Thermochimica Acta, 44 (1981) 29—36
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL DECOMPOSITION OF BASIC ALUMINIUM POTASSIUM SULFATE. PART II. KINETICS OF THE REACTION

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(Received 30 July 1980)

ABSTRACT

The kinetics of individual stages of thermal dissociation of basic aluminium potassium sulfate (BAPS) were studied thermogravimetrically under isobaric and isothermal conditions at a reduced pressure of the order of 10^{-3} hPa and in the atmosphere of gaseous products of the reaction (H_2O, SO_2).

The kinetic parameters of all the reaction stages have been identified and the nature of the stages and the effect of changes of the reaction conditions on the course of the processes have been determined.

INTRODUCTION

The aim of the work was to study the kinetics and the macromechanism of individual stages [1] of the thermal dissociation of basic aluminium potassium sulfate (BAPS) which is an admixture (up to 10% by wt.) of the products of hydrolysis of alums in the Bretsznajder method. Investigations of this kind make it possible to determine the kinetic parameters and the nature of the process, as well as to establish the effect of change in reaction conditions on the course of the process.

The kinetics and macromechanism of the thermal dissociation of basic aluminium ammonium sulfate, which is the main product of the hydrolysis of alums, have been studied in some detail [2]. No such studies have been performed, as yet, on the decomposition of BAPS.

EXPERIMENTAL

BAPS samples obtained by roasting this compound to constant weight at 378, 643, and 843 K were used for the studies. The kinetics of the first and second stages of dehydration were studied on preparations obtained during roasting the BAPS at 378 and 643 K, and the kinetics of desulfuration (third stage) were determined for samples of BAPS roasted at 843 K [1]. In all the kinetic experiments the initial mass of the samples was 10 mg, and the degree of transformation during each stage of dissociation was determined with respect to the mass decrement found in preliminary roasting of the compound at the given temperature.

The kinetics of each dissociation stage of BAPS were studied by gravimetric method under isothermal and isobaric conditions. The experiments were carried out under reduced pressure of the order of 10^{-3} hPa and under different but constant pressures of H_2O vapor (in the first and second stages) or SO_2 (in the third stage) in a common glass vacuum apparatus fitted with a quartz spiral as a weighing element. The sensitivity of the weighing element permitted the determination of the weight loss with a precision of 10^{-7} g.

In the course of the studies of the first and second stages of decomposition in the atmosphere of H_2O vapor the necessary pressure of p_{H_2O} was achieved using the known pressures of water vapor over saturated solutions of some salts at 293 K, e.g. $LiCl \cdot H_2O$, 3.4 hPa; $Zn(NO_3)_2 \cdot 6\,H_2O$, 9.8 hPa; NH_4Cl, 18.5 hPa, etc. The necessary value of p_{H_2O} was obtained as follows: the apparatus was joined with a container filled with a saturated solution of an appropriate salt cooled to about 90 K and the whole was evacuated to a pressure of 10^{-4} hPa. The pump was then disconnected and the container thawed; the measurements were started after the required pressure had been established within the measuring set.

In the third stage of decomposition the necessary pressure of SO_2 was obtained by introducing an appropriate amount of SO_2 to the formerly evacuated system.

The experimental data of the reaction rate studies were processed by kinetic analysis methods involving computer calculations. The possibility of using commonly applied equations has been checked [3]. The selected models were checked for every individual kinetic curve. The criterion of the best fit of the given kinetic equation was the standard deviation of the $f(\alpha)_{exp}$ from the $f(\alpha)_{calc}$. The necessary calculations were performed with the use of a MERA 305 computer in the language MINI MERA BASIC.

The investigated process of thermal dissociation of BAPS under the applied experimental conditions can best be described by two models:

(1) the Kolmogorov—Erofeev—Avrami model

$$\alpha = 1 - e^{-kt^n}$$

has been utilized for the description of the first and the second stages of the dissociation in the following log form

$$\log[-\log(1 - \alpha)] = n \log t + \log(k \log e)$$

(2) the Bronstein—Ginstling model of three-dimensional diffusion

$$(1 - 2/3\alpha) - (1 - \alpha)^{2/3} = kt$$

has been used for the description of the third stage of decomposition.

Models 1 and 2 have been used for evaluation of mean values of the rate constant (k) at definite temperatures (T). The obtained k, T pairs have been utilized for identification of the kinetic parameters (by the least squares method), namely the activation energy (E) and the pre-exponential coefficient in the Arrhenius equation (A).

