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Thermal decomposition of gypsum

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Abstract

The decomposition of $CaSO_4 \cdot 2H_2O$ under the conditions of TA consists of two consecutive reactions, firstly $CaSO_4 \cdot 0.5H_2O$ then $CaSO_4$III being formed. The dehydration is a two-step process even when the TA curves illustrate that it is a one-step reaction. The water loss process takes place with a significant delay owing to protracted nucleus formation on the one hand and to interface processes occurring within the grains and to the reduction in the degree of dispersion caused by the sintering of the grains on the other hand.

INTRODUCTION

We are inclined to regard the mechanism and kinetics of the decomposition of salt hydrates as simple and well interpretable processes although they are in general even more complicated than the dissociation processes of inorganic compounds [1,2]. The decomposition of salt hydrates may generally take place in several different ways (eqns. (1)–(12)). The water loss process of salt hydrates is greatly influenced by the experimental conditions. This influence is sometimes so effective that it may even shift the transformation process from one mechanism to another one [2]. The occurrence of the transformations may also be influenced by nucleus formation and nucleus growth, as well as by topochemical and structural factors. The present authors found a characteristic example of the effect of the last two factors in an examination of the decomposition of $CaSO_4 \cdot 2H_2O$.

In the course of time, owing to the industrial significance of $CaSO_4 \cdot 2H_2O$, the mechanism of its decomposition has been investigated by many researchers, although they have not reached identical conclusions on certain points [3–23].

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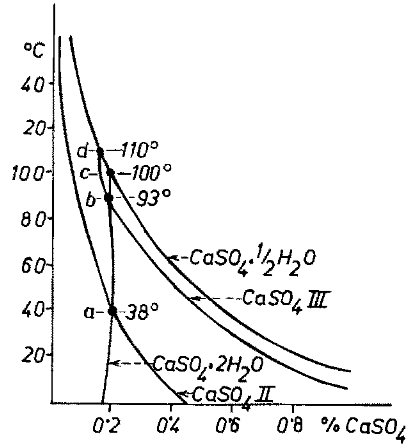

Fig. 1. Phase diagram of the system $CaSO_4$–H_2O. Points a, b, c and d are the incongruent melting points in accordance with eqns. (1), (4), (7) and (8).

On the basis of the phase diagram of the system $CaSO_4(s)$–$H_2O(i)$ (Fig. 1) [3] it may be concluded that if the thermoanalytical examination were carried out in a quasi-closed space, e.g. in a labyrinth or conic crucible [24–26], then the $CaSO_4 \cdot 2H_2O$ would melt incongruently at 38°C (point a) and $CaSO_4II(s)$ and the saturated solution (L(sat)) would be formed and within the crucible would be in equilibrium with water vapour (G):

$$CaSO_4 \cdot H_2O(s) \xrightleftharpoons[\text{incongruent melting}]{38^\circ C} CaSO_4II(s) + L(sat) + G \tag{1}$$

By raising the temperature further the water would escape in gaseous form somewhat over 100°C in the course of isothermal boiling [2,26]:

$$L(sat) \xrightleftharpoons[\text{boiling}]{100^\circ C} CaSO_4II(s) + nH_2O(g) \tag{2}$$

By using an open sample holder the water would evaporate (eqn. (3)) from the saturated solution under 100°C:

$$L(sat) \xrightleftharpoons[\text{evaporation}]{<100^\circ C} CaSO_4II(s) + nH_2O(g) \tag{3}$$

Should the transformation not take place for any reason, then the next possibility (point b) is the incongruent melting of $CaSO_4 \cdot 2H_2O$ at 93°C. In this case $CaSO_4III$ and similarly the saturated solution and vapour phase would be formed [3]:

$$CaSO_4 \cdot 2H_2O(s) \xrightleftharpoons[\text{incongruent melting}]{93^\circ C} CaSO_4III(s) + L(sat) + G \tag{4}$$

$$L(sat) \xrightleftharpoons[\text{isothermal boiling}]{100^\circ C} CaSO_4III(s) + nH_2O(g) \tag{5}$$

$$L(sat) \xrightleftharpoons[\text{evaporation}]{<100^\circ C} CaSO_4III(s) + nH_2O(g) \tag{6}$$

