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Kinetics of the isothermal dehydration of $Li_2SO_4 \cdot H_2O$ in vacuo

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Abstract

Although the dehydration of lithium sulfate monohydrate in vacuum ($\approx 10^{-4}$ Torr) has a simple appearance, the kinetics is not so simple as the reaction mechanism, which can be expressed by a single function model $F(\alpha)$. The kinetics is represented by the combination of A_2 and R_2 functions.

The initial acceleratory stage described by the A_2 equation seems to be related to the nucleation and nuclei growth process controlled by the diffusion of dissociated water molecules. When the two-dimensional phase boundary is formed around the specimen by the growing nuclei, the dehydration seems to be controlled by the advance of the interface and to have the characteristics of the R_2 model function.

The values of activation energies and pre-exponential factors were 22.1 kJ mol^{-1} and 1.45 s^{-1} for the A_2 process, and 29.3 kJ mol^{-1} and 12.1 s^{-1} for the R_2 process, respectively.

INTRODUCTION

Several studies have been carried out on the kinetics of the thermal dehydration of lithium sulfate monohydrate [1–7].

Koga and Tanaka [6] showed that the kinetics of the dehydration in nitrogen flow was described by the combination of a random nucleation and growth (Avrami–Erofe'ev) equation A_m $(2 < m < 3)$ and a phase boundary controlled equation R_n $(2 < n < 3)$. The values of activation energies reported by these authors were 90–115 kJ mol^{-1} for both the A_m and the R_n processes.

In contrast, however, Okhotnikov et al. [7] have reported that the initial dehydration stage of single crystal specimens in vacuo may be dependent upon the diffusion of the dehydrated water molecules. Other kinetic data on the dehydration in vacuo have scarcely been reported.

It is well-known that the kinetics of thermal dehydration of hydrates is

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affected by the measuring conditions. In this paper, the kinetics and mechanisms of the overall dehydration of a crystalline powdered specimen of $Li_2SO_4 \cdot H_2O$ in vacuo ($\approx 10^{-4}$ Torr) have been studied by means of isothermal thermogravimetry.

EXPERIMENTAL SECTION

Lithium sulfate monohydrate was purchased from Wako Pure Chemical Industries Ltd., Osaka. The specimen was sieved to a narrow fraction of 100–150 mesh.

The isothermal dehydration was followed with a Shinku–Riko TGD-5000RH differential microbalance equipped with a gold image furnace [8, 9]. After the specimen of about 5 mg was weighed into a platinum crucible and placed in the microbalance, the reaction system was degassed to below 5×10^{-4} Torr for 3 h before the experiment. The furnace was controlled at given temperatures between 70 and 135°C, and maintained within ±0.5°C until the dehydration was complete.

The TG output voltages were amplified and recorded on a microcomputer (Epson QC-10 II) via an A/D converter (Datel–Intersil 7109 modified to 13 bit). About 1000 data points were collected at given time intervals for each dehydration process, and the fraction of dehydration α was calculated from these data [8–12].

The X-ray powder diffraction patterns were obtained with a Rigaku Geigerflex RDA 3C diffractometer equipped with a standard high-temperature sample holder. Cu Kα radiation, a nickel filter and a graphite monochrometer were used for all measurements. The diffraction data were collected at 0.02° intervals.

RESULTS AND DISCUSSION

Figure 1 shows the plots of α against the time of the reaction at various temperatures. The $\alpha(t)$ curves consist of two stages, i.e. a former acceleratory stage ($\alpha < \approx 0.5$) and a latter deceleratory stage ($\alpha > \approx 0.5$).

The dehydration was analyzed kinetically by the integral method according to the following procedure. The kinetics of a solid-state reaction can be represented by the general equation

$$F(\alpha) = kt \tag{1}$$

where k is the rate constant and $F(\alpha)$ is a function depending on the reaction mechanism. Many theoretical model functions are known for $F(\alpha)$ [13–16]. The mechanism of the present dehydration, i.e. the model function, was determined on the basis of the linearity of the plots of the $F(\alpha)$ functions calculated from α against time t for the dehydration according to eqn. (1).

