THERMOGRAVIMETRIC EXAMINATION OF THE DEHYDRATION PROCESS OF CALCIUM BROMIDE HYDRATE UNDER QUASI ISOTHERMAL AND QUASI ISOBARIC CONDITIONS

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ABSTRACT

The dehydration process of calcium bromide hexahydrate has been investigated using the quasi isothermal–quasi isobaric thermogravimetry method. It was found that in a self-generated atmosphere (labyrinth crucible), the path of the process is indicated by the intermediate formation of tetra-, di- and monohydrates. In the course of the reaction, crystalline, saturated solution and water vapour phases form a state of quasi equilibrium. If the sample contacts a water vapour atmosphere lower than 1 atm pressure (open crucible), it loses first 3, then 2 and finally 1 moles of water. The actual existence of the detected $CaBr_2 \cdot 3H_2O$ intermediate is questionable.

INTRODUCTION

Thermal transformations are usually composed of overlapping partial processes. Interpretation of such processes on the basis of conventional thermoanalytical curves is often difficult. A characteristic example of this can be seen in Fig. 1 which illustrates the simultaneously recorded TG, DTG and DTA curves of $CaBr_2 \cdot 4.5H_2O$. These curves were obtained by using a heating rate of 10°C min^{-1} and a covered crucible. With this experiment, we wished to find out of what single partial processes the dehydration is composed and what intermediate products are being formed in the course of transformation. However, on the basis of these curves, the single partial processes could not be identified unambiguously and with certainty. On the basis of the TG curve, only the intermediate formation of $CaBr_2 \cdot H_2O$ could be regarded as probable.

In the inorganic chemistry literature[1], seven hydrates of calcium bromide are mentioned with 6, 4, 3, 2, 1.5, 1 and 0.5 moles of H_2O, respectively. The phase equilibrium examination of the water–salt system, however, only proved the existence of hexa-, tetra- and dihydrates[2]. The phase transition of hexa- and tetrahydrates was found to be at 34°C, while that of tetra- and dihydrates at 55°C.

Amirova et al.[3] found in their thermogravimetric examinations that five water molecules of the hexahydrate were lost in a single step while the loss of the last

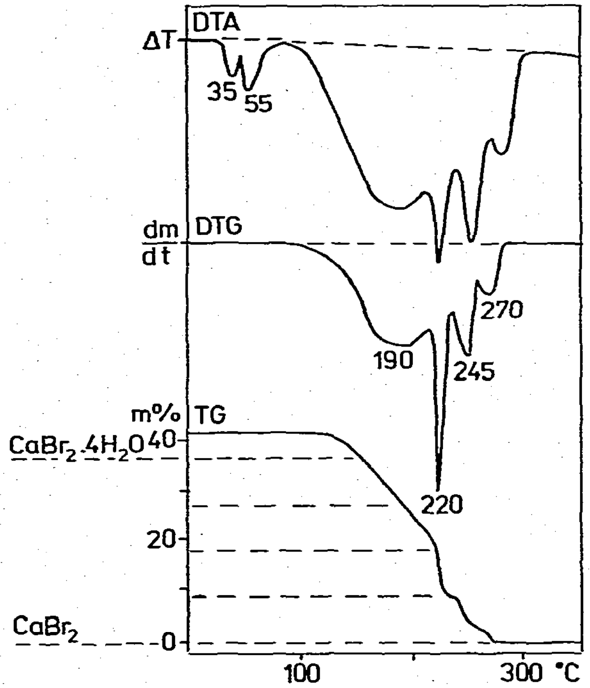

Fig. 1. Dehydration of $CaBr_2 \cdot 4.5H_2O$. Simultaneous TG, DTG and DTA measurements under dynamic heating conditions.

water molecule occurred in two stages, in the course of which 0.5 moles of water escaped each time. Buzágh-Gere et al.[4] who investigated calcium bromide of various water contents by TG measurements under different experimental conditions, found that the monohydrate could always be detected as the final intermediate. Depending on the water content, the endothermic peak corresponding to the melting of the hexahydrate and the transformation of the tetrahydrate appeared in the DTA curve. These last two processes were identified in a quantitative DTA apparatus in a closed sample holder at 32.5 °C and 51 °C, respectively.