RESULTS AND DISCUSSION

The results of the decomposition rate studies of BAPS have been given in the form of kinetic curves illustrating the isothermic relationship between the transformation degree (α) and time (t). Figure 1 represents the relation $\alpha - t$ for the first, second and third stages of decomposition in vacuum and, as an example, for the second stage of decomposition under pressure of H_2O vapor $p_{H_2O} = 9.8$ hPa. Figures 2 and 3 represent the relation between α and time according to the Kolmogorov—Erofeev—Avrami model (second stage of decomposition) and according to that of Bronstein and Ginstling (third stage).

The values of kinetic parameters E and A for the processes carried out in vacuum and under pressure of H_2O vapor are presented in Tables 1 and 2.

Analysis of the kinetic data, the studies of dissociation stages and of intermediate dissociation products of BAPS [1] showed that the first stage of decomposition proceeding with evolution of three molecules of water without the destruction of the initial alunite structure is effected in two steps differing in the kinetic parameters E and A.

From the description of the kinetic data by means of the Kolmogorov—Erofeev—Avrami equation with the value of the parameter $n = 0.5$ it results that the dehydration process proceeds in the diffusion region. The tempera-

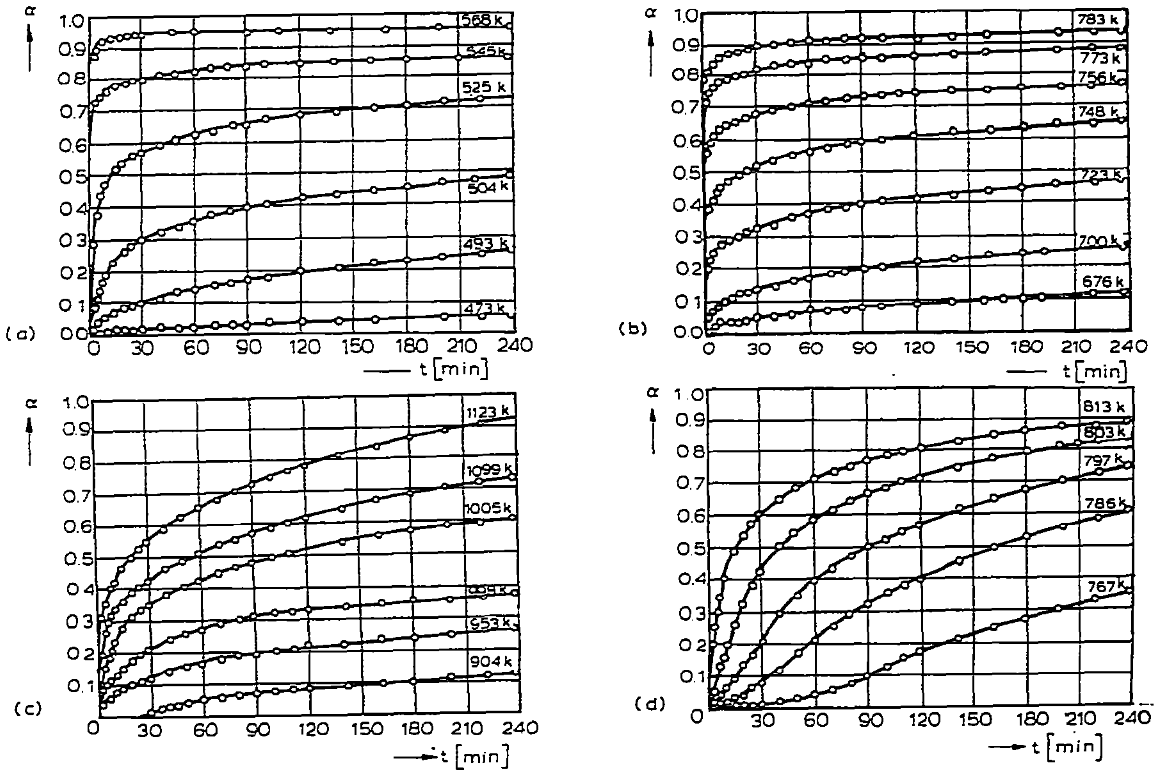

Fig. 1. Examples of kinetic curves: a, b, c = first, second, and third stage of decomposition in vacuum; d = second stage of decomposition under H_2O vapour pressure of $p_{H_2O} = 9.8$ hPa.

