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Note

THERMAL DECOMPOSITION OF BASIC ALUMINIUM POTASSIUM SULFATE. PART III. GENERAL REGULARITIES OF THERMAL DISSOCIATION

JANUSZ PYSIAK and ALEKSANDRA GLINKA

Institute of Chemistry, Płock Branch of Warsaw Technical University, 09-400 Płock (Poland)

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Among the most frequently observed empirical relationships concerning the thermal dissociation of solids are:

the Zawadzki—Bretsznajder [1,2] relation which describes the relationship between the activation energy and the pressure in the reaction system;

the existence of an isokinetic temperature [3] at which the rate constants of decomposition under different pressures become equal to each other;

the compensation effect [3,4] which interrelates the pre-exponential factor in the Arrhenius equation with the activation energy; and

a specific correlation between the activation energy and the supersaturation [5]. According to the latter the activation energy of a dissociation process calculated from the reaction rates at different temperatures under constant supersaturation is constant and equal to the Arrhenius activation energy of a process carried out under considerably reduced pressure (in vacuum).

Recently it has been shown that the above relationships are interrelated and may be regarded as a direct consequence of considering the Arrhenius equation as a projective correlation [4]. The existence of such correlations has hitherto been established for relatively simple reactions, such as the thermal decomposition of carbonates, dehydration of crystal hydrates, etc.

The aim of the present work was to utilize these relationships for a description of much more complex systems as well as to gain additional information on the kinetics and mechanism of the dissociation of basic aluminium potassium sulfate (BAPS). The adequateness of kinetic studies reported in a previous part of the work [6] was also checked.

RESULTS AND DISCUSSION

The Zawadzki—Bretsznajder relationship, to be denoted as the $E = \mathrm{f}(p)$ relation, has been searched for by graphical representation of the rate constant k as a function of the reciprocal temperature for each stage of the dehydration process (Fig. 1).

It follows from the presented data, that with increasing p_{H_2O} (with

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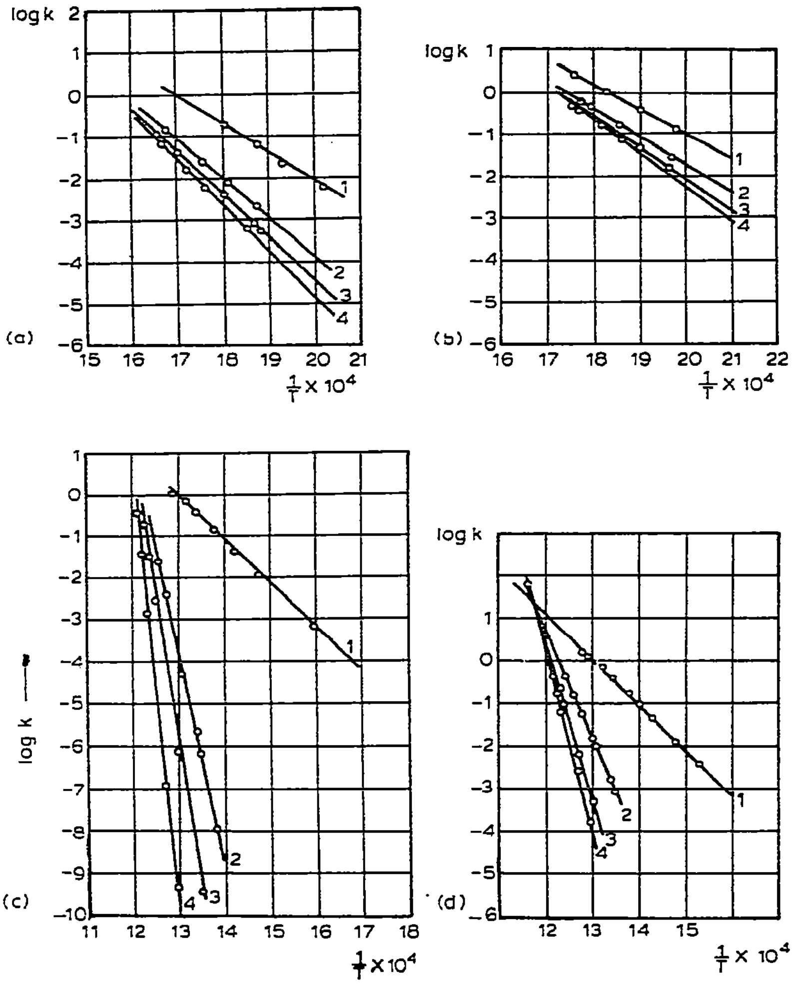