According to point c in Fig. 1 the sample may melt incongruently even at 100°C [3] but in this case the equilibrium in a closed system would set in only at over 100 kPa pressure:

$$CaSO_4 \cdot 2H_2O(s) \underset{\substack{\text{incongruent}\\ \text{melting}}}{\overset{\substack{>100\ \text{kPa}\\ \sim 100°\text{C}}}{\rightleftharpoons}} CaSO_4 \cdot 0.5H_2O(s) + L(sat) + G \tag{7}$$

In an open system, e.g. under the conditions of conventional thermal analysis, this transformation could not take place at all. The same is valid also for the reaction according to eqn. (8), which in principle can take place at 110°C (point d) [3]:

$$CaSO_4 \cdot 0.5H_2O(s) \underset{\substack{\text{incongruent}\\ \text{melting}}}{\overset{\substack{>100\ \text{kPa}\\ 110°\text{C}}}{\rightleftharpoons}} CaSO_4III(s) + L(sat) + G \tag{8}$$

Earlier, by tensiometric measurements it has been shown [3] that in a vapour space of pressure lower than 100 kPa, equilibrium conditions may develop also in the following systems:

$$CaSO_4 \cdot 2H_2O(s) \rightleftharpoons CaSO_4II(s) + 2H_2O(g) \tag{9}$$

$$CaSO_4 \cdot 2H_2O(s) \rightleftharpoons CaSO_4III(s) + 2H_2O(g) \tag{10}$$

$$CaSO_4 \cdot 2H_2O(s) \rightleftharpoons CaSO_4 \cdot 0.5H_2O(s) + 1.5H_2O(g) \tag{11}$$

$$CaSO_4 \cdot 0.5H_2O \rightleftharpoons CaSO_4III(s) + 0.5H_2O(g) \tag{12}$$

These possibilities are therefore remarkable because such experimental conditions exist for thermoanalytical examination in which open sample holders are used.

Curves 1–4 in Fig. 2 show how the decomposition pressure changes for reactions (9)–(12). In the case of reactions (11) and (12) the changes in the decomposition pressure are shown consecutively by curves 5 and 6 where the molar ratio is also taken into account.

EXPERIMENTAL

In order to demonstrate the effect of the experimental conditions exerted upon the course of the decomposition of $CaSO_4 \cdot 2H_2O$ the authors carried out simultaneous TG, DTG and DTA examinations in series.

They changed the conditions in the following way. In the first case shown in Fig. 3 they changed the sample holders (multiplate sample holder, covered and uncovered conventional crucibles, conic and labyrinth crucibles [24–26]) while they left the amount of sample (100 mg) and the rate of heating (1 and 10°C min^{-1}) unchanged. In the second case shown in Fig. 4 they changed the heating rate (0.5, 1, 2.5, 5, 10°C min^{-1}) while the amount of the sample (10 mg and 100 mg respectively) and the sample

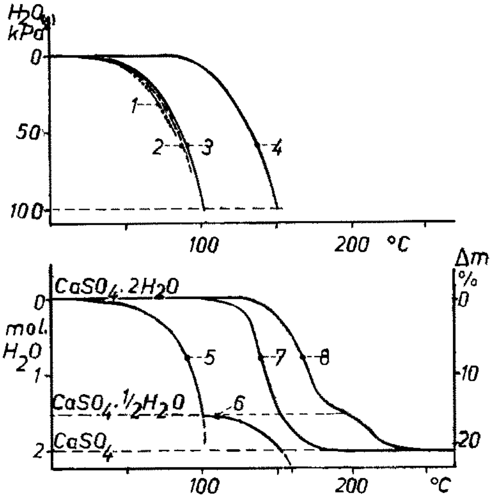

Fig. 2. Theoretical (curves 1–6) and experimental (curves 7 and 8) courses of the decomposition of $CaSO_4 \cdot 2H_2O$, showing the correlation between decomposition pressure and temperature in the case of reactions (9) and (10) (curves 1 and 2) and reactions (11) and (12) (curves 3–6) respectively. The corresponding DTG curves of the TG curves 7 and 8 are illustrated in Fig. 3 (curves 6 and 10).