This problem had already been examined earlier[5] with the help of quasi isothermal–quasi isobaric thermogravimetry[6, 7]. Our recent investigations resulted in further information regarding this question which is reported in the present work.

EXPERIMENTAL

We performed our examination by means of a Q-Derivatograph (Hungarian Optical Works, Budapest) which is equally suitable for the performance of simultaneous TG, DTG and DTA examinations under dynamic heating conditions and of quasi isothermal–quasi isobaric TG measurements[6, 7]. Characteristic of the latter measuring technique is that transformations connected with weight change take place at a strictly constant rate and are slower by one or two orders of magnitude compared with transformations occurring under conventional conditions. According to experience, the partial pressure of the sample contacting gaseous decomposition products stays constant (quasi isobaric) during the whole transformation process. This latter condition is especially valid for the so-called labyrinth crucible in which the gaseous products establish the so-called self-generated atmosphere of 1 atm pressure. The temperature of the sample, according to these special experimental conditions, also changes in a quite different way and yields further information.

The rate of transformation was selected to be 0.5 mg min^{-1}. The weight of the sample varied around 300 mg. Sample holders of four different types were used. The applied atmosphere was air.

The measurements were carried out with analytically pure $CaBr_2 \cdot 6H_2O$ prepared by Merck. The water content of the preparate was actually less than theoretical at about 4.5 moles of H_2O. Despite this, on heating, the material behaved in the same way as $CaBr_2 \cdot 6H_2O$ except for the amount of the weight loss.

DISCUSSION

The TG curves of Fig. 2 demonstrate the dehydration process of a calcium bromide sample containing about 4.5 moles of water of crystallisation examined under quasi isothermal heating conditions in a labyrinth crucible (curve 1), in a covered (curve 2) and uncovered crucible (curve 3) as well as on the multiplate sample holder (curve 4). In the four different types of sample holder, the conditions for the removal of the liberated water significantly differed from one another; thus it is self-evident that the four curves became shifted in phase in comparison with one another.

It seems that the various experimental conditions caused not only changes in the kinetics of the transformation but also in its mechanism. The inflexion points in curve 1 correspond to the compositions of $CaBr_2 \cdot 2H_2O$ and $CaBr_2 \cdot H_2O$, while in curves 2–4, they correspond to $CaBr_2 \cdot 3H_2O$ and $CaBr_2 \cdot H_2O$.

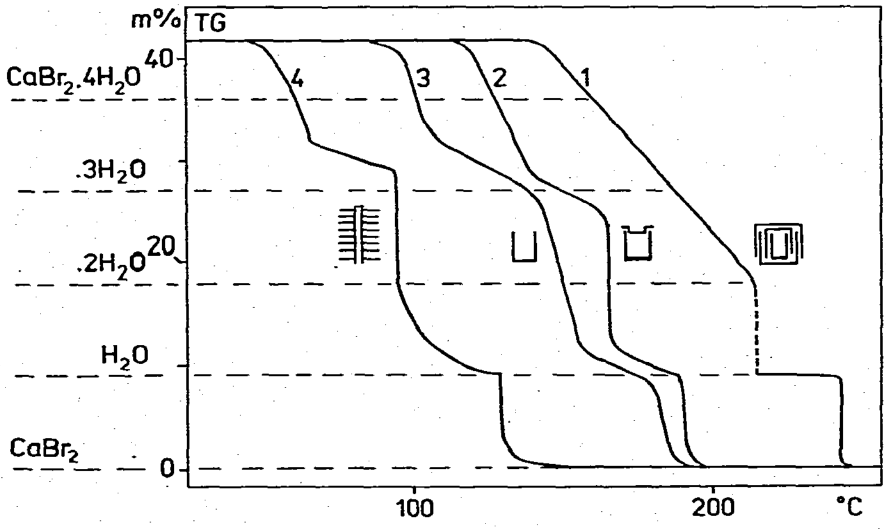

Fig. 2. Dehydration of $CaBr_2 \cdot 4.5\ H_2O$. Quasi isothermal–quasi isobaric measurements carried out with different types of sample holder.

