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EXAMINATION OF PHASE EOUILIBRIUM OF THE $Ca(NO_3)_2-H_2O$ SYSTEM WITH QUASI-ISOTHERMAL–QUASI-ISOBARIC THERMOGRAVIMETRY AND DTA

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By means of the quasi-isothermal–quasi-isobaric thermogravimetry (Q-TG) technique ideal experimental conditions can be realized. This provides a possibility to compare the measured data with data from other phase equilibrium (solubility, tension) examinations.

On the example of the $Ca(NO_3)_2-H_2O$ system it is demonstrated that the phase diagrams can be used to interpret thermoanalytical (especially Q-TG) curves, or conversely, the results of thermoanalytical (Q-TG, DTA) examinations can serve for the control of equilibrium data of phase diagrams or to supply missing data.

In a previous paper [1] on the example of $Ca(NO_3)_2 \cdot 4\,H_2O$ we discussed the advantages of quasi-isothermal–quasi-isobaric thermogravimetry (Q-TG). Due to its ideal experimental conditions, in contrast with conventional thermoanalytical methods, this technique permits a comparison of the obtained data with the results of other phase equilibrium measurements and in this way facilitates the interpretation of Q-TG curves.

However, not only may phase diagrams help in the evaluation of thermoanalytical curves, but conversely, equilibrium data of phase diagrams may be checked or missing data can be acquired through thermoanalytical examinations. This possibility may be of great use in cases when other physicochemical methods fail. One example arises in solubility examinations of very soluble compounds, where the concentrated and viscous solution sticks to the surface of the crystals in an unremovable way. If the ratio of the solution and the solid phase is shifted in the direction of the latter, then their separation or determination in the presence of one another is a rather difficult task. It is also difficult to determine the boiling points of extremely concentrated solutions.

The quasi-isothermal–quasi-isobaric technique is especially suitable for the performance of this kind of examination. The advantages of this technique are connected with the very accurate weight measurements and the circumstance that the examination is carried out under quasi-equilibrium conditions and without separation. However, it also has the disadvantage that information is furnished only after the beginning of weight change. Phase transformations taking place in the low-temperature region and connected solely with enthalpy changes can therefore be examined for lack of a better procedure only with conventional thermoanalytical methods such as DTA or DSC.

In the present paper we report control results on the phase diagram and tension curve of the $Ca(NO_3)_2-H_2O$ model system by quasi-isothermal–quasi-isobaric thermogravimetry and by DTA.

Experimental

Method

The principle of quasi-isothermal–quasi-isobaric thermogravimetry [2–4] and the interpretation of the curve obtained are described in detail in our earlier paper [1].

Experimental conditions

Figure 1 demonstrates magnified parts of the Q-TG curves of the dehydration of $Ca(NO_3)_2 \cdot 4\,H_2O$ (sample 1) alone (curve 1) and of $Ca(NO_3)_2 \cdot 4\,H_2O$ mixed in various proportions with $Ca(NO_3)_2$. In these latter experiments we assumed that, until weight change begins, the solution formed on the melting of $Ca(NO_3)_2 \cdot 4\,H_2O$ dissolves the $Ca(NO_3)_2$ either totally (curves 2–5) or partially (curve 6), in accordance with the solubility. We selected the proportions of the components so that the solutions to be formed should contain the following amounts of $Ca(NO_3)_2$: 72.6, 74.4, 76.6, 79.0 and 80.3% (samples 2–6 corresponding to curves 2–6).

