

Mechanism of thermal dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

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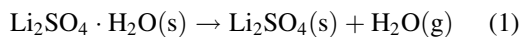
Abstract

The kinetic characteristics (the product partial pressures P and activation energies E_a) of the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ reported in a number of available publications have been analysed with the supposition of dissociative evaporation of the hydrate in the form of Li_2SO_4 and H_2O molecules. Despite the considerable differences in the measurement conditions, the experimental values of P and E_a have been found to be in good agreement with theoretical calculations. The calculations took into account the depressing effect of water vapor on the dehydration rate and partial transfer of the energy released in the condensation of $\text{Li}_2\text{SO}_4(\text{g})$ to the reactant. The agreement between the calculated and experimental data supports the proposed mechanism of dehydration. © 1998 Elsevier Science B.V.

Keywords: Dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; Dissociative evaporation; Effect of H_2O vapor; Kinetic parameters

1. Introduction

The kinetics and mechanism of the thermal dehydration of crystalline hydrates are dealt with, in numerous publications, the results having been partially summarized in some books and review articles [1–5]. One of the most popular subjects of investigation is lithium sulphate monohydrate, whose dehydration is considered to be a single rate process:



Interest in this compound has increased still more in the early 90s in connection with an attempt to use the process of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration as a 'kinetics standard' [6]. A recent comparison of the results of kinetics studies carried out in different laboratories

has revealed, however, a substantial dependence of the measured kinetic parameters on the mass and prehistory of the sample, the particle size, the presence of water vapor in the environment, the heating rate, the calculational mode and the fraction decomposed. As a consequence, the idea of using reaction (1) as a kinetics standard was rejected [6]. The inadequacy of the generally accepted concepts, which are incapable of explaining the behavior of this and similar reactions, pointed out already in Refs. [2,4], has become all the more obvious.

The present work is an attempt at analyzing the available experimental data on the kinetics of dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, based on an untraditional approach to the process of thermal decomposition of solids, which is treated as dissociative evaporation of the reactant, followed by condensation of the molecules of the nonvolatile products. This approach has been successfully used in the interpretation of the

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mechanism and kinetics of the thermal decomposition of nitrates [7–10], azides [11], carbonates [12] and of a number of other metal compounds [13]. Direct observation of the primary products of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ decomposition in vacuum by quadrupole mass spectrometry (QMS) has shown that the dehydration of this compound also proceeds by congruent gasification of all reaction products, including $\text{Cu}(\text{NO}_3)_2$ molecules [10].

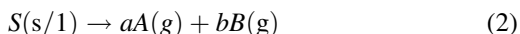
The method to be employed below consists in comparing experimental data on the kinetic parameters with their calculated values. The calculations are based on the classical evaporation model of Hertz–Langmuir, extended by the present author to the cases of dissociative evaporation of compounds [7–14].

2. Theoretical

The scheme employed in the theoretical calculation of the main kinetic parameters of the decomposition process (the flux of the gaseous product J , the rate constant k , the product partial pressure P and the parameters of the Arrhenius equation, E_a and A) has been described in a number of our recent publications [11–14]. Therefore, we are going to present below only some final relations necessary for the calculations in this work.

2.1. Decomposition in vacuum

In the case of a compound S decomposed in vacuum into gaseous products A and B



the flux of product A can be expressed through the partial pressure P_A (in atm) of this product corresponding to the hypothetical equilibrium of reaction (2) in the form

$$J_A = \frac{\gamma M P_A}{(2\pi \overline{MRT})^{1/2}} \quad (3)$$

where M is the molar mass of compound, γ the coefficient of conversion from atmospheres to pascals and R the gas constant. Here \overline{M} is the geometric mean of the molar masses of all gaseous particles, i.e.

$$\overline{M} \equiv M_A^{a/\nu} \times M_B^{b/\nu} \quad (4)$$

where

$$\nu \equiv a + b \quad (5)$$

The flux of gaseous products J is connected with the rate constant k . For spherical particles, the fraction decomposed is described by the contracting volume model

$$\frac{d\alpha}{dt} = 3(1 - \alpha)^{2/3}k \quad (6)$$

Taking into account some obvious relationships: $\alpha \equiv 1 - m/m_0$, $m = (4/3)\pi r^3 \rho$ and $J = -(dm/dt)(4\pi r^2)^{-1}$, where m , r and ρ are the mass, radius and density of reactant spherical particle(s), we obtain on rearrangement of Eq. (6) a simple expression

$$J = \rho r_0 k \quad (7)$$

From Eqs. (3) and (7), we have

$$P_A = \frac{(2\pi \overline{MRT})^{1/2}}{\gamma M} J = \frac{(2\pi \overline{MRT})^{1/2}}{\gamma M} \rho r_0 k \quad (8)$$

This equation can be used for the calculation of the actual partial pressures of product A from the experimental J or k values in vacuum.

