THERMAL DISSOCIATION OF BASIC ALUMINIUM AMMONIUM SULFATE IN VACUUM

PART III. MATHEMATICAL MODEL OF THE PROCESS

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A mathematical model of the thermal decomposition of basic aluminium ammonium sulfate has been developed. The construction of the model consisted in simulation of TG and DTG curves, with the use of kinetic parameters identified on the basis of results obtained in measurements of the rate of thermal dissociation of the compound under isothermal and non-isothermal conditions.

Our previous works [1, 2] were devoted to investigations of the stages and the kinetics of the vacuum decomposition of basic aluminium ammonium sulfate. It was established that the compound decomposes in three stages. The first stage, which proceeds at 378 − 623 K, is connected with partial dehydration of the compound. The characteristic processes of the second stage (623 − 873 K) are further dehydration of the compound and liberation of ammonia. In the third stage (873 − 1273 K) desulfuration of the basic salt takes place. Further investigations were devoted to studies of the kinetics of thermal decomposition under isothermal and isobaric conditions within all three stages of the decomposition.

The results obtained made it possible to identify (by examination of more than ten mathematical models) the kinetic parameters of thermal decomposition of basic aluminium ammonium sulfate (see Table 1), with consideration to mathematical models allowing a good correlation of the results obtained in the studies on the rate of dissociation. The kinetic parameters found in that way were then used for simulation of the TG and DTG curves of the compound studied.

The same paper also contains the methods for identification of the kinetic parameters of thermal dissociation of basic aluminium ammonium sulfate, based on studies of the rate of decomposition of that compound under non-isothermal conditions.

Mathematical treatment of the results of kinetic studies and the results of calculations

The kinetic parameters of thermal decomposition of basic aluminium ammonium sulfate (see Table 1), obtained by means of isothermal methods, have been utilized for simulation of the TG and DTG curves obtained in vacuum at a heating rate of 2 K/min. The simulation consisted in numerical integration of a system of equations: a reaction rate equation in a form depending on the accepted model of the

Table 1

Kinetic parameters calculated from data obtained during the thermal

Model	Stage I			
	E_1	A_1	E_2	A_2
	kJ/mole^{-1}	min^{-1}	kJ/mole	min^{-1}
Jander	154.2	$0.23 \cdot 10^{12}$	110.6	$0.21 \cdot 10^7$
Ginstling–Brounstein	149.6	$0.76 \cdot 10^{11}$	93.4	$0.38 \cdot 10^5$
Erofeew	—	—	94.3	$0.89 \cdot 10^6$

process, and an equation characterizing the assumed rate of the increase of temperature. The mathematical model of thermal decomposition of basic aluminium ammonium sulfate has been developed under the assumptions that the decomposition proceeds in three stages and that the kinetics of the process in all three stages under isothermal conditions may be described by the Jander and Ginstling–Brounstein equations.

Hence the simulation of the thermogravimetric curves consists in numerical integration (within each stage of the dissociation) of a system of two equations

$$\frac{d[(1 - 2/3\alpha) - (1 - \alpha)^{2/3}]}{dt} = A \exp\left[\frac{-E}{RT}\right] \tag{3a}$$

$$\frac{dT}{dt} = q = 2 \text{ degree/min} \tag{3b}$$

$$\frac{d\{[1 - (1 - \alpha)^{1,3}]^2\}}{dt} = A \exp\left(\frac{-E}{RT}\right) \tag{4a}$$

$$\frac{dT}{dt} = q = 2 \text{ degree/min} \tag{4b}$$

In calculations of the TG curve the initial mass of the substance involved in the given stage was assumed to be equal to the final mass of the preceding stage; the initial mass of basic aluminium ammonium sulfate was 5 mg. The systems of equations (3) and (4) were integrated by the Runge-Kutta method of 4th order, according to the flow diagram presented in Fig. 1. In Fig. 2 the results of the calculations are compared with experimental data, viz. with the TG and DTG curves obtained in the decomposition of basic aluminium ammonium sulfate in vacuum at a heating rate of 2 degree/min.