The Q-TG curves in Fig. 1 were recorded with a Q-derivatograph (Hungarian Optical Works, Budapest). A mixture of about 600 mg in the labyrinth sample holder was examined in the presence of air to a transformation rate of 0.6 mg min^{-1}. The total

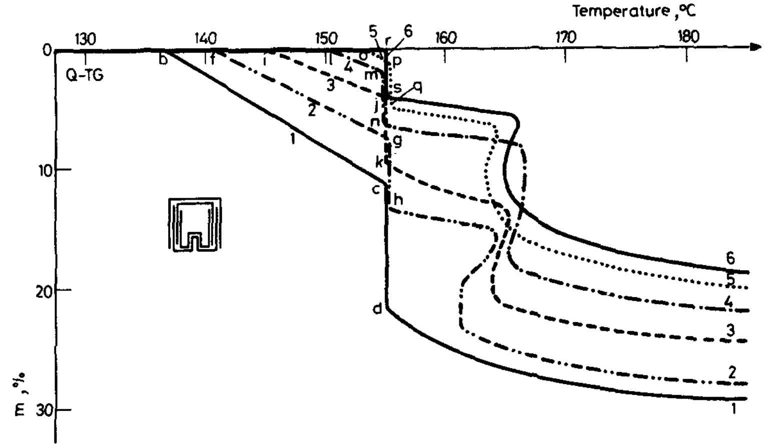

Fig. 1 Q-TG curves of $Ca(NO_3)_2-H_2O$ system containing various amounts of $Ca(NO_3)_2$

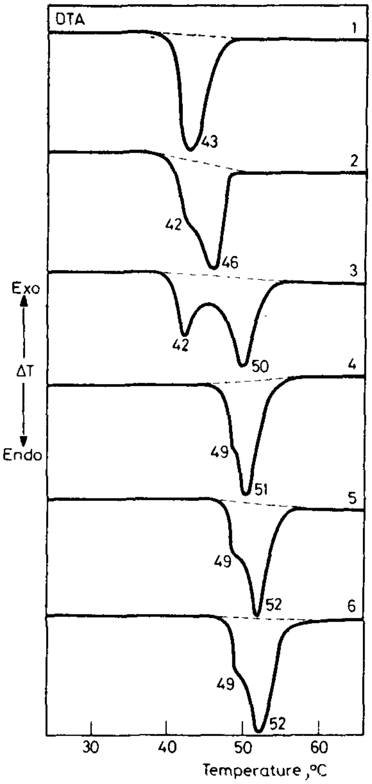

Fig. 2 DTA curves of $Ca(NO_3)_2$–H_2O system containing various amounts of $Ca(NO_3)_2$

weight loss of the sample varied in the range 100–200 mg, the dehydration requiring about 3–6 hours.

We also traced the DTA curves (Fig. 2) of the above $Ca(NO_3)_2$–H_2O systems with various compositions. One of our aims was to check that part of the phase diagram which lies in the lower temperature region.

There is also another way to prepare $Ca(NO_3)_2$–H_2O systems, which differs from the method described above. Setting of the appropriate water content can be achieved not only through the dissolution of $Ca(NO_3)_2$, but also by expelling the water excess under strictly controlled conditions (Q-TG). We prepared the samples for the DTA examinations in this way. For this purpose about 100 mg of $Ca(NO_3)_2 \cdot 4\,H_2O$ was weighed in a small crucible, which was then placed into the inner part of the six-part labyrinth crucible and the Q-TG examinations were started.

As soon as the samples had lost so much weight that the residues contained 72.6, 74.4, 76.6, 79.0 and 80.3% of $Ca(NO_3)_2$ (samples 2–6), the examinations were interrupted by lifting the furnace. The samples were thereafter kept at about – 15° in a

