# INVESTIGATION OF RATE OF THERMAL DISSOCIATION OF BASIC ALUMINIUM POTASSIUM SULPHATE IN HYDROGEN ATMOSPHERE

B. Pacewska

INSTITUTE OF CHEMISTRY IN PLOCK BRANCH OF WARSAW UNIVERSITY OF TECHNOLOGY, 09-400 PLOCK, POLAND

The rate of release of sulphur oxides from basic aluminium potassium sulphate was studied in a hydrogen atmosphere under isothermal-isobaric conditions, and the kinetic parameters of the process were determined by the statistical criteria method.

The desulphurization of alunite in a hydrogen atmosphere occurs in two stages [1]. The first stage, in the temperature range 823-943 K, involves the following reactions:

$$2\,KAl(SO_4)_2 = K_2SO_4 + Al_2(SO_4)_3$$

$$Al_2(SO_4)_3 + 3\,H_2 = \gamma\text{-}Al_2O_3 + 3\,SO_2 + 3\,H_2O$$
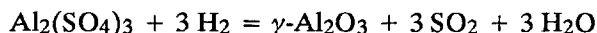
A stable mixture of γ-Al_2O_3 and K_2SO_4 is formed. The washing-out of the K_2SO_4 from this mixture gives a possibility of obtaining an active form of aluminium oxide.

The second stage, in the temperature range 943-1123 K, involves the reaction

$$K_2SO_4 + Al_2O_3\,d + 4\,H_2 = K_2O\cdot Al_2O_3 + H_2S + 3\,H_2O$$
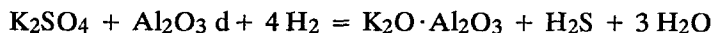
When the temperature is increased up to about 1223 K, the potassium aluminate is transformed into KAl_5O_8:

$$K_2O\cdot Al_2O_3 + 4\,Al_2O_3 = K_2O\cdot 5\,Al_2O_3$$

At a temperature close to 1223 K, the phase change of γ-Al_2O_3 into α-Al_2O_3 occurs. In the gaseous phase, sulphur oxides are reduced by hydrogen.

The ains of the present work were to establish the kinetics of desulphurization in the first stage of thermal decomposition of basic aluminium potassium sulphate in a hydrogen atmosphere, and to use the statistical criteria method to determine the kinetic parameters of this stage.

Experimental

The basic aluminium potassium sulphate had the following chemical composition (weight percentages): Al_2O_3 – 30.94; K_2O – 10.55; SO_3 – 41.71; H_2O – 16.8. The kinetic studies were carried out in the temperature range 823-943 K (cf. Fig. 1).
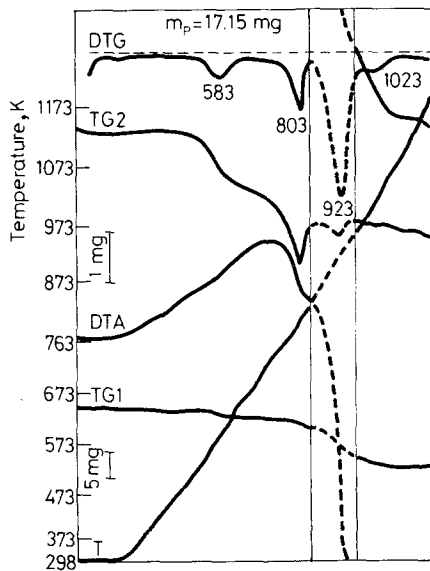

Fig. 1 TG curves of basic aluminium potassium sulphate in a hydrogen atmosphere

The kinetic isothermal measurements were made with a Mettler thermoanalyzer. 25 mg samples were heated initially at a rate of 40 deg/min in an argon atmosphere up to 873 K in order to attain complete dehydration of the compound, after which hydrogen was introduced into the reaction zone

and kinetic measurements were carried out under isobaric and isothermal conditions at temperatures of 823, 863, 883, 893, 903 and 923 K.