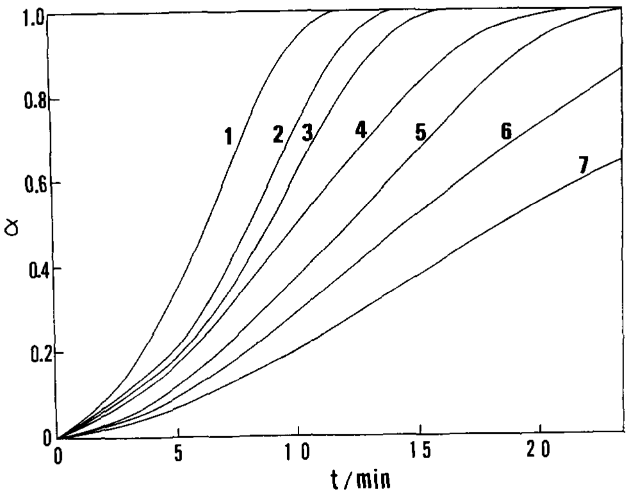

Fig. 1. Plots of α vs time: 1, 134.2°C; 2, 126.5°C; 3, 114.5°C; 4, 102.2°C; 5, 95.2°C; 6, 84.2°C; 7, 73.8°C.

Figure 2 shows typical plots of $F(\alpha)$ vs. t for the present dehydration. It is interesting that the former acceleratory stage can be described by an Avrami–Erofe'ev equation (A2) [13–16]

$$[-\ln(1-\alpha)]^{1/2} = k_{A_2}t \qquad (2)$$

and the latter deceleratory stage can be a two-dimensional phase boundary equation (R2) [13–16]

$$1-(1-\alpha)^{1/2} = k_{R_2}t \qquad (3)$$

This kinetic behavior of the dehydration is similar to that for the dehydration at atmospheric pressure reported by Koga and Tanaka [6].

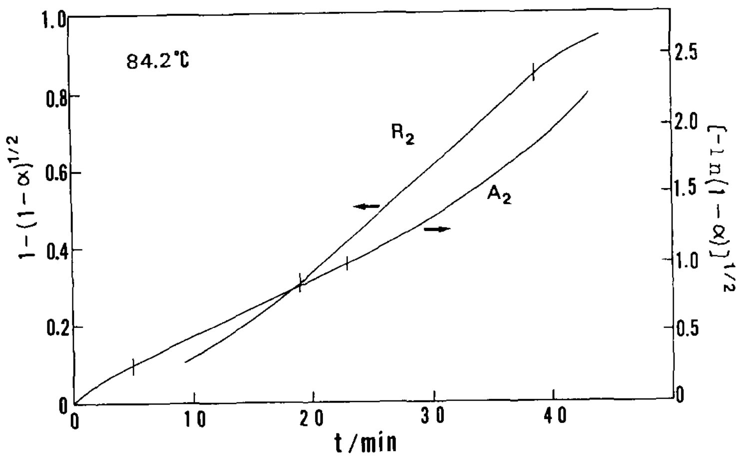

Fig. 2. Typical $F(\alpha)$ vs. t plots.

TABLE 1

$F(\alpha)$ and $\ln k$ for the dehydration of $Li_2SO_4 \cdot H_2O$ in vacuo

T/°C	$F(\alpha)$	Range of α	C [a]	$\ln(k/s^{-1})$
73.8	A_2	0.09–0.72	0.9999	−7.31
	R_2	0.42–0.99	0.9997	−7.71
84.2	A_2	0.06–0.62	0.9999	−7.06
	R_2	0.51–0.98	0.9998	−7.38
95.2	A_2	0.01–0.51	0.9999	−6.83
	R_2	0.42–0.98	0.9997	−7.04
102.2	A_2	0.02–0.58	0.9998	−6.65
	R_2	0.49–0.98	0.9998	−6.97
114.5	A_2	0.01–0.51	0.9996	−6.51
	R_2	0.57–0.97	0.9997	−6.64
126.5	A_2	0.01–0.52	0.9997	−6.29
	R_2	0.54–0.98	0.9998	−6.35
134.2	A_2	0.02–0.51	0.9991	−6.15
	R_2	0.55–0.99	0.9996	−6.17

[a] Correlation coefficient.

Table 1 shows the values of both rate constants k_{A_2} and k_{R_2}. The initial acceleratory periods of experimental $\alpha(t)$ curves fit well with the theoretical $\alpha(t)$ curves calculated using the rate constants k_{A_2} and the latter deceleratory periods fit with the theoretical curves calculated using the rate constants k_{R_2} (Fig. 3).

