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THERMOGRAVIMETRIC EXAMINATION OF THE DEHYDRATION OF CALCIUM NITRATE TETRAHYDRATE UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS

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The progressive nature of the process of dehydration of $Ca(NO_3)_2 \cdot 4\,H_2O$ has been shown not to be due to consecutive decomposition reactions, as believed so far, but is the result of various physical processes, such as the incongruent melting of the material, the boiling and evaporation of the unsaturated or saturated solution formed, as well as the crust formation and drying of the surface of the solidifying residue. The quasi-isothermal—quasi-isobaric thermogravimetric technique and the phase diagram of the $Ca(NO_3)_2$—H_2O system were used to evaluate the results.

There are many contradictory data in the literature regarding the process of dehydration of calcium nitrate tetrahydrate [1–9]. The cause of this is that it is rather difficult to interpret the conventional thermoanalytical curves.

The simultaneous TG, DTG and DTA curves in Fig. 1 indicate that the thermal decomposition of the hydrated salt under the given conditions takes place in four steps. Although the existence of $Ca(NO_3)_2 \cdot 3\,H_2O$ and $Ca(NO_3)_2 \cdot 2\,H_2O$ is known, it is impossible that in the present case the formation of these intermediates causes the stepwise transformation. These intermediates decompose even above 52° (Fig. 7), while the TG and DTG curves reveal that the four subsequent processes in question took place with maximum rate at 120°, 155°, 160° and 210°, respectively. What then was the cause of the gradual water loss?

We also observed that, even under identical experimental conditions, the courses of the curves could not be reproduced. Further, when the experimental conditions were varied in a set manner, the courses of the curves changed not in the expected way but irregularly and apparently randomly. Curves 2 and 3 in Fig. 2 show examples of this. These curves were obtained in covered and uncovered crucibles, respectively, but under otherwise identical conditions. The courses of these curves relative to each other are not regular. Despite the fact that the liberated water vapour can depart more easily from the uncovered crucible than from the covered one [10], the water loss ended at a higher temperature in the former crucible than in the latter one. How can this contradiction be explained?

Only the results of our experiments carried out by using the quasi-isothermal—quasi-isobaric technique could give answers to these questions.

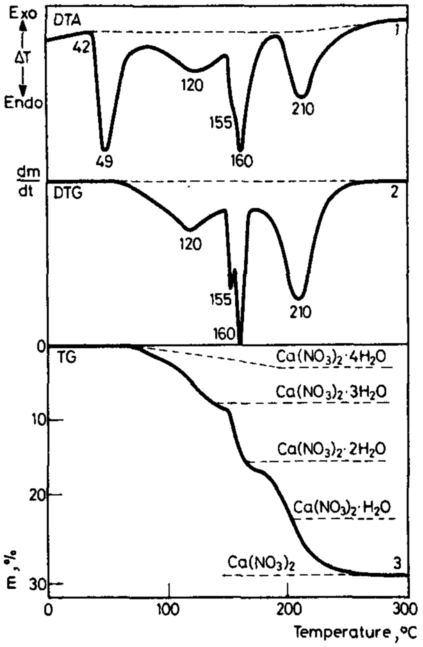

Fig. 1 Simultaneous TG, DTG and DTA curves of $Ca(NO_3)_2 \cdot 4\,H_2O$

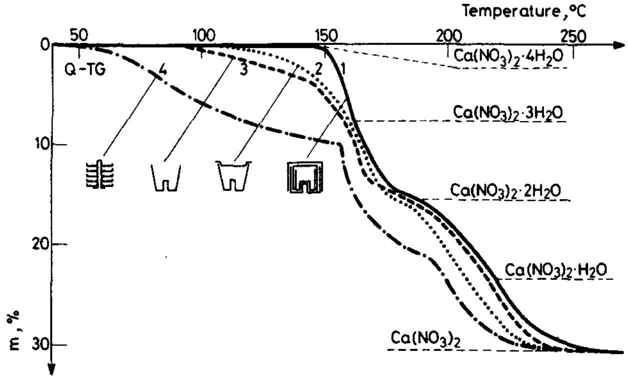

Fig. 2 TG curves of $Ca(NO_3)_2 \cdot 4\,H_2O$ traced using labyrinth (curve 1), covered (curve 2), uncovered (curve 3), crucibles and multiplate sample holder (curve 4)

