DEHYDRATION KINETICS OF LITHIUM SULFATE MONOHYDRATE SINGLE CRYSTALS

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Abstract

Some peculiar properties of lithium sulfate monohydrate dehydration kinetics are investigated. Experiments were carried out under both isothermal and non-isothermal conditions on the bulk single crystals (~1 cm). Under both heating modes some new data were obtained. Uncommon high dehydration process rate under isothermal conditions and linear dependence of this rate under non-isothermal ones were discovered. Experiments over the water saturated porous ceramics drying and over the water vapors transmitting through the layer of preliminary dehydrated lithium sulfate were carried out. It is attempted to explain observed phenomena considering heat- and mass-transfer conditions.

Keywords: activation energy, lithium sulfate monohydrate, non-isothermal kinetics, single crystals, thick product layers

Introduction

A large number of papers dealing with dehydration of lithium sulfate monohydrate has been published until today. It was stated by means of X-ray diffraction studies that the size of the formed reaction zone in the direction of its propagation is about 100 µm for the decomposition of this crystalhydrate [1]. It can be demonstrated, using the presently accepted notions of theoretical heterogeneous kinetics, that the rate of reaction zone propagation (and thus the rate of decomposition) is constant at constant temperature [2]. This conclusion has been experimentally confirmed only for the samples with rather small linear dimensions. Researchers investigated mainly either powder samples [3–6] or very small single crystals [5–7], or cuts obtained from larger single crystal samples [8, 9]. A typical size of the particles of a compound under investigation in powder samples was $\sim 2 \cdot 10^{-4}$ m [6, 7], the thickness of single crystal cuts studied in [8, 9] was $(1–2) \cdot 10^{-4}$ m. As one can easily notice, in all these cases the size of body subjected to thermal decomposition is comparable with the size of reaction zone itself; it can be assumed that under these conditions the reaction zone

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does not have enough time to form completely and to reach a stationary character. Because of this, we were interested in how the reaction zone would propagate under the conditions when the size of the sample in the direction of its propagation is much bigger than the size of reaction zone. It is evident that the experiments should involve rather large single crystal samples with easily controlled geometry and constant area of the reaction zone since the reaction rate is directly proportional to this area [2]. Another question that we were interested in was the effect of temperature on decomposition rate. The data obtained under isothermal heating and described in the papers cited above suggest that the reaction rate increases with temperature according to the Arrhenius law. Activation energies for this type of process which are about 90 kJ mol^{-1} are given in [7–9]. Besides, the results of these studies confirm that the reaction rate remains constant at constant temperature. It could be expected that in the experiments with large single crystal samples with non-isothermal heating regime the rate of dehydration will also obey the Arrhenius law, i.e. kinetic curves would be exponential. Because of this, we used both isothermal and non-isothermal heating regimes; in the latter case temperature was increased linearly with time.

Experimental

Figure 1 shows a scheme of experimental set-up and the section of the sample. Single crystals to be used as the samples were grown by slow evaporation at 80°C. The ini-
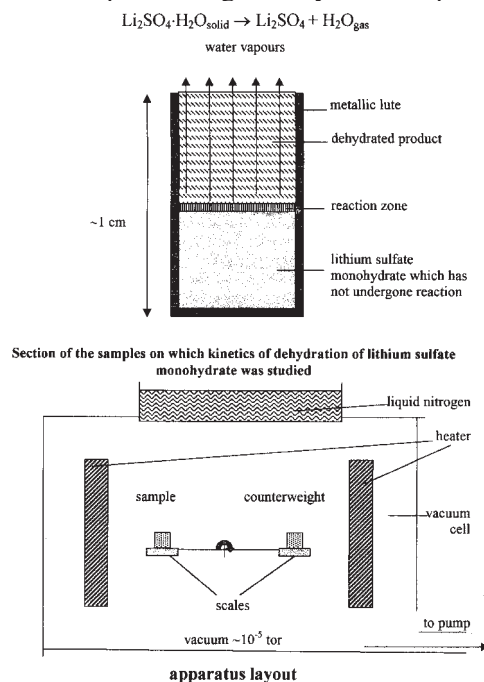