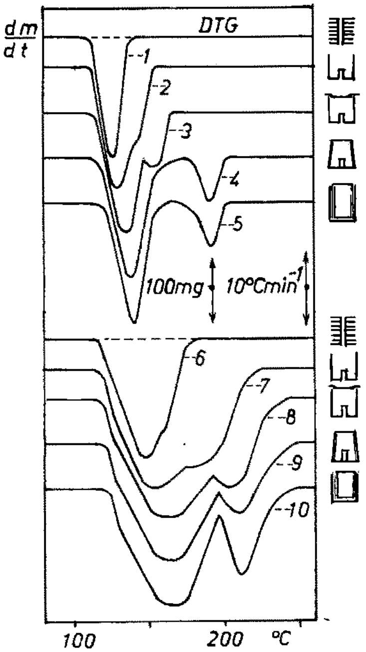

Fig. 3. DTG curves obtained for the decomposition of $CaSO_4 \cdot 2H_2O$ on changing the type of the sample holder used.

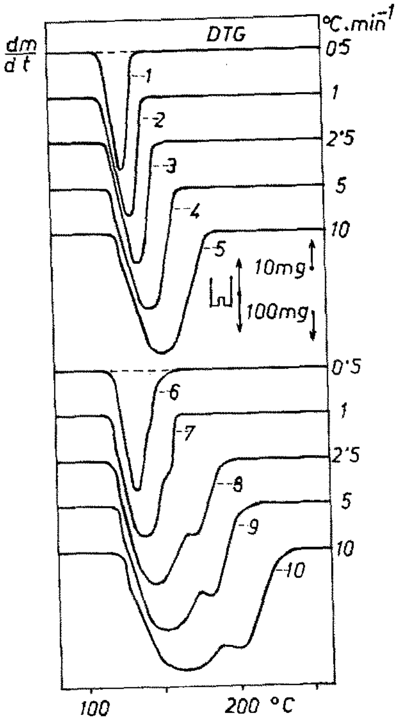

Fig. 4. DTG curves obtained for the decomposition of $CaSO_4 \cdot 2H_2O$ on changing the rate of heating.

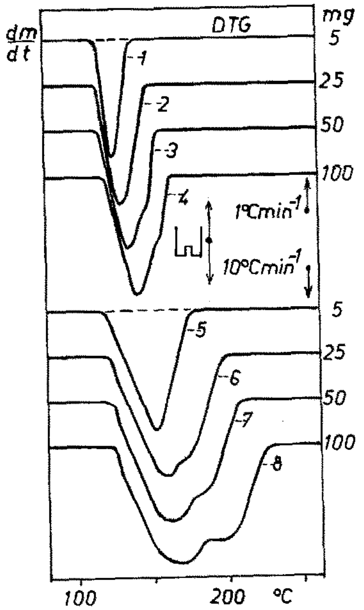

Fig. 5. DTG curves obtained for the decomposition of $CaSO_4 \cdot 2H_2O$ on changing the amount of the sample.

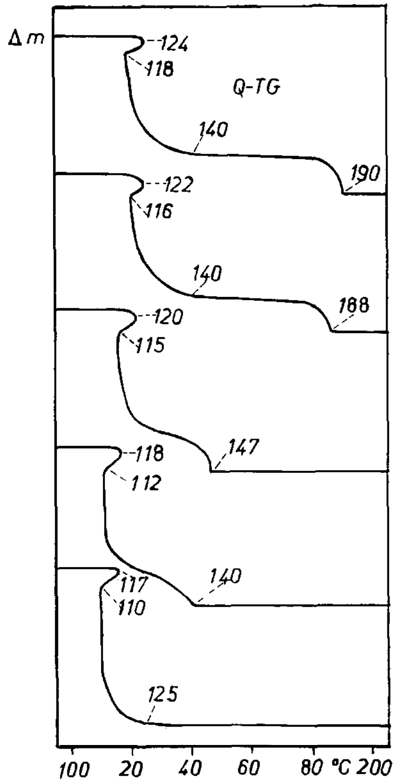

Fig. 6. Q-TG curves obtained for the decomposition of $CaSO_4 \cdot 2H_2O$ on changing the type of the sample holder.