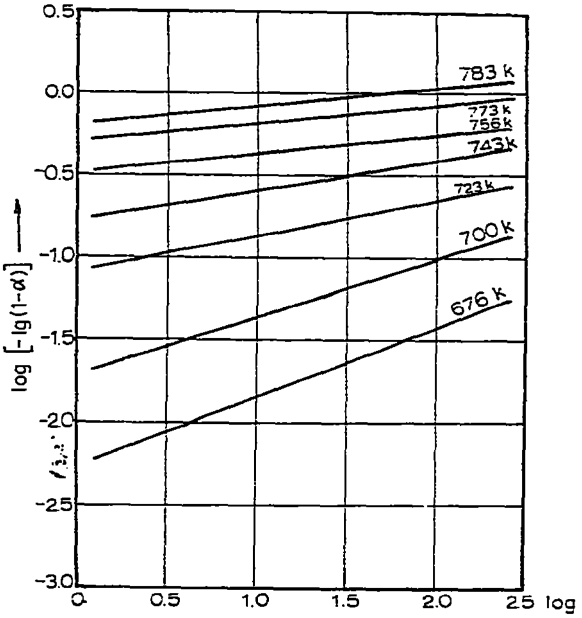

Fig. 2. Examples of the relationship between log[—log(1 — α)] and log t for the second stage of BAPS decomposition in vacuum.

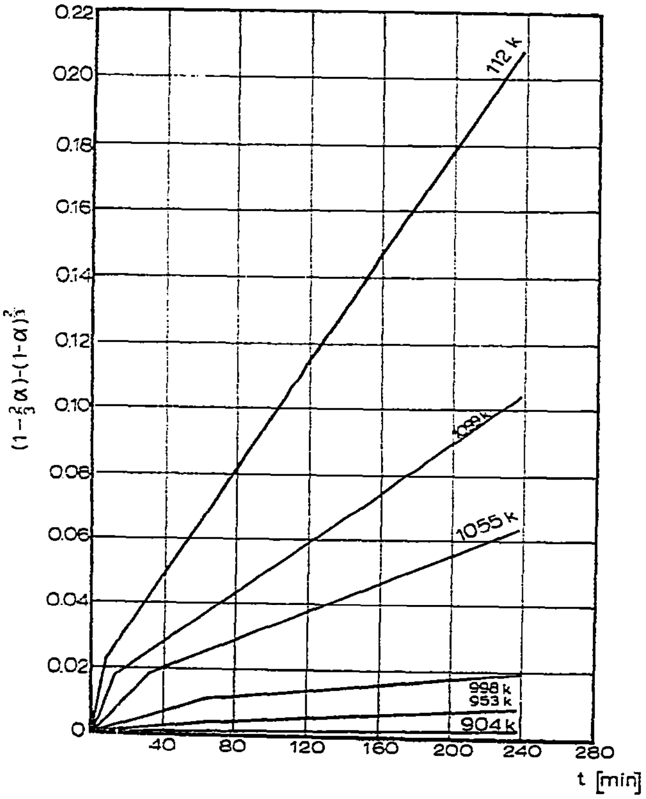

Fig. 3. Examples of the relationships between (1 — 2/3α) — (1 — α)$^{2/3}$ and t for the third stage of BAPS decomposition in vacuum.

TABLE 1

Kinetic parameters of the thermal decomposition of BAPS in vacuum

Model	First stage			
	First step		Second step	
	E_1 (kJ mole^{-1})	A_1 (min^{-1})	E_2 (kJ mole^{-1})	A_2 (min^{-1})
Kolmogorov-Erofeev-Avrami 3D-diffusion-controlled	139.5	0.15×10^{14}	111.4	0.53×10^{11}

ture coefficients of the reaction ($\gamma = k_{T+10}/k_T$) equal to 1.89 and 1.66 for the first and second steps, respectively, as well as high activation energy values suggest that the decomposition proceeds in the intermediate (kinetic—diffusion) region. The rate of the process is controlled by both the kinetics of the reaction and by the rate of diffusion of the gaseous reaction product (H_2O) through the layer of a solid reaction product formed on the surface of substrate grains.

An increase in pressure of the gaseous reaction product does not alter essentially the mechanism of the process during the first dissociation stage. It influences, however, the values of the kinetic parameters (see the data in Tables 1 and 2). This stage proceeds in two steps, also under the pressure of H_2O vapor and it may be described by the Kolmogorov—Erofeev—Avrami equation. The higher values of temperature coefficients (close to 2) and the value of the n parameter approaching 1.0 indicate that an increase of temperature in the presence of H_2O vapor has a more distinct effect on the course of the process than does the increase in counterpressure. The effect of diffusion, more pronounced in the second step of the process, is probably due to the increased thickness of the reaction product layer on the substrate grains.