Fig. 1 Sample section and apparatus layout

tial crystals of monoclinic syngony were up to 0.02 m long in the direction [010]. Then they were rounded off to cylinder and covered with metal grease on all the surface except one end. This grease prevented dehydration from the covered surface. It hardened within 24 h and possessed high thermal conductivity. This was necessary, on one hand, to provide correct functioning of thermocouple temperature measurer, and on the other hand, to prevent the so-called self-cooling effect. The essence of this effect is that temperature in the reaction zone of endothermal process (in particular, dehydration of crystal hydrates) is somewhat lower than the ambient temperature. According to [10], the difference between temperatures can reach 10 K (for potash alum). This question is still under investigation (e.g. [5]) but it remains not clear yet. We performed thermocouple measurements aiming at the estimation of this effect and obtained 2–4 K. However, these data are only preliminary. The use of metal grease with high thermal conductivity allows to provide efficient heat transfer to the reaction zone and to minimize self-cooling. An open edge of the sample was then polished with an abrasive to increase the defects content. After such a treatment, the reaction was initiated simultaneously over the entire surface; thus we obtained the process geometry that could be well controlled and easily described. The set-up used in these experiments was developed and patented by the researchers of our Institute. The sample was placed on one cup of electron balance; a counter-weigh made of the same metal grease was placed on another. Temperature on the sample surface (to be more accurate, on the surface of the grease) was measured using a thermocouple that was inserted into the bottom of the balance cup. After the sample and the counter-weigh were mounted, the balance chamber was tightly closed and evacuated with a magnetic discharge pump till the residual pressure of ~10^{-3} Pa. After stable pressure was achieved, the furnace was switched on and heating began, either isothermal or non-isothermal. In the latter regime, temperature was increased linearly with time. In
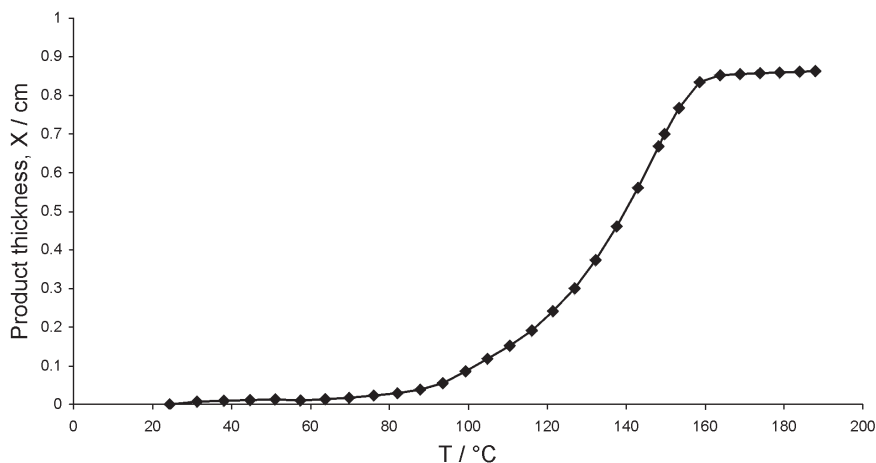
Fig. 2 A typical kinetic curve in experiments on non-isothermal dehydration of lithium sulfate monohydrate. Presented example was obtained under 0.019 K s^{-1} heating rate

order to stabilize the vacuum, a freezer was used. It was filled with liquid nitrogen. Water vapor was frozen out with its help. The decrease of sample mass due to water removal during dehydration was recorded, as well as the temperature on the sample surface.

Results and discussion

Results of experiments with non-isothermal heating regime

Theoretically, one could expect that a single experiment in non-isothermal regime could give all the Arrhenius parameters. A classical approach was used in [8, 9] to determine activation energy for the dehydration of lithium sulphate monohydrate. The data reported by these authors ideally fit the straight line in the co-ordinates $\ln(w)$–$1/T$. It seemed probable that the rate of dehydration in non-isothermal regime would also increase according to the Arrhenius law, i.e. exponentially.

