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DEHYDRATION OF MAGNESIUM SULPHATE HEPTAHYDRATE INVESTIGATED BY QUASI ISOTHERMAL—QUASI ISOBARIC TG *

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ABSTRACT

With the help of the quasi isothermal—quasi isobaric technique, completed with DTA and thermomicroscopic examinations, several new observations have been made regarding the dehydration process of $MgSO_4 \cdot 7\ H_2O$. It was found that under given conditions the material, first at 50°C and then at 95°C, melts in an incongruous way. In the course of the latter transformation, a ternary system consisting of solid $MgSO_4 \cdot 3\ H_2O$, a solution phase saturated with respect to the trihydrate, and a water vapour phase, is formed. The saturated solution reaches its boiling point at 105°C. Without any temperature change, the system loses four moles of water and solid $MgSO_4 \cdot 3\ H_2O$ remains. This decomposes at 115°C and a mixture consisting of $MgSO_4 \cdot H_2O$ and $MgSO_4 \cdot 2\ H_2O$ forms, the proportion of which depends on the experimental conditions. At 150°C, the latter compound loses one mole of water. The $MgSO_4 \cdot H_2O$ maintains constant weight up to 310°C, above which temperature the remaining water of crystallization is removed.

INTRODUCTION

In studies on the course of reactions leading to equilibrium, conventional thermoanalytical examinations often yield a distorted picture which is more characteristic of the experimental conditions than of the transformation itself. The interpretation of the curves becomes even more difficult if the conversion consists of several overlapping partial reactions. A good example of this may be given by the dehydration of magnesium sulphate heptahydrate examined by several authors [1—12] using conventional thermoanalytical methods. The course of this process was found to be different.

The problem is well illustrated in Fig. 1 where the DTA, DTG and TG curves [1—3] are traced by means of the derivatograph. From the course of the curves, one could draw the conclusion that the dehydration is composed of six partial reactions. This conclusion could even be supported by literature data [13], according to which, for example with the help of chemical preparation methods, eight various hydrates of this salt can be obtained.

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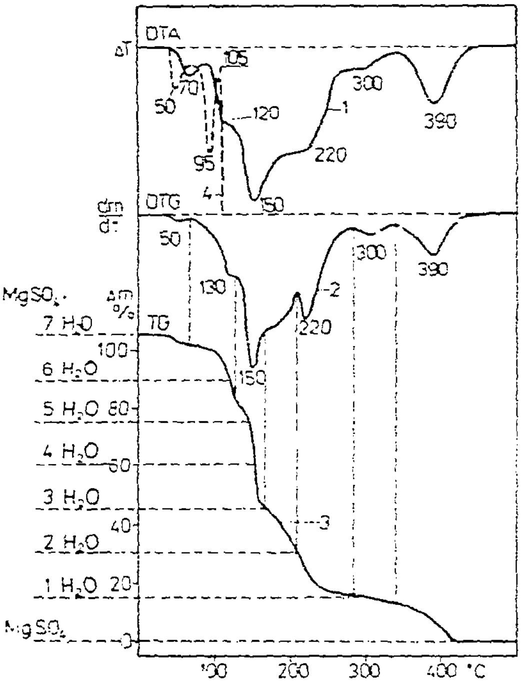

Fig. 1. Dehydration of $MgSO_4 \cdot 7\ H_2O$.

EXPERIMENTAL

Since the above interpretation of the curves seemed to us improbable, we examined this problem with the help of the quasi isothermal—quasi isobaric measuring technique [14—16]. The essence of this technique lies in a special heating controller, which is incorporated in the derivatograph [16]. This technique ensures that the transformations take place at a strictly constant rate which is lower by two orders of magnitude than in the case of conventional heating. The heating program is based on the "feed-back" principle regulated by the transformation itself. In this way, overlap of the transformations can be avoided. But the essence of this technique is the application of a so-called "labyrinth crucible" [14—16], within which, at the very beginning of the reaction, the so-called "self-generated" atmosphere, whose composition remains constant, is being formed. This condition also contributes to the course of the reactions leading to an equilibrium which becomes regular and unambiguous.

With the help of examinations carried out by means of a thermomicroscope and a DTA apparatus, it was found that the heptahydrate incongruously melted, first at 50°C and then at 95°C. It is to be noted that, in the case of both examinations, efforts were made to ensure that, up to the melting point, the sample should not lose much water by dehydration. This involved blocking the free orifice of the sample holder capillary of the Kofler microscope by means of a loose fitting glass rod. For the same purpose, instead of the conventional open crucible (Fig. 1, curve 1) a pair of labyrinth crucibles (Fig. 1, curve 4) was used in the DTA examination.

