

Dehydration of α -CaSO₄·0.5H₂O

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Thermal dehydration of α -CaSO₄·0.5H₂O investigated by nonisothermal thermogravimetry proceeds in air as a first-order reaction

$$-\ln(1 - \alpha) = kt$$

where α is the fraction decomposed at time t .

Термическая дегидратация α -CaSO₄·0,5H₂O, которую мы определили при помощи неизотермической термогравиметрии, осуществляется на воздухе по реакции первого порядка

$$-\ln(1 - \alpha) = kt$$

где α является степенью разложения за период t .

The thermal dehydration of α -CaSO₄·0.5H₂O was studied by several authors. Šatava and Šesták [1—3] found out by isothermal and nonisothermal thermogravimetry that this dehydration in air is controlled by the kinetic equation of the first order (F_1): $-\ln(1 - \alpha) = kt$. The dehydration does not exhibit any incubation period and the rate-determining process is random nucleation. The activation energy ($E \approx 125 \text{ kJ mol}^{-1}$) is independent of partial pressure $p_{\text{H}_2\text{O}}$. The frequency factor corresponds to $Z \approx 8 \times 10^{14} \text{ s}^{-1}$. The values of kinetic constants found in nitrogen stream were lower.

On the other hand, Ball and Norwood [4] used isothermal thermogravimetry in nitrogen stream ($p_{\text{H}_2\text{O}} = 2.4 \text{ kPa}$) and found the dehydration to be due to one-dimensional diffusion (D_1): $\alpha^2 = kt$. The corresponding activation energy and frequency factors were $E \approx 94 \text{ kJ mol}^{-1}$ and $Z \approx 6 \times 10^{10} \text{ s}^{-1}$. Above the equilibrium temperature (424 K) the dehydration is significantly affected by parallel structural transformation α -CaSO₄ III \rightarrow CaSO₄ II [5].

Negro and Stafferi [6] ascertained by the method of DTA in air that the dehydration obeyed the kinetic Avrami equation (A_2): $[-\ln(1 - \alpha)]^{1/2} = kt$. The rate-determining process was random nucleation and the two-dimensional growth

of nuclei. The activation energy and frequency factor obtained by these authors were $E \approx 75 \text{ kJ mol}^{-1}$ and $Z \approx 10^{11} \text{ s}^{-1}$.

Recently, *Lehmann* and *Rieke* [7] found for dehydration by the use of nonisothermal thermogravimetry $E \approx 107 \text{ kJ mol}^{-1}$ and reaction order $n = 0.64$.

According to the existing publications [1—4, 6, 7] three different kinetic equations and two different rate-determining processes have been found for the dehydration of $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. The aim of this study was to find out the most probable kinetics of the mentioned process.

Experimental

We used $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ of high purity prepared in laboratory from precipitated gypsum (Merck) by the method described by *Combe* and *Smith* [8]. The dislocations in crystals which are centres of crystallization of CaSO_4 II were eliminated by milling to specific surface $S \approx 4000 \text{ cm}^2/\text{g}^{-1}$ according to Blaine [9, 10].

The measurements were carried out with the Du Pont Instrument 951 TGA adjusted for nonisothermal thermogravimetry. Samples of 0.02 g, heating rate 5°C min^{-1} , medium: air ($p_{\text{H}_2\text{O}} \approx 1.33 \text{ kPa}$).

The method of *Šatava* and *Škvára* [11—13] was used for evaluation.

Results and discussion

The probability that the dehydration of $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is controlled by the kinetic equation obtained thermogravimetrically for $\alpha = 0.1\text{—}0.9$ may be generally expressed by the correlation coefficient r of linear regression of the functional relation between $\log g(\alpha)$ and T^{-1} [11—13]. The obtained results are summarized in Table 1. The dehydration found experimentally in the sense of kinetic equations D_1 , F_1 and A_2 [1—4, 6] is represented in Fig. 1.

It results from the table that the dehydration according to kinetic models involving the nucleation (F_1 , A_2 , A_3) as rate-determining process is more probable than that according to models where the rate-determining process is diffusion or phase boundary reaction (D_1 , D_2 , D_3 , D_4 , R_2 , R_3).

However, equal values of correlation coefficients for kinetic equations F_1 , A_2 , and A_3 do not allow to determine the most probable kinetics of dehydration. Therefore we used the values of frequency factor and activation energy as deciding criteria of probability for the kinetics of dehydration of $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. For monomolecular reactions in the solid phase it ought to be $Z \approx 10^{14}\text{—}10^{16} \text{ s}^{-1}$ and $E \approx 83\text{—}250 \text{ kJ mol}^{-1}$ [14—16]. These requirements are fulfilled according to Table 1 by the dehydration proceeding as a first-order reaction, which is in agreement with papers [1—3].

Table 1

Kinetic parameters of thermal decomposition of $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$

Function	Rate-determining process	r	Z/s^{-1}	$E/kJ\text{mol}^{-1}$
D_1	Diffusion	0.993	—	—
D_2	Diffusion	0.990	—	—
D_3	Diffusion	0.996	—	—
D_4	Diffusion	0.992	—	—
F_1	Random nucleation	0.999	3×10^{14}	128
A_2	Random nucleation	0.999	5×10^5	63
A_3	Random nucleation	0.999	4×10^2	40
R_1	Phase boundary reaction	0.993	—	—
R_3	Phase boundary reaction	0.996	—	—

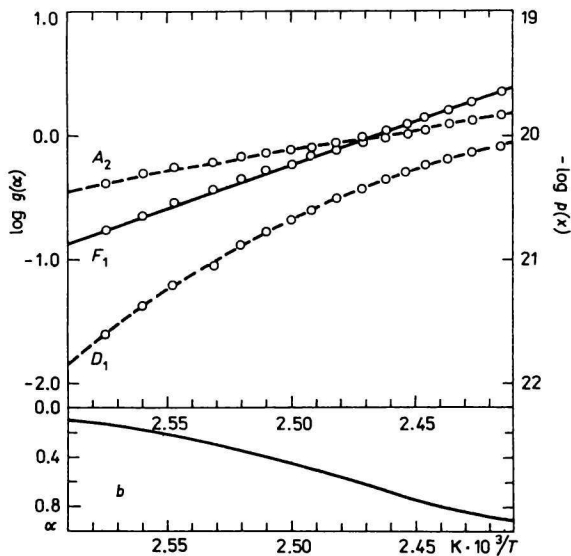


Fig. 1a. Experimental dependence of $\log g(\alpha)$ on T^{-1} according to kinetic equations D_1 , F_1 , and A_2 for dehydration of $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ in air.

Fig. 1b. Variation of the degree of transformation of $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ with temperature in the presence of air.

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