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THERMAL DISSOCIATION OF BASIC ALUMINIUM AMMONIUM SULFATE IN VACUUM

PART II. KINETICS OF THE PROCESS

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Investigations were carried out on the kinetics of thermal decomposition of basic aluminium ammonium sulfate in vacuum. The kinetic model of dissociation of the compound was identified. The results of the kinetic studies and the mechanism of the process are discussed.

In a previous work we reported the stages of thermal decomposition of basic aluminium ammonium sulfate. The results created the possibility for more detailed studies on the kinetics of these stages.

Earlier studies by many authors [1 – 10] have led to different results, which cannot be interpreted in an uniequivocal manner. The difficulties in interpretation arise from the multistage character of the decomposition and uncertainty about the intermediates of the dissociation.

In the present work the object of our studies was to establish the kinetics of thermal dissociation of basic aluminium ammonium sulfate, which is a starting material in the final technological operation in Bretsznajder's acidic method of producing metallurgical aluminium oxide. The kinetic measurements were carried out in vacuum, i.e. at a pressure of 10^{-3} hPa, in the temperature ranges 378 – 623 K (1st stage), 623 – 873 K (2nd stage) and 873 – 1273 K (3rd stage).

The measurements allowed appropriate selection of the kinetic equations and determination of the parameters of the processes.

Experimental

The kinetic studies were carried out in a common glass vacuum apparatus fitted with a quartz helix as a weighing element. The elongation of the spiral was measured by means of a cathetometer with a precision of 0.005 mm, which permitted the determination of weight loss with precision of about 10^{-7} g. The weight of the samples was of the order of 10 mg. The starting material for the 1st stage of decomposition was basic aluminium ammonium sulfate dried to constant weight at 378 K. The samples were subjected to thermal decomposition under isobaric and isothermal conditions, under a pressure of 10^{-3} hPa at temperatures of 473, 523, 543, 563, 578 and 598 K.

In the 2nd stage the starting material was basic aluminium ammonium sulfate preliminary decomposed by igniting to constant weight (about 8 hours) at 623 K. Samples of the material were subjected to thermal decomposition under conditions as above, at temperatures of 648, 673, 723, 753, 793 and 816 K. In the 3rd stage the starting material was the basic salt ignited previously for about 8 hours at 873 K. The kinetic measurements were made at 891, 903, 943, 1008, 1093, 1143 and 1208 K.

The transformation degree was determined from the relation:

$$\alpha = \frac{\Delta m_t}{\Delta m_{max}}$$

where Δm_t = weight loss of the sample after time t;
Δm_{max} = maximum loss in weight of the sample in the given stage of decomposition*.

The following procedure was applied. A quartz crucible filled with the sample material was suspended on the quartz spiral, and the reactor was closed and evacuated. When the pressure fell to about 10^{-3} hPa, the sample was weighed and then brought into the zone of previously established, constant temperature. In the construction of kinetic curves and in the analysis of experimental data, all values measured during the initial 2–3 min were rejected, as in that time the decomposition proceeded under unsteady conditions.

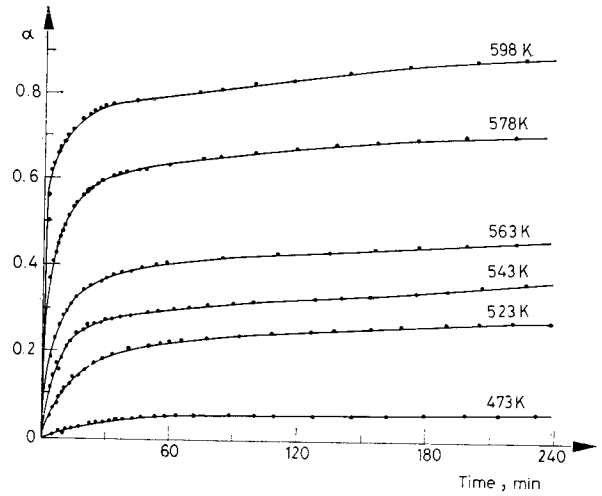

Fig. 1. Kinetic curves of the 1st stage of thermal decomposition of basic aluminium ammonium sulfate in vacuum ($p = 10^{-3}$ hPa)

* Δm_{max} was determined from the TG curve taken in vacuum at a heating rate of 2 degree/ /min. Thus, Δm_{max} was equal to the loss of sample weight during preliminary decompositions at 378, 623, and 873 K, respectively.