Experimental

We performed our experiments with a Q-derivatograph (Hungarian Optical Works, Budapest) using either a dynamic heating programme [10] (5 deg min^{-1} heating rate) or the quasi-isothermal–quasi isobaric technique [10–12] (0.6 mg min^{-1} rate of weight change). The measurements were made with different types of sample holders, in the presence of air, using about 600 mg of sample. The total weight loss was about 200 mg, the dehydration requiring around 5 hours.

Figure 1 shows the simultaneous TG, DTG and DTA curves produced when material situated in an open crucible was subjected to the dynamic heating programme.

The TG curves in Fig. 2 were also obtained by using the dynamic heating programme and under identical experimental conditions, with the exception that different kinds of sample holders were applied: labyrinth (curve 1), covered crucible (curve 2), open crucible (curve 3) and multiplate sample holder (curve 4).

Figure 3 shows the thermogravimetric curves for pure water using the quasi-isothermal– quasi-isobaric measuring technique (Q-TG curves) and the four different kinds of sample holders. In order to render the boiling and evaporation steady, about 200 mg of the water examined was soaked up by 600 mg of silica glass powder.

Figure 4 illustrates the Q-TG curves of $Ca(NO_3)_2 \cdot 4\,H_2O$. The four kinds of curves were traced using the four different types of sample holders.

Curve 2 in Fig. 5 demonstrates the equilibrium conditions of the $Ca(NO_3)_2$–H_2O system. The phase diagram was constructed by Ewig, Krey, Law and Lang [16] on the basis of solubility examinations. Sections A–C, C–D, D–E and E–F illustrate the saturation curves of $Ca(NO_3)_2 \cdot 4\,H_2O$, $Ca(NO_3)_2 \cdot 3\,H_2O$, $Ca(NO_3)_2 \cdot 2\,H_2O$ and $Ca(NO_3)_2$, respectively, while sections C–G, H–D, D–I and E–G border the metastable domains of the same salts. Sections A–C–D–E–F in curve 2 distinguish the solid (S) and liquid (L) domains.

Curve 1 in Fig. 5 was constructed by us in the knowledge of the related temperature *vs.* composition pairs which could be read from curve 1 in Fig. 4. With this, we

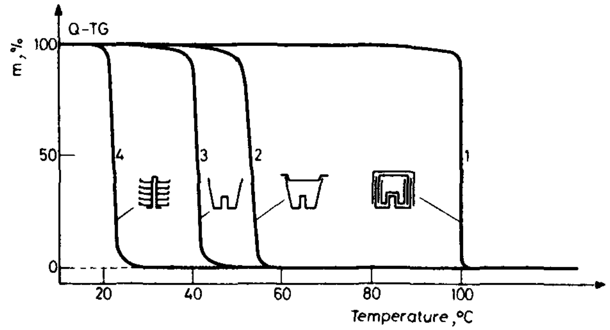

Fig. 3 Q-TG curves recorded of water using labyrinth (curve 1), covered (curve 2), uncovered (curve 3), crucibles and multiplate sample holder (curve 4)