Fig. 1. Relation between log k and $1/T$. a, b = First and second step of the first stage of BAPS dehydration, respectively; c, d = first and second step of the second stage of BAPS dehydration, respectively. 1, Vacuum; 2, $p_{H_2O} = 3.4$; 3, $p_{H_2O} = 9.8$; 4, $p_{H_2O} = 18.5$ hPa.

increasing pressure of the gaseous reaction product) the straight lines tend to be shifted to the left. This corresponds to a shift of the region of temperatures ΔT at which the reaction runs at a measurable rate. The increase in p_{H_2O} is followed by an increase of the slope of the lines and, consequently, by an increase of the Arrhenius activation energy. The experimental data given in Fig. 1 enable the determination (by means of extrapolation) of the isokinetic temperature (β).

The dehydration of BAPS also involves the compensation effect, according to which the increase in activation energy must be compensated for by an increase of the pre-exponential factor in the Arrhenius equation. The relation between log A and E (Fig. 2) is a straight line described by the equation

$$\log A = a + bE$$

in which usually $a = 0$, and the value of $b(b_{\text{exp.}})$ may be derived, for successive stages of the dehydration, from the slope of the straight lines. It is also

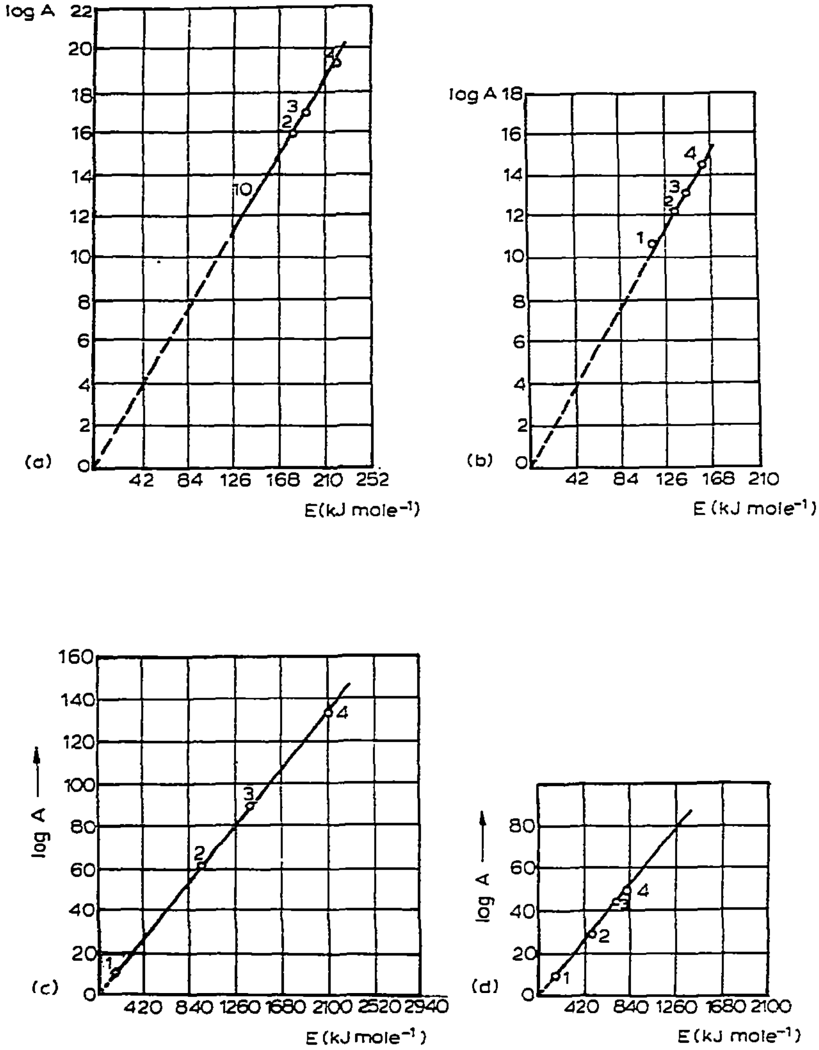

Fig. 2. Compensation relationship between log A and E. a, b = First and second step of the first stage of BAPS dehydration, respectively; c, d = first and second step of the second stage of BAPS dehydration, respectively. 1, Vacuum; 2, $p_{H_2O} = 3.4$; 3, $p_{H_2O} = 9.8$; 4, $p_{H_2O} = 18.5$ hPa.

possible to calculate the value of b (the so-called $b_{calc.}$) from the obtained values of the isokinetic temperature ($b_{calc.} = 1/R\beta$ [4], where R is the gas constant).