Experimental results and methods of their processing

Figures 1 – 3 represent the results obtained in 3 experimental series corresponding to individual stages of thermal dissociation of basic aluminium ammonium sulfate: preliminary dehydration at 473 – 598 K, further dehydration and removal of ammonia at 648 – 816 K, and desulfuration of the compound at 891 – 1208 K.

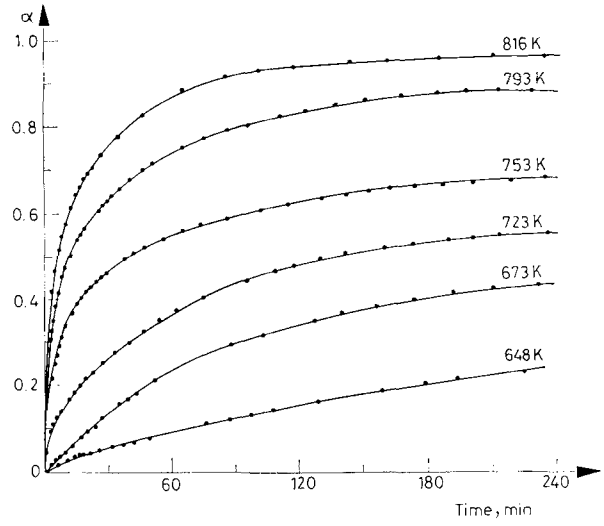

Fig. 2. Kinetic curves of the 2nd stage of thermal decomposition of basic aluminium ammonium sulfate in vacuum ($p = 10^{-3}$ hPa)

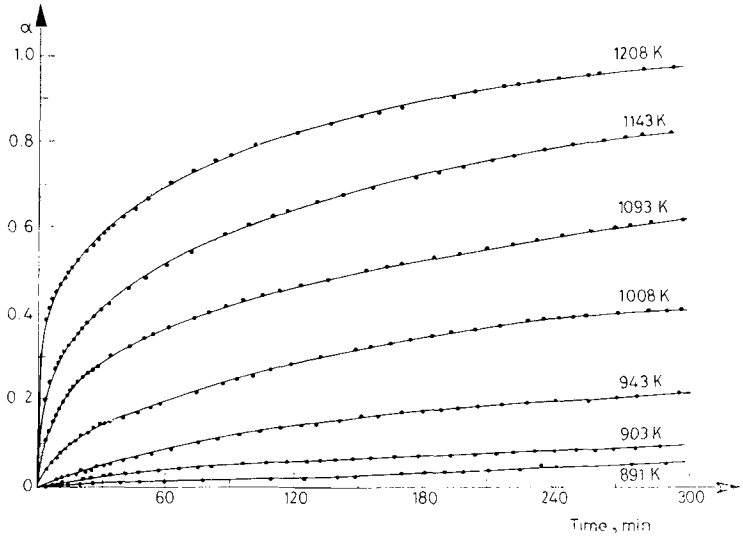

Fig. 3. Kinetic curves of the 3rd stage of thermal decomposition of basic aluminium ammonium sulfate in vacuum ($p = 10^{-3}$ hPa)

Table 1

Kinetic equations

Lp	Equation $t = f(\alpha)$	n	$t = f(\alpha)$
1	Power law α^n	1	α
2		2	α^2
3		1/2	$\alpha^{1/2}$
4		1/3	$\alpha^{1/3}$
5		1/4	$\alpha^{1/4}$
6	Contracting geometry $1 - (1 - \alpha)^{1/n}$	2	$1 - (1 - \alpha)^{1/2}$
7		3	$1 - (1 - \alpha)^{1/3}$
8	Erofeev $[-\ln(1 - \alpha)]^{1/n}$	1	$-\ln(1 - \alpha)$
9		3/2	$[-\ln(1 - \alpha)]^{2/3}$
10		2	$[-\ln(1 - \alpha)]^{1/2}$
11		3	$[-\ln(1 - \alpha)]^{1/3}$
12		4	$[-\ln(1 - \alpha)]^{1/4}$
13	2D diffusion controlled $(1 - \alpha)\ln(1 - \alpha) + \alpha$	—	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
14	Ginstling-Brounstein $(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$	—	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$
15	Jander $[1 - (1 - \alpha)^{1/3}]^2$	—	$[1 - (1 - \alpha)^{1/3}]^2$
16	Prout-Tompkins $\ln \frac{\alpha}{1 - \alpha}$	—	$\ln \frac{\alpha}{1 - \alpha}$
17	Second order $\frac{1}{1 - \alpha} - 1$	—	$\frac{1}{1 - \alpha} - 1$
18	Exponential $\ln \alpha$	—	$\ln \alpha$