2.2. Decomposition in a foreign-gas environment

In a foreign-gas environment, the evaporation rate is limited by the diffusion of molecules from the near-surface boundary layer. In this case, instead of Eq. (8), we have [14]

$$P_A = \frac{zRT}{\gamma \overline{MD}} J = \frac{zRT}{\gamma \overline{MD}} \rho r_0 k \quad (9)$$

Here z is the distance from the vaporization surface to the sink, where the particle concentration drops to zero, and \overline{D} is the geometric mean of the coefficients of diffusion of the gaseous particles, i.e.

$$\overline{D} = D_A^{a/\nu} \times D_B^{b/\nu} \quad (10)$$

The dependence of diffusion coefficient on temperature is described by the equation

$$D = D_0(T/T_0)^n \quad (11)$$

where $T_0 = 273$ K. If one of the gaseous product condenses, the effective value of its diffusion coefficient

can be calculated from the obvious equality

$$D_{\text{eff}} = \frac{zRT}{(2\pi MRT)^{1/2}} \quad (12)$$

based on the supposition that the flux of this product in a foreign-gas environment has a maximum value, namely, that in vacuum.

Eqs. (9)–(12) should be used for the calculation of the actual partial pressure of product A from the experimental J or k values in a foreign-gas environment.

2.3. Calculation of the equilibrium partial pressure

A theoretical value of the partial pressure of product A can be calculated from the equilibrium constant K_P for the reaction (2). In the absence of reaction products in the reactor atmosphere, the situation corresponding to the *equimolar* evaporation mode, the partial pressure can be expressed as

$$P_A^e = a \left(\frac{K_P}{F} \right)^{1/\nu} = \frac{a}{F^{1/\nu}} \exp \frac{\Delta_r S_T^0}{\nu R} \exp \left(- \frac{\Delta_r H_T^0}{\nu RT} \right) \quad (13)$$

where

$$F \equiv a^a \times b^b \quad (14)$$

and

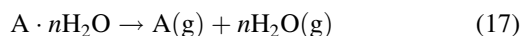
$$K_P = P_A^a \times P_B^b \quad (15)$$

Here $\Delta_r H_T^0$ and $\Delta_r S_T^0$ are, respectively, the changes of the enthalpy and entropy in the process (2). If the partial pressure P'_X of one of the gaseous components greatly exceeds the equilibrium pressure P_X of the same component released in the decomposition and if, in addition to that, the magnitude of P'_X remains constant in the process of decomposition, we call such evaporation mode *isobaric*. In this case,

$$P_A^i = a \left[\frac{K_P}{F} \left(\frac{x}{P'_X} \right)^x \right]^{1/\nu-x} = a \left[\frac{1}{F} \left(\frac{x}{P'_X} \right)^x \right]^{1/\nu-x} \times \exp \frac{\Delta_r S_T^0}{(\nu-x)R} \exp \left[- \frac{\Delta_r H_T^0}{(\nu-x)RT} \right] \quad (16)$$

As can be seen from Eqs. (13) and (16), the calcu-

lated activation energies for the decomposition of the hydrate



should be different for the equimolar and isobaric modes of dehydration, i.e.

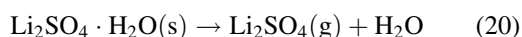
$$E_a^e = \Delta_r H_T^0 / \nu \quad (18)$$

for the equimolar mode and

$$E_a^i = \Delta_r H_T^0 \quad (19)$$

for the isobaric one.

For the reaction of interest to us



Eqs. (13) and (16) take on a simplified form

$$P_A^e = \exp \frac{\Delta_r S_T^0}{2R} \exp \left(- \frac{\Delta_r H_T^0}{2RT} \right) \quad (21)$$

and

$$P_A^i = \frac{1}{P'_{\text{H}_2\text{O}}} \exp \frac{\Delta_r S_T^0}{R} \exp \left(- \frac{\Delta_r H_T^0}{RT} \right) \quad (22)$$

2.4. Variation of P_A for comparable values of $P'_{\text{H}_2\text{O}}$ and $P_{\text{H}_2\text{O}}$

For comparable values of $P'_{\text{H}_2\text{O}}$ and $P_{\text{H}_2\text{O}}$ the partial pressure of the product A should satisfy, in contrast with Eq. (22) which is valid only for $P'_{\text{H}_2\text{O}} \gg P_{\text{H}_2\text{O}}$ the relation:

$$P_A = \frac{K_P}{P_{\text{H}_2\text{O}} + P'_{\text{H}_2\text{O}}} \quad (23)$$

Under the condition of congruent evaporation, we have

$$P_{\text{H}_2\text{O}} = P_A \quad (24)$$

Substituting P_A for $P_{\text{H}_2\text{O}}$ in Eq. (23) in accordance with Eq. (24), we obtain a quadratic equation:

$$P_A^2 + P'_{\text{H}_2\text{O}} P_A - K_P = 0 \quad (25)$$

which yields

$$P_A = - \frac{1}{2} P'_{\text{H}_2\text{O}} + \left[\frac{1}{4} (P'_{\text{H}_2\text{O}})^2 + K_P \right]^{1/2}. \quad (26)$$

Strictly speaking, Eq. (26) should be used in all cases when $P'_{\text{H}_2\text{O}} > 0$.