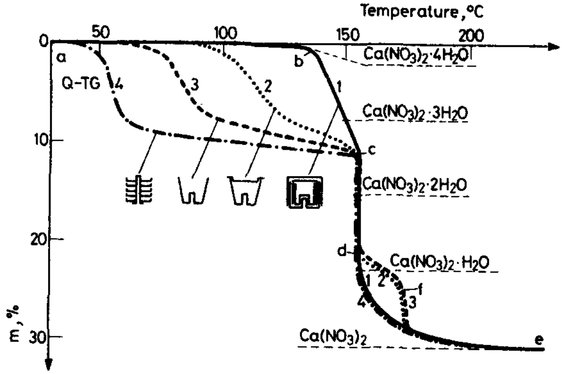

Fig. 4 Q-TG curves of $Ca(NO_3)_2 \cdot 4H_2O$ traced using labyrinth (curve 1), covered (curve 2), uncovered (curve 3), crucibles and multiplate sample holder (curve 4)

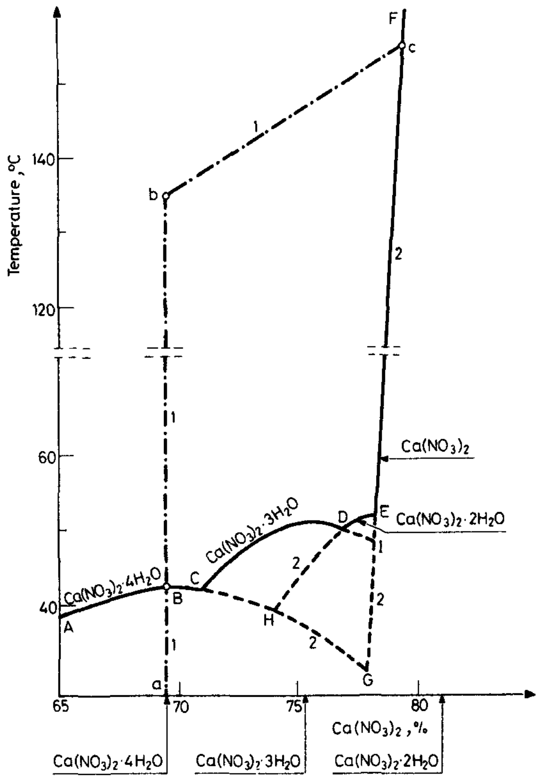

Fig. 5 Phase diagram of $Ca(NO_3)_2$—H_2O system according to Ewig et al. (curve 2); curve 1 constructed on the basis of curve 1 in Fig. 4

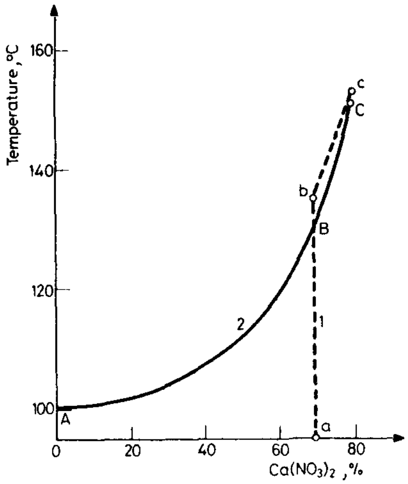

Fig. 6 Changes in the boiling point of the system $Ca(NO_3)_2$—H_2O in function of composition according to Ewig (curve 2); curve 1 constructed on the basis of curve 1 in Fig. 4

wished to demonstrate the way in which the composition of the solution formed by melting of $Ca(NO_3)_2 \cdot 4\ H_2O$ changed as a function of temperature if the transformation was examined in a labyrinth crucible with the quasi-isothermal—quasi-isobaric technique.

In Fig. 6 curve 2 illustrates the way in which, according to Ewig [17], the boiling point of the $Ca(NO_3)_2$—H_2O system changes as a function of the composition. In the knowledge of curve 1 in Fig. 4, we constructed curve 1 in Fig. 6. This latter curve demonstrates the changes in the boiling point of the unsaturated solution in the course of the Q-TG examination.