However, the course of curves 2–4 is not quite unambiguous. The vertical sections of the curves, in contrast to expectations, do not show the partial reactions as strictly isothermal processes, while the inflexion points indicating the formation of $CaBr_2 \cdot 3H_2O$ as intermediate, show differences from the theoretical water content. This phenomenon can probably be explained in the following way. It is known that $CaBr_2 \cdot 6H_2O$ melts in its own water of crystallisation at 35 °C. In such cases, due to the loss of water on the surface of the sample, a compact crust is immediately formed which from time to time is ruptured by the pressure of water vapour. We also observed this crust formation in the present investigation. However, this process may distort the whole course of the transformation, as we earlier observed[8] in the case of $CoCl_2 \cdot 6H_2O$. Accordingly, it is hard to decide with certainty, whether $CaBr_2 \cdot 3H_2O$ was actually being formed as an intermediate product, or whether, in the course of the drying of the solution phase, a change occurred which caused the inflexion point in question in the TG curve.

In the labyrinth crucible (curve 1), i.e. in a self-generated atmosphere, the dehydration took place in a different way. After the sample melted in its own water of crystallisation, a saturated solution and a solid phase of composition $CaBr_2 \cdot 4H_2O$ were being formed. At 55 °C, this phase-equilibrium ended and $CaBr_2 \cdot 2H_2O$ came into existence. In Fig. 1, the endothermic maxima at 35 and 55 °C of the DTA curve indicate these processes.

Accordingly, in the labyrinth crucible (Fig. 2, curve 1) above 55 °C, solid $CaBr_2 \cdot 2H_2O$, a saturated solution and a water vapour phase were in a state of equilibrium.

At 140 °C, the saturated solution reached its boiling point and the pressure of the water vapour its 1 atm pressure within the crucible. Between 140 and 215 °C, the system gradually lost 3 moles of H_2O while the solution gradually dried up. However, the composition of the solid phase did not change and $CaBr_2 \cdot 2H_2O$ remained. When the solution phase disappeared, a strange phenomenon occurred. The weight of the sample changed with extreme rapidity (dotted portion of curve 1) to correspond to the composition of $CaBr_2 \cdot H_2O$.

The probable explanation of this phenomenon is as follows. $CaBr_2 \cdot 2H_2O$ is stable up to 215 °C only in a ternary system. In a binary system, i.e. in the absence of the solution phase, when the solid sample contacts only the water vapour of 1 atm pressure, the decomposition temperature is actually 205 °C as was shown by the results of our further investigations (see Figs. 3–6). Accordingly, when at 215 °C with the drying up of the solution phase the ternary system changed into a binary one, the equilibrium of the system became suddenly overbalanced and $CaBr_2 \cdot 2H_2O$, being in an overheated state, suddenly decomposed.

We proved the correctness of this explanation in an indirect way with several experiments. We started from the idea that, if we can remove the last traces of the solution phase, which stabilizes $CaBr_2 \cdot 2H_2O$, before the overheating of the system and ensure thereafter sufficient time for the formation of nuclei of the new solid

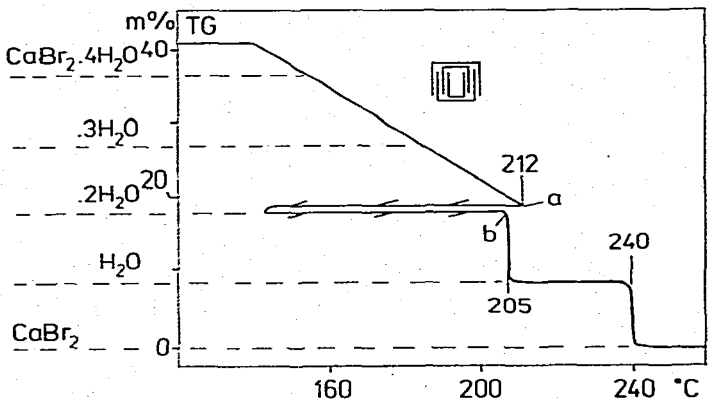

Fig. 3. TG curve analogous to curve 1 in Fig. 2 with the difference that the examination was interrupted at point a and continued at point b.