2.5. Impact of the condensation energy on the decomposition rate

The gasification mechanism of the decomposition process assumes that the stage of dissociative evaporation of the reactant is accompanied by a stage in which the nonvolatile product condenses with a release of a considerable condensation energy. Thermal decomposition rate calculations made for a number of compounds (nitrates, azides, nitrides and sulphates) [9–13] disregarded the possible effect of this additional source of energy. It was assumed that this energy is dissipated in the bulk of the product. The real decomposition rates found for some compounds, for instance, carbonates [12], have turned out to be, however, substantially (by three orders of magnitude) higher than the calculated values. This discrepancy was attributed [12] to a partial transfer of condensation energy from the nonvolatile decomposition product to the reactant by activated water molecules occupying one of the 'excited vibrational-rotational levels of the ground electronic state with energies ranging from 19 to 210 kJ mol⁻¹'. Unfortunately, both the mechanism and the characteristics of the partial transfer of condensation energy to the reactant remain unclear. Nevertheless, it can be assumed that this transfer occurs in the course of decomposition of other compounds as well, especially when one of the reaction products is water.

In order to take into account the influence of this effect on the dehydration rate, it was proposed [15] to introduce into calculations of the enthalpy of the decomposition reaction an additional term $\tau \Delta_c H_T^0$ where the coefficient τ corresponds to the fraction of the condensation energy $\Delta_c H_T^0$ transferred to the reactant. For reaction (20), we can write

$$\begin{aligned} \Delta_r H_T^0 = & \Delta_f H_T^0[\text{Li}_2\text{SO}_4(\text{g})] + \Delta_f H_T^0[\text{H}_2\text{O}(\text{g})] \\ & - \Delta_f H_T^0[\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}(\text{s})] \\ & + \tau \Delta_c H_T^0[\text{Li}_2\text{SO}_4(\text{g})] \end{aligned} \quad (27)$$

In the absence of a quantitative transfer model, the magnitude of τ coefficient for the process under study is chosen from considerations of the best fit of the calculations to experiment. The change in the entropy of the

decomposition reaction is calculated without including any corrections for the condensation.

2.6. Selection of initial parameters

An additional difficulty in the kinetics calculation for reaction (20) is connected with the absence of data characterizing the enthalpy of formation $\Delta_f H_T^0$ and the entropy S_T^0 of gaseous $\text{Li}_2\text{SO}_4(\text{g})$ in the available reference books [16,17]. Both these quantities were evaluated by us from the known values of the enthalpy of formation and entropy for $\text{Li}_2\text{SO}_4(\text{s})$ [16] and from the differences in the enthalpies of formation and entropies for the gaseous and solid M_2SO_4 averaged over Na, K, Rb and Cs: 338 ± 10 kJ mol⁻¹ and 194.2 ± 3.5 J mol⁻¹ K⁻¹. Table 1 lists the initial values of the thermodynamic functions for all components of reactions (1) and (20), and Table 2, all the other parameters necessary for subsequent calculations.

3. Results and discussion

3.1. Product partial pressures

Out of a large number of publications dealing with the thermal dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, we shall use for the analysis Refs. [19–27]. The measurement conditions and the main kinetic parameters obtained in these works are summarized in Table 3. All authors used $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single-crystal or powder samples with a known particle size, which permits one to relate the experimental values of the Arrhenius parameters (A and E_a) to the absolute values of the product partial pressure. Significantly different techniques and measuring conditions were used in different laboratories.

Okhotnikov et al. [19] studied the kinetics of dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ by means of a quartz-crystal microbalance under a dynamic vacuum of $\approx 4 \times 10^{-10}$ atm. The samples were polished to form 5 mm \times 3 mm \times 0.3 mm parallelepipeds. To eliminate the nucleation stage, the largest plane was ground with fine-grain abrasive. The gaseous molecules of water condensed on the surface of the quartz crystal located above and parallel to the sample surface. The kinetic parameters derived from isothermal measurements within the 300–400 K range were found to be: $E_a = 87.1 \pm 0.8$ kJ mol⁻¹ and $A = 1.4 \times 10^8$ kg m⁻² s⁻¹ (in units of the mass

Table 1
Thermodynamic functions [16,17] used in the calculations

Species	State of aggregation	$\Delta_r H_{298}^0$ (kJ mol ⁻¹)	S_{298}^0 (J mol ⁻¹ K ⁻¹)	Ref.
H ₂ O	g	-241.8±0.1	188.7±0.1	[16]
Li ₂ SO ₄	g	-1098.0±10	308.2±4.0	[16]
Li ₂ SO ₄	s	-1436.0±0.5	114.0±0.2	[16]
Li ₂ SO ₄ ·H ₂ O	s	-1736.4±1.3	146.4±0.6	[17]

Table 2
Parameters used in the calculations of dehydration rates

Parameter	Symbol	Value
Molar mass of Li ₂ SO ₄ ·H ₂ O	<i>M</i>	0.124 kg mol ⁻¹
Molar mass of Li ₂ SO ₄	<i>M</i>	0.106 kg mol ⁻¹
Mean molar mass of gaseous products	\bar{M}	0.044 kg mol ⁻¹
Density of Li ₂ SO ₄ ·H ₂ O	ρ	2050 kg m ⁻³
Coefficient of diffusion of H ₂ O in N ₂ at 273 K [18]	<i>D</i> ₀	2.04×10 ⁻⁵ m ² s ⁻¹
Power degree in Eq. (11)	<i>n</i>	2.072
Enthalpy of reaction (20) at $\tau=0$	$\Delta_r H_{298}^0$	396.6 kJ mol ⁻¹
Entropy of reaction (20)	$\Delta_r S_{298}^0$	350.5 J mol ⁻¹ K ⁻¹
Condensation heat of Li ₂ SO ₄ (g)	$\Delta_c H_{298}^0$	-338.0 kJ mol ⁻¹
Gas constant	<i>R</i>	8.3145 J mol ⁻¹ K ⁻¹
Pressure conversion factor	γ	101325 Pa atm ⁻¹

density of H₂O flow). Somewhat later, Kirdyashkina and Okhotnikov [20] repeated these measurements using crystalline Li₂SO₄·H₂O samples shaped as discs, 1 mm thick and 6 mm in diameter. The kinetic parameters found in the 315–362 K range were: $E_a=84.9\pm 2.1$ kJ mol⁻¹ and $A=1.3\times 10^7$ kg m⁻² s⁻¹.