Good agreement of the calculations with the experimental results was found for the two initial stages of decomposition: 1st stage — partial dehydration of the

dissociation of basic aluminium ammonium sulfate under isothermal conditions

Stage II				Stage III	
E_1	A_1	E_2	A_2	E_1	A_1
kJ/mole	min^{-1}	kJ/mole	min^{-1}	kJ/mole	min^{-1}
108.5	$0.22 \cdot 10^5$	82.1	$0.48 \cdot 10^3$	147.1	$0.32 \cdot 10^4$
96.4	$0.23 \cdot 10^4$	73.7	$0.12 \cdot 10^2$	127.8	$0.30 \cdot 10^3$
108.1	$0.18 \cdot 10^6$	—	—	132.0	$0.65 \cdot 10^4$

compound, and 2nd stage — further dehydration and removal of 2 moles of ammonia. Difference occurred in the 3rd stage of decomposition, i.e. in the desulfura-
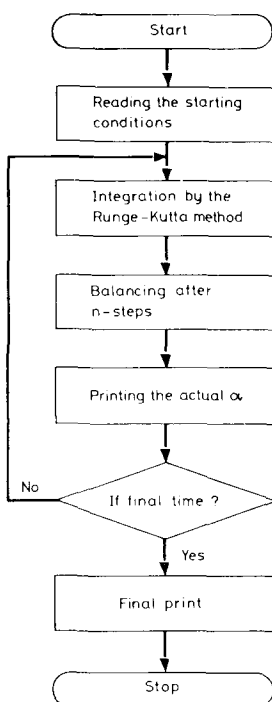

Fig. 1. Flow diagram of the simulation of the thermogravimetric curves, with the use of kinetic parameters calculated from data obtained during the thermal dissociation of basic aluminium ammonium sulfate under isothermal conditions
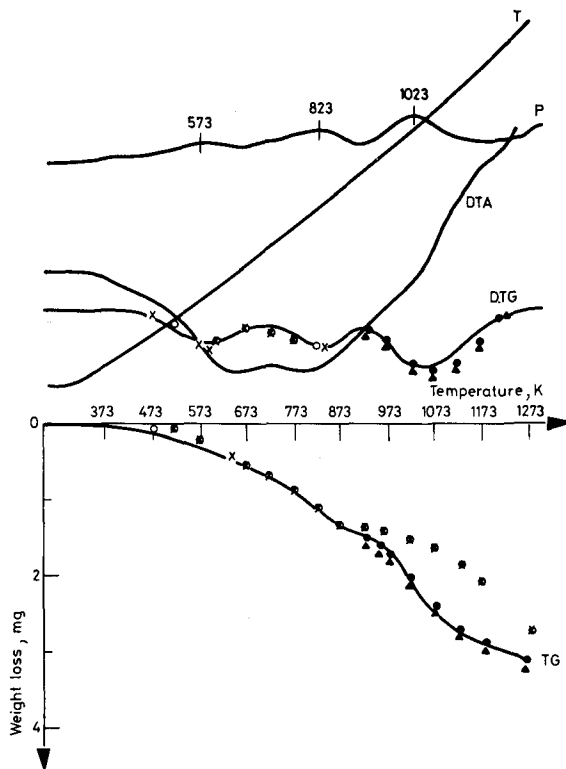
Fig. 2. Results of simulation of the thermogravimetric curves: × — Jander model applied to data from isothermal decomposition; ○ — Ginstling—Brounstein model applied to data from isothermal decomposition; ⊙ — Jander model applied to data from non-isothermal decomposition; ▲ — Ginstling—Brounstein model applied to data from non-isothermal decomposition. P: total pressure of the gaseous decomposition products