The kinetic curves were used for identification of the parameters of the kinetic model of thermal dissociation. The identification was based on analysis of the 18 kinetic equations collected in Table 1. The inclusion of the equations was based on the frequency of their usage for describing the kinetics of thermal dissociation of solids, and also on the fact that the same set of equations was used by Johnson and Gallagher [6] for the identification of the kinetic parameters of similar compounds.

For determination of each of the kinetic curves, linear regression coefficients were found for all 18 equations (mathematical models) used. The calculation was accomplished by means of a Honeywell H-2040 digital computer according to the flow-diagram shown in Fig. 4. The criterion for the selection of the optimum equation (model) was the value of the standard deviation between $f(\alpha)_{calc.}$ and $f(\alpha)_{exptl.}$, expressed as a percentage of $f(\alpha)$.

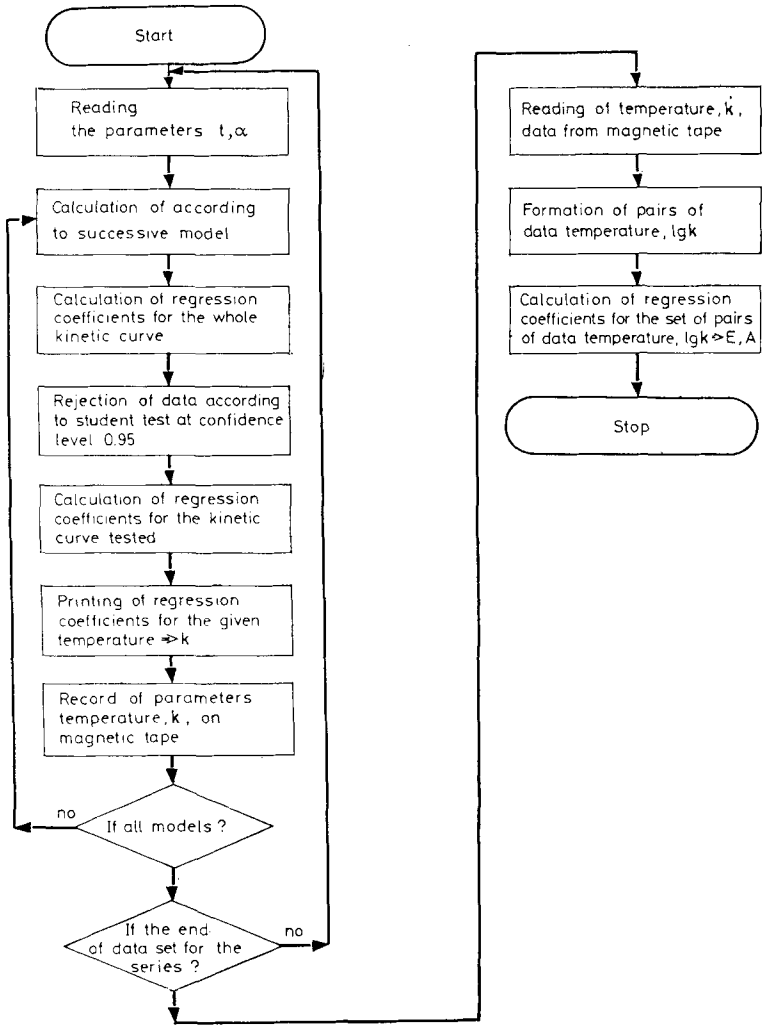

Fig. 4. Flow-diagram of identification of kinetic parameters with the use of experimental data obtained during thermal dissociation of basic aluminium ammonium sulfate under isothermal conditions