The behaviour experimentally observed was found to be quite different from the expected one. Figure 2 shows a typical dependence of the mass of water lost by the sample on temperature. Though we recorded the decrease of the sample mass M, in order to make things more clear we present our data in the co-ordinates X–T where X is the distance at which the reaction front has moved. The parameters M and X are linked by the equation $M = XS\rho_{H_2O}$ where S is the area of sample, $\rho_{H_2O} = 0.29$ g cm^{-3} is the density of water in lithium sulphate monohydrate. After differentiation with respect to temperature, the primary kinetic curves obtained in the experiment were straightened in the dX/dT–T co-ordinates. So, in these experiments the reaction rate was not exponential (Arrhenius) but linear function of temperature. Curves shown in Fig. 3 (where the data are presented in the co-ordinates $X^{1/2}$–T) confirm this assumption. One can see that in these co-ordinates experimental points fall within straight lines; so, the dependence of sample mass loss on temperature is quadratic.
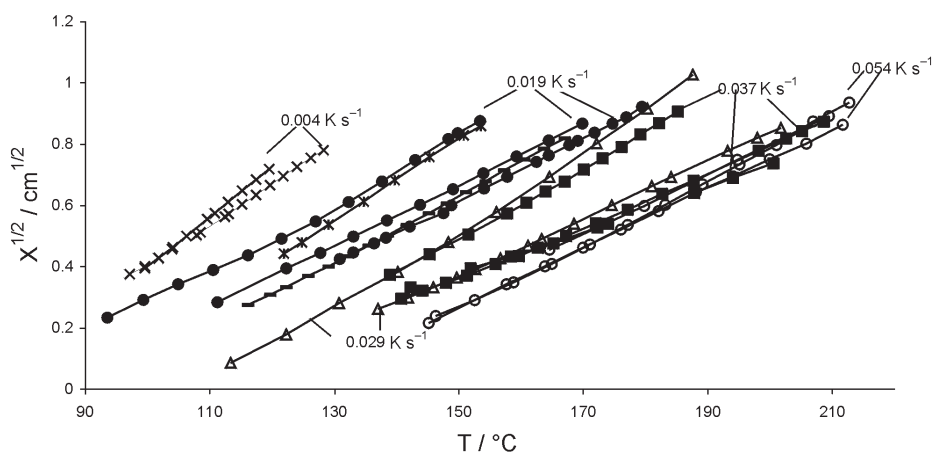

Fig. 3 Linear ranges in non-isothermal experiments

Thus, our experiments under the conditions of non-isothermal heating demonstrated that the process rate increases not according to the Arrhenius law but linearly (at least within a wide range of transformation degrees); so, it is impossible to obtain all the Arrhenius parameters from a single experiment. Of course, we do not suspect that the Arrhenius law does not work in this case. The reasons for such a behaviour of the system should be searched for. These results, together with others, will be discussed in detail below.

Results of experiments with isothermal heating regime

The goal of the present series of experiments was to obtain activation energies of the process under investigation that could not be determined from non-isothermal experiments. It was also interesting to compare the results obtained with the results of [8, 9] where activation energies were obtained using thin cuts of single crystals. Stationary regions of curves obtained in isothermal experiments that were then used to build a plot in the Arrhenius co-ordinates are shown in Fig. 4.
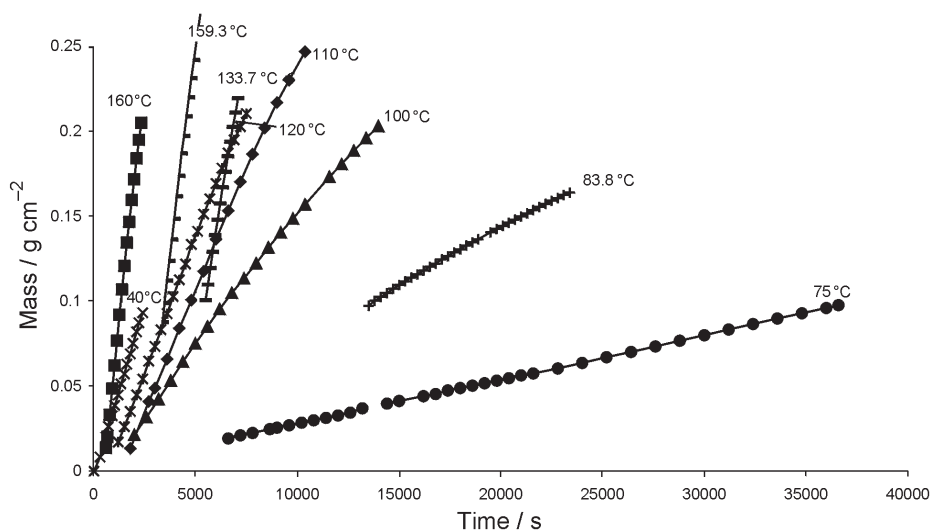

