

THERMOANALYTICAL STUDY OF EQUILIBRIUM CONDITIONS IN THE SYSTEM $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 - \text{H}_2\text{O}$

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The phase diagram of the system $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 - \text{H}_2\text{O}$ (abbr.: C.U.-W.) is not known in domains containing less than 25% water, as conventional solubility examinations are not suitable for determination of the solubility equilibria between very concentrated and viscous solution and solid C.U. The unknown domain of the phase diagram has been established by means of thermoanalytical methods.

DTA studies revealed that C.U.3W. separates from solutions containing 7–21% water, while C.U. separates from more concentrated solutions.

C.U.3W. and C.U. form an eutectic mixture with melting point 28°C and composition C.U.3W.:C.U. = 36.64.

Quasi-isothermal–quasi-isobaric thermogravimetry showed the boiling point of the solution saturated with respect to C.U. to be 200°C, the composition being C.U.:W. = 97:3. The course of the tension curve of the phase diagram was determined by investigation of systems containing different amounts of water.

The equilibrium conditions in the $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 - \text{H}_2\text{O}$ system (abbreviated below to C.U.-W.) are known in general terms. The phase diagram, however, has not yet been determined. Figure 1 illustrates the solubility isotherms [1, 2] of the system at 0, 20, 40 and 55°. The areas HMF, JNF, KOF and LRF mark the stability domains of the complex $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3 \text{H}_2\text{O}$ (C.U.3W.) at each temperature, while the area RPG shows the stability region of anhydrous C.U.

C.U.3W. is one of the well-defined compounds in the C.U.-W. system. It has potential as a fertilizer and an investigation of all aspects of its stability is therefore of practical significance.

The stability conditions prevailing along the straight line AG in Fig. 1 can be more easily appreciated with the help of the phase diagram of C.U.3W. in Fig. 2.

This diagram shows that the solubility of C.U.3W. is known only up to the point E. This is probably due to the fact that separation of the phases and their determination in the presence of one another using conventional methods of solubility analysis are very difficult in those regions where the solution in equilibrium with the solid phase is extremely concentrated and viscous.

We recently developed a method [3] based on quasi-isothermal–quasi-isobaric thermogravimetry (Q–TG) [4–6] and DTA investigations. This method can be applied with advantage to those problems which cannot be solved with conventional methods. We employed it to determine the missing part of the phase diagram of the C.U.-W. system.

Experimental

Materials

For the DTA measurements (Fig. 3) C.U.-xW. mixtures containing different amount of water were prepared by means of the quasi-isothermal–quasi-isobaric technique.

$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ were mixed in a 1:1 molar ratio, and the mixture was introduced into a small crucible used for DTA measurements; this was then placed in the centre of the labyrinth sample holder. Thereafter, regular Q–TG experiments were carried out, with the difference that they were interrupted at the moment when the calculated amount of excess water had departed from the system. Before the DTA examination, the system was solidified by cooling at -15° . It was observed that the C.U.-xW. systems are inclined to supercooling, but if the cooled viscous material is stirred with a needle or if microcrystals of C.U.3W. are added, solidification is immediate.

For the Q–TG measurements (Fig. 5) C.U.-xW. systems of various compositions were prepared in essentially the same way, but with the difference that the samples were placed directly in the labyrinth crucible and were examined without deep-cooling; it was not necessary here to obtain a well-defined solid phase because the material melted anyhow during the Q–TG measurements.

Experimental conditions

The conventional DTA [6] and Q–TG measurements [4–6] were carried out with a Q-Derivatograph (Hungarian Optical Works, Budapest).

Figure 3 illustrates the DTA curves recorded for $\text{Ca}(\text{NO}_3)_2$ – $\text{CO}(\text{NH}_2)_2$ systems containing 4, 3, 2.5, 1.75, 1.5, 1.25, 1.0, 0.7 or 0.4 moles of water (curves 1–10). The weight of the samples was about 50 mg. The heating rate was $0.5 \text{ degree min}^{-1}$.

Q–TG curves for the systems containing 4, 3, 2, 1.5, 1.0 and 0.5 moles of water (curves 1–6) were also recorded and are shown in Fig. 5. The labyrinth crucible [5–7] was used with a transformation rate of 0.3 mg min^{-1} and a sample size of about 500 mg.