Table 2

Rate constants of desulfuration of basic aluminium ammonium sulfate

Temperature, T	Ginstling—Brounstein		Jander	
	Rate constant — k	Standard deviations	Rate constant — k	Standard deviations
K	min^{-1}	%	min^{-1}	%
891	$1.160 \cdot 10^{-6}$	4.30	$1.150 \cdot 10^{-6}$	4.35
903	$3.470 \cdot 10^{-6}$	0.86	$3.550 \cdot 10^{-6}$	0.85
943	$2.090 \cdot 10^{-5}$	1.53	$2.203 \cdot 10^{-5}$	1.45
1008	$8.401 \cdot 10^{-5}$	1.20	$9.444 \cdot 10^{-5}$	1.06
1093	$1.967 \cdot 10^{-4}$	1.67	$2.428 \cdot 10^{-4}$	1.13
1143	$4.387 \cdot 10^{-4}$	1.37	$6.281 \cdot 10^{-4}$	0.55
1208	$7.931 \cdot 10^{-4}$	1.11	$1.527 \cdot 10^{-3}$	1.30

The calculations showed that the results of kinetic studies on the thermal dissociation of basic aluminium ammonium sulfate may be described in all three stages with the aid of the equations derived by Ginstling and Brounstein:

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

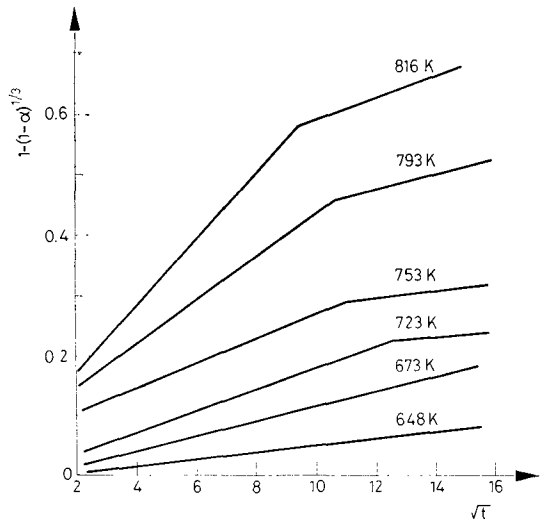

Fig. 5. Example of relationship between $1 - (1 - \alpha)^{1/3}$ and $t^{1/2}$ for the 2nd stage of decomposition of basic aluminium ammonium sulfate

or that of Jander:

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

where α = degree of transformation;
t = time in min;
k = rate constant in min^{-1}

In Table 2 and in Fig. 5 we have given examples of rate constants from Eqs (1) and (2), standard deviations for the 3rd stage of the dissociation, i.e. desulfuration of the compound (Table 2) and the values of the relation

$$[1 - (1 - \alpha)^{1/3}]^2 = f(t)$$

for the 2nd stage of thermal dissociation of basic aluminium ammonium sulfate (Fig. 5)

For corresponding pairs of values (k, T) found by means of Eqs (1) and (2), we have calculated the Arrhenius activation energy (E) and the pre-exponential factor (A) (see Table 3). This Table also gives the results of attempts to represent

Table 3

Kinetic parameters of thermal decomposition of basic aluminium ammonium sulfate in vacuum

Model	Stage I				Stage II				Stage III	
	E_1,	A_1,	E_2,	A_2,	E_1,	A_1,	E_2	A_2	E_1,	A_1,
	kJ/mole	min^{-2}	kJ/mole	min^{-1}	kJ/mole	min^{-1}	kJ/mole	min^{-2}	kJ/mole	min^{-1}
Jander	154.2	$0.23 \cdot 10^{12}$	110.6	$0.21 \cdot 10^{7}$	108.5	$0.22 \cdot 10^{5}$	82.1	$0.48 \cdot 10^{3}$	147.1	$0.32 \cdot 10^{4}$
Ginstling-Brounstein	149.6	$0.76 \cdot 10^{11}$	93.4	$0.38 \cdot 10^{5}$	96.4	$0.23 \cdot 10^{4}$	73.7	$0.12 \cdot 10^{2}$	127.8	$0.30 \cdot 10^{3}$
Erofeev	—	—	94.3	$0.89 \cdot 10^{6}$	108.1	$0.18 \cdot 10^{6}$	—	—	132.0	$0.65 \cdot 10^{4}$

the kinetics of thermal dissociation of basic aluminium ammonium sulfate by means of the Kolmogorov-Erofeev-Avrami equation involving the variable kinetic parameter n.