Fig. 4 Stationary regions of curves obtained in isothermal experiments

The results are shown in Fig. 5. Activation energy obtained in our experiments using the least squares method was 50.6 kJ mol^{-1}. This is much different from the value reported in [8, 9] ($\approx$87 kJ mol^{-1}). Besides, the enthalpy of dehydration for $Li_2SO_4 \cdot H_2O$ is known from literature to be 60.1 kJ mol^{-1} [11] which is higher than the activation energy for the same process obtained in our experiments. This fact is surely due to the multistage character of dehydration process. It is also noteworthy that the value obtained by us is close to the heat of water evaporation (40.6 kJ mol^{-1}). This will also be discussed below. Now we shall pay attention to the following. One can see when comparing our results with the results of [8, 9] shown in the same Fig. 5 that
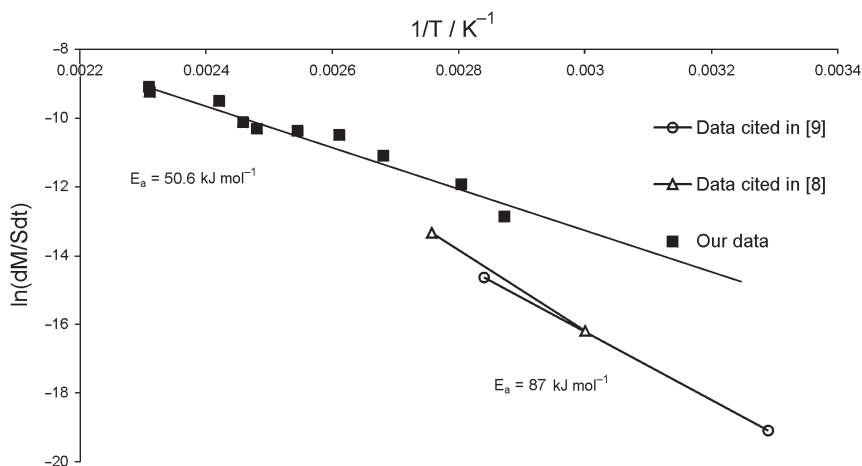
Fig. 5 Isothermal kinetics data

in our experiments, for the rest conditions kept constant, dehydration rate was several times higher, in spite of the fact that substantial layers of anhydrous products were accumulated during the experiment which did not happen in the experiments described in the mentioned works. Unexpectedly high process rate is likely to be the most interesting effect observed by us during the present study.

Additional experiments

It was reasonable to assume that the layer of solid product which was absent in the earlier works was responsible for the observed phenomena. In order to test this assumption, we performed experiments on drying the porous ceramics saturated with water, and on passing water vapor through the layer of lithium sulfate dehydrated preliminarily. For the experiments on drying the ceramics, the scheme was the same as for the monohydrate except that ceramic cylinder preliminarily saturated with water was used instead of a rounded single crystal. The structure of the samples in the experiments on passing water vapor through the layer of dehydrated lithium sulfate is shown in Fig. 6. A cylinder of dehydrated salt was glued with metallic grease into a metal yoke; a pellet of humid porous ceramics was used as a source of water vapor. The results of these experiments are compared with the results on dehydration of lithium sulfate monohydrate in Figs 7 and 8. One can see that the shapes of kinetic curves for non-isothermal dehydration of lithium sulfate monohydrate, drying porous ceramics and the transfer of water vapor through dehydrated lithium sulfate are rather similar to each other. This suggests that the mechanisms that govern these processes are also similar.
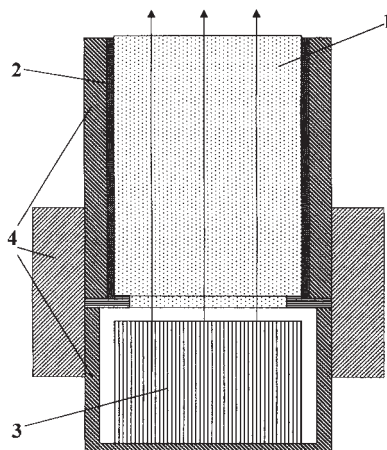
Fig. 6 Sample section in experiments over the water vapours transmitting; 1 – preliminarily dehydtrated lithium sulfate, 2 – metallic lute, 3 – porous ceramics saturated with liquid water, 4 – metal casting

