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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

KINETICS OF THERMAL DISSOCIATION OF BASIC ALUMINIUM AMMONIUM SULFATE IN A HYDROGEN ATMOSPHERE

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The rate of release of sulfur oxides from basic aluminium ammonium sulfate (BAAS) under isothermal, isobaric conditions in a hydrogen atmosphere was studied.

Twomethods of selection of the $g(\alpha)$ function which best describes the isothermal experimental data are discussed.

The first method is based on statistical criteria and the second one on the the use of a reduced-time scale. Kinetic parameters for the thermal decomposition of BAAS in a hydrogen atmosphere are reported.

In a previous study [1] we reported the stages of thermal decomposition of BAAS in a hydrogen atmosphere . The results pointed to the influence of a hydrogen atmosphere only on the last stage of the BAAS dissociation process i. e. desulfuration of this compound (Fig. 1).

The desulfuration in a hydrogen atmosphere probably occurs as follows:

$$2AlH(SO_4)_2 + H_2 = Al_2(SO_4)_3 + SO_2 + 2H_2O$$

$$Al_2(SO_4)_3 + 3H_2 = Al_2O_3 + 3SO_2 + 3H_2O$$

$$2AlH(SO_4)_2 + 2H_2 = Al_2O(SO_4)_2 + 2SO_2 + 3H_2O$$

$$Al_2O(SO_4)_2 + 2H_2 = Al_2O_3 + 2SO_2 + 2H_2O$$

In the present work, the object of our studies was to establish the kinetics of desulfuration of BAAS in a hydrogen atmosphere. The selection of the appropriate kinetic equations and determination of the kinetic parameters of the process are also considered.

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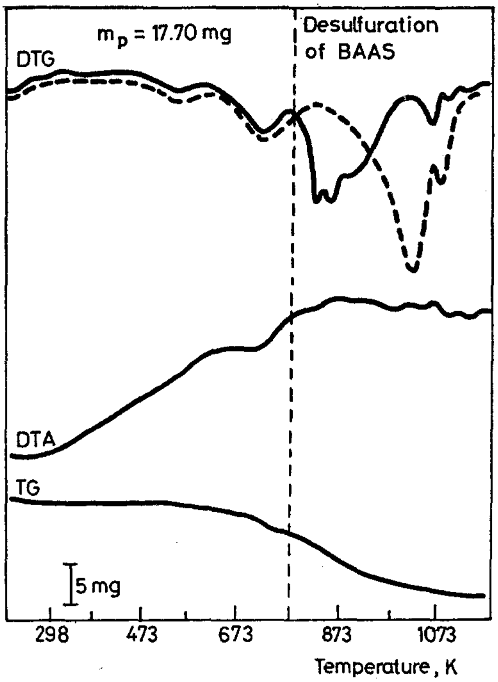

Fig. 1 Thermogravimetric analyses of BAAS made using a Mettler thermoanalyser —— in a hydrogen atmosphere ------ in argon; heating rate: 15 deg/min

Experimental

The kinetic studies were carried out using a Mettler thermoanalyzer. The starting material for measurements was BAAS, which had been preliminary decomposed at 843 K in an air atmosphere. Under these conditions, water (except one mole) and ammonia released from the basic salt.

25 mg samples were heated at 40 deg/min in an argon atmosphere up to the set isothermal temperature. After reaching this temperature, the gas atmosphere was changed to hydrogen. Kinetic measurements were made at 798 K, 823 K, 848 K, 873 K, 898 K and 973 K. The degree of transformation was determined from the fractional mass loss based on complete decomposition of all BAAS to aluminium oxide.

Results and kinetic analysis

Figure 2 shows the α, time curves for the reaction at the series of different isothermal temperatures.

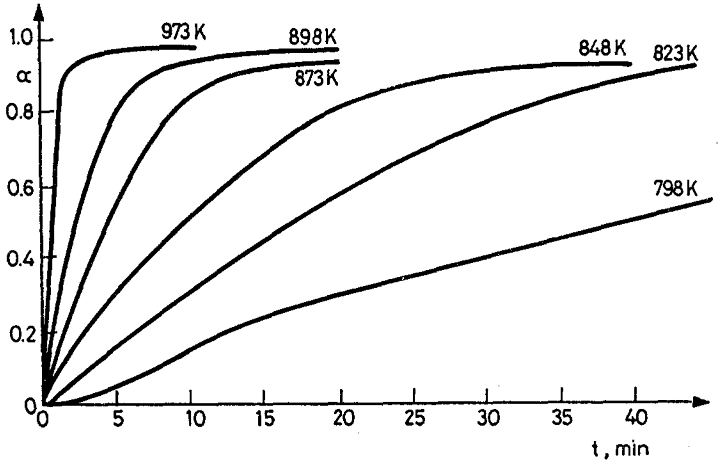

Fig. 2 Degree of transformation, α, *vs* time for the desulfuration of BAAS in a hydrogen atmosphere of a series of isothermal temperatures