Discussion of results

The results of the experiments and the calculations have shown that the removal of 4 moles of H_2O in the 1st stage of decomposition proceeds in 2 steps. The complex nature of this stage is probably due to different modes of water binding in the starting material. The differences in water binding may also account for the existence of at least 2 absorption maxima in the range 3000–3700 cm^{-1} in the infrared spectrum of the basic salt [11].

The description of the kinetic data by Eqs (1) and (2) seems to suggest that the 1st stage of dehydration proceeds in the diffusion region, which is in disagreement with the comparatively high activation energie (150 kJ/mole, 93 kJ/mole) and temperature coefficients, $\frac{k_T + 10}{k_T}$ (1.75 and 1.50) for the 1st and 2nd steps of that stage of thermal dissociation, respectively. This apparent discrepancy can easily be explained if one considers the effect of grain size distribution on the possibility of kinetic description of dissociation of a polydisperse material. In the case of the Rosin-Ramler-Stirling distribution (usually encountered in crystallized material), the mathematical description of the dissociation is only possible with the use of diffusion equations [12].

On the basis of the above considerations, one can suppose that in fact 1st stage of decomposition of the basic salt is effected in the transition region (kinetic and diffusional), and that the rate of the process is therefore controlled both by the kinetics and by the diffusion of a gaseous reaction product (H_2O) through the layer of solid product formed on the substrate grains. It seems that in the second step the effect of diffusion is much more distinct, probably owing to the increased layer thickness of the solid reaction product. Further dehydration of the compound and removal of 2 moles of ammonia (2nd stage of the dissociation) is accompanied by destruction of the alunite structure of the material.

This stage of thermal decomposition of basic aluminium ammonium sulfate also proceeds in two steps, probably because of the difference in temperatures at which the evolution of water and of ammonia from the compound begins.

In the first step of this stage, up to 723 K, the dehydration of the compound continues, and above 723 K the evolution of water and of ammonia proceed simultaneously.

Similarly as in the 1st stage, the kinetics of the process may be represented only by Eqs (1) and (2). An additional difficulty in interpretation of the kinetic data is the effect of two independent variables. The values of the activation energies (96 and 74 kJ/mole) and temperature coefficients (1.25 and 1.19) may be accounted for by the diffusional (or at least diffusional – kinetic) nature of the process. A similar conclusion may also be drawn from the value of $n = 0.5$.

In the 3rd stage of the decomposition, *viz.* during desulfuration of the compound, the intermediates ($Al_2(SO_4)_3$ and $AlH(SO_4)_2$) are decomposed [11].

Despite the very complex mechanism of the process, its kinetics may be described by Eqs (1) and (2) within a wide interval of values of α (0.1 – 1.0). The activation energy (128 kJ/mole) (see Table 3), the temperature coefficient of the process (1.19) and the value of $n = 0.5$ may be accounted for by the fact that the desulfuration proceeds in the diffusion region. The rate-limiting process may be the diffusion of sulfur oxides, oxygen or water vapour in the layer of the solid reaction product (γ-Al_2O_3), although the effects of other factors, connected with the complex character of the solid-phase transformation, cannot be excluded.

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Résumé — La cinétique de la décomposition thermique sous vide du sulfate basique d'aluminium et d'ammonium a été étudiée. On a identifié les paramètres du modèle cinétique de la dissociation de ce composé. Les résultats des études cinétiques et le mécanisme du processus de décomposition sont discutés.

Zusammenfassung — Es wurde die Kinetik der thermischen Zersetzung von basischem Ammoniumaluminiumsulfat im Vakuum untersucht. Die Parameter für das kinetische Modell der Dissoziation von der Verbindung wurden identifiziert und die Ergebnisse der kinetischen Untersuchungen im Zusammenhang mit dem Verfahrensmechanismus besprochen.

Резюме — Исследована в вакууме кинетика термического разложения основного сульфата алюминия — аммония. Определены кинетические параметры всех стадий процесса и установлена математическая модель термического разложения соединения в соответствии с механизмом процесса.