It is known that the R_2 reaction is characterized by the rapid initial production of a complete reactant–product interface around the preferred

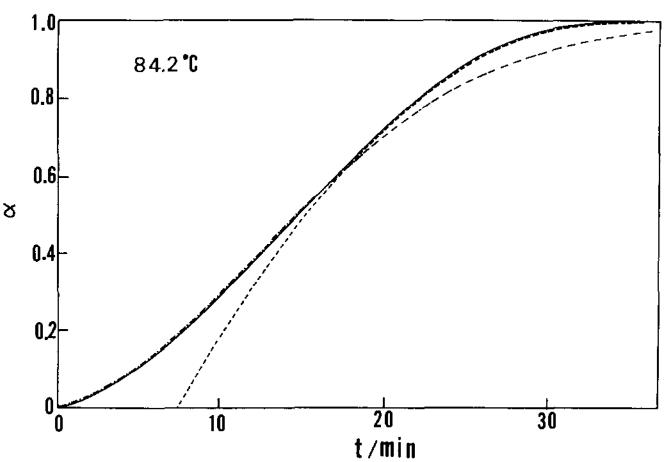

Fig. 3. The fitness of the theoretical curve for the experimental $\alpha(t)$ plots: ———, experimental plot; -·-·-, theoretical A_2 plot ($k_{A_2}/s^{-1} = 8.57 \times 10^{-4}$); ----, theoretical R_2 plot ($k_{R_2}/s^{-1} = 6.23 \times 10^{-4}$).

TABLE 2

Activation energy and pre-exponential factor for the dehydration of $Li_2SO_4 \cdot H_2O$ in vacuo

	A_2	R_2
$E/\mathrm{kJ\,mol^{-1}}$	22.1	29.3
$A/\mathrm{s^{-1}}$	1.45	12.1

crystallographic surfaces, and its rate is determined by the two-dimensional advance of the reaction interface. However, the A_2 equation is the kinetic expression concerning random nucleation and nuclei growth process. Hulbert pointed out the relationship between nuclei growth and the diffusion process of migrating species as follows [16]. If the nucleation rate is constant, the nuclei grow two-dimensionally and the growth rate is controlled by the diffusion of the migrating species, and the A_2 equation can be derived on the basis of the overall rate constant given by

$$k_{A_2} = (\pi hID/2)^{1/2} \tag{4}$$

where I is the nucleation rate per unit volume, h is the thickness of the specimen, and D is the diffusion coefficient of the migrating species.

The values of activation energies and pre-exponential factors for the A_2 and R_2 functions (Table 2) were determined from the Arrhenius plots (Fig. 4). The values are lower than those reported for the dehydration at atmospheric pressure. This fact seems to be ascribable as follows. Under vacuum, the dissociated water molecules may diffuse easily from the specimen, which will presumably accelerate the rate of the complete dehydration.

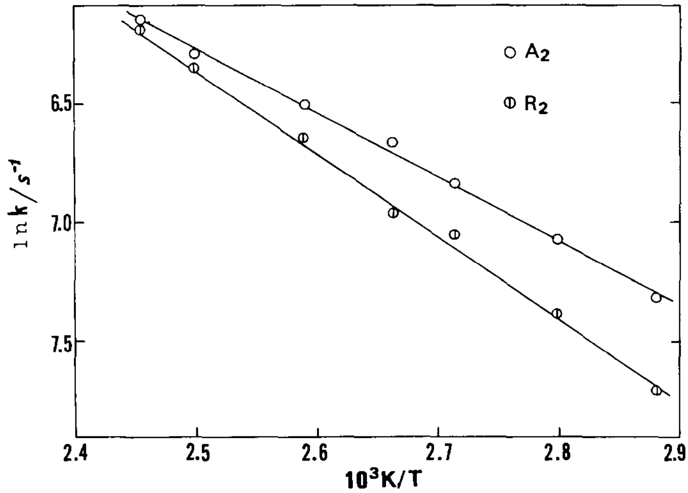

Fig. 4. Arrhenius plots of k_{R_2} and k_{A_2}.

Okhotonikov et al. [7] reported that in vacuo (6.7×10^{-5} Pa) the initial process of the dehydration of $Li_2SO_4 \cdot H_2O$ was controlled by the diffusion of water molecules from the semi-infinite medium produced. We could not detect the metastable phase from the X-ray diffraction profile of the dehydrated product under our experimental conditions. However, the fact that the initial dehydration process can be described by the A_2 equation indicates that the growth of nuclei may be controlled by the diffusion process of water molecules.

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