Bertrand et al. [21] reported on isothermal TG measurements of the dehydration rate constant of Li₂SO₄·H₂O as a function of water-vapor partial pressure (0.1–4 Torr) in a reaction system evacuated preliminarily to 10⁻⁵ Torr at several different temperatures: 58, 63, 71, 81 and 86°C. The rate constant k_a was calculated from the equation

$$k_a t = [1 - (1 - \alpha)^{1/3}]r \quad (28)$$

where $r=0.048$ mm is the average radius of sample particles. Using parts of the $k_a=f(P_{H_2O})$ curves obtained at different temperatures (before the onset of the Topley–Smith effect), one can readily calculate

the activation energy for the dehydration of Li₂SO₄·H₂O. By averaging the values of E_a found from a comparison of the $k_a=f(P_{H_2O})$ curves for the temperatures 58 and 71°C and 81 and 86°C [21], we came to $E_a=192\pm 10$ kJ mol⁻¹. Taking this value of E_a and the values of the rate constants for $P'_{H_2O}=1$ Torr and the above temperatures, we obtained $A=4.8\times 10^{24}$ s⁻¹.

The kinetic studies of Galwey et al. [22] and Brown et al. [23] were performed on single-crystal and powder Li₂SO₄·H₂O samples. The kinetic parameters were obtained from isothermal measurements of the pressure of the water vapor evolved in a pre-evacuated, constant-volume apparatus. The final pressure P'_{H_2O} by the end of decomposition was 5–6 Torr, so that the mean value of P'_{H_2O} (at $\alpha=0.5$) for the decomposition process should be equal ca. 3 Torr or 4×10^{-3} atm. The measurement temperature was varied within the 360–400 K range.

Tanaka et al. [24–27] used TG for the isothermal kinetic study and TG–DSC for the non-isothermal studies. The flow of nitrogen with the concentration of H₂O vapor of ca. 10⁻³% at a rate of 30 ml min⁻¹ was used. The heating rate was varied from 0.47 to 8.04 K min⁻¹. Single crystals and crushed crystals of various particle size fractions were used. Of many kinetics results given in these works [24–27], we included in Table 3 the data calculated for the R3 model and corresponding to the change of α in the 0.1–0.9 range.

The original E_a and A values were used for the calculation of the rate constant k and product partial pressure P_A at the mean decomposition temperature for the different studies. Eq. (8) was used in the case of experiments in vacuum [19–23] and Eqs. (9)–(12) in the case of experiments in a foreign-gas environment [24–27]. The distance z in the last case was assumed to be 5 mm. This value, in our opinion, is close to the

Table 3
Kinetic parameters for the thermal dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

Method	Atmosphere	Temperature range (K)	r (m)	E_a (kJ mol ⁻¹)	A (s ⁻¹)	k_{373} (s ⁻¹)	P_A/atm at 373 K		Ref.
							experiment	calculation	
Quartz-crystal microbalance	Dynamic vacuum 4×10^{-10} atm	300–400		87.1	1.4×10^8 ^a		1.4×10^{-6}	3.8×10^{-5}	[19]
Quartz-crystal microbalance	Dynamic vacuum 4×10^{-10} atm	315–362		84.9	1.3×10^7 ^a		2.6×10^{-7}	3.8×10^{-5}	[20]
TG isothermal	$P_{\text{H}_2\text{O}} = 1$ Torr	331–359	4.8×10^{-5}	192.0	4.8×10^{24}	6.3×10^{-3}	2.2×10^{-6}	1.1×10^{-6}	[21]
EGA (constant- volume reactor)	$P_{\text{H}_2\text{O}} \approx 3$ Torr	360–400	1.6×10^{-3}	79.9	6.6×10^6	4.3×10^{-5}	5.1×10^{-7}	3.7×10^{-7}	[22]
EGA (constant- volume reactor)	$P_{\text{H}_2\text{O}} \approx 3$ Torr	349–377	7.5×10^{-5}	93.0	8.0×10^9	7.6×10^{-4}	4.2×10^{-7}	3.7×10^{-7}	[22]
EGA (constant- volume reactor)	$P_{\text{H}_2\text{O}} \approx 3$ Torr	362–402	1.6×10^{-3}	106.3	2.8×10^{10}	3.6×10^{-5}	4.3×10^{-7}	3.7×10^{-7}	[23]
EGA (constant- volume reactor)	$P_{\text{H}_2\text{O}} \approx 3$ Torr	324–365	7.5×10^{-5}	87.0	9.9×10^8	6.5×10^{-4}	3.6×10^{-7}	3.7×10^{-7}	[23]
TG isothermal	N_2 flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	385–400	1.2×10^{-3}	111.8	2.0×10^{11}	4.4×10^{-5}	3.7×10^{-5}	3.3×10^{-5}	[24]
TG isothermal	N_2 flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	358–372	7.5×10^{-5}	90.2	4.0×10^9	9.4×10^{-4}	5.0×10^{-5}	3.3×10^{-5}	[24]
TG-DSC non-isothermal	N_2 flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	0.5–8.0 ^b	1.2×10^{-3}	84.1	2.6×10^7	4.3×10^{-5}	3.6×10^{-5}	3.3×10^{-5}	[24]
TG-DSC non-isothermal	N_2 flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	0.5–8.0 ^b	7.5×10^{-5}	114.9	4.9×10^{12}	4.0×10^{-4}	2.1×10^{-5}	3.3×10^{-5}	[24]
TG-DSC non-isothermal	N_2 flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	388–408 1.0 ^b	1.2×10^{-3}	92.5	2.0×10^8	2.2×10^{-5}	1.9×10^{-5}	3.3×10^{-5}	[25]
TG-DSC non-isothermal	N_2 flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	1.0–8.0 ^b	1.3×10^{-4}	115.5	4.0×10^{12}	2.7×10^{-4}	2.5×10^{-5}	3.3×10^{-5}	[25]

