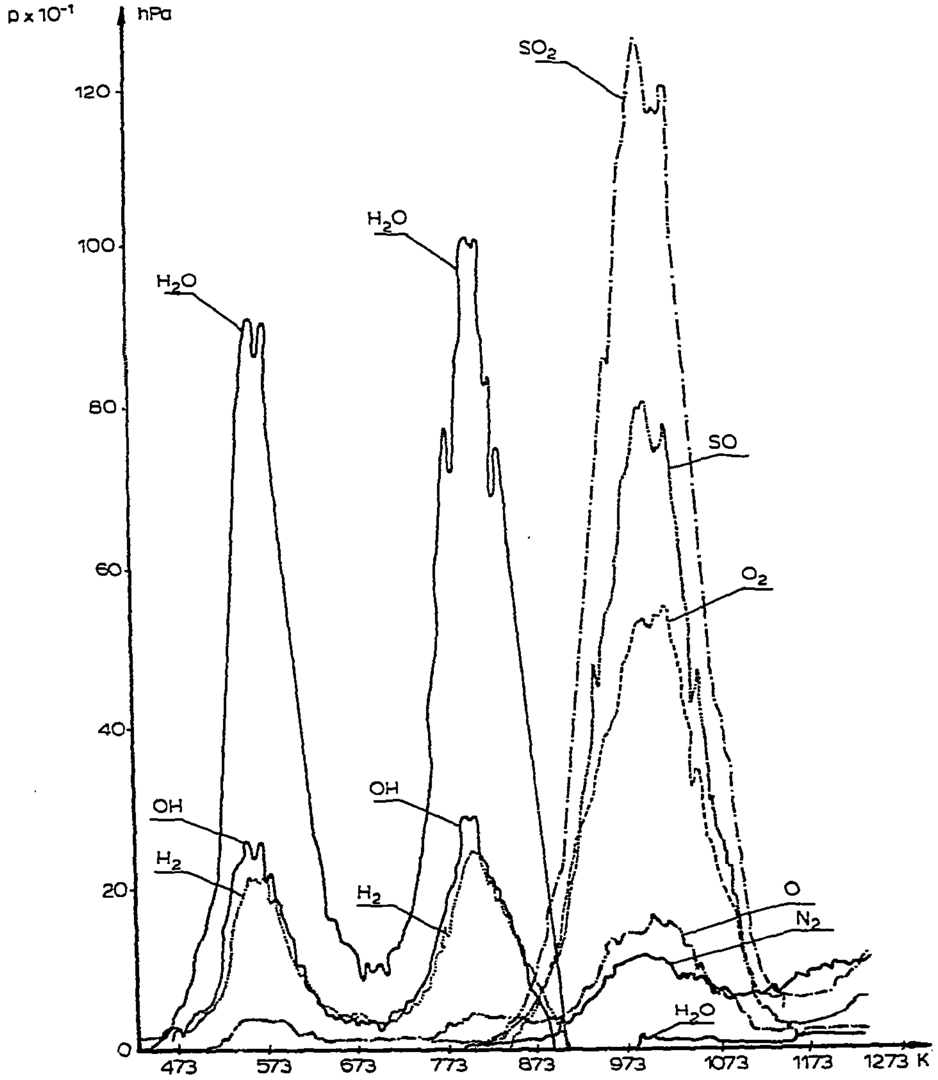


Fig. 4. Temperature dependence of the partial pressure of the gaseous decomposition products at a heating rate of 2 K min^{-1}.