Discussion of the results

It is evident that it is impossible to understand the above-mentioned features of the system behavior without considering mass and heat transfer. The physics of heat and mass exchange is the area that is far from being complete and clear; analytical calculations proposed in this research area can be used only for not very complicated systems. In the majority of cases empirical or semi-empirical approach is to be used. In the system under consideration, we can reveal three aspects that affect its kinetic characteristics. These are
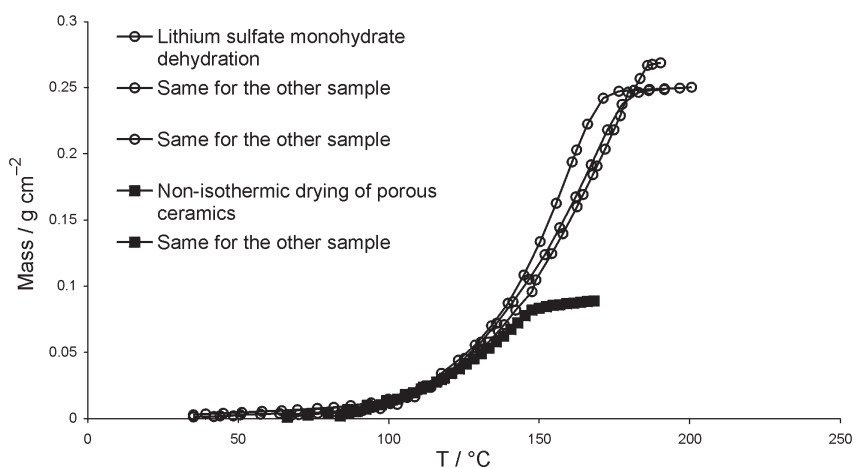

Fig. 7 Non-isothermal kinetics of lithium sulfate monohydrate dehydration compared to that for the water saturated porous ceramics drying with a heating rate of 0.019 K s^{-1} (X-axes are reduced)
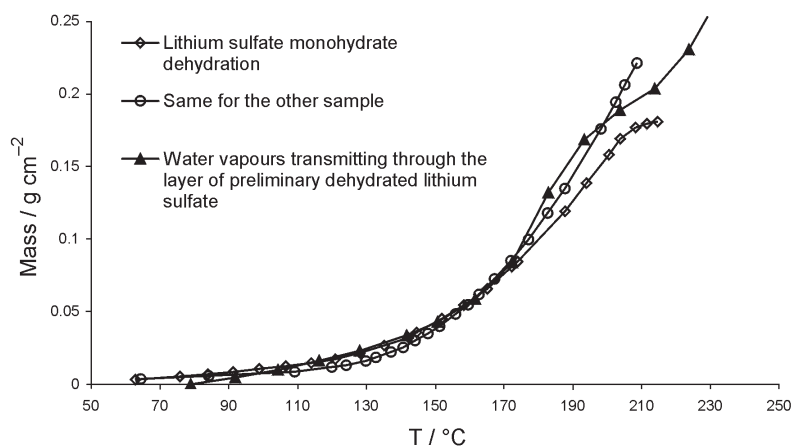
Fig. 8 Non-isothermal dehydration kinetics of lithium sulfate monohydrate compared
to that for over the water vapours transmitting through the layer of preliminarily
dehydrated lithium sulfate with a heating rate of 0.037 K s^{-1}

heat and mass transfer, and physicochemical features of this very compound (lithium sulfate monohydrate and its anhydrous form). We tried to consider all the three aspects keeping in mind that the transfer of mass and heat are the processes very closely connected with each other. It can be assumed that the layer of dehydrated product which was absent from the reaction systems in earlier works is now responsible for the observed effects. In order to confirm this statement, we made experiments involving drying porous
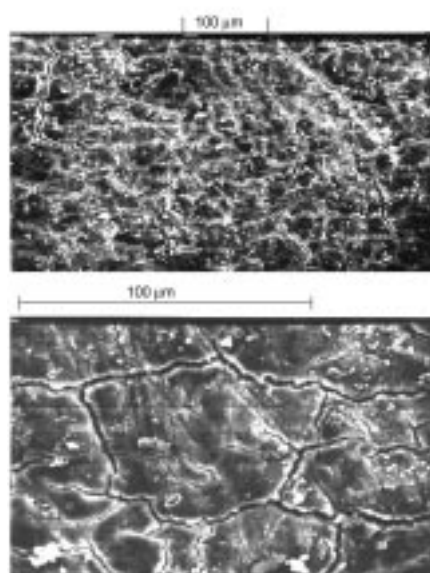
Fig. 9 Photos of dehydrated lithium sulfate surface