Kinetic parameters were determined using a statistical method [2]. The selection of the $g(\alpha)$ function which best describes the experimental results was made from the 17 kinetic equations collected in Table 1. These equations are frequently used to describe the kinetics of thermal decomposition of solids in general [3, 4], and also for the identification of the kinetic parameters of compounds similar to BAAS [5]. Previously we used them for the identification of the kinetic parameters of decomposition of BAAS in vacuum [8].

Two models for describing experimental data, based on the least-squares method (LSM), were considered.

Model 1: $g(\alpha) = kt$
Model 2: $g(\alpha) = kt + b$

where k = rate constant in $\min^{-1}$, t = time in min, b = constant.

The second model seems to be more appropriate since:

(a) in the initial stage of measurements, errors connected with unstabilised experimental conditions can occur.

Table 1 Kinetic functions for description of the thermal decomposition of solids and symbols of the equations according to [3]

No	Equation	n	$g(\alpha)$	Symbols [3]
1		1	α	
2	Power law	2	α^2	D1
3		1/2	$\alpha^{1/2}$	
4	α^n	1/3	$\alpha^{1/3}$	
5		1/4	$\alpha^{1/4}$	
6	Contracting geometry	2	$1-(1-\alpha)^{1/2}$	R2
7	$1-(1-\alpha)^{1/n}$	3	$1-(1-\alpha)^{1/3}$	R3
8		1	$-\ln(1-\alpha)$	F1
9		3/2	$[-\ln(1-\alpha)]^{2/3}$	
10	Erofeev	2	$[-\ln(1-\alpha)]^{1/2}$	A2
11	$[-\ln(1-\alpha)]^{1/n}$	3	$[-\ln(1-\alpha)]^{1/3}$	A3
12		4	$[-\ln(1-\alpha)]^{1/4}$	A4
13	2D diffusion controlled $(1-\alpha)\ln(1-\alpha)+\alpha$	–	$(1-\alpha)\ln(1-\alpha)+\alpha$	D2
14	Ginstling-Brounstein $(1-2/3\alpha)-(1-\alpha)^{2/3}$	–	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	D4
15	Jander $[1-(1-\alpha)^{1/3}]^2$	–	$[1-(1-\alpha)^{1/3}]^2$	D3
16	Prout-Tompkins $\ln\frac{\alpha}{1-\alpha}$	–	$\ln\frac{\alpha}{1-\alpha}$	B1
17	Second order $\frac{1}{1-\alpha}-1$		$\frac{1}{1-\alpha}-1$	F2

(b) the deviation of experimental points ($g(\alpha)$ values) for equations of the type $y = ax + b$ were smaller than for equations of the type $y = ax$.

The following parameters were calculated to aid the selection of the $g(\alpha)$ function, which best describes the experimental results:

1. the correlation coefficient, r
2. a weighted correlation coefficient
3. the sum of the squares of the residuals

$$R = \frac{1}{n} \sum_{i=1}^{n} (\alpha_{\mathrm{calc},i} - \alpha_{\mathrm{exp},i})^2$$

where n = the number of experimental α values,

$\alpha_{\mathrm{exp,i}}$ = the fractional decomposition for a given time t,

$\alpha_{\mathrm{calc,i}}$ = the α value calculated at time t, on the basis of the selected g(α) function.

4. the ratio of the standard deviation of the constant to its actual value (s_k/k)
5. criterion s determined from the relation

$$s = \frac{1}{N} \sum_{i=1}^{l} \sum_{j=1}^{n_i} (\alpha_{\mathrm{exp,ij}} - \alpha_{\mathrm{calc,ij}})^2$$

where l = the number of different isothermal temperatures,

n_i = the number of α values obtained at temperature T_i,

N = the sum of n_i,

$$N = \sum_{i=1}^{l} n_i$$

$\alpha_{\mathrm{exp,\,ij}}$ = the fractional decomposition determined experimentally,

$\alpha_{\mathrm{calc,\,ij}}$ = the fractional decomposition calculated from the Arrhenius equation for a given $g(\alpha)$.