tion of the compound. The differences probably arise from a different mechanism of the process under a programmed increase of temperature as compared with that operative under isobaric and isothermal conditions, for which the kinetic parameters have been determined. This supposition is confirmed by the thermogravimetric examination of basic aluminium ammonium sulfate at different heating rates [1]. For a rate of 2 degree/min a single peak is observed in the P, DTG and partial pressure curves, and a corresponding endothermic effect in the DTA curve. Increase of the heating rate to 6 and 10 degree/min leads to the separation of peaks, which might be accounted for by a change in the mechanism of the process. For this reason the identification of the kinetic parameters of desulfuration of basic aluminium ammonium sulfate has been based on data obtained in decomposition under non-
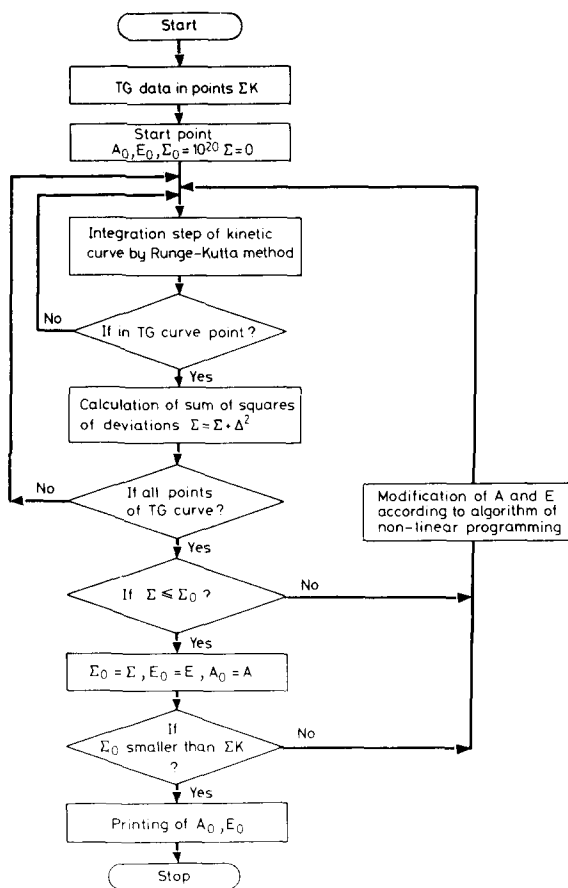
Fig. 3. Flow diagram for identification of kinetic parameters, with the use of data obtained during the thermal dissociation of basic aluminium ammonium sulfate under non-isothermal conditions

isothermal conditions, i.e. with utilization of T and TG curves taken in vacuum at a heating rate of 2 degree/min in the temperature range $873-1273$ K. The calculations were performed by the non-linear regression method, under the assumption that thermal dissociation of the compound may be described by the Ginstling–Brounstein and Jander models, by minimalizing the sum of the squares of the points calculated (with respect to their equivalents on the TG curve) in the space of the kinetic parameters A and E. The starting points were the activation energies (E) and pre-exponential coefficients (A) found under the non-isothermal conditions. The calculations were carried out according to the flow diagram presented in Fig. 3.

The results of calculations are given in Fig. 2 and in Table 2.

Table 2

Kinetic parameters calculated from data obtained during the thermal dissociation of basic aluminium ammonium sulfate under non-isothermal conditions

Model	Stage III	
	E	A
	kJ/mol^{-1}	min^{-1}
Jander	161.2	$0.16 \cdot 10^6$
Ginstling–Brounstein	153.8	$0.44 \cdot 10^5$

Conclusions

The performed calculations have shown that the mathematical model of thermal dissociation of basic aluminium ammonium sulfate may represented in two ways:
1. Assuming that the rate of decomposition of the compound is described by the Ginstling–Brounstein equation, one obtains:

at temperatures $378 - 623$ K:

$$\frac{\mathrm{d}\,[(1 - 2/3\alpha) - (1 - \alpha)^{2/3}]}{\mathrm{d}t} = 7.6 \cdot 10^{10} \exp\left(\frac{-149,600}{RT}\right)$$

at temperatures $623 - 873$ K:

$$\frac{\mathrm{d}\,[(1 - 2/3\alpha) - (1 - \alpha)^{2/3}]}{\mathrm{d}t} = 2.3 \cdot 10^3 \exp\left(\frac{-96,400}{RT}\right)$$

at temperatures $873 - 1273$ K:

$$\frac{\mathrm{d}\,[(1 - 2/3\alpha) - (1 - \alpha)^{2/3}]}{\mathrm{d}t} = 4.4 \cdot 10^4 \exp\left(\frac{-153,800}{RT}\right)$$