TG-DSC non-isothermal	N ₂ flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	1.0–8.0 ^b	6.4×10^{-5}	136.0	4.5×10^{15}	4.1×10^{-4}	1.9×10^{-5}	3.3×10^{-5}	[25]
TG non-isothermal	N ₂ flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	362–379 0.6 ^b	6.4×10^{-5}	165.3	5.0×10^{19}	3.6×10^{-4}	1.7×10^{-5}	3.3×10^{-5}	[26]
TG non-isothermal	N ₂ flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	368–386 1.2 ^b	6.4×10^{-5}	161.9	1.3×10^{19}	2.8×10^{-4}	1.3×10^{-5}	3.3×10^{-5}	[26]
TG non-isothermal	N ₂ flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	372–396 2.4 ^b	6.4×10^{-5}	127.6	2.0×10^{14}	2.7×10^{-4}	1.3×10^{-5}	3.3×10^{-5}	[26]
TG-DSC non-isothermal	N ₂ flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	0.5–8.0 ^b	1.3×10^{-4}	115.4	4.0×10^{12}	2.8×10^{-4}	2.6×10^{-5}	3.3×10^{-5}	[27]
TG-DSC non-isothermal	N ₂ flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	0.5–8.0 ^b	7.5×10^{-5}	114.1	4.0×10^{12}	4.2×10^{-4}	2.2×10^{-5}	3.3×10^{-5}	[27]
TG-DSC non-isothermal	N ₂ flow $P_{\text{H}_2\text{O}} \approx 10^{-5}$ atm	0.5–8.0 ^b	6.4×10^{-5}	135.4	3.2×10^{15}	3.5×10^{-4}	1.6×10^{-5}	3.3×10^{-5}	[27]

^a In $\text{kg m}^{-2} \text{s}^{-1}$ of H₂O flow.

^b The heating rate in K min^{-1} .

height of platinum crucibles with dehydrated samples used in experiments in a flow of nitrogen. For non-volatile Li_2SO_4 molecules, the effective value of the diffusion coefficient was calculated from Eq. (12). Taking into account the dependence of D_{eff} on z , the actual dependence of P_A on z is proportional of \sqrt{z} . Hence, the possible uncertainty in the estimation of the z -value within, for example, a factor of 2 introduces only $\sqrt{2}$ variation in P_A .

The preliminary examination of the experimental P_A values leads to some, at first sight unexpected, conclusions.

1. In spite of great differences in E_a and A values obtained for the decomposition $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in a flow of nitrogen, the discrepancy between P_A values is rather small and ranges from $1.3 \times 10^{-5} \text{ s}^{-1}$ to $5.0 \times 10^{-5} \text{ s}^{-1}$ for all 13 independent series of measurements [24–27].
2. The P_A values in the case of isothermal measurements in a pre-evacuated, constant-volume apparatus [22,23] are two orders of magnitude lower than that in a flow of nitrogen.
3. The P_A values for the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ under a high-vacuum [19,20] are 1–2 orders of magnitude lower than that in a flow of nitrogen.

The first two conclusions will be discussed later on, after a comparison of experimental and theoretical results. Now let us consider the last conclusion. On closer inspection of measurement conditions with the quartz-crystal microbalance [19,20], it becomes evident that the most probable reason of this discrepancy lies in an intensive cooling of the dehydrated sample by the quartz crystal. The quartz crystal was maintained at 78 K (the boiling point of liquid nitrogen), which is ca. 300 K lower than that of the thermostatically controlled support for the sample. It means that the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal was heated from below by the support and was cooled from above through the heat consumption in the course of dehydration and the radiative heat transfer from the sample surface to the quartz crystal. As a result, the dehydrated sample surface had a temperature much below of that for the support. The difference should be higher for a thicker sample. Indeed, as can be seen from Table 3, the P_A value for the 1 mm thick sample [20] is 5.4 times lower than that for the 0.3 mm thick sample [19]. Therefore, the results of kinetics measurements in

Refs. [19,20] must be taken as essentially underestimated. For the further comparison of experimental and theoretical P_a values, we shall use the results obtained only in Refs. [21–27].