Procedure, discussion

DTA examinations were first performed with solid C.U.-W. systems containing different amounts of water in order to determine the missing part of the phase diagram

(Fig. 2). On cooling, the system C.U.-4W. yielded first the solid C.U.3W. complex, and thereafter, at a temperature below 0° , an eutectic mixture of C.U.3W. and ice separated. In the DTA examination the same processes took place, but in the reverse direction. The DTA apparatus did not permit measurements below 0° , so we could not observe the melting of the eutectics. The wide spectrum of curve 1 in Fig. 3 indicated only the subsequent process. According to this, the liquid formed from the melted eutectics immediately began to dissolve the remaining solid C.U.3W. Due to the

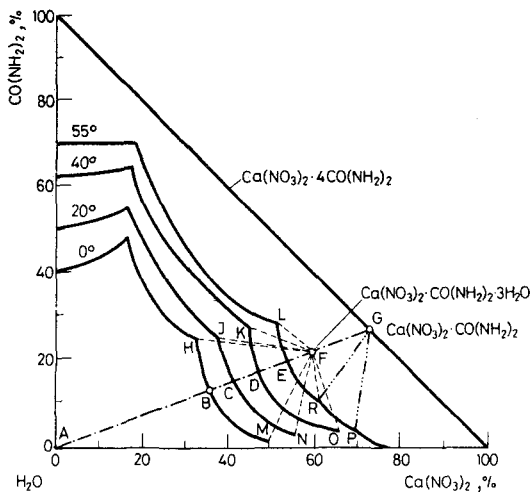


Fig. 1 Phase diagram of the $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ system. Isotherms of 0° and 55°C were determined by [1] while isotherms of 20° and 40°C by [2]

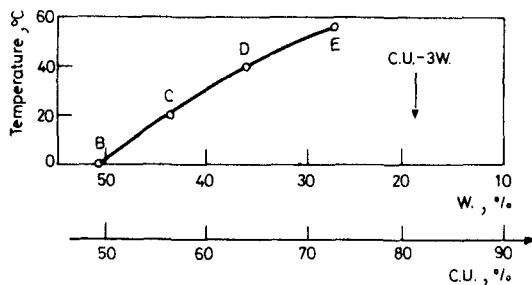


Fig. 2 Phase diagram of the binary system: $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ (C.U.-W.)

character of this process, it extended over a rather wide temperature interval. It would therefore be senseless to give the "onset" temperature, and it was more correct to characterize the process by its peak temperature. In the present case this is 59° and can be interpreted as the temperature at which the dissolution of C.U.3W. is completed. This point is indicated in the phase diagram of the binary C.U.-W. system (point *a* in Fig. 4).

It can be assumed that only the pure C.U.3W. complex could separate from the solution of the system C.U.3W. Consequently, the DTA peak at 60° in curve 2 in Fig. 3 indicates the melting of the complex. This is in good agreement with the literature data. Otherwise, as could be expected, the transformation temperature was the highest in this case (point *b* in Fig. 4).

In curves 3–7 in Fig. 3 the DTA peaks at 28° indicate the melting of the eutectic mixture of C.U.3W. and of water-free C.U. (points *i–n* in Fig. 4), while the peaks at 58, 53, 50, 46 and 42° denote the end of the dissolution of the solid C.U.3W. complex (points *c–g* in Fig. 4).

In curve 8 in Fig. 3 only a single peak appears at 28°, demonstrating that the composition of the eutectic mixture was C.U.:W = 1:1 (molar ratio). This also means that in systems which contain less water than this molar ratio the solid C.U.3W. could be present only in the eutectics.

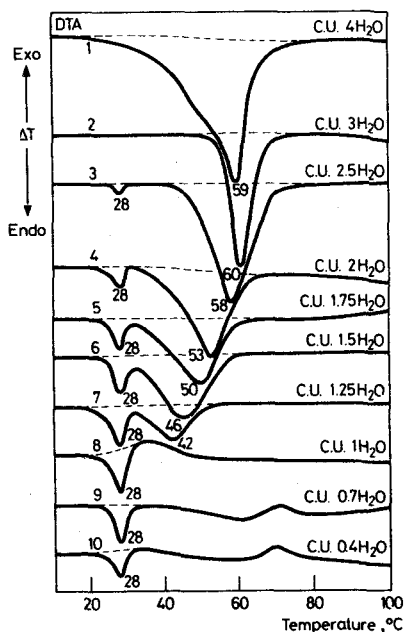


Fig. 3 DTA curves of solid $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ (C.U.-W.) systems with various water contents