In the case of curves 2 and 3 in Fig. 4, between points *d* and *f* a crust was being formed on the surface of the sample. We performed a special experiment, the result of which is demonstrated in Fig. 7. We repeated the recording of curve 3 of Fig. 4 with the difference that at the moment corresponding to point *f* in Fig. 4 we interrupted the examination (point *f* in Fig. 7), cooled the sample down, thoroughly mixed it by means of a needle and restarted the Q-TG examination (point *g*). Curve 2 indicated that the departure of water continued not at the temperature (175°) at which the heating was interrupted, but at that (155°) (point *h*) at which the crust formation began (point *d*).

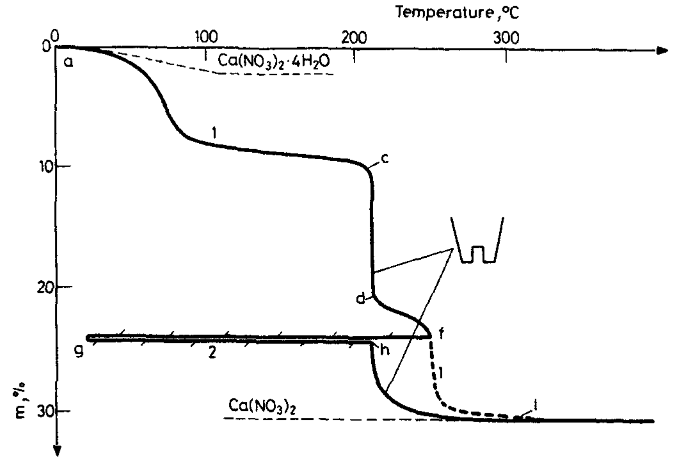

Fig. 7 Q-TG curves of $Ca(NO_3)_2 \cdot 4\,H_2O$ traced in interrupted experiments

Theoretical basis of interpretation of Q-TG curves

The essence of the quasi-isothermal–quasi-isobaric measuring technique [10–12] lies in a special heating controller, incorporated in the derivatograph, which controls the course of the transformations so that these take place at a strictly constant rate (0.2–1.0 mg min^{-1} weight change) several orders of magnitude lower than in the case of the conventional dynamic heating technique. If no transformation occurs, the temperature increases rapidly (about 2–5 deg min^{-1}), while during transformations it does not increase at all or only exceedingly slowly (quasi-isothermal).

The application of a "labyrinth crucible" also belongs to the essence of the method. In this sample holder the $AB_{(s)} \rightleftharpoons A_{(s)} + B_{(g)}$ type reactions leading to equilibrium take place in a "self-generated" atmosphere, i.e. isothermally and at the temperature where the decomposition pressure of the compound reaches atmospheric pressure.

Experience shows [13–15] that similar processes take place in solutions formed in the course of the melting of salt hydrates. In such cases the interpretation of the Q-TG curves involves the following train of thought, applied in the instance of $Ca(NO_3)_2 \cdot 4\,H_2O$ too (Fig 4). The results of experiments carried out with pure water (Fig. 3) also justified this kind of interpretation.

After the melting of the salt hydrates the solution begins to evaporate. The water vapour gradually drives out the air from the crucible. The mixture of air and water vapour streaming outwards from the crucible through the tight channel system formed by the walls of the crucibles impedes air from streaming back into the crucible. The partial pressure of the water vapour within the crucible gradually increases as the temperature rises, so as constantly to maintain equilibrium with the increasing tension of the solution. At the boiling point of the liquid, both the partial pressure of the vapour and the tension of the solution reach atmospheric pressure.

Small amounts of water vapour can expel the air from the crucible and therefore it is found that, up to the boiling point, the weight of the liquid decreases to only a negligible extent (Fig. 4). For instance, when 200 mg of water was examined (curve 1 in Fig. 3), up to 100° a weight loss of only 3 mg was observed.

In the case of pure water the whole amount departs at 100° (curve 1 in Fig. 3). Unsaturated solutions gradually lose water after reaching the boiling point, whereupon both their concentration and the boiling point corresponding to the concentration increase (section *b—c* of curves 1 in Figs 4, 5 and 6). Meanwhile, by means of the heating controller the rate of vapour departure is kept constant at a value selected in advance, creating an appropriate difference between the temperatures of the solution and its vicinity.

