DEHYDRATION KINETICS OF $K_2AlF_5 \cdot H_2O$

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ABSTRACT

The dehydration kinetics of $K_2AlF_5 \cdot H_2O$ have been studied by isothermal and dynamic thermogravimetry. Reduced time plots of isothermal measurements show a phase-boundary-controlled reaction. For the interpretation of the dynamic measurement, the Coats–Redfern integral method was used. Kinetic parameters obtained isothermally as well as dynamically show the kinetic compensation effect. High temperature X-ray diffractometry supports the idea of a chain-controlled topotactic reaction mechanism.

INTRODUCTION

Recently, we have tried to correlate the dehydration temperatures and the dehydration enthalpies of $K_2MF_5 \cdot H_2O$ compounds with their crystal structures [1]. It was shown that, for these compounds, thermal analysis cannot be used to distinguish between coordinated and structural water. On the other hand, the dehydration temperatures as well as the dehydration enthalpies could be correlated with the crystal field stabilization energy.

The data obtainable from TG and DTA depend not only on the nature of the process but also on the number of experimental parameters. In an attempt to obtain reliable characteristics for the reactions mentioned, we have determined more details of the dehydration of $K_2AlF_5 \cdot H_2O$.

EXPERIMENTAL

$K_2AlF_5 \cdot H_2O$ was prepared as described elsewhere [2]. The whole sample (about 15 g) was homogenized in a mortar for an hour before use.

The thermoanalytical curves were produced by means of Mettler TA1 thermoanalyzer using Pt crucibles. A TD1 sample holder was used for simultaneous TG–DTA runs with sample masses of 100 mg, reference material α-Al_2O_3, flow rate 5 l h^{-1} and heating rates 1, 2, 4 and 6 K min^{-1}. A TG sample holder with flat crucibles of 12 and 8 mm in diameter, flow

rate $1 \, l \, h^{-1}$ and heating rates 0.5, 1, 2 and 4 K min^{-1} were used for sample masses of 50 and 10 mg, respectively.

Isothermal mass losses were measured at 65, 62, 60 and 57°C for 50 mg samples, and at 65, 60, 57 and 55°C for 10 mg samples.

DSC measurements were made on a Mettler TA 2000C apparatus with 40 mg samples and a 6 K min^{-1} scan speed.

Electron micrographs were taken on a JSM-U2 JEOL electron raster microscope.

X-ray powder photographs were made using a high temperature Lenne de-Wolf camera using Cu $K\alpha$ radiation. The heating rate was 100 K h^{-1}.

RESULTS AND DISCUSSION

Samples of the particle size and shape shown in Fig. 1 were used for thermal analysis. Typical dehydration curves for dynamic and for isothermal runs are shown in Figs. 2 and 3, respectively, whereas Table 1 shows the influence of experimental parameters on the reaction temperature. On the DTA curve, there is an additional exothermal effect between 300 and 330°C (peak temp. at 318°C), which corresponds to a monotropic phase change of the anhydrous compound. The enthalpy of the phase change, determined by DSC, is 6.5 ± 0.5 kJ mol^{-1}.
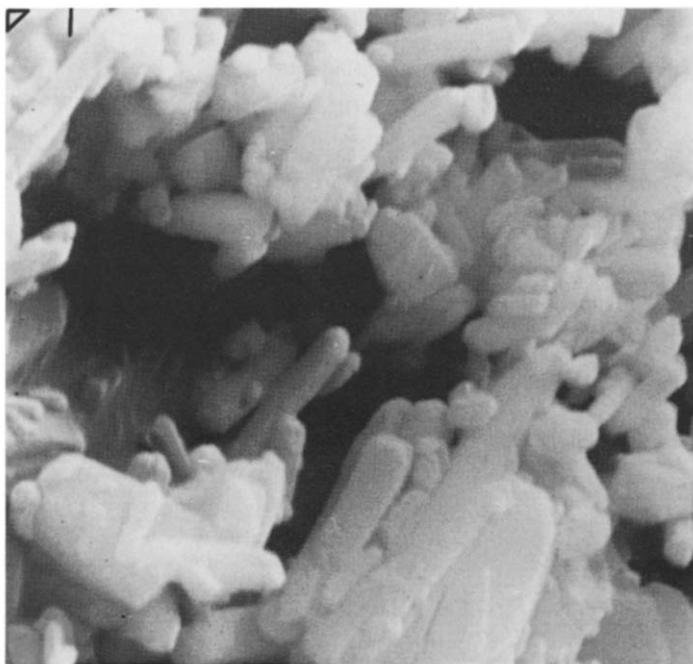