holder used (uncovered crucible) were left unchanged. In the next experiments, illustrated in Fig. 5, the amount of the sample was changed (5, 25, 50, 100 mg) while the heating rate (1 and 10°C min^{-1}) and the shape of the sample holder (open crucible) remained the same. In Figs. 3–5 of the simultaneously recorded TG, DTG and DTA curves, only the DTG curves are depicted since these curves accentuate all the details of the course of the transformations. For the sake of comparison the maximum amplitudes of the DTG curves are drawn on an identical scale. Since the course of the DTA curves was essentially in agreement with that of the DTG curves, the DTA curves are not illustrated.

Figure 6 shows the so-called Q-TG curves obtained by means of the quasi-isothermal–quasi-isobaric measuring technique [24–26]. Here the sample holders were changed while the amount of the sample (200 mg) and the rate of the transformation 0.5 mg min^{-1} ($\Sigma\Delta m = 200$ mg) were left unchanged.

Curve 10 in Fig. 3 is identical with curve 2 in Fig. 7. The latter curve was derived using the Derivatograph C. The result is the so-called DDTG curve (curve 3).

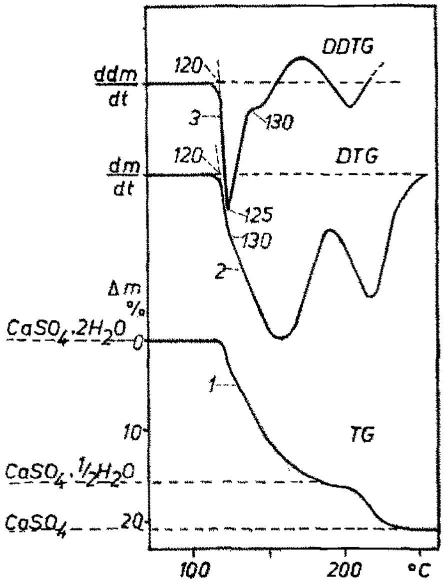

Fig. 7. TG, DTG and DDTG (second derivative) curves obtained for the decomposition of $CaSO_4 \cdot 2H_2O$.

The above experiments were carried out by means of Derivatograph C [27] (produced by the Hungarian Optical Works, MOM, Budapest). The $CaSO_4 \cdot 2H_2O$ sample was of commercial origin and of pro analyse purity.

DISCUSSION

The results of simultaneous TG, DTG, DTA (Figs. 3–5 and 7) and Q-TG investigations under quasi-isothermal quasi-isobaric conditions (Fig. 6) indicate that the dehydration of $CaSO_4 \cdot 2H_2O$ took place not according to eqns. (1)–(10), but to eqns. (11) and (12).

It could be excluded, for example, that the water loss process took place in accordance with eqns. (1)–(8). By applying a quasi-closed sample holder (conic crucible) to ensure a water vapour atmosphere of 100 kPa partial pressure [24,26], no endothermal maxima appeared in the DTA curves in the vicinity of 38, 93, 100 and 110°C respectively. The maxima would have indicated the incongruent melting of $CaSO_4 \cdot 2H_2O$ or the boiling of the saturated solution. Even the literature does not mention such maxima.

It is improbable that this compound decomposes according to eqns. (9)–(10) because in a space containing only a small amount of water vapour a one-step process was always observed. Every curve in Figs. 3–7 uniformly proved that of the two reactions (eqns. (11) and (12)), owing to the effect of the decrease in the partial pressure of water vapour, the latter became much more shifted in the direction of lower temperatures than the former.

Therefore in the presence of a small amount of water vapour, reactions (11) and (12) followed each other very closely and fused to such an extent that the courses of the curves could not be distinguished any more. This supposition was also confirmed by the fact that no borderline existed between the different courses of the single and double peaks; the transition between them was unbroken (Figs. 3–5).

The earlier observation [3] that $CaSO_4III$ and even $CaSO_4 \cdot 0.5H_2O$ are strongly hygroscopic seems also to prove that the dehydration takes place via reactions (11) and (12).