The theoretical values of P_A at 373 K were calculated with Eqs. (26) and (27) taking into account the enthalpy and entropy of reaction (20), the partial pressure of H_2O vapor listed in Table 3 and the coefficient $\tau=0.6$. The choice of the τ coefficient equal to 0.6 corresponds to the best agreement of experimental and calculated data. In all cases, the discrepancy between experimental and calculated P_A values is not higher than a factor of 2.5, in spite of the fact that the absolute values of P_A are varied through a range of two orders of magnitude.

It can be seen from a comparison of experimental and calculated data that the reason why the P_A values measured in a constant-volume apparatus [22,23] are two orders of magnitude lower than those in a flow of N_2 [24–27] is the difference in the partial pressure of H_2O vapor (4×10^{-3} and 10^{-5} atm). As follows from Eq. (26), for a fixed value of $P_{\text{H}_2\text{O}}$, the P_A values should be identical for any different conditions, irrespective of the measurement technique (isothermal or non-isothermal) and particle size. This explains, in particular, the close proximity of experimental P_A values obtained in different studies [24–27].

3.2. Activation energies

As follows from the theoretical considerations (see Eqs. (18) and (19)), the value of the activation energy depends on the dehydration mode and, for the equimolar mode ($P'_{\text{H}_2\text{O}} \ll P_{\text{H}_2\text{O}}$) is ν times less than that for the isobaric mode ($P'_{\text{H}_2\text{O}} \gg P_{\text{H}_2\text{O}}$). For $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, the ν value is equal to 2. Taking into account $\tau=0.6$, we obtain $E_a^i = \Delta_r H_{298, \tau=0.6}^0 \approx 194 \text{ kJ mol}^{-1}$ for the isobaric mode and $E_a^e = \Delta_r H_{298, \tau=0.6}^0 / 2 \approx 97 \text{ kJ mol}^{-1}$ for the equimolar mode.

If the equilibrium pressure $P_{\text{H}_2\text{O}}$ evolved during thermal dehydration (internal pressure) is not much lower than the partial pressure $P'_{\text{H}_2\text{O}}$ in a foreign gas (external pressure), we should expect it to reach and surpass this value with increasing temperature. In this case, decomposition will crossover from the isobaric to the equimolar mode. For illustration, Fig. 1 presents the variation of $\log P_A$ calculated from Eq. (26) with

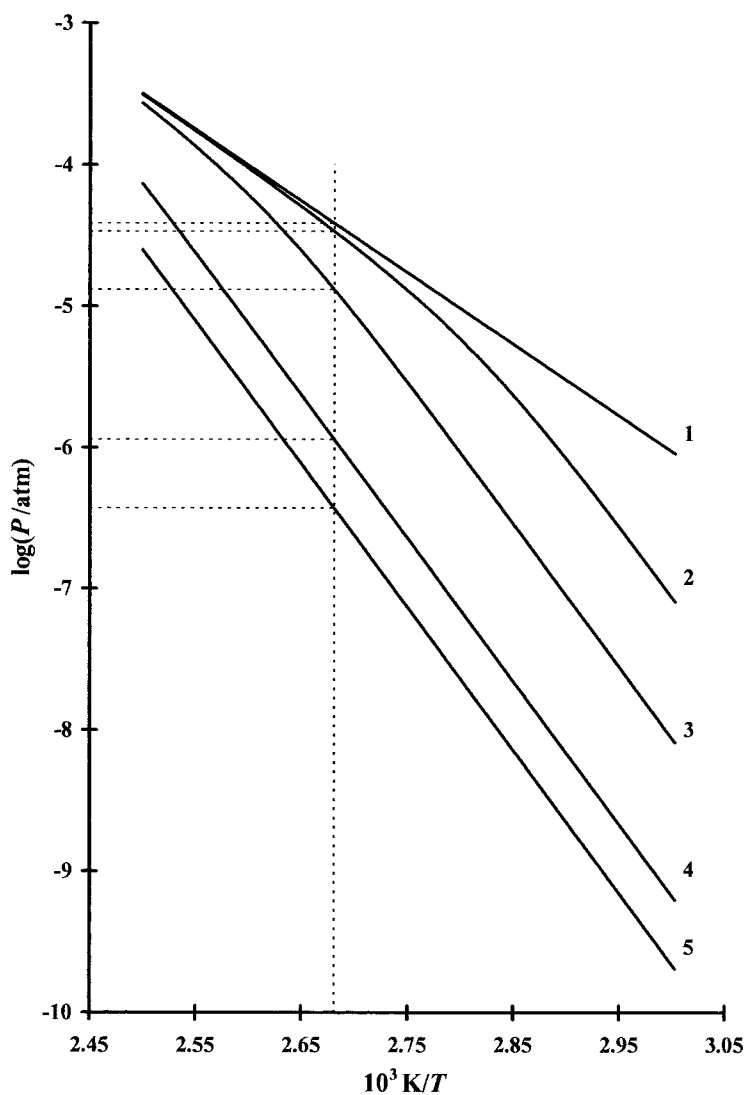


Fig. 1. Calculated temperature dependence of the equilibrium Li_2SO_4 partial pressure for the dissociative evaporation of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ at the different external partial pressures of H_2O vapor: (1) 4×10^{-10} atm, (2) 10^{-5} atm, (3) 10^{-4} atm, (4) 1.3×10^{-3} atm and (5) 4×10^{-3} atm. Dotted lines correspond to the P_A values at $T=373$ K.