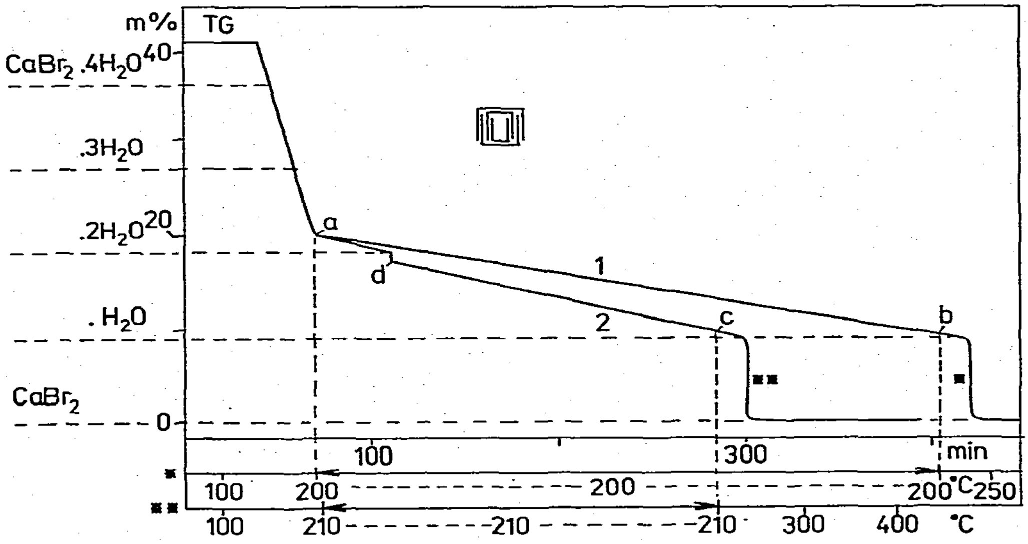

Fig. 4. TG curves analogous to curve 1 in Fig. 2 obtained with the difference that, in the case of curve 1, the temperature between points a and b was maintained at 200°C while, in the case of curve 2, the temperature was maintained at 210°C between points a and c.

phase, then the decomposition of $CaBr_2 \cdot 2H_2O$ would take place in a quasi isothermal way and under conditions of quasi equilibrium.

Therefore, we repeated our earlier experiment (Fig. 2, curve 1) with the difference (Fig. 3) that we suddenly stopped the heating at 212°C (point a) before the start of the rapid decomposition due at 215°C and allowed the temperature of the sample to fall by about 60°C whereupon we continued the experiment. During this process, which lasted about half an hour, according to the curve the solution phase disappeared completely, whereupon the $CaBr_2 \cdot 2H_2O$ (without overheating) really decomposed at 205°C (point b). Furthermore, this decomposition did not take place with the extreme rapidity it did earlier, but at a very low and constant rate (0.5 mg min^{-1}) characteristic of quasi isothermal processes.

In our opinion, the results of two further experiments, illustrated in Fig. 4, also supported the correctness of the above suggestion. Both experiments were performed in the way already known until the composition of about $CaBr_2 \cdot 2.2H_2O$ was attained. From this time on (point a), the temperature of the sample was maintained strictly at 200°C (curve 1) and 210°C (curve 2) for 4–6 h until the sample arrived at a composition of about $CaBr_2 \cdot H_2O$ (points b and c). After this, the quasi isothermal heating control was applied again. According to the curves, the phase transition from a ternary to a binary system caused an inflexion point (point d) in the curve (curve 2) and a sudden change in the system if the temperature of the sample was kept at 210°C, i.e. at a higher temperature than that of the decomposition (205°C) while if the temperature of the sampl[illegible]t at 200°C during the dehydration process, the decomposition too[illegible] stant rate (curve 1).