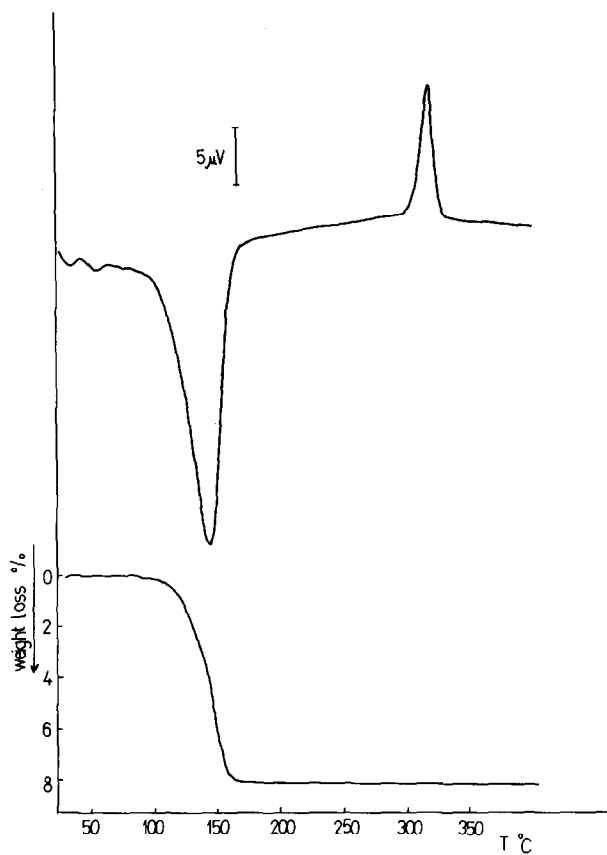Fig. 1. Electron micrograph of $K_2AlF_5 \cdot H_2O$ (magnification $\times 10\,000$).
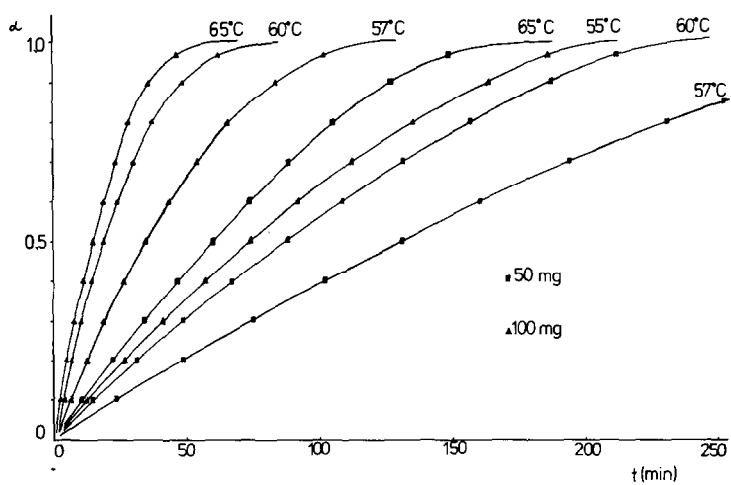
Fig. 2. TG and DTA curves of $K_2AlF_5 \cdot H_2O$.

Fig. 3. Isothermal mass loss plots of $K_2AlF_5 \cdot H_2O$.