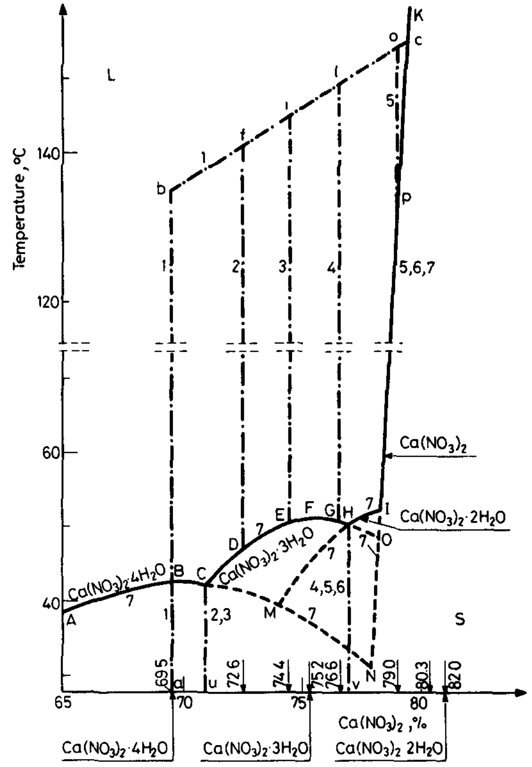

Fig. 3 Phase diagram of $Ca(NO_3)_2$–H_2O system according to Ewig et al. (curve 7); curves 1–6 constructed on the basis of curves 1–6 in Fig. 1

refrigerator until solidification. It should be noted that these samples are inclined to undercooling. On several occasions we observed that, instead of the corresponding stable salt hydrate, the metastable one was formed.

The DTA curves were recorded with a Q-derivatograph, in the presence of air, at a heating rate of 1 deg min^{-1}.

Curves 7 in Fig. 3 show the equilibrium conditions of the $Ca(NO_3)_2$–H_2O system. The phase diagram was prepared by Ewig, Krey, Law and Lang [5] on the basis of solubility examinations. Curves 1–6 of this figure were constructed by us in the knowledge of the corresponding solution composition *vs.* temperature pairs read off Q-TG curves 1–6 in Fig. 1.

Curve 7 in Fig. 4 demonstrates the way in which, according to Ewig [6], the boiling point of the $Ca(NO_3)_2$–H_2O system changes as a function of the composition. Curves 1–6 of this figure were similarly constructed by us in the knowledge of curves 1–6 of Fig. 1. These latter illustrate the changes in the boiling point of the solution during the Q-TG examination of samples with various compositions.

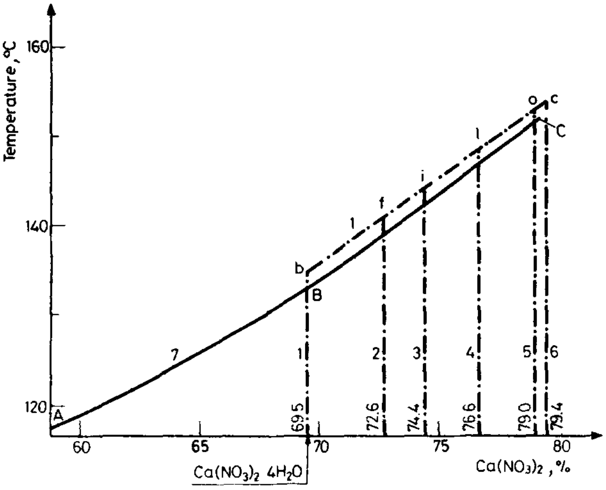

Fig. 4 Changes in the boiling point of the system $Ca(NO_3)_2$—H_2O in function of composition according to Ewig (curve 7); curves 1—6 constructed on the basis of curves 1—6 in Fig. 1