The transformation degree was determined from the relation

$$\alpha = \frac{\Delta m}{\Delta m_{max}} \tag{1}$$

where Δm = weight loss of the sample after time t,

Δm_{max} = maximum weight loss of the sample in the first stage, corresponding to the release of 3 mol of SO_3 from the compound. Kinetic curves are shown in Fig. 2.
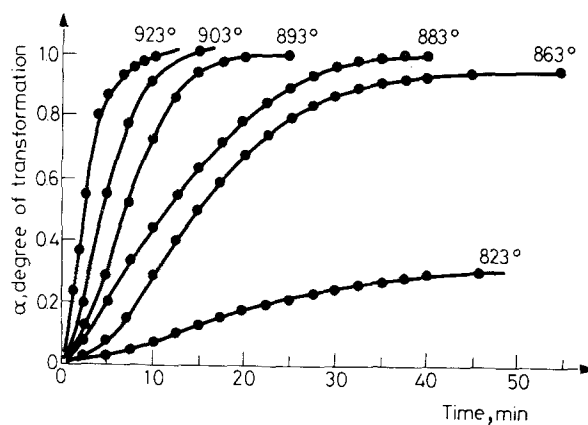

Fig. 2 Kinetic curves of the first stage of desulphurization of basic aluminium potassium sulphate in a hydrogen atmosphere

The kinetic parameters were determined with the statistical criteria method [2]. The $g(\alpha)$ function describing the experimental results was selected from among 18 functions most often used in investigations of the kinetics of thermal decomposition of solids (Table 1).

Two variants for the description of the experimental data were considered by means of the least squares method:

$$\text{Variant 1: } g(\alpha) = k \cdot t \tag{2}$$
$$\text{Variant 2: } g(\alpha) = k \cdot t + b \tag{3}$$

where k = rate constant; t = time and b = constant.

Table 1 Kinetic functions for the description of the thermal decomposition of solids

No	$g(\alpha)$	No	$g(\alpha)$
1	α	10	$[-\ln(1-\alpha)]^{1/2}$
2	α^2	11	$[-\ln(1-\alpha)]^{1/3}$
3	$\alpha^{1/2}$	12	$[-\ln(1-\alpha)]^{1/4}$
4	$\alpha^{1/3}$	13	$(1-\alpha)\ln(1-\alpha)+\alpha$
5	$\alpha^{1/4}$	14	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
6	$1-(1-\alpha)^{1/2}$	15	$[1-(1-\alpha)^{1/3}]^2$
7	$1-(1-\alpha)^{1/3}$	16	$\ln[\alpha]/(1-\alpha)$
8	$-\ln(1-\alpha)$	17	$1/(1-\alpha)-1$
9	$[-\ln(1-\alpha)]^{2/3}$	18	$\ln\alpha$

The following criteria were used to select the $g(\alpha)$ best describing the experimental results:

1. Correlation coefficient r.

2. A correlation coefficient considering weights.

3. For the given temperature, the following parameter was calculated:

$$R = 1/n \sum_{i=1}^{n} (\alpha_{\exp,i} - \alpha_{\text{calc},i})^2 \qquad (4)$$

where n = number of experimental α values,

$\alpha_{\exp,i}$ = degree of transformation (Eq. 1) at a given time,

$\alpha_{\text{calc},i}$ = α value calculated for a given time on the basis of the corresponding $g(\alpha)$ function ($k \cdot t$ or $k \cdot t + b$).

4. The ratio S_k/k the ratio of the standard discrepancy and the rate constant of the reaction).

5. Criterion S:

$$S = 1/N \sum_{i=1}^{l} \sum_{j=1}^{n_i} (\alpha_{\exp,ij} - \alpha_{\text{calc},ij})^2 \qquad (5)$$

where l = number of temperatures,

n_i = number of degrees of transformation at temperature i,

N = the sum of n_i: $N = \sum_{i=1}^{l} n_i$,

$\alpha_{\exp,ij}$ = degree of transformation determined experimentally,

$\alpha_{\text{calc},ij}$ = degree of transformation determined from the Arrhenius equation for a given $g(\alpha)$ [2].

The $g(\alpha)$ functions best describing the experimental results should meet the following conditions:
- the values of criteria 1 and 2 should be as close as possible to one;
- the values of criteria 3, 4 and 5 should be minimum as compared with the values of these criteria for other $g(\alpha)$ functions considered.

The calculations were carried out on an IBM-XT computer with a program written in BASIC.