RESULTS AND DISCUSSION

From the investigation of the dehydration of magnesium sulphate heptahydrate under quasi isothermal—quasi isobaric conditions, curve 1 in Fig. 2 was obtained. For the sake of comparison, the conventional TG curve (Fig. 2, curve 2) is also shown.

According to Fig. 2, curve 1, the material maintained constant weight up to 105°C. The next section of weight stability appeared at the level corresponding to the trihydrate. We therefore supposed that, after the second incongruous melting (95°C), the system consisted of three phases, viz. solid trihydrate, a solution phase saturated with respect to the trihydrate, and a water vapour phase, all in equilibrium with one another. The saturated solution reached its boiling point at 105°C. Thereupon, without change in the temperature, the sample lost four moles of water, while solid trihydrate separated from the solution. The water loss therefore occurred at a constant temperature, because the solution was saturated and its concentration was not changing.

When the last traces of water were lost from the solution phase, the temperature again began to increase, while the weight of the sample remained constant. At 130°C, the trihydrate started to decompose. However, the temperature soon fell again to 110°C where it remained constant until the formation of the next intermediate. Accordingly, under the ideal conditions mentioned above, the decomposition temperature of the trihydrate was 115°C. The initial overheating of the sample to 130°C can probably be explained by the difficulty of nucleus formation [16]. The next intermediate contained 1.67 moles of water. This water content was arrived at by the decomposition of two-thirds of the trihydrate to the dihydrate, while one-third decomposed directly to the monohydrate.

At 150°C, the dihydrate decomposed to the monohydrate, which proved to be very stable and maintained constant weight up to 310°C. The decomposition of the monohydrate was also introduced by delayed nucleus formation, as can be seen from the transitional overheating of the sample (330°C).

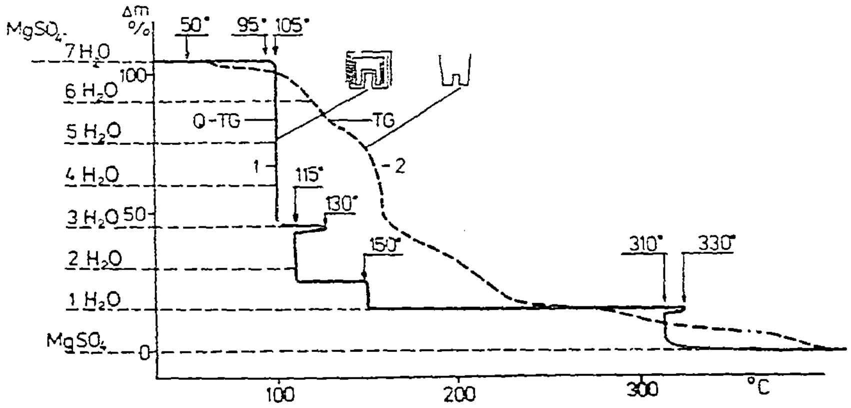

Fig. 2. Dehydration of $MgSO_4 \cdot 7H_2O$. Curve 1, under quasi isothermal—quasi isobaric conditions. Curve 2, conventional TG curve.

But this decomposition process also takes place in an isothermal way.

The question arose as to what would be the situation if the dehydration process was interrupted in its initial period by cooling the sample and subsequently restarting the examination. Would the ternary system of reduced water content become a concentration domain which would be favourable to the formation of another hydrate?

In order to answer this question a new kind of experiment was performed, the result of which is demonstrated in Fig. 3. Curve 1 is already known from Fig. 2. Curve 2 was obtained by interrupting the examination when the water content of the sample decreased to six moles. The section of curve 2 between 105 and 150°C, obtained in the course of the newly started experiment, proves that in this case too, the trihydrate was first formed and that this decomposed similarly to mixtures of di- and monohydrates. However, the proportions of these two hydrates became just the reverse. The mixture consisted of one-third dihydrate and two-thirds monohydrate. By repeating the experiment, the proportion of these components occasionally differed. Consequently, the composition changed from case to case. This proves, in an indirect way, that the intermediate formed was not a defined compound but a mixture of two compounds.

In the frame of the next experiment, we interrupted the examination at a water content of 5.5 moles. According to curve 3 of Fig. 3, under the given conditions, only the monohydrate was formed and no tri- or dihydrates.