The way in which the phase equilibrium conditions changed between 140 and 205°C cannot be stated, of course, on the basis of the TG curve. However, the results of our experiment, illustrated in Fig. 5, may serve with certain explanatory data. Among other things, we can say that the gradual disappearance of the solution phase

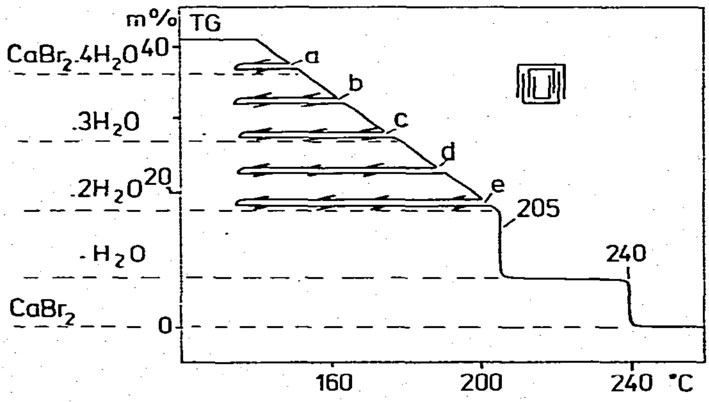

Fig. 5. TG curve analogous to curve 1 in Fig. 2 with the difference that the experiment was interrupted at points a, b, c, d and e.

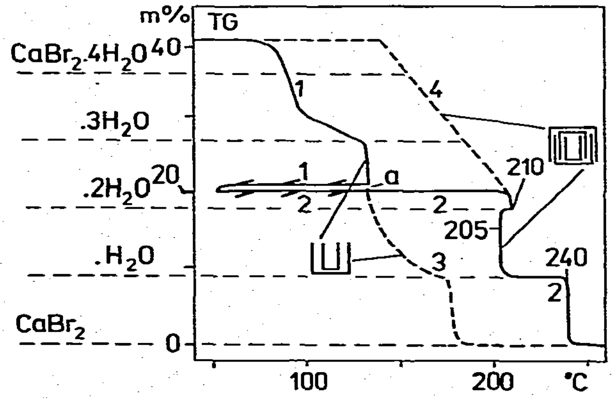

Fig. 6. TG curves. The experiment started in open crucible (curve 1), was interrupted at point a and was continued in a labyrinth crucible (curve 2). Complementary curves 3 and 4 are analogous to curves 1 and 3 in Fig. 2.

between 140 and 205 °C had not been a simple evaporation process. In this latter case, the process must have taken place at a constant temperature while from the saturated solution, solid $CaBr_2 \cdot 2H_2O$ would have been gradually formed in an amount proportional to the water lost. In contrast to this, the temperature increased linearly proportionally with the reduction of the water content. This unknown process differed from the former one essentially. In order to prove that this unknown process took place under quasi equilibrium conditions, we recorded the curve shown in Fig. 5. The experiment was carried out by using the labyrinth crucible and the quasi isothermal heating technique in the known way with the difference that the heating was stopped at points a, b, c, d and e, respectively, and every time the temperature of the sample dropped below 100 °C the heating was started again. As Fig. 5 shows, the weight loss process always continued at the same temperature at which it had previously been stopped. This proves that the corresponding temperature and composition values illustrated by the TG curve between 140 and 205 °C also describe a sequence of quasi equilibrium states.

The experimental results shown in Fig. 6 illustrate another noteworthy phenomenon. In this case, the sample was placed into the lower parts of the labyrinth crucible which was left uncovered this time. Accordingly, curve 1 was obtained by using an open crucible and the quasi isothermal heating technique. As soon as the composition of the sample became $CaBr_2 \cdot 2.2H_2O$, the heating was interrupted (point a) and the reaction was quenched by the sudden cooling down of the sample. After the sample was cooled down, the upper covering parts of the crucible were put in place and a new examination was started, now with the application of the complete labyrinth crucible. As curve 2 shows, the decomposition took place according to the changed experimental conditions ($p_{H_2O} = 1$ atm), i.e. as if the experiment had originally been begun by using the labyrinth crucible. Curves 3 and 4, drawn with dotted lines, demonstrate the course of the TG curve as if the whole experiment had been carried out with the open and the labyrinth crucible, respectively, as in the examinations illustrated earlier in Fig. 2.

Summing up, it can be stated that by applying the quasi isothermal–quasi isobaric measuring technique, i.e. under quasi equilibrium conditions the dehydration of $CaBr_2 \cdot 6H_2O$ is characterized by the subsequent formation of tetra-, di- and monohydrate intermediates.

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