However, the boiling point increases only up to the point where the solution becomes saturated (points *c* of curves in Figs 4, 5 and 6). Since the composition of the solution can no longer change thereafter, its temperature cannot change either (section *c—d* of curve 1 in Fig. 4, points *c* of curves 1 in Figs 5 and 6). The heat taken up by the system subsequently is consumed only for the removal of water at constant temperature while an equivalent amount of solid salt separates from the solution.

We have observed [10] that if we exchanged the labyrinth crucible for a covered crucible, an uncovered one or a multiplate sample holder, then in the case of $AB_{(s)} \rightleftharpoons A_{(s)} + B_{(g)}$ type reactions the partial pressure of the gaseous decomposition products in the direct vicinity of the solid product decreased from 100 to 20, 5 and 1 kPa, respectively. Due to this, the transformation temperatures decreased depending on the applied sample holder, while both the partial pressure and the transformation temperature remained constant in each of the transformation processes.

In contrast, the change of the sample holders did not influence the course of reactions not leading to equilibrium. Consequently, the two reaction types can clearly be distinguished. With the change of the sample holder the process of evaporation of liquids also changes, in such a characteristic way that one can differentiate between water, unsaturated and saturated solutions.

Water evaporates far below the boiling point. The rate of evaporation depends primarily on the shape of the sample holder, because this defines the magnitude of two basic factors: the heat absorbance surface and the free surface layer of the water. Accordingly, the evaporation occurs at the temperature at which the sample holder allows the weight of the sample to decrease at the preselected rate (curves 2, 3 and 4 in Fig. 3).

Unsaturated solution situated in an open sample holder likewise evaporates at a rate depending on the shape of the sample holder. However, the shape of the Q-TG curve is also influenced by the circumstance that the tension of the solution decreases with the progress of the evaporation process, due to the increasing concentration. Accordingly, in order to ensure that the rate of the weight change remains constant it is necessary for the temperature to increase gradually.

The tension of the saturated solution generally decreases to such an extent that, independently of the shape of the sample holder, the water vapour can escape at the preselected rate only at the boiling point of the solution. This is why, when sample holders of various shapes are applied, the Q-TG curves separate from one another when unsaturated solution is evaporating, and why they are congruent in the case of saturated solutions (Fig. 4, curves 2, 3 and 4).

Discussion

One of the advantages of the quasi-isothermal–quasi-isobaric thermogravimetric (Q-TG) technique is that ideal experimental conditions can be achieved whereby, in contrast with the conventional measuring technique, the data obtained can be compared with the results of other phase-equilibrium examinations, which facilitates the interpretation of the Q-TG curves.

In the interpretation of the present curves (Fig. 4) we made use of the phase diagram of the $Ca(NO_3)_2$–H_2O system (Fig. 5) and the boiling point curve of the $Ca(NO_3)_2$-containing unsaturated solution (Fig. 6).

In this way we found that at the very beginning of the examination $Ca(NO_3)_2 \cdot 4 H_2O$ melted at 42.7° while a saturated homogeneous solution was formed (intersection point B of curves 1 and 2 in Fig. 5) which with increase of temperature got unsaturated. Up to the boiling point the extent of unsaturation hardly changed with the rising temperature (slope of section E–F of curve 2 in Fig. 5).