inverse temperature (within the 300–400 K range) for the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ at the external pressures $P'_{\text{H}_2\text{O}}$ corresponding to the experimental conditions in Refs. [19–27]. As is evident from Fig. 1, the crossover from the isobaric to the equimolar mode (see curve 2 for $P'_{\text{H}_2\text{O}} = 10^{-5}$ atm) turns out to be fairly smooth, corresponding to a change in P_A of ca. one order of magnitude. The change of the slope for

this curve is accompanied by gradual changing of the E_a value from 194 to 97 kJ mol^{-1} . Therefore, for comparable values of internal and external pressures of H_2O vapor, the activation energy for the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ may vary, depending on the temperature, by a factor of 2. As we shall see below, these theoretical conclusions are in complete agreement with experiments.

1. In 'pure' equimolar and 'pure' isobaric modes, the E_a values are equal to 86 kJ mol^{-1} [19,20] and 192 kJ mol^{-1} [21], respectively, which are in agreement with the theoretically estimated values of 97 and 194 kJ mol^{-1} .
2. The E_a values measured in Refs. [22,23] are underestimated, most likely, because of the great uncertainty of the rate constant measurements. Indeed, in the process of isothermal measurements in a constant-volume apparatus [22,23], the $P'_{\text{H}_2\text{O}}$ value gradually increased in proportion to the fraction decomposed. It means that in the range of α from 0.1 to 0.9 the rate constant should be gradually reduced nine times. This conclusion is in agreement with the experiments (see, for example, Fig. 3 and particularly Fig. 4 of Ref. [23]). It follows herefrom that any small tendency in a shift of averaged k values to higher α values with temperature should reduce the slope of the Arrhenius graph and hence the E_a value.
3. The variations of E_a values in non-isothermal experiments [24–27] can be explained as follows from Fig. 1, by the difference in the temperature range used for determination of E_a . In its turn, the

- temperature range must depend on the sample particle size, heating rate and fraction decomposed. Practically all experimental data presented in Refs. [24–27] support these expectations. For example, an increase of particle radius from 6.4×10^{-5} up to $1.2 \times 10^{-3} \text{ m}$ reduced the E_a value from 136 to 92.5 kJ mol^{-1} [25]. With an increase of the heating rate from 0.55 to 2.4 K min^{-1} , the E_a value decreased from 170.7 to $136.4 \text{ kJ mol}^{-1}$ [26]. Finally, an increase of fraction dehydrated from 0.1 to 0.9 reduced the E_a value from 189 to 107 kJ mol^{-1} (for the sample with the particle radius $6.4 \times 10^{-5} \text{ m}$) and from 152 to 95 kJ mol^{-1} (for the sample with the particle radius $1.3 \times 10^{-4} \text{ m}$) [24]. The same regularities were observed by Huang and Gallagher [28] who used TG–DSC measurements for powders and single crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Higher activation energies (up to 220 kJ mol^{-1}) were associated with a small α and a small particle size.
4. As can be seen from Fig. 1, the effect of variations of external H_2O vapor pressure on the dehydration rate of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (in the 10^{-5} – 10^{-4} atm range) should be significant at low temperatures and

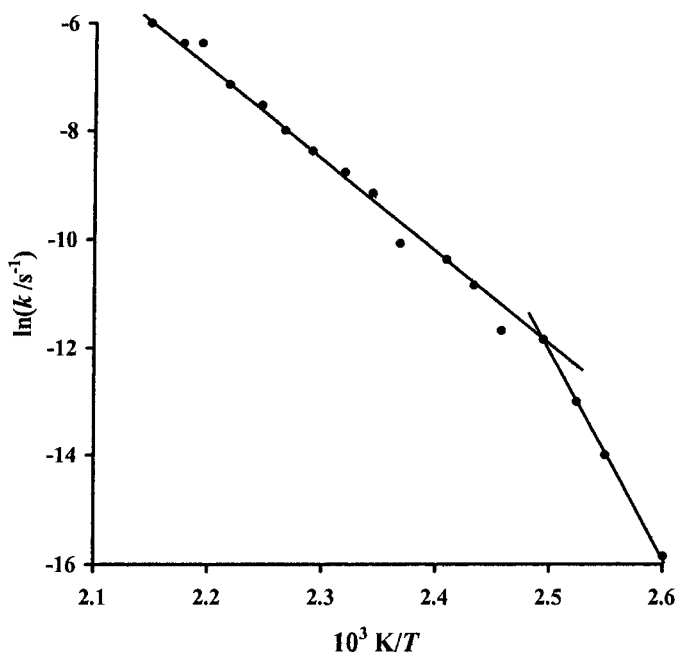


Fig. 2. Arrhenius plot for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ under an atmosphere of air. (Reproduced from Dollimore et al. [29], by permission of the Journal Editor).