In the second stage of thermal dissociation of BAPS the remaining molecules of water are evolved and the alunite structure of the compound is destroyed. The kinetics of the process, as in the first stage, are well described by the Kolmogorov—Erofeev—Avrami equation within the whole variability range, with the n value below 0.5, which suggests the diffusional character of the process. As in the first stage, however, both the temperature coefficient (1.58) and the activation energy (200.5 kJ mole^{-1}) suggest that the decomposition probably proceeds in the kinetic—diffusion region. Due to the presence of water vapor the course of the reaction differs from that in vacuum. The reaction proceeds in two steps differing in the kinetic parameters. The high values of the temperature coefficients indicate that the effect of temperature and water vapor pressure is similar to that in the first stage. A small effect of diffusion is observed in the passage from the first to the second step of this stage.

The kinetics of the third stage of the dissociation obey the Bronstein—Ginstling equation (3D-diffusion controlled). Calculations show that the

Second stage		Third stage			
E_1 (kJ mole^{-1})	A_1 (min^{-1})	First step		Second step	
		E_1 (kJ mole^{-1})	A_1 (min^{-1})	E_2 (kJ mole^{-1})	A_2 (min^{-1})
200.5	0.48×10^{14}				
		215.9	0.36×10^8	174.9	0.16×10^6

process is effected in two steps with different values of the kinetic parameters E and A (see the data in Table 1). The temperature coefficients, 1.27 and 1.22, respectively, for the first and the second steps evidence that the desulfuration proceeds in the diffusion region * and it is a complex process.

According to the Lorant thesis [5] the decomposition of the alunite structure may be accompanied by the following series of reactions: $AlK(SO_4)_2$; $Al_2(SO_4)_3$; $Al_2O(SO_4)_2$; $Al_2O(SO_3)_2$; K_2SO_4, and γ-Al_2O_3. An additional difficulty in the interpretation of the steps of the desulfuration process is the actual impossibility of determining precisely and reliably the composition of the gas phase.

Unlike the water vapor effect on the dehydration of BAPS, no effect of SO_2 on desulfuration of that compound has been observed. The course of the reaction in SO_2 atmosphere is identical with that in air or in an inert gas. This is in agreement with the results of thermodynamic calculations which indicate that at temperatures where desulfuration is effected the equilibrium of the reaction $SO_3 \rightleftharpoons SO_2 + \frac{1}{2}/O_2$ has been shifted completely toward the formation of SO_2, thus the change in pressure of SO_2, which is not the primary product of the reaction, has practically no effect on the course of the dissociation of BAPS.

CONCLUSIONS

(1) The first stage of BAPS dehydration in vacuum proceeds in two steps differing in the values of kinetic parameters E and A. Both these steps are probably effected in the kinetic—diffusion region and an increase of pressure of the gaseous reaction product (p_{H_2O}) does not alter the mechanism of the process, although the increase in the decomposition temperature due to

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* The use of diffusion equations for describing a process characterized by high values of activation energy and temperature coefficients may arise from the fact that those equations have been derived for a single grain model and thus they are valid for descriptions of systems of uniform size grains. The material under study is a polydisperse system with grain size distribution corresponding to the Rosin—Ramler—Stirling distribution model. In such a case the experimental kinetic curves may be described only by diffusion models [4].

TABLE 2

Kinetic parameters of the thermal decomposition of BAPS under H_2O vapour pressure

Pressure (hPa)	Model	First stage				Second stage			
		First step		Second step		First step		Second step	
		E_1 (kJ $mole^{-1}$)	A_1 (min^{-1})	E_2 (kJ $mole^{-1}$)	A_2 (min^{-1})	E_1 (kJ $mole^{-1}$)	A_1 (min^{-1})	E_2 (kJ $mole^{-1}$)	A_2 (min^{-1})
3.4	Kolmogorov—Erofeev—Avrami	181.4	0.11×10^{17}	134.1	0.18×10^{13}	966.1	0.14×10^{63}	462.8	0.53×10^{30}
9.8	Kolmogorov—Erofeev—Avrami	194.8	0.11×10^{18}	144.1	0.11×10^{14}	1395.1	0.15×10^{90}	707.9	0.89×10^{45}
18.5	Kolmogorov—Erofeev—Avrami	222.4	0.30×10^{20}	159.8	0.30×10^{15}	2112.8	0.87×10^{134}	789.2	0.74×10^{50}

increase of water vapor pressure has a stronger effect on the course of the process than does the increase of counterpressure.

(2) The second stage of dehydration of BAPS in vacuum proceeds in a single step both kinetic- and diffusion-controlled. In the atmosphere of water vapor the process proceeds in two steps differing in the values of the kinetic parameters E and A, which may be accounted for by differences in the bonding of the water in the compound studied.

(3) The desulfuration of BAPS proceeding in the third stage of thermal dissociation is a very complex process. A mathematical description of this process is, however, fairly simple, and the kinetic data show that the reaction proceeds in two steps and is diffusion-controlled. The pressure of SO_2 has no effect on either the rate or the nature of the desulfuration process.

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