The values of $b_{calc.}$, $b_{exp.}$, and isokinetic temperature are given in Table 1. It follows from the presented data that the values of $b_{calc.}$ are in fair agreement with those of $b_{exp.}$ found from the slope of the lines represented in Fig. 2.

The accordance of the values of $b_{calc.}$ and $b_{exp.}$ is not surprising, as the magnitudes k, E, T, and A are interrelated by the Arrhenius equation, and the pair E, A is in a dual correlation with the pair k, T (which means that the magnitudes log A and E are in a linear relationship only in cases where the

TABLE 1

Isokinetic temperatures and values of the coefficient *b* in the compensation equation

First stage						Second stage					
First step			Second step			First step			Second step		
β_1(K)	$b_{1\text{calc.}}$	$b_{1\text{exp.}}$	β_2(K)	$b_{2\text{calc.}}$	$b_{2\text{exp.}}$	β_1(K)	$b_{1\text{calc.}}$	$b_{1\text{exp.}}$	β_2(K)	$b_{2\text{calc.}}$	$b_{2\text{exp.}}$
625	0.35	0.36	608	0.36	0.38	833	0.26	0.26	851	0.26	0.26

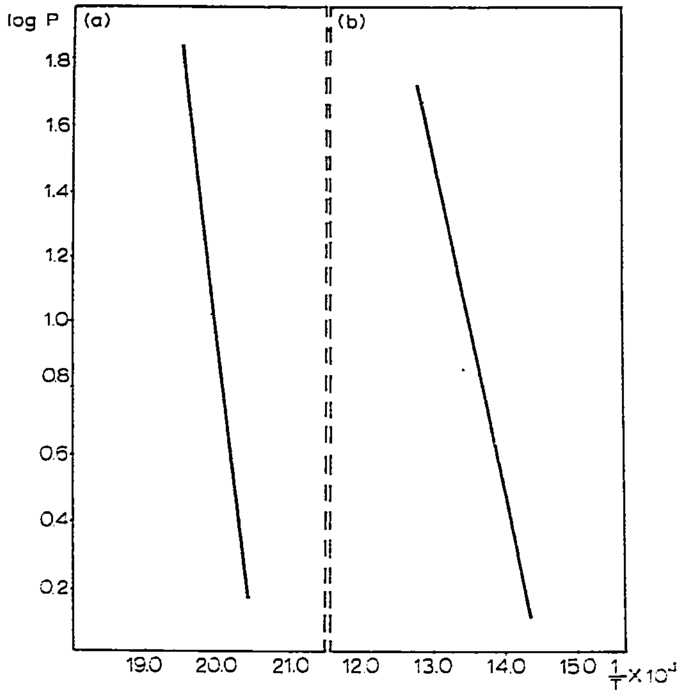

Fig. 3. Relation $p_{0_{H_2O}} = f(T)$: a and b refer to the first and the second stage of BAPS dehydration.

magnitudes log k and $1/T$ are in a pencil correlation [1].

We have also checked another relationship, characteristic for thermal dissociation reactions, according to which the activation energy of thermal decomposition calculated from reaction rates at different temperatures and constant supersaturation (i.e. at constant p_0/p where p_0 is equilibrium pressure and p is the pressure of the gaseous product in the reaction system) is constant and equal to the activation energy of the process carried out under highly reduced pressure.

To calculate the activation energies at constant supersaturation it is necessary to know the equilibrium pressures of water vapor (p_0) over BAPS; these data are not to be found in the literature and their precise determination by experiment is very difficult. However, use may be made of the apparent equilibrium pressures, p_0^*, which can be found by extrapolation of kinetic data (decomposition rates) obtained under different pressures up to such conditions where the reaction practically stops. The data obtained by such reasoning are represented in Fig. 3. From the obtained relationship, $p_0^* = F(T)$, it is possible to calculate the pressure (p) under which constant supersaturation is retained at a given temperature [5].

Calculations show (see Table 2 and Fig. 4) that changes of the ratio p_0/p_{H_2O} within 1.5—10.0 do not influence the activation energy; only slight differences are observed between the obtained values which are very close to the value of E in the process carried out in vacuum.

TABLE 2

Values of E and log A under constant supersaturations p_0/p_{H_2O}

p_0/p_{H_2O}	First stage				Second stage			
	First step		Second step		First step		Second step	
	E_1 (kJ mole^{-1})	log A_1	E_2 (kJ mole^{-1})	log A_2	E_1 (kJ mole^{-1})	log A_1	E_2 (kJ mole^{-1})	log A_2
1.5	139.9	9.8	114.4	9.1	191.0	4.6	200.7	9.4
2.0	141.6	10.1	113.1	9.0	191.0	5.5	201.9	9.9
3.0	132.0	9.3	109.8	8.7	194.8	6.8	193.9	9.8
4.0	132.0	9.3	113.5	9.1	198.7	7.8	201.9	10.7
10.0	137.0	10.0	106.4	8.6	196.5	9.6	192.7	11.1
Vacuum	139.5	13.1	111.4	10.7	200.5	13.6	200.5	13.6

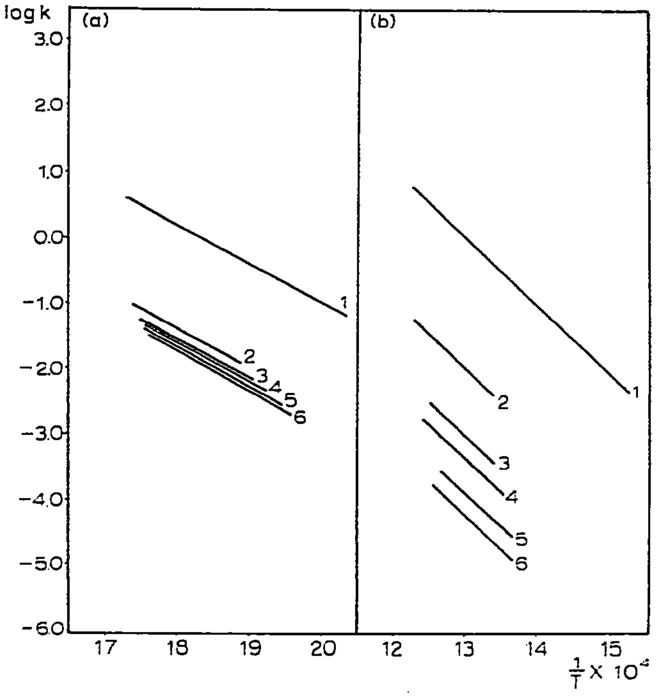

Fig. 4. Examples of relationships between log k and $1/T$ for p_0/p_{H_2O} = const. for first and second stage of BAPS dehydration. 1, Vacuum; 2, $p_0/p_{H_2O} = 10$; 3, $p_0/p_{H_2O} = 4$; 4, $p_0/p_{H_2O} = 3$; 5, $p_0/p_{H_2O} = 2$; 6, $p_0/p_{H_2O} = 1.5$.

CONCLUSIONS

The thermal decomposition of basic aluminium potassium sulfate follows the known relationships observed in thermal dissociation. It has been shown that the process follows the Zawadzki—Bretsznajder relationship, and depicts the existence of an isokinetic temperature and compensation effect. A relationship $p_{0_{H_2O}} = f(T)$ has been derived for BAPS and utilized for the calculation of the activation energy under constant but different values of supersaturation.

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