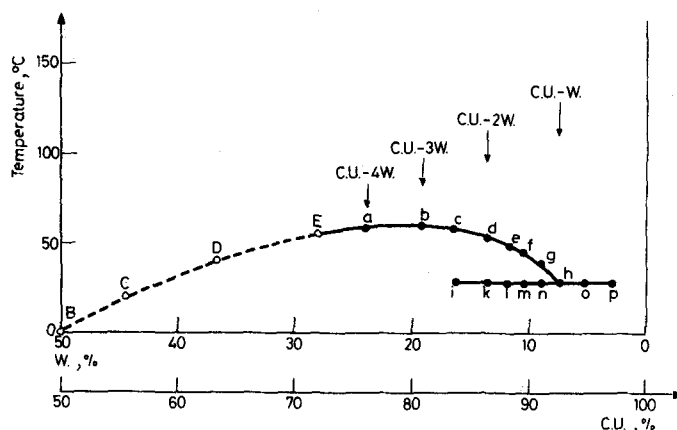


Fig. 4 Phase diagram of the binary system $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ (C.U.-W.). The already known phase line (B-E) completed by sections (a-h and i-p) obtained on the basis of DTA measurements

This is supported by the fact that in curves 9 and 10 in Fig. 3 we cannot detect any peak indicative of the presence of C.U.3W. apart from the peak at 28° which indicates the melting of the eutectics (points o and p in Fig. 4).

Since the literature does not report hydrates which contain less water than C.U.3W. does, we presumed that to the right-hand side of the eutectic point, and above it, equilibrium is established between the anhydrous salt and the solution.

In order to determine approximately the stability region of the anhydrous complex in addition to the eutectic point, at least a further single point in the phase diagram had to be determined, at which equilibrium exists between the solution and the solid anhydrous complex. The boiling point of the saturated solution can be used for this purpose. This can be determined relatively easily and exactly by means of Q-TG measurement [3].

In the present case we traced the Q-TG curves (curves 1-6 in Fig. 5) for six systems containing different amounts of water. The manner of interpretation of the Q-TG curves is somewhat different from that for TG curves [6]. For example, Q-TG curve 2 in Fig. 5 can be interpreted in the following way. The C.U.3W. complex melted at 60° (point b), but under the given conditions (labyrinth crucible) the initially saturated, but later unsaturated solution did not begin to lose water up to 135° (straight section up to point s).

The solution began to boil at 135° (point s) and gradually lost water, its concentration increasing along with its boiling point (curve section s-z). At 200° the solution became saturated (point z). Thereafter, the solution continued boiling, losing water gradually, but its concentration did not change further because the solid anhydrous salt separated out in an amount proportional to the amount of the de-

parting water. Since the composition of the saturated solution did not change, its boiling point stayed constant too, while the solution and the solid phases remained in equilibrium with one another. This gave the missing point.

In Fig. 5 the further courses of the Q-TG curves (curve 1-6) relative to one another prove that the boiling point of the unsaturated solution changes as a function of the composition for the other C.U.-xW. systems in the same way as observed in the case of curve 2. This change has also been indicated in the phase diagram (curves 1-6 in Fig. 6). All of these curves meet at a single point, i.e. at the boiling point (point z) of the saturated solution at 200°, with a composition 97% $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2$ and 3% H_2O .

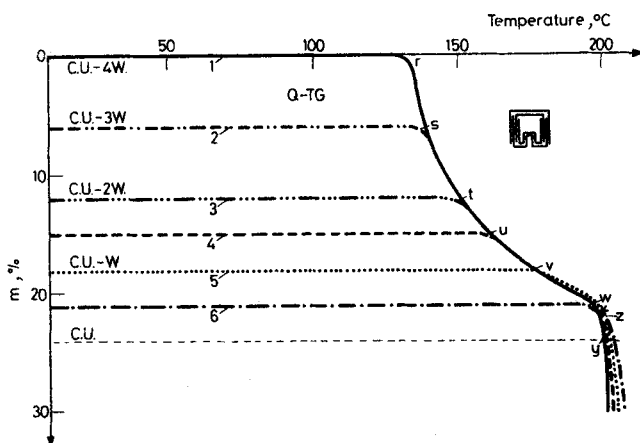


Fig. 5 Q-TG curves of solid $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ (C.U.-W.) systems containing various amounts of water

The unknown part of the curve in the phase diagram, starting from the eutectic point (point *h*), and along which the saturated solution is in equilibrium with the solid anhydrous salt, must pass through point *z*.

It can therefore be supposed that no serious error will be made if these two points are connected by a straight line and this line is regarded as belonging to the phase diagram.