Table 2 presents values of the Arrhenius activation energy E, the pre-exponential factor A and S (criterion 5) for the four $g(\alpha)$ functions best describing the experimental data with the use of all five statistical criteria. Figure 3 illustrates the Arrhenius relationship for a case when the experimental results are described with the kinetic equation (Eq. 1 in Table 2).
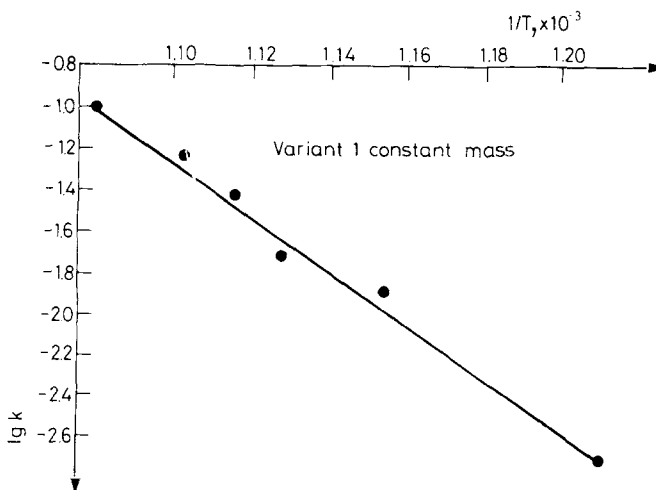

Fig. 3 Example of the relationship between $\log k$ and $1/T$

Table 2 Examples of values of A, E and criterion S for variant 1 with the use of constant weights

$g(\alpha)$	A, min^{-1}	E, kJ/mol	S
9	$1.10\ 10^{11}$	205.96	0.004450
7	$2.12\ 10^{11}$	219.55	0.005513
6	$2.97\ 10^{10}$	203.95	0.007303
10	$1.02\ 10^{10}$	188.44	0.007967

Discussion

The process of release of decomposition products of basic aluminium potassium sulphate in a hydrogen atmosphere occurs with a measurable rate in the temperature range 823-923 K. At 923 K, a degree of transformation close to one is achieved in about 10 minutes, in accord with earlier results [1]. The influence of the hydrogen atmosphere is evident and probably involves mainly the reduction of SO_3, the original product of decomposition. This can be especially important near the lower limit of the temperature range of this stage, when the equilibrium of the reaction $SO_3 \rightleftarrows SO_2 + \frac{1}{2}O_2$ favours the formation of SO_3 [3].

Analysis of the kinetic data (examples are given in Table 2) demonstrates that the rate of release of sulphur oxides from basic aluminium potassium sulphate in a hydrogen atmosphere can be described with comparably good accuracy by four kinetic equations deduced for very different process models (Eqs 6, 7, 9 and 10 in Table 2).

If "the kinetic law" cannot be combined with "the process mechanism", then the process should be described by the equation containing the lowest number of constants (at the best, only one, i.e. the rate constant).

In our case these conditions can be met by the equation of the kinetic region of reaction (Eq. 7 in Table 2), i.e. the Spencer-Topley equation.

Conclusions

1. The release of sulphur oxides from basic aluminium potassium sulphate in a hydrogen atmosphere occurs in two stages:
- in the temperature range 823-943 K, a solid mixture of K_2SO_4 and γ-Al_2O_3 is formed:
- above 943 K, potassium sulphate undergoes decomposition.

2. The first stage of the decomposition can be described with the equation of the kinetic region of reaction, with the kinetic parameters

$$E = 219.55 \text{ kJ/mol and } A = 2.12 \cdot 10^{11} \text{ min}^{-1}$$

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References

1 B. Pacewska and J. Pysiak, Thermal Decomposition of Basic Aluminium-Potassium Sulfate in Hydrogen Atmosphere (in press)
2 C. Rózycki and M. Maciejewski, Thermochim. Acta, 96 (1985) 91.
3 J. Pysiak and B. Pacewska, J. Thermal Anal., 19 (1980) 79.

Zusammenfassung — Es wurde in Wasserstoff unter isothermen-isobaren Bedingungen die Geschwindigkeit der Freisetzung von in basischem Aluminium-kaliumsulfat in Form von Aluminiumsulfat gebundenen Schwefeloxiden untersucht und die kinetischen Größen dieses Prozesses bestimmt.