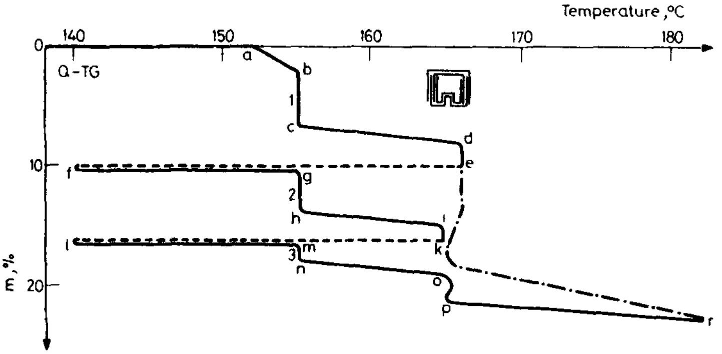

Fig. 5 Q-TG curves of $Ca(NO_3)_2 \cdot 4H_2O$ traced in interrupted experiments

In order to prove that a crust was formed on the sample surface in the case of curves 2—6 of Fig. 1 after points *h*, *k*, *n*, *q* and *s*, similarly as in our earlier investigations [1] we performed a special experiment, the result of which is illustrated in Fig. 5. We repeated the recording of curve 4 of Fig. 1 with the difference that at the moment corresponding to point *e* (after the presumed formation of the crust) we interrupted the examination, cooled the sample down, thoroughly mixed it with a needle and thereafter restarted the Q-TG examination (point *f*). As a result we obtained curve 2. By interrupting this experiment too (point *k*), destroying the newly formed crust again, and restarting the examination (point *l*), we obtained curve 3 which is similar in character to the two earlier curves.

These curves indicate that in the course of the restarted experiment the water loss continued not at the temperature (points *g* and *m*) at which the experiment was interrupted (points *e* and *k*), but at the temperature at which the process was taking place before the crust formation (points *c* and *h*). In our opinion this circumstance lends support to our supposition.

Discussion

Analysis of the Q-TG curves of $Ca(NO_3)_2$—H_2O systems with various compositions (curves 1—6 in Fig. 1) and comparison of the measured data with the phase diagram (Fig. 3) of the system and its boiling point curve (Fig. 4) permits the following conclusions.

After samples 1—4 melted, at temperatures corresponding to their composition (Figs 2 and 3), saturated solutions were formed (curve sections B—b, D—f, E—i and G—l in Fig. 3), which with increase of temperature got unsaturated. After the melting, up to 130° sample 5 was composed of saturated solution and solid $Ca(NO_3)_2$ (curve section I—P in Fig. 3); at 130° the solid dissolved (point P in Fig. 3) and with further rise in temperature the solution became unsaturated (curve section P—o in Fig. 3). An unsaturated solution was not formed from sample 6 (curve section I—c in Fig. 3).

For samples 1—5 the changes in the boiling points corresponding to the compositions of the unsaturated solutions are illustrated by curve sections b—c, f—g, i—j, l—m and o—p in Fig. 1 and sections b—c, f—c, i—c, l—c and o—c in Figs 3 and 4). The solution became saturated in every case at 155° and a $Ca(NO_3)_2$ content of 79.4% (points *c, g, j, m, p* and *r* in Fig. 1 and point *o* in Figs 3 and 4). The departure of the remaining water continued thereafter without any changes in the temperature (sections c—d, g—h, j—k, m—n, p—q and r—s in Fig. 1 and point *c* in Figs 3 and 4). Since the solution was originally saturated, in the case of sample 6 no changes in the boiling point could be observed (points *r* and *s* in Fig. 1). As the sections following points *d, h, k, n, q* and *s* in curves 1—6 of Fig. 1 were distorted by the crust formation on the sample surface, these could no longer provide useful information.

When the results of the examinations were interpreted and evaluated from our original point of view, it turned out that point *c* of Fig. 3 lay on curve I—K, and curves b—c and B—C of Fig. 4 were nearly congruent. Accordingly, the solubility and tension studies carried out by Ewig et al. [5] and our Q-TG examinations led to nearly identical results. It follows from this that, if necessary, the missing data of a phase diagram may possibly be obtained with the help of Q-TG measurements carried out according to the above principle.

We performed the joint interpretation of the DTA curves of the samples solidified by deep-freezing (Fig. 2) and the phase diagram of the system (Fig. 3) in the following way.

Sample 1: The DTA curve of $Ca(NO_3)_2 \cdot 4\,H_2O$ of theoretical composition is represented by curve 1 in Fig. 2. The endothermic peak at 43° in this curve indicates the congruent melting of the salt hydrate. This follows from the fact that curve A–B–C in Fig. 3 has a maximum at point B (42.7°). The path of the phase transformation can be characterized by points a–B–b.