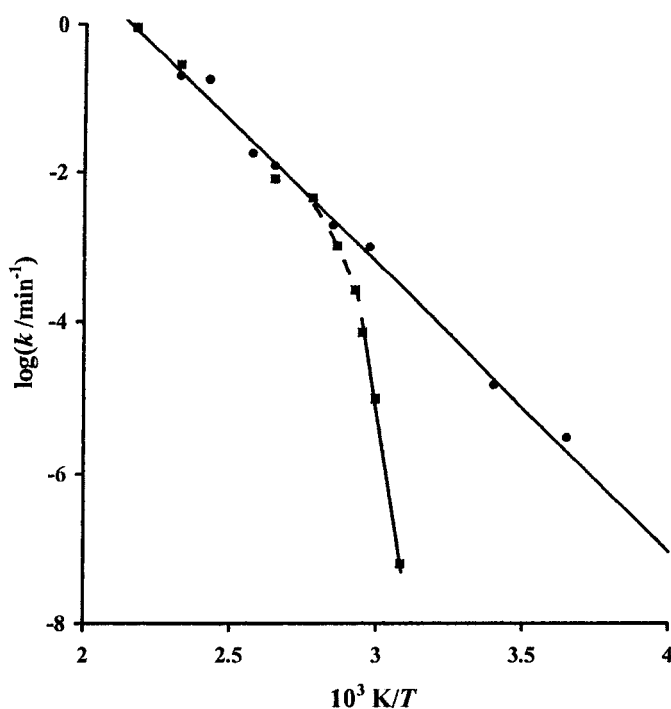


Fig. 3. Arrhenius plots for the dehydration of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ vacuum (●) and under an atmosphere of water vapor at $P'_{\text{H}_2\text{O}} = 10$ Torr (■). (Reproduced from Pavlyuchenko et al. [30], by permission of the authors).

negligible at high temperatures (>400 K). This theoretical conclusion explains the results of TG measurements of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration by Huang and Gallagher [28] in dry and water saturated N_2 . The effect of the water vapor increase was significant only for the powdered samples (dehydrated at temperatures <400 K) particularly during the early stage of the dehydration. For single crystals (dehydrated at temperatures >400 K), the dehydration was only marginally affected.

The same theoretical conclusions, in particular, the existence of two distinct (isobaric and equimolar) modes of decomposition can be extended to the dehydrations of other hydrates. As an example, the Arrhenius plots for the dehydration of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [29] and $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ [30] are reproduced in Figs. 2 and 3. In the work by Dollimore et al. [29], non-isothermal TG under a dynamic atmosphere of air was used. In the work by Pavlyuchenko et al. [30], isothermal TG under high vacuum (10^{-8} atm) and an atmosphere of H_2O vapor at $P'_{\text{H}_2\text{O}} = 10$ Torr was used.

In both cases, we can observe two regions of the Arrhenius plots: isobaric and equimolar, at lower and higher temperatures, respectively. The slopes of the Arrhenius plot in these regions are in close agreement with the theoretical predictions: the ratio E_a^i/E_a^e is equal to $281/147 \approx 1.9$ [29], instead of the expected 2, for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and to $515/65 \approx 8$ [30], instead of the expected 9, for $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$.

4. Conclusions

Based on the mechanism of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration through dissociative evaporation of the hydrate in the form of Li_2SO_4 and H_2O molecules, we have attempted to substantiate theoretically the effect of water vapor on the dehydration rate and to calculate the product partial pressures and activation energies under the conditions used in the available publications. In order to fit the calculated to experimental values of the kinetic parameters, the calculations of the enthalpy of the reaction included partial transfer of

the energy released in $\text{Li}_2\text{SO}_4(\text{g})$ condensation to the reactant. Unfortunately, there is presently no physical model of this transfer. Therefore, the choice of the coefficient τ did not have any theoretical substantiation.

Nevertheless, this concept has provided a quantitative interpretation for the depressing action of water vapor on the hydrate decomposition rate, and offered an explanation for the apparent differences in the kinetics of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration, when one compares the values of E_a obtained by different authors. Despite the significant differences between the methods and conditions of these studies, the product partial pressures and activation energies turn out to be in good agreement with theoretical calculations. In this connection, it is difficult to agree with the pessimistic conclusion of the Kinetic Committee of the International Confederation for Thermal Analysis and Calorimetry [6] concerning the unsuitability of using the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration reaction as a kinetic standard.

We are aware that the material presented in this work is not enough to allow ultimate conclusions on the dehydration mechanism as a whole and that further research is needed, primarily for other hydrates. Nevertheless, we would like to draw the attention of researchers to a tempting possibility opened by the mechanism of dissociative evaporation in gaining a better understanding of the physics underlying the dehydration process. We believe that many of the kinetic features of the process which still have not found convincing interpretation (such as the existence of an induction period, the effect of surface defects and solid products on the formation and growth of nuclei, self-localization of the process, the Topley–Smith effect and impedance effect) can find a simple explanation within the mechanism of dissociative evaporation, if one takes into account the stage of condensation of the nonvolatile component from oversaturated vapor and partial transfer of condensation energy from the product to the reactant. The most convincing evidence for or against this mechanism could be obtained by studying the composition of the primary products of dehydration by EGA/QMS techniques, which have been used recently in investigating the mechanism of decomposition of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ [10]. Although, the first experiments of this kind were carried out more than 30 years ago in a study of NaN_3

and TiN_3 decomposition products [31], this method is practically not in use in the field of thermal analysis.

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