In the course of our Q-TG examinations ideal equilibrium conditions were best approached when the labyrinth sample holder was used. Curve 1 in Fig. 4 was traced in this way. It can be seen that the sample did not lose water until the solution reached the boiling point corresponding to the composition of the solution (section *a–b* of curves 1 in Figs 4, 5 and 6). According to the literature [17] this boiling point is at 132° (point B in Fig. 6). We found the boiling point to be at 135° (points *b* in Figs 4, 5 and 6). Above 135° the unsaturated solution gradually lost water. With increasing concentration the boiling point of the solution also gradually increased (section *b–c* of curves 1 in Figs 4, 5 and 6). As soon as the temperature of the solution reached 155° and the composition of the solution attained a $Ca(NO_3)_2$ content of 79.4%, the solution became saturated (point *c* of curves 1 in Figs 4, 5 and 6). Subsequently, the composition and the temperature of the boiling solution remained constant (section *c–d* of curve 1 in Fig. 4, point *c* of curves 1 in Figs 5 and 6), while solid $Ca(NO_3)_2$ separated out corresponding to the amount of water vapour departing from the solution.

After two-thirds of the water had escaped, the character of the process changed. According to section *d–e* in curve 1 of Fig. 4, the water could depart at the constant preselected rate only if the temperature of the sample was raised with increasing rapidity. This phenomenon is probably due to the circumstance that it became increasingly difficult for the water to escape from the mixture of solid crystals in viscous, very concentrated (about 80% of $Ca(NO_3)_2$ and 20% of H_2O) solution. The process lost its balance and the simple evaporation was replaced by a very complicated, undefined process depending on many factors, which could perhaps best described by the word "drying".

In most cases the drying was accompanied by formation of a compact layer on the surface of the product (section *d–f–e* in curves 2 and 3 of Fig. 4). The water vapour could diffuse through only with difficulty. This caused a further hindrance in the departure of the water, and consequently the temperature of the process became significantly higher.

The course of curves 2, 3 and 4 in Fig. 4 is also informative. In this case the first third of the water did not escape during the boiling of the solution, but simply evaporated at significantly lower temperatures. The more open the sample holder applied, the lower was the temperature of the departure of the water, showing that the solution was still unsaturated in this period of the examination. The solution became saturated at the point where the curves became congruent (section *c–d* curves 1–4 in Fig. 4).

Returning to the question posed in the introduction, we may state that the progressive nature of the conversion $Ca(NO_3)_2 \cdot 4\,H_2O \rightleftharpoons Ca(NO_3)_2 + 4\,H_2O$ was not the result of consecutive decomposition reactions, but was due to physical processes such as evaporation, boiling of unsaturated and saturated solutions, drying processes and formation of a solid crust.

However, the course and overlapping of these partial processes were influenced by the conditions of conventional thermoanalytical examinations to such an extent that, even in the knowledge of the phase diagram of the $Ca(NO_3)_2$–H_2O system, these processes could not be recognized in the curves.

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Zusammenfassung — Es wurde bewiesen, dass der progressive Charakter des Dehydrationsvorganges vom $Ca(NO_3)_2 \cdot 4 H_2O$ nicht den aufeinanderfolgenden Dekompositionsreaktionen zuzuschreiben ist, wie es bisher gedacht wurde, sondern ein Ergebnis verschiedener physikalischen Prozesse ist, wie das inkongruente Schmelzen des Materials, das Sieden und die Verdampfung der sich bildenden ungesättigten oder gesättigten Lösung, wie auch Verkrustung und Trocknung der Oberfläche des festwerdenden Materials. Zur Auswertung der Ergebnisse wurde die quasi-isothermische—quasi-isobare thermogravimetrische Methode und das Phasendiagramm des $Ca(NO_3)_2$—H_2O-Systems gebraucht.

Резюме — Показано, что последовательность процесса дегидратации $Ca(NO_3)_2 \cdot 4 H_2O$ обусловлена не ступенчатым характером реакций разложения, как это было принято, а является результатом различных физических процессов, таких как инконгруэнтное плавление вещества, кипение и испарение образующегося ненасыщенного и насыщенного раствора, образование корки и высушивание поверхности затвердевающегося остатка. В исследованиях был применен квазиизотермический—квазиизобарный термогравиметрический метод, а для оценки полученных результатов была использована фазовая диаграмма системы $Ca(NO_3)_2$—H_2O.