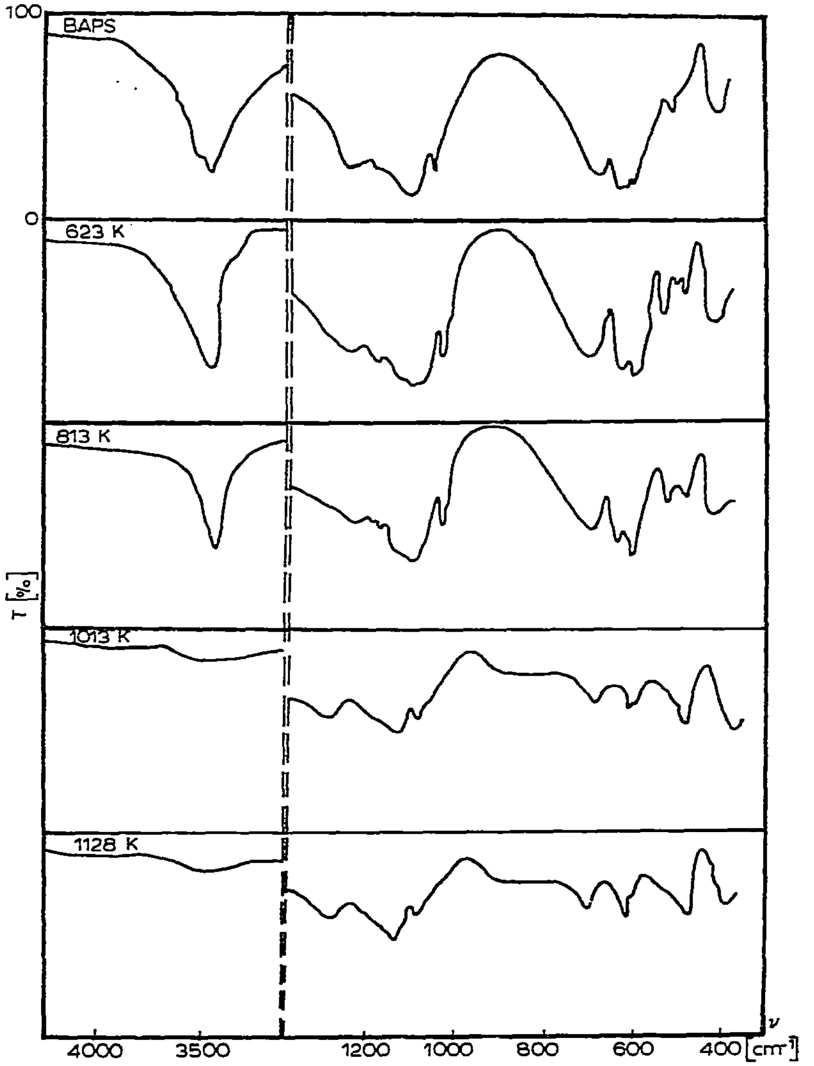


Fig. 5. Infrared spectra of the starting material and partially dissociated samples.

partially decomposed samples. The absorption bands observed in the 700—800 cm^{-1} range may be due to stretching vibrations of the =Al—O—Al= group [8, 9]. An analogous absorption band has also been observed in the IR investigation of the solid products of basic aluminium ammonium sulphate desulphuration [1]. Here the final products of the decomposition are γ-Al_2O_3 and K_2SO_4.

The gaseous products of the first and the second stages of decomposition contain water, whereas those produced in the third stage contain SO_2, SO, and O_2. No SO_3 has been found in the gaseous products. The absence of SO_3 may be explained in terms of equilibrium constants and equilibrium stages of the dissociation $SO_3 \rightleftharpoons SO_2 + 1/2\ O_2$. Under experimental conditions the equilibrium of this reaction may be considered as shifted completely to the right. The problem of the occurrence of SO in the gaseous products of the

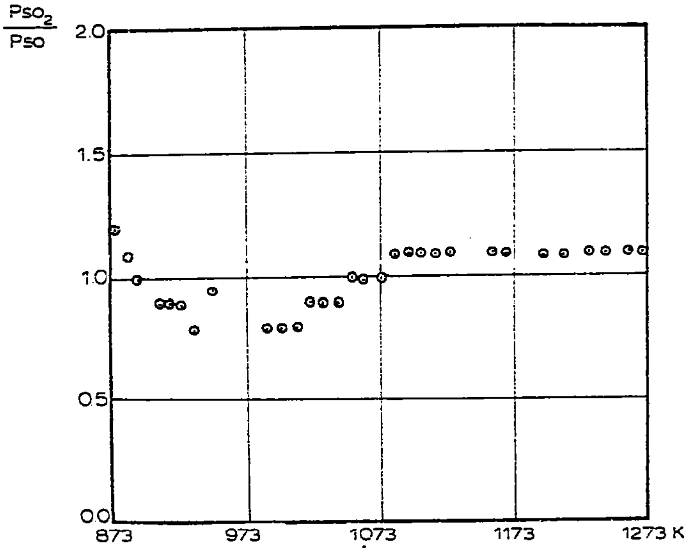


Fig. 6. Influence of temperature on the p_{SO_2}/p_{SO} ratio.

desulphuration of BAPS is uncertain as we have no direct evidence of SO being a primary product of thermal dissociation of the compound.

The thermodynamic data of the reactions $SO_3 \rightleftharpoons SO + O_2$ and $SO_2 \rightleftharpoons SO + 1/2\ O_2$ indicate that SO cannot be formed during the dissociation of SO_3 or SO_2. Thus the presence of SO in the gaseous desulphuration products may be accounted for either by destruction of SO_2 molecules in the ionisation chamber of the mass spectrometer or the fact that SO is a primary product of the decomposition. The changes in the ratio p_{SO_2}/p_{SO} in the course of the desulphuration step show that in the temperature range 870—1200 K its value is close to one which evidences that SO may occur independently of SO_2 and SO_3 (see Fig. 6). One may assume, therefore, that the presence of SO is due not only to the fragmentation in the mass spectrometer in such a case (according to results of a model cracking the ratio p_{SO_2}/p_{SO} should be 0.49 [5]), but is also a result of the formation of that compound as a primary product of the dissociation.

CONCLUSIONS

The thermal decomposition of basic aluminium potassium sulphate proceeds essentially in three stages. The results of experimental studies lead us to suggest the following scheme for the dissociation.