TABLE 1

Initial, inflection and final temperatures as a function of sample mass and heating rate

Sample mass (mg)	Heating rate (°C min^{-1})	Initial temp. (°C)	DTG peak (°C)	Final temp. (°C)
10	0.5	51	71.5	84
	1	50	78	90
	2	50	82	100
	4	51	86	110
50	0.5	49	90	107
	1	49	96	120
	2	49	105	134
	4	49		160
100	1	62	117	130
	2	63	129	145
	4	63	145	153
	6	65	151	180

Isothermal measurements were tested by reduced time plots [3], which showed that the best fit was for the R2 mechanism (Fig. 4), in accordance with the shape of the particles (Fig. 1). Activation energy calculated by the Wiedemann method [4] is 90.7 kJ mol^{-1} for 50 mg samples and 145.9 kJ mol^{-1} for 10 mg samples.

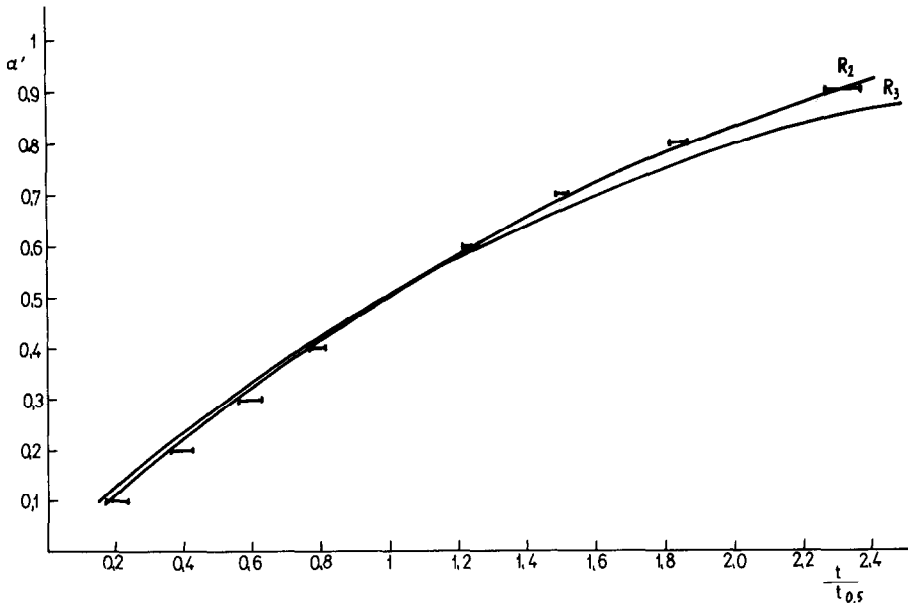Fig. 4. Reduced time plots for $K_2AlF_5 \cdot H_2O$.

TABLE 2

Kinetic parameters for dehydration of $K_2AlF_5 \cdot H_2O$

Sample mass (mg)	Heating rate (°C min^{-1})	Validity range of α	n	E (kJ mol^{-1})	lg A
10	0.5	0.15–0.95	1.00	160	22.99
	1	0.15–0.90	0.667	113	15.01
		0.15–0.90	1.00	129	18.15
	2	0.10–0.90	0.667	113	15.03
		0.15–0.95	1.00	132	18.54
	4	0.20–0.85	0.667	102	13.27
		0.15–0.85	1.00	119	16.64
50	0.5	0.05–0.95	0.667	118	14.94
		0.05–0.95	1.00	132	17.68
	1	0.05–0.97	1.00	112	14.68
	2	0.15–0.95	0.667	80	9.33
		0.10–0.95	1.00	94	12.00
	4	0.05–0.90	0.667	74	8.83
100	1	0.05–0.95	0.50	82	9.31
		0.05–0.95	0.667	88	9.74
	2	0.05–0.95	0.50	70	7.55
		0.05–0.95	0.667	74	7.86
	4	0.05–0.95	0.50	61	6.44
		0.05–0.95	0.667	66	6.67
	6	0.05–0.95	0.50	58	5.93
		0.05–0.95	0.667	61	6.13

The kinetic parameters for dynamic TG measurements were calculated using the Coats–Redfern integral method [5], with values of 0.0, 0.5, 0.667 and 1.0 as orders of the reaction. Regression analysis was used for the calculation of the kinetic parameters. The results, with a correlation coefficient of at least 0.999, are given in Table 2. Most measurements obey two orders of reaction between 0.5 and 1.0 (Table 2), indicating that the dehydration can be described as a phase-boundary-controlled reaction or as random nucleation according to the first-order law.