For the $g(\alpha)$ function, which best describes the experimental data:

(a) values of criteria 1 and 2 should be close to one

(b) values of criteria 3, 4 and 5 should be lower than values of these criteria for other $g(\alpha)$ functions considered.

The calculations were carried out on an IBM-XT computer using a program written in BASIC. Values of the criteria (r, R, s_k/k i s) for the selection of $g(\alpha)$ function and the activation energy (E), Arrhenius pre-exponential factor (A) for model 1 and weighted LSM are shown in Table 2.

Examination of these calculations led us to the conclusion that the function $g(\alpha) = -\ln(1-\alpha)$ best describes the desulfuration reaction of BAAS.

Rate constants calculated from the above function are presented in Table 3. In Figs 3 and 4, the Arrhenius plots (log k *vs.* $1/T$) for model 1 and 2, respectively, are given. Values of the kinetic parameters identified using the function $g(\alpha) = -\ln(1-\alpha)$ both for model 1 and 2 are collected in Table 4. Independently, the well-known method for the selection of the $g(\alpha)$ function based on reduced-time plots, was applied. The "reduced time" t_{red} is usually defixed as the ratio $t/t_{0.5}$, where $t_{0.5}$ denotes the time at which fractional decomposition $\alpha = 0.5$ at the given temperature. If the experimental

Table 2 Isothermal decomposition of BAAS in a hydrogen atmosphere. The values of the criteria *r*, *R* and s_k/k given for temperature 848 K. The values of Arrhenius equation parameters (*E*, Jmol^{-1}; A, min^{-1}) and criterion *s* for model 1 and weighted LSM

No*	*r*	*R*		sk/*k*		*A*,	*E*,	*s*
		Model 1	Model 2	Model 1	Model 2	min^{-1}	Jmol^{-1}	
12	0.9303	0.0852	0.1246	0.0233	0.0070	7.2268×10^{4}	103120	0.0356
2	0.9792	0.0553	0.0656	0.0032	0.0024	9.1200×10^{6}	140646	0.0137
3	0.8823	0.1115	0.1688	0.1108	0.0102	2.2217×10^{4}	93957	0.1090
4	0.8638	0.1194	0.1844	0.1746	0.0115	1.5704×10^{4}	91262	0.1604
5	0.8544	0.1232	0.1923	0.2175	0.0122	1.3283×10^{4}	89963	0.1891
6	0.9747	0.0545	0.0725	0.0033	0.0019	1.0818×10^{6}	124070	0.0101
7	0.9837	0.0407	0.0579	0.0016	0.0011	2.7534×10^{6}	132572	0.0036
8	0.9863	0.0295	0.0530	0.0008	0.0008	7.4975×10^{7}	146616	0.0015
9	0.9846	0.0611	0.0561	0.0045	0.0008	1.0040×10^{7}	132370	0.0058
10	0.9750	0.0886	0.0721	0.0127	0.0013	3.3294×10^{6}	124858	0.0154
11	0.9606	0.1169	0.0915	0.0322	0.0022	1.0414×10^{6}	117102	0.0371
12	0.9520	0.1312	0.1017	0.0504	0.0027	5.7267×10^{5}	113159	0.0558
13	0.9769	0.0939	0.0691	0.0052	0.0019	2.9941×10^{8}	168668	0.0120
14	0.9649	0.1173	0.0861	0.0077	0.0024	4.0512×10^{8}	181113	0.0140
15	0.9271	0.1590	0.1279	0.0149	0.0049	5.3347×10^{9}	199142	0.0201
16	0.9671	0.4092	0.0832	0.0244	0.0015	1.5267×10^{11}	207690	0.0392
17	0.9159	0.0847	0.1385	0.0096	0.0072	7.6858×10^{8}	160779	0.0083

* Number of the function g(α,) is according to Table 1

curves are transformed to this coordinate system [6] they may be identical for experiments carried out at various isothermal temperatures, thus showing that one form of the $g(\alpha)$ function describes the decomposition of the compound investigated over the temperature range studied (so-called isokinetic behaviour).

The selection of the $g(\alpha)$ based on the comparison of the experimental α, t_{red} curve with theoretical curves calculated for the functions $g(\alpha)$ is very subjective.

In this paper a more objective method for selecting the $g(\alpha)$ function was used.

The sum :

$$D_{\mathrm{i}} = \sum_{i=1}^{m} [(t/t_{0.5})_{\mathrm{exp,ij}} - (t/t_{0.5})_{\mathrm{ij}}]^2$$

is calculated,

where $(t/t_{0.5})_{\mathrm{exp},j}$ and$(t/t_{0.5})_{i,j}$ are the experimental and theoretical calculated reduced-time values for degree of transformation *j*, respectively.