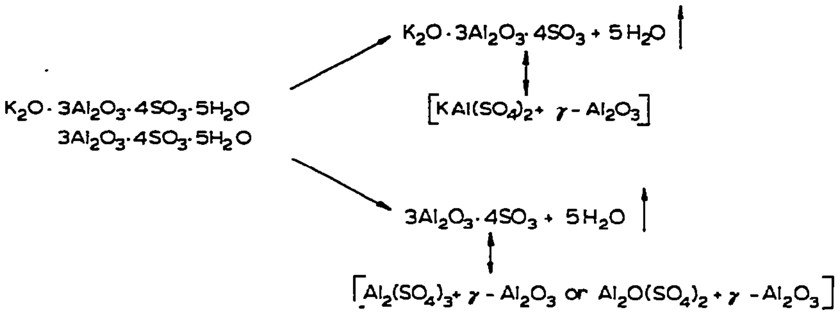
First stage — partial dehydration of the starting material at 470—670 K

$$K_2O \cdot 3\ Al_2O_3 \cdot 4\ SO_3 \cdot 8\ H_2O = K_2O \cdot 3\ Al_2O_3 \cdot 4\ SO_3 \cdot 5\ H_2O + 3\ H_2O\uparrow$$

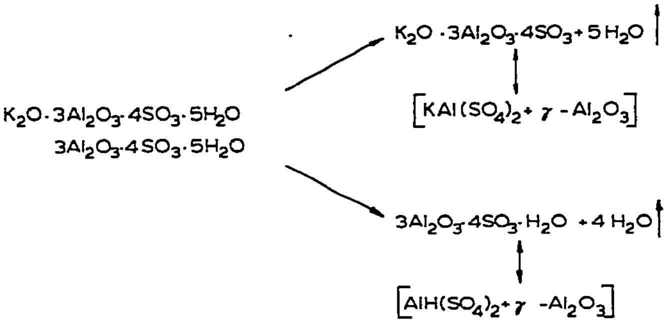
$$H_2O \cdot 3\ Al_2O_3 \cdot 4\ SO_3 \cdot 8\ H_2O = 3\ Al_2O_3 \cdot 4\ SO_3 \cdot 5\ H_2O + 4\ H_2O\uparrow$$

Second stage — further dehydration at 670—870 K

(a) complete dehydration



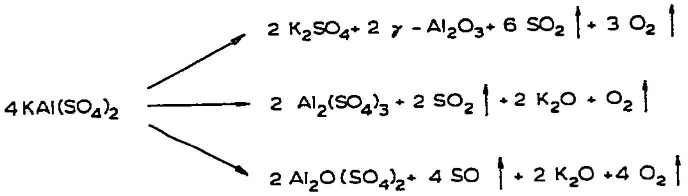
(b) partial dehydration



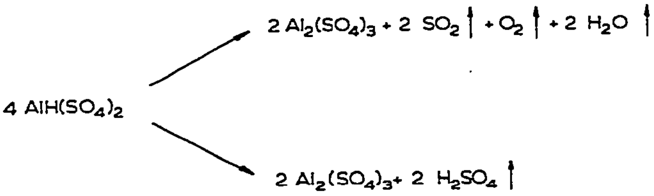
Third stage — desulphuration at 870—1200 K

Decomposition of the sulphates:

(a) aluminium potassium sulphate



(b) aluminium hydrogen sulphate (acid sulphate)



(c) aluminium sulphate

$$2\,Al_2(SO_4)_3 = 2\,\gamma\text{-}Al_2O_3 + 6\,SO_2\uparrow + 3O_2\uparrow$$

$$Al_2(SO_4)_3 = Al_2O(SO_4)_2 + SO_2\uparrow + \tfrac{1}{2}O_2\uparrow \text{ (or } SO + O_2)$$

(d) alumoxane sulphate

$$Al_2O(SO_4)_2 = Al_2O(SO_3)_2 + O_2\uparrow$$

$$Al_2O(SO_3)_2 = \gamma\text{-}Al_2O_3 + 2\,SO_2\uparrow \text{ (or } SO + O_2)$$

In the first stage of decomposition (470—670 K) the starting material loses three molecules of water and the solid reaction product retains the alunite structure of the substrate.

The second stage (670—870 K) is characterised by a further loss of water, destruction of the initial alunite structure, and formation of aluminium potassium sulphate $KAl(SO_4)_2$, aluminium sulphate $Al_2(SO_4)_3$, and aluminium oxide γ-Al_2O_3.

In the third stage (870—1200 K) both aluminium potassium sulphate and aluminium sulphate formed in the destruction of the alunite structure decompose to give the final product which is γ-Al_2O_3. The intermediate products of decomposition of $KAl(SO_4)_2$ are aluminium sulphate and potassium sulphate. The subsequent decomposition of aluminium sulphate probably leads to successive formation of alumoxane sulphate and sulphite.

The gaseous products of the decomposition are sulphur dioxide, sulphur trioxide, and oxygen. It seems highly probable that SO may be one of the primary products of the decomposition.

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