ceramics and passing water vapor through anhydrous lithium sulfate. Unfortunately, we cannot state that any clear and unambiguous answer could be obtained from these experiments. On the one hand, the similarity of the curve shapes shown in Figs 7 and 8 is the evidence of qualitative similarity of dehydration, drying and water vapor passing through the layer of anhydrous sulfate. At the same time, it was reported in [9] that the process rate was independent of the thickness of the solid product layer. This was confirmed in our experiments on isothermal kinetics (Fig. 4). Under the conditions of isothermal heating, dehydration rate remains practically constant in spite of the accumulation of reaction product, this layer reaching the thickness of $(8–9) \cdot 10^{-3}$ m that is much more than the values reported in [9] (10^{-3} m). It is evident that in this case the thickness of this layer has no effect on kinetics. An attempt to explain this fact can be based on the presence of the developed net of cracks formed in the product (Fig. 9). It is clear that the net of cracks simplifies the transport of vapor through the product layer, compared to simple diffusion through it. Water vapor pressure in the reaction zone also remains unknown. It is clear that, whatever thorough was pumping out, zero pressure in the sample cannot be achieved. The released water vapor is to pass through the layer of solid product in order to leave the sample. So, water vapor pressure in the reaction zone and in the dehydrated lithium sulfate is not zero. As it was already mentioned in the Experimental section, this should have a strong effect on the process rate. The pressure profile (which is unknown) over the sample length is also of interest. The shape of this profile is very likely to have even a stronger effect on the process than pressure does. Turning back to the question concerning the similarity of kinetic curves for dehydration, drying ceramics and passing water vapor, we can try to explain this phenomenon on the basis of the data presented in [12] where it was shown that drying can be frontal similarly to dehydration. On this basis, the similarity of kinetic curves can be understood but this does not explain why the process rate is constant under isothermal conditions and grows linearly under non-isothermal heating. It seems impossible to outline the role of heat exchange conditions in this system. Since experiments were conducted in vacuum and there was no direct contact between the sample and heater (Fig. 1), heat transfer was carried out practically only due to energy transfer by radiation. It is evident that in this case some lag should be observed since the sample temperature increases lagging behind the heater temperature. The studies into the effect of this factor were hindered also by the fact that heat conductivity of lithium sulfate monohydrate has been unknown till recently [13]. It is also necessary to keep in mind the self-cooling effect (see Experimental section) which should undoubtedly influence the entire dehydration process. Finally, one should not forget physicochemical features of the compound under investigation. At present, our hypothesis assumes the presence of critical conditions under which the formation of the layer of saturated aqueous lithium sulfate solution becomes possible (this is the so-called melting in solution). Assumptions of this type appeared also earlier ([14] and references therein). However, no undeniable confirmations of the existence of this effect had ever been presented. Theoretical possibility of the existence of these conditions could be demonstrated with the help of the *P–T* diagrams for saturated vapor pressure over lithium sulfate monohydrate and over saturated aqueous solution of lithium sulfate but, unfortunately, no data on saturated aqueous solution are available in literature. This situation can be due

to the existence of branched net of cracks in the product (Fig. 9). It was shown in the theory of drying [15] that the conditions may be created when capillary porous matter is dried so that water vapor will evaporate at the bottom of a capillary and condense at the outlet. It is clear that water vapor pressure inside the sample can be much more than the equilibrium value which would help melting of the salt. However, the question concerning the reasonableness of spreading these conclusions to our system remains disputable. From this point of view, the work [16] is very interesting. These authors consider the possibility of the formation of aqueous solution of calcium chloride in microporous silica gel matrix. The authors explain this phenomenon by the interaction of the substance under investigation with the matrix or by dimensional effects in pores which helps to confirm the assumption concerning the effect of cracks in solid product on the creation of critical conditions inside it. On the basis of this hypothesis, it is easy to explain why the process activation energy determined by us ($\sim$50 kJ mol^{-1}) is close to water evaporation heat ($\sim$40 kJ mol^{-1}). To our regret, we do not know the heat of water evaporation from saturated lithium sulfate solution. It may also be close to 50 kJ mol^{-1}. This item requires additional investigations. Anomalously high dehydration rate in isothermal studies is also easily explained. It is evident that the rate of water evaporation, even from saturated solution, is higher than the rate of water removal from lattice. Since the hypothesis allows to explain many experimental facts satisfactorily, at present we are collecting additional information to confirm or reject this hypothesis.

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