Comparing the correlations of the decomposition pressure and temperature of $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 0.5H_2O$ (curves 3–6 in Fig. 2), and the course of the DTG and TG curve respectively (curves 7 and 8) one can conclude that in every case the whole water loss process was significantly delayed in comparison with the theoretical progress.

In the case of reactions leading to equilibrium the course of TA curves is basically defined by the correlation between decomposition pressure and temperature. Every deviation from the theoretical progress indicates the influence of a foreign effect [24]. Under the theoretical conditions of the two consecutive reactions the first reaction (curves 3 and 5 in Fig. 2) could have begun even at room temperature and could have ended at 103°C. Instead, even by using the multiplate sample holder, water loss began only at about 115°C and the sample lost 1.5 mol of H_2O up to 150°C (curve 7). The delay was even longer when the labyrinth crucible was used (curve 8). This phenomenon was on the one hand due to nucleus formation and on the other to interface processes taking place inside the individual grains [1] and to the decrease in the degree of dispersion caused by the sintering of the grains.

We can conclude indirectly that nucleus formation takes place from the fact that varying the type of the sample holder (Fig. 3), the rate of the heating (Fig. 4), and the amount of the sample (Fig. 5) did not change the decomposition which took place consistently at about 115–125°C while the changes in the partial pressure of water vapour should have manifested themselves at the onset temperature values. It is to be noted that these changes already revealed themselves in the second section of the curves.

It is very difficult to detect the phenomenon of nucleus formation from conventional TA curves, even from DTG curves of high resolution. However, if we derive the high resolution curves by means of computer-controlled TA equipment, e.g. Derivatograph C [27] or Derivatograph PC [28], then on the so-called DDTG curve, this process can be identified. For example, in contrast with the DTG curve, the DDTG curve in Fig. 7 shows unambiguously that the transformation was initiated by a small but unusually quick weight-loss process (peak at 140°C) which at the beginning immediately showed an accelerating tendency, soon followed by a decay, characteristic of nucleus formation.

More convincing are the beaklike peaks appearing simultaneously immediately at the beginning of the weight loss in the Q-TG curves (Fig. 6) indicating overheating of the sample [24–26]. These beaks imply that nucleus formation could begin and proceed at the preselected rate (e.g. 0.5 mg min^{-1}) only at a higher temperature. When a sufficient amount of nuclei was formed the temperature began to drop gradually to the value at which the inhibition ceased and the transformation could take place at an unaltered rate.

The fact that the decomposition of $CaSO_4 \cdot 2H_2O$ is initiated by nucleus formation had already been observed earlier by optical methods [8,16].

On the basis of the anisothermal course of the vertical part of the Q-TG curves (Fig. 6) between 120 and 140°C we may assume the probable formation of a compact new solid phase. It is known [1,24–26] that decomposition reactions leading to equilibrium take place under quasi-isothermal and quasi-isobaric conditions isothermally, provided that the new solid phase formed within the grains becomes porous in structure [1]. Otherwise, if the new phase does not recrystallize, and owing to shrinkage, no pores and channels are formed, its structure remains compact. Therefore the gaseous decomposition products can diffuse through this layer only with difficulty and as a result the decomposition temperature is shifted towards higher temperatures. With increasing thickness of this layer the resistance to gas diffusion continuously increases and the course of the Q-TG curves, similarly to the curves in Fig. 6 becomes anisothermal.

There are many literature reports of results which prove that on heating, the grains of anhydrous $CaSO_4$ become sintered. This process already begins in the last stage of the dehydration (120–200°C). Under a low partial pressure of water vapour, firstly β-$CaSO_4$III with a large inner surface area is formed, later, or directly in the presence of much water vapour, α-$CaSO_4$III with a more compact inner structure is formed. On further raising the temperature (200–400°C) the water-soluble and rehydratable α-$CaSO_4$III transforms into the practically insoluble and not rehydratable $CaSO_4$II. It was also shown by X-ray examination that the crystal structure does not change during these processes. Accordingly it can be assumed that the diffusion of the departing water molecules is also hindered by the sintering of the grains.

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