We also studied the question of how the thermal decomposition of magnesium sulphate heptahydrate would change if the sample were examined on the large surface of the multiplate sample holder spread in a thin layer. In this way, viz. in the vicinity of the sample, the concentration of water vapour is lower by two orders of magnitude [16]. Curve 2 in Fig. 4 was obtained under these conditions. It is rather difficult to interpret this curve. The question therefore remains unanswered as to whether the inflection seen at the composition $MgSO_4 \cdot 6\,H_2O$ in curve 2 can be explained by the formation of the hexahydrate or the simultaneous formation of two intermediates, similar to the case of the sections between 115 and 150°C of curves 1 and 2 in Fig. 3. We have every reason to suppose that in this case also the

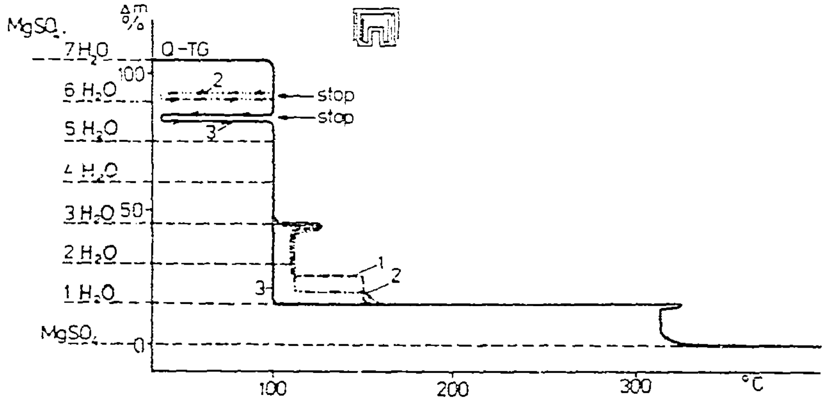

Fig. 3. Examination under quasi isothermal and quasi isobaric conditions in the labyrinth crucible. Curve 1, without interruption; curves 2 and 3, with interruption.

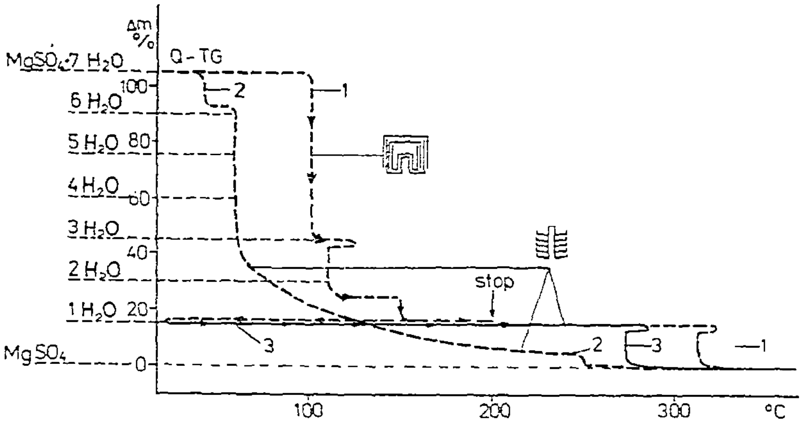

Fig. 4. Examination under quasi isothermal and quasi isobaric conditions. Curve 1, labyrinth crucible; curve 2, multiplate sample holder; curve 3, examination begun in the labyrinth crucible, stopped at 200°C and restarted on the multiplate sample holder.

dehydration was composed of several partial reactions which completely overlapped.

In a further experiment the monohydrate was prepared. The heptahydrate was heated in the labyrinth crucible up to 200°C and then rapidly cooled. Consequently, up to 200°C the water content of the sample changed according to curve 1. Thereafter, spreading the monohydrate in a thin layer on the multiplate sample holder, the experiment was restarted. As curve 3 shows, this time a special memory effect was observed. Despite the condition that with the application of another type of sample holder the partial pressure of the water vapour in the vicinity of the sample decreased by about two orders of magnitude, the weight of the sample remained constant up to 270°C, i.e. the material decomposed as if it had been examined in the labyrinth crucible, as if it had remembered the conditions of its preparation. But it is also remarkable that the decomposition of the monohydrate took place in the labyrinth crucible (curve 1) at a temperature higher than 40°C than on the multiplate sample holder (curve 3). This means that the solid phase in contact with the higher partial water vapour pressure shifted the decomposition in the direction of higher temperatures. From this, it follows that the decomposition of the monohydrate can be regarded as a process which leads to equilibrium.

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