2. Use of the Jander model for the mathematical description of the experimental data gives:

at temperatures $378 - 623$ K:

$$\frac{\mathrm{d}\,\{[1 - (1 - \alpha)^{1/3}]^2\}}{\mathrm{d}t} = 2.3 \cdot 10^{11} \exp\left(\frac{-154,200}{RT}\right)$$

at temperatures $623-873$ K:

$$\frac{d\{[1-(1-\alpha)^{1/3}]^2\}}{dt} = 2.2 \cdot 10^4 \ \exp\left(\frac{-108,500}{RT}\right)$$

at temperatures $873-1273$ K:

$$\frac{d\{[1-(1-\alpha)^{1/3}]^2\}}{dt} = 1.6 \cdot 10^5 \ \exp\left(\frac{-161,200}{RT}\right)$$

The bases for identification of mathematical models describing the 1st and the 2nd stages of the decomposition were the kinetic parameters determined during the studies on thermal dissociation under isothermal conditions. Since the approximation gave fairly accurate results, the proposed models are suitable for representation of the shapes of TG and DTG curves within the first and the second stages of thermal dissociation of basic aluminium ammonium sulfate.

The shapes of the TG and DTG curves obtained for the third stage of decomposition under steady increase of temperature cannot be simulated on the basis of kinetic parameters A and E identified in isothermal investigations. Hence, the construction of the mathematical model of the third stage of dissociation under non-isothermal conditions was based on the multiple regression method, which served for determination of the kinetic parameters under a steady increase of temperature (2 degree/min). A comparison of the kinetic parameters thus found (activation energy E and the pre-exponential factor A) with the values of A and E determined during isothermal studies (see Tables 1 and 2) shows that either method gives very close values of the activation energy. The higher rate of dissociation under non-isothermal conditions is due to the fact that the pre-exponential factor is greater by about two orders. The lack of a general theory of this factor does not allow precise analysis of its changes. One may assume, however, that increase of the value of A may be due to a change in the course of the decomposition resulting from the different experimental conditions. The presented considerations lead to the conclusion that construction of a mathematical model of a process (based on kinetic parameters determined under different conditions) requires a thorough knowledge of the mechanism of dissociation and the possibilities of its change under the given experimental conditions.

References

1. J. PYSIAK and B. PACEWSKA, J. Thermal Anal., 19 (1980) 79.
2. J. PYSIAK and B. PACEWSKA, J. Thermal Anal., 19 (1980) 89.

RÉSUMÉ — Un modèle mathématique décrivant la décomposition thermique du sulfate basique d'aluminium et d'ammonium est présenté.

La méthode consiste à simuler les courbes thermogravimétriques TG et TGD à l'aide des paramètres cinétiques identifiés sur la base des résultats des déterminations isothermes et non-isothermes de la vitesse de la dissociation du composé.

ZUSAMMENFASSUNG — Es wurde das mathematische Modell fur thermische Zersetzung des basischen Ammoniumaluminiumsulfats bearbeitet. Die Struktur des Modells bestand in der Nachbildung von thermogravimetrischen Kurven TG, DTG mittels der kinetischen Parameter, die auf Grund der isothermen und der nichtisothermen Ergebnisse der Untersuchungen nach der Dissoziationsgeschwindigkeit von Verbindungen identifiziert wurden.

Резюме — Разработана математическая модель термического разложения основной двойной соли сернокислого алюминия и сернокислого аммония. Построение модели заключается в моделировании термогравиметрических кривых ТГ и ДТГ с использованием кинетических параметров, установленных на основании результатов, полученных при измерении скорости термической диссоциации этого соединения в изотермических и неизотермических условиях.