The value of D_i is calculated for particular temperatures and various functions denoted $i = 1\dots n$, and the value D_{sum}, being the sum of the values D_i for particular temperatures, can be calculated. The minimum value of D_{sum} determines the function $g(\alpha)$ which best describes the experimental data over the range of temperatures studied.

Table 3 Rate constants of desulfuration of BAAS calculated using the function $g(\alpha,) = -\ln(1-\alpha,)$for description of the kinetic curves

	Model 1			Model 2	
T, K	*k*, min^{-1}	Residual	*k*, min^{-1}	*a*	Residual
798	0.01698	5.385×10^{-8}	0.01765	–0.01829	8.672×10^{-8}
823	0.03842	6.713×10^{-7}	0.04077	–0.03662	1.236×10–6
848	0.07181	4.478×10^{-6}	0.07069	0.01183	1.402×10–5
873	0.15210	1.898×10^{-5}	0.15940	–0.03199	5.360×10–5
898	0.26180	1.066×10^{-4}	0.24480	0.05462	3.863×10–4
973	0.87980	4.052×10^{-3}	0.69610	0.29660	1.461×10–2

The values of D_{sum} for appropriate functions tested are shown in Table 5. Figure 5 represents experimental results of desulfuration of BAAS in a hydrogen atmosphere described by the function $g(\alpha) = -\ln(1-\alpha)$ in the temperature range 798–973 K.

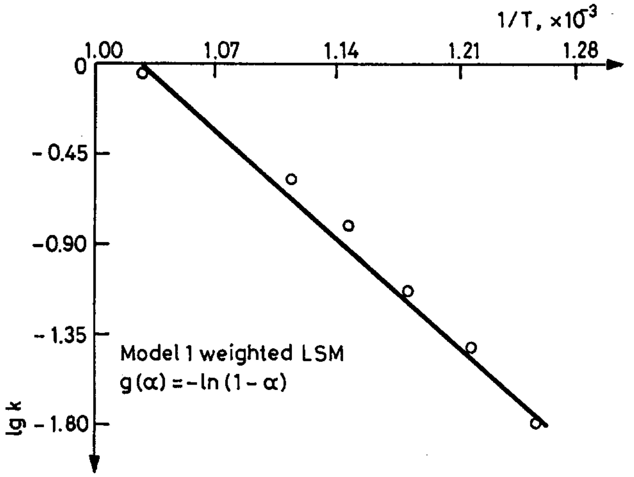

Fig. 3 Arrhenius relationship calculated by non linear LSM

Table 4 Values of Arrhenius parameters calculated by nonlinear LSM method for the function $g(\alpha) = -\ln(1-\alpha)$

Model 1		Model 2	
E, kJ mol^{-1}	A, min^{-1}	E, kJ mol^{-1}	A, min^{-1}
160.04	5.125×10^8	160.83	5.867×10^8

Table 5 Values of the D_{sum} calculated for reduced-time $t_{red} = t/t_{0.5}$ and for different functions $g(\alpha)$

No*	Dsum
8	43.995
13	57.160
14	81.817
2	88.704
7	115.284
9	148.600
6	149.724
10	208.842
1	227.986
11	265.826
12	292.436
3	298.736
4	320.918
5	331.840
15	357.529
17	3439.968

* Number of the function g(α) is according to Table 1

Discussion

It has been found [1] that the presence of hydrogen in the environment on the reaction influences on the BAAS desulfuration process. In hydrogen, desulfuration of the basic salt at a fixed rate occurs at lower temperatures than in air or in vacuum [8, 9]. The influence of a hydrogen atmosphere is probably in reduction of the primary gaseous dissociation product SO_3. This is especially important near the lower limit of the temperature range of this stage, when the equilibrium of the reaction:

$SO_3 \leftrightarrow SO_2 + 1/2O_2$ is transferred towards SO_3 [9].