Sample 2: In the course of the preparation of the sample containing 72.6% of $Ca(NO_3)_2$ from the unsaturated warm solution by cooling (curve 2 in Fig. 3), first (point D) the trihydrate separated (47.0°) and subsequently, at the eutectic point (point C) (42.6°) the eutectic mixture of the tetra- and trihydrates was formed. The DTA curve of the sample solidified by deep-freezing (curve 2 in Fig. 2) traced the reverse of this process, with an inflexion point of 42° and a peak temperature of 45°. The path of the transformation is marked by points u–C–D–f.

Sample 3: The solid phase separated from unsaturated solution containing 74.4% of $Ca(NO_3)_2$ was composed of the same components as the two earlier samples, since the phase transformation took place in a similar way (i–E–C–u). Of course, the proportions of the separated phases were different. The DTA curve (curve 3 in Fig. 2) again showed the melting of the eutectic at 42°, but the second maximum appeared at a somewhat higher temperature (50°). However, this is in accordance with the fact that in curve C–F–H of Fig. 3 a higher temperature (50.5°) corresponded to point E than to point D.

Sample 4: From the unsaturated solution containing 76.6% of $Ca(NO_3)_2$, first (point G in Fig. 3) the trihydrate separated (52.0°) in the course of cooling and then, at the eutectic point H (50.6°), the tri- and dihydrate-containing eutectic mixture was formed. This is in accordance with the circumstance that in the DTA curve (curve 4 in Fig. 2) an inflexion point appeared at 49° and a maximum at 51°. The path of the transformation: points v–H–G–l.

Sample 5: The unsaturated solution containing 79.0% of $Ca(NO_3)_2$ became saturated at point P (130°) on cooling. During further cooling solid $Ca(NO_3)_2$ gradually separated out. Separation of the dihydrate started at point I (52.0°), while at point H (50.6°) the eutectic mixture of di- and trihydrates also separated. The 49° inflexion point and the 52° maximum in the DTA curve (curve 5 in Fig. 3) demonstrate the same processes taking place in the reverse direction. The path of the transformation: v–H–I–P–o.

Sample 6: Even at the boiling point, the system containing 80.3% of $Ca(NO_3)_2$ was composed to a greater part of saturated solution and to a lesser part of solid $Ca(NO_3)_2$. The path of the solidification (c–I–H–v) and the phase composition of the solidified system were nearly the same as those for sample 5. Consequently, it is understandable that the DTA curve 6 in Fig. 2 and curve 5 (traced for sample 5) have similar courses.

Thus, with the above principle the DTA technique can be used to check or supplement the equilibrium data of phase diagrams.

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Zusammenfassung — Mit Hilfe des quasi-isothermischen–quasi-isobaren thermogravimetrischen (Q-TG) Verfahrens können ideale Versuchsbedingungen realisiert werden. Das ermöglicht es, die gemessenen Daten mit von anderen Phasengleichgewicht-Untersuchungen (Lösbarkeit, Tension) stammenden Daten zu vergleichen.

Durch das Beispiel des $Ca(NO_3)_2$–H_2O-Systems wurde es gezeigt, dass die Phasendiagramme zur Erklärung von thermoanalytischen (insbesondere Q-TG) Kurven können angewandt werden, oder umgekehrt, die Ergebnisse der thermoanalytischen (Q-TG, DTA) Untersuchungen als Kontrolle der Gleichgewichtsdaten der Phasendiagramme dienen können, oder die fehlenden Daten liefern können.

Резюме — С помощью квазиизотермического–квазиизобарного термогравиметрического метода (Q–ТГ) могут быть реализованы идеальные экспериментальные условия. Этим самым представляется возможность сопоставлять измеряемые данные с данными других фазовых равновесий (растворимость, упругость). На примере системы $Ca(NO_3)_2$–H_2O было показано, что фазовая диаграмма может быть использована для интерпретации термоаналитических (особенно Q–ТГ) кривых или наоборот, результаты термоаналитических исследований могут служить для контроля равновесных данных фазовых диаграмм или при использовании недостающих данных.