In the present case the phase line ends at point *z*. Earlier results indicated that when the last traces of water are driven from the system, the anhydrous C.U. complex hitherto stabilized by water immediately decomposes to its components and the urea then begins to decompose [7].

The steep slope of the phase line *h-z* determined in this way also explains why only a single peak appeared in DTA curves 9 and 10. After the eutectic of the solid containing 0.7 and 0.4 mole water melted, the liquid formed began to dissolve the

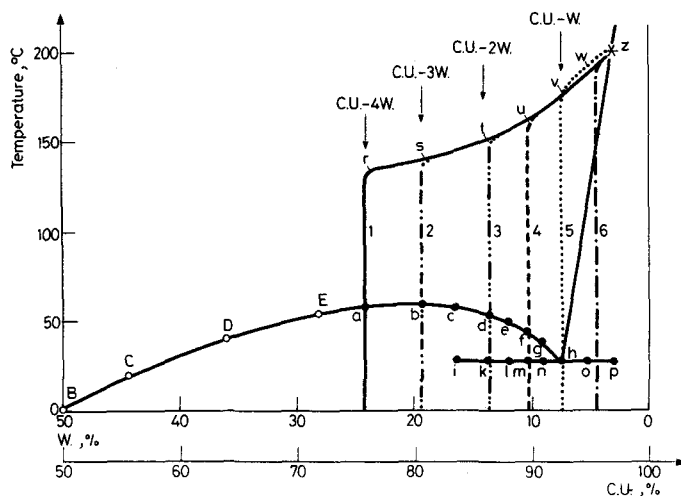


Fig. 6 Phase diagram of the binary system: $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ (C.U.-W.). Phase line B-E already known the new phase lines a-h and i-p constructed on the basis of DTA curves while section h-r on the basis of the Q-TG curve. Curves 1-6 illustrate the changes in the composition of the C.U.-xW. systems against temperature in the course of the Q-TG examination

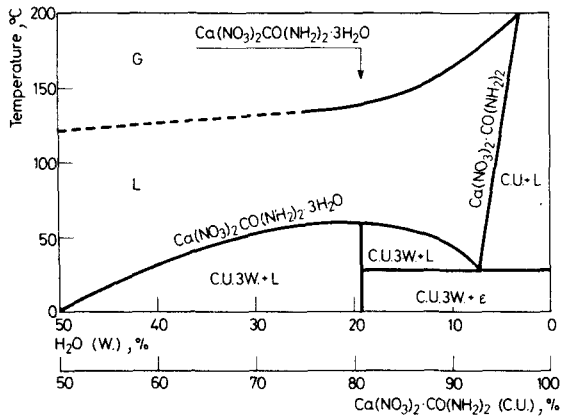


Fig. 7 New phase diagram of the binary system: $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ (C.U.-W.). G: water vapour, L: liquid, ε: eutectics

solid anhydrous salt, but in a process associated with a relatively small thermal effect. In the case of curve 9, this extended over a temperature interval of about 100°, while in the case of curve 10 the range was even broader. For this reason the DTA apparatus was not able to sense the thermal effect.

During the boiling in the labyrinth crucible, the liquids formed from systems with various water contents were in contact with water vapour at atmospheric pressure (ca. 100 kPa), and so the saturation of the solutions took place under quasi-equilibrium conditions. Hence, it is easy to see that the section $r-z$ of the phase line in Fig. 7 is identical with the corresponding section of the equilibrium tension curve of the C.U.-W. system.

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Zusammenfassung – Das Phasendiagramm des Systems $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 - \text{H}_2\text{O}$ (C.U.-W.) ist nicht für das Gebiet mit weniger als 25% Wasser bekannt, da herkömmliche Löslichkeitsuntersuchungen nicht zur Bestimmung von Löslichkeitsgleichgewichten zwischen sehr konzentrierten und viskosen Lösungen und festem C.U. geeignet sind. Der unbekannte Teil des Phasendiagramms wurde mittels thermoanalytischer Methoden ermittelt.

DTA-Untersuchungen ergaben, dass sich C.U.3W. aus 7–21% Wasser enthaltenden Lösungen, C.U. dagegen aus konzentrierteren Lösungen abscheidet.

C.U.3W. und C.U. bilden eine eutektische Mischung mit einem Schmelzpunkt von 28°C und einer Zusammensetzung C.U.3W.:C.U. = 36:64. Quasi-isotherme/quasi-isobare Thermogravimetrie ergibt für die an C.U. gesättigte Lösung einen Siedepunkt von 200°C. Das C.U.:W.-Verhältnis dieser Lösung ist 97:3. