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COMPENSATION EFFECT IN THE THERMAL DECOMPOSITION PROCESS OF BASIC ALUMINIUM SALTS

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ABSTRACT

The Zawadzki–Bretsznajder relationship and the compensation effect in the isothermal–isobaric decomposition process of aluminium salts were studied. From our own studies and the critical analysis of kinetic data of other authors, the dual nature of these correlations was confirmed. It was also found that the constant *a* need not have a value of zero in the compensation equation.

INTRODUCTION

The influence of the pressure of a gaseous reaction product on the course of the thermal dissociation of a solid, the Zawadzki–Bretsznajder relationship, was first observed in the 1930s [1]. This relationship was observed repeatedly and was regarded as normal behaviour in the thermal dissociation of solids [2]. More recently, new aspects of this problem have been revealed as the result of expressing the Arrhenius equation as a projection correlation [3]. Such a treatment of the Arrhenius equation demonstrated that, in addition to the Zawadzki–Bretsznajder relationship, another regular feature of thermal dissociation, the compensation effect (equation), is also characteristic of the Arrhenius equation. Consequently, the existence of the so-called "isokinetic point" has been proved and its coordinates can be used to determine both constants of the compensation equation.

The existence of an isokinetic point allows both these relationships to be combined and demonstrates their mathematical duality. Thus it is possible to determine the interdependence of a pencil correlation, i.e. the Zawadzki–Bretsznajder relationship, and a linear correlation, i.e. the compensation effect; the common deviation factor of these correlations is the pressure of a gaseous decomposition product. Therefore, expressing the Arrhenius equation in the form of a projection line

$$R \ln k + E\frac{1}{T} - R \ln A = 0 \qquad (1)$$

one can illustrate the Zawadzki–Bretsznajder relationship as a pencil correlation (Fig. 1a) of the type $k = g(T)$, since, if the three values ln k_0, $1/T_0$ and R are treated as projection coordinates of the point, then eqn. (1) becomes the pencil equation with a common point (ln k_0 $(1/T_0)$. This means that pairs of values (A,E) and (k,T) are correlated in the correct scales and, for a pair (k_0,T_0), called an isokinetic pair, and any (A,E), eqn. (1) is satisfied.

The existence of an isokinetic point for a linear correlation is called the compensation effect (Fig. 1b) described by the equation

$$\ln A = a + bE \tag{2}$$

in which a and b are constants.

Coordinates of an isokinetic point (ln k_0, $1/T_0$) satisfy the Arrhenius equation

$$\ln k_0 = \ln A - \frac{E}{RT_0} \tag{3}$$

in which the linear pair (A,E) can take various values correlated by the compensation relationship, eqn. (2). Comparing eqns. (2) and (3), one can determine the constants a and b which equal ln k_0 and $1/RT_0$, respectively.

In the literature, for example ref. 4 and citations therein, it is generally agreed that in eqn. (2), a takes a value of zero. This is justified only when k_0 equals 1. The value of b, in the range 0–1, was discussed earlier [5].

RESULTS

In this paper, an attempt is made to prove the above views on the basis of a critical analysis of the results of the kinetics of the thermal dissociation of basic aluminium potassium sulphate [6] and of our own studies on the thermal decomposition of basic aluminium ammonium sulphate. Measure-

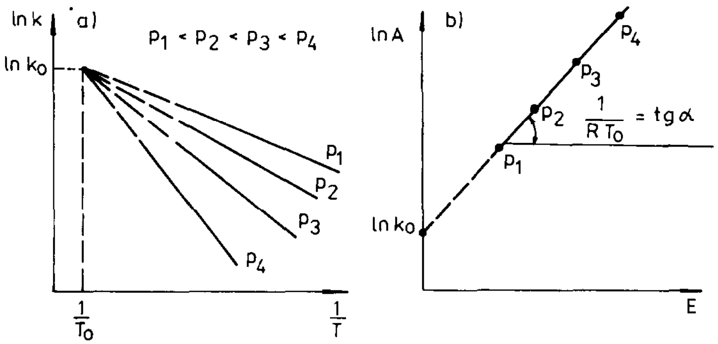

Fig. 1. Zawadzki–Bretsznajder relationship, a; compensation relationship, b.

TABLE 1

Kinetic parameters of the thermal decomposition of basic aluminium potassium sulphate in vacuum and under steam pressure

p_{H_2O}	Model	Stage I				Stage II			
		E_1 (kJ mol^{-1})	A_1 (min^{-1})	E_2 (kJ mol^{-1})	A_2 (min^{-1})	E_1 (kJ mol^{-1})	A_1 (min^{-1})	E_2 (kJ mol^{-1})	A_2 (min^{-1})
Vacuum	Kołmogorow–Jerofiejew Avrami	139.5	0.15×10^{14}	111.4	0.53×10^{11}	200.5	0.48×10^{14}	200,5	0.48×10^{14}
3,4		181.4	0.11×10^{17}	134.1	0.18×10^{13}	966.1	0.14×10^{63}	462,8	0.53×10^{30}
9,8		194.8	0.11×10^{18}	144.1	0.11×10^{14}	1395.1	0.15×10^{90}	707,9	0.89×10^{45}
18,5		222.4	0.30×10^{20}	159.8	0.30×10^{15}	2112.8	0.87×10^{134}	789,2	0.74×10^{50}

TABLE 2

Kinetic parameters of the thermal decomposition of basic aluminium ammonium sulphate in vacuum and under steam and ammonia pressure

Stage	Model	Composition of gaseous phase	p (hPa)	Step I		Step II	
				E_1 (kJ mol^{-1})	A_1 (min^{-1})	E_2 (kJ mol^{-1})	A_2 (min^{-1})
I	Jander	H_2O	10^{-3}	107.3	1.19×10^6		
			9.8	150.0	3.77×10^8		
			18.5	172.9	9.02×10^9		
II			10^{-3}	191.9	1.58×10^{11}		
		H_2O	3.4	259.8	1.26×10^{16}		
		(623–743 K)	9.8	290.4	1.58×10^{18}		
			18.5	399.7	3.98×10^{25}		
			10^{-3}	108.5	2.20×10^4	108.5	2.20×10^4
		NH_3	6.7	120.3	2.96×10^5	99.6	6.77×10^2
		(623–873 K)	13.3	150.4	2.04×10^7	112.7	8.14×10^3
			20.0	165.9	2.08×10^8	103.7	1.22×10^3

ments were made in isothermal–isobaric conditions under different pressures of a gaseous reaction product. The calculated kinetic parameters of decomposition of basic aluminium potassium sulphate and basic aluminium ammonium sulphate are shown in Tables 1 and 2. Figure 2 shows the Zawadzki–Bretsznajder relationship and the compensation equation for stage I of the decomposition of basic aluminium potassium sulphate, i.e. an initial dehydration, and Fig. 3 shows stage II of the dissociation of the compound in which the rest of the water is lost.

Table 3 shows the values of coordinates of isokinetic points (log k_0, T_0) and values of the constants a and b (calculated and experimental) for each stage of the decomposition of basic aluminium potassium sulphate. The analysis of these data shows that the values of a are different from zero and equal the logarithm of the constant speed of a kinetic point. Earlier accepted values of a, in this case zero [6], were corrected in the compensation equation here.

Figure 4 shows the Zawadzki–Bretsznajder relationship and the compensation equation for stage I of the decomposition of basic aluminium ammonium sulphate, i.e. an initial dehydration, and for stage II of the dissociation of this compound in which the rest of the water and a complete ammonium group is lost.

Table 4 lists values of coordinates of isokinetic points (log k_0, T_0) and constants a and b (calculated and experimental) for each stage of the decomposition of basic aluminium ammonium sulphate.

No Zawadzki–Bretsznajder relationship and, hence, no compensation effect were observed in stage II of the decomposition above 743 K in a steam atmosphere. This may be because of the relatively narrow temperature

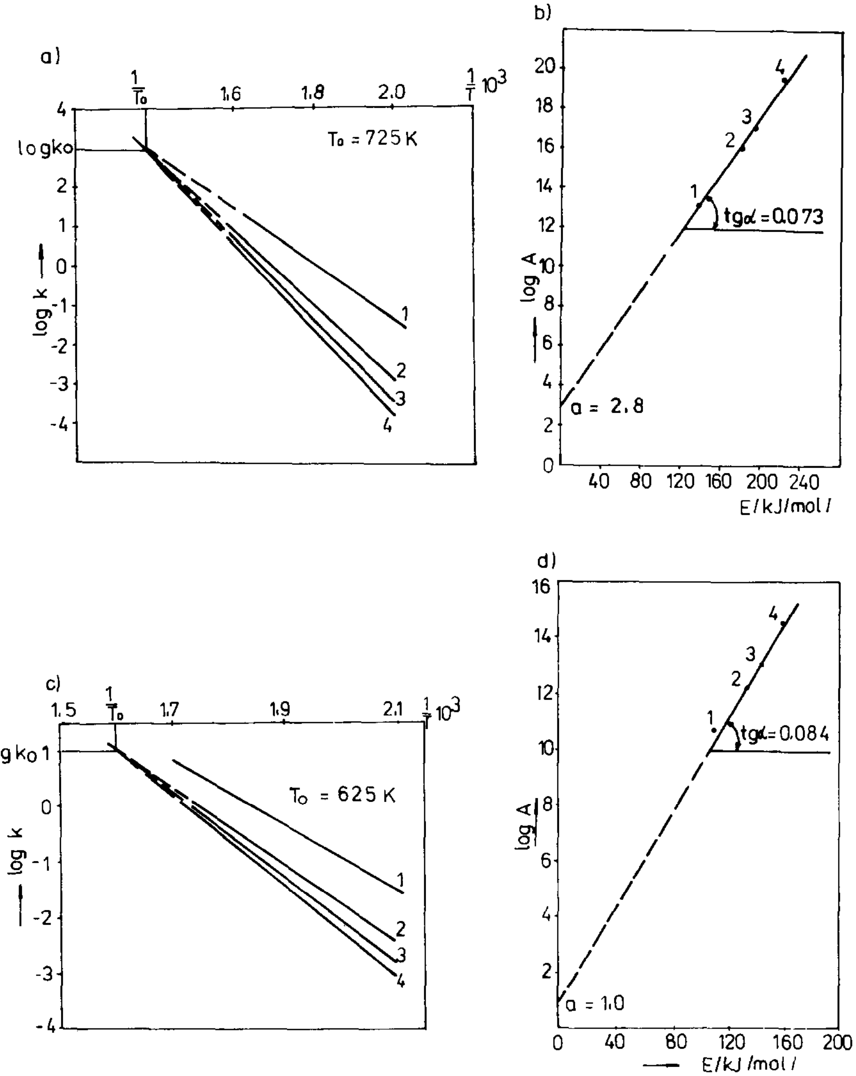

Fig. 2. Zawadzki–Bretsznajder relationship and the compensation equation for stage I of basic aluminium potassium sulphate decomposition: a and b, step I; c and d, step II. Points: 1, vacuum; 2, $p_{H_2O} = 3.4$ hPa; 3, $p_{H_2O} = 9.8$ hPa; 4, $p_{H_2O} = 18.5$ hPa.

range of this stage and also may be the result of disturbances in the course of the reaction caused by the presence of interfering sulphur oxides formed in the initial stage. Nor were these relationships observed in step II of the second decomposition stage of this compound in an ammonium atmosphere. The reaction course in the atmosphere of gaseous products is complicated at this stage. This complication is also caused by the simultaneous dehydration of the compound and separation of ammonium during stage II and, in such

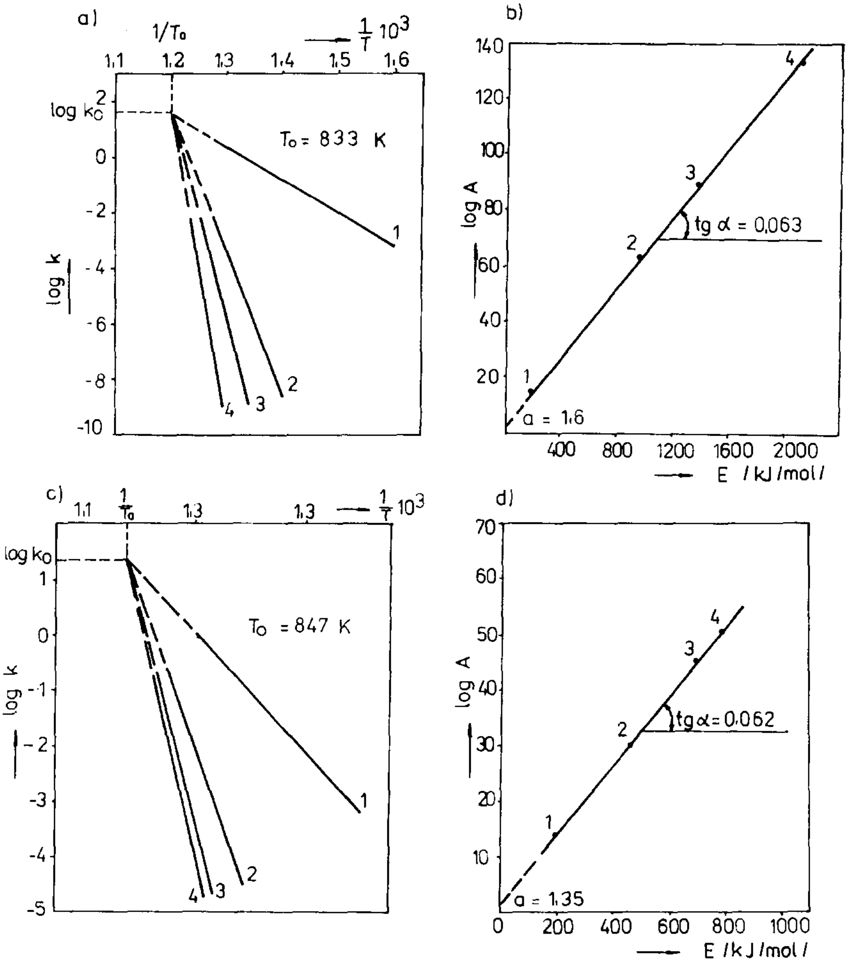

Fig. 3. Zawadzki–Bretsznajder relationship and the compensation relationship for stage II of basic aluminium potassium sulphate decomposition: a and b, step I; c and d, step II. Points: 1, vacuum; 2, $p_{H_2O} = 3.4$ hPa; 3, $p_{H_2O} = 9.8$ hPa; 4, $p_{H_2O} = 18.5$ hPa.

TABLE 3

Values of coordinates of isokinetic points and constants *a* and *b* in compensation equations for the decomposition of basic aluminium potassium sulphate

Stage	Step	T_0 (K)	log k_0	*a*(exp.)	*b*(calc.)	*b*(exp.)
I	I	725	2.80	2.80	0.072	0.073
	II	625	1.00	1.00	0.084	0.084
II	I	833	1.60	1.60	0.063	0.063
	II	847	1.35	1.35	0.062	0.062

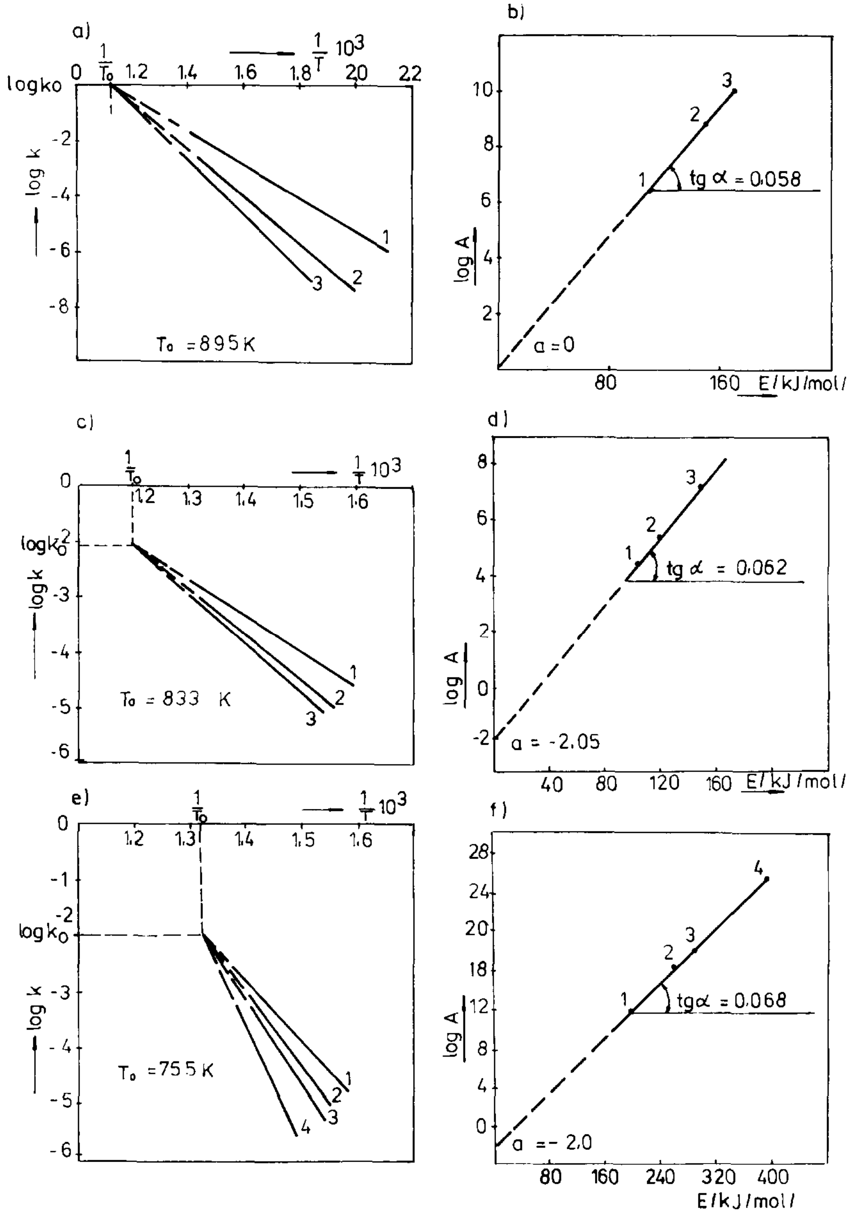

Fig. 4. Zawadzki–Bretsznajder relationship and the compensation equation for basic aluminium ammonium sulphate decomposition. a and b, Stage I — points: 1, $p_{H_2O} = 3.4$ hPa; 2, $p_{H_2O} = 9.8$ hPa; 3, $p_{H_2O} = 18.5$ hPa. c and d, Stage II — points: 1, $p_{NH_3} = 6.7$ hPa; 2, $p_{NH_3} = 13.3$ hPa; 3, $p_{NH_3} = 20.0$ hPa. e and f, Stage II — points: 1, vacuum; 2, $p_{H_2O} = 3.4$ hPa; 3, $p_{H_2O} = 9.8$ hPa; 4, $p_{H_2O} = 18.5$ hPa.

a case, the observed reaction speed and kinetic parameters (E,A) describe the overall process, whereas the influence of steam and ammonium is studied separately.

TABLE 4

Values of coordinates of isokinetic points and constants *a* and *b* in compensation equations for the thermal decomposition of basic aluminium ammonium sulphate

Stage	Composition of gaseous phase	T_0	$\log k_0$	a(exp.)	b(calc.)	b(exp.)
I	H_2O	895	0.00	0.00	0.058	0.058
II (623–743 K)	H_2O	755	−2.00	−2.00	0.069	0.068
II (623–873 K)	NH_3	833	−2.05	−2.05	0.063	0.062

CONCLUSIONS

1. The course of the thermal decomposition of basic aluminium salts in isothermal–isobaric conditions under various pressures of gaseous decomposition products and the calculation of the kinetic parameters reveal that the Zawadzki–Bretsznajder relationship and the compensation effect result from the application of the Arrhenius equation to describe the experimental data.
2. The coordinates of the isokinetic point ($\ln k_0$, $1/T_0$) simultaneously provide the values of the constants *a* and *b* in the compensation equation.
3. Experimental and calculated results confirm that the deviation factor of the dual correlations: a linear, i.e. the compensation effect; and a pencil correlation, i.e. Zawadzki–Bretsznajder relationship, is the pressure of gaseous reaction products.

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