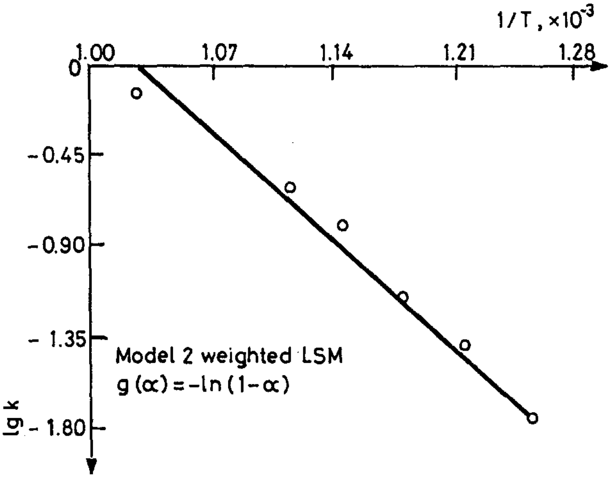

Fig. 4 Arrhenius relationship calculated by linear LSM

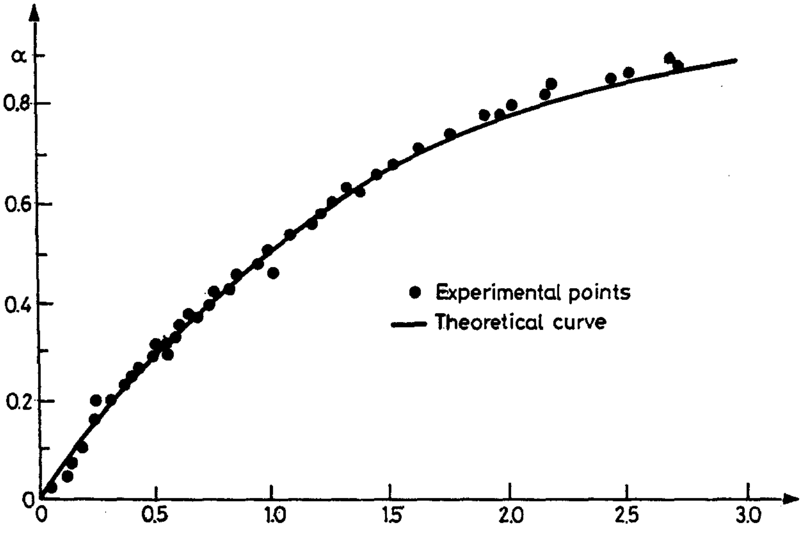

Fig. 5 Experimental results for decomposition of BAAS in a hydrogen atmosphere in the temperature range 798 K – 973 K described by the function $g(\alpha) = -\ln(1-\alpha)$; $t_{\rm red}$ calculated for $\alpha = 0.5$

The process of desulfuration of BAAS is complicated and occurs in several steps.

From consideration of the kinetic results (Tables 2–5), it was found that in spite of the complicated desulfuration process of BAAS the kinetics can be described by the simple first-order function $g(\alpha) = -\ln(1-\alpha)$ over practically the complete range of degree of transformation, α, from 0 to 1.

The values of the kinetic parameters calculated by the weighted LSM method are: $E = 160\ \text{kJ}\cdot\text{mol}^{-1}$ and $A = 5.12\times10^{8}\ \text{min}^{-1}$.

In the case in question, where reactions proceed in a parallel and multistage way, the determined kinetic parameters give information only about the whole course of complex physicochemical phenomena occuring during dissociation. Thus, "kinetic law" cannot be univocally correlated with the mechanism of basic salt dissociation.

Conclusions

1. The presence of hydrogen in the environment of the reaction causes the last stage of decomposition of BAAS, i.e. desulfuration of the compound, to occur at a given rate at lower temperatures in H_2 than in air or vacuum.
2. At 973 K, the degree of transformation is close to one after 10 min of decomposition. Low temperature of desulfuration of BAAS is very important to obtain aluminium oxides with special properties.
3. Selection of the function $g(\alpha)$ which best described experimental data was made by means of statistical criteria and by using a reduced-time method.
4. The kinetics of the desulfuration of BAAS can be described by the function $g(\alpha) = -\ln(1-\alpha)$ over virtually the whole range $0 < \alpha < 1$.
5. The values of the kinetic parameters are: $E = 160\ \text{kJ}\cdot\text{mol}^{-1}$ and $A = 5.12\times10^{8}\ \text{min}^{-1}$.

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Zusammenfassung — Unter isothermen, isobaren Bedingungen wurde die Geschwindigkeit der Freisetzung von Schwefeloxiden aus basischem Aluminiumammoniumsulfat (BAAS) untersucht.

Es werden zwei Verfahren zur Auswahl derjenigen $g(\alpha)$-Funktion diskutiert, die die isothermen Ergebnisse am besten wiedergibt.

Das erste Verfahren beruht auf statistischen Kriterien, dem zweiten lag eine reduzierte-Zeitskala zugrunde. Kinetische Parameter für die thermische Zersetzung von BAAS in Wasserstoff werden beschrieben.