A linear relationship between lg A and E, known as the compensation effect, has often been observed for decomposition reactions [6–8]. For $K_2AlF_5 \cdot H_2O$, this dependence is shown in Fig. 5 and can be expressed as lg $A = -4.33 \pm 1.71 \times 10^{-1} E$. Inspection of Tables 1 and 2 shows that the apparent activation energy decreases with increasing sample mass and/or heating rate, respectively. In other words, E decreases with increasing reaction temperature. A similar relationship has been observed by Gallagher and Johnson [7] when studying the effect of experimental conditions on the kinetic parameters.

The structure of $K_2AlF_5 \cdot H_2O$ consists of AlF_6 octahedra, connected to infinite trans-chains by sharing of common vertices [9]. Potassium cations
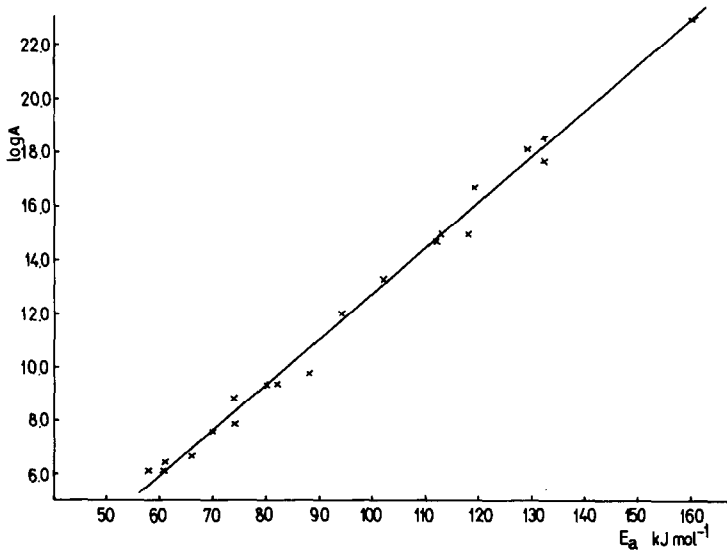
Fig. 5. Kinetic compensation effect for $K_2AlF_5 \cdot H_2O$.

TABLE 3

X-ray powder patterns of $K_2AlF_5 \cdot H_2O$ at various temperatures

$T = 20\,°C$		$45 < T < 230\,°C$		$T = 230\,°C$	
d (Å)	I	d (Å)	I	d (Å)	I
6.16	3	6.17	3	5.07	1
		6.05	3	4.93	2
		4.32	2	3.07	5
3.63	1			2.51	3
3.22	3	3.20	2	2.17	3
3.08	2	3.04	2	2.08	1
2.93	2			1.771	3
2.85	2	2.83	4	1.662	1
2.77	2	2.72	1	1.533	1
2.70	2				
2.63	1				
2.38	5	2.63	5		
2.32	3				
		2.14	3		
2.05	3				
		1.906	3		
1.884	3				
1.758	1	1.786	2		
1.717	1	1.705	2		
		1.682	1		
1.606	1				
1.597	1	1.591	1		
1.534	1	1.536	1		
		1.512	1		

and water molecules are located between the anionic chains. X-ray powder patterns of $K_2AlF_5 \cdot H_2O$ at various temperatures are given in Table 3. The initial pattern does not change very much during the dehydration as shown by the X-ray powder data for $K_2AlF_5 \cdot H_2O$ below 230°C.

In a similar study, the dehydration of $Rb_2MnF_5 \cdot H_2O$ was followed by X-ray diffractometry on single crystals [10]. It was found that the initial octahedral chains remain unchanged with a minimum contraction of 0.7%. Water molecules left the crystals parallel to anionic chains.

The X-ray data on the dehydration of $K_2AlF_5 \cdot H_2O$ thus support the idea of a chain-controlled topotactic reaction similar to that proposed for $Rb_2MnF_5 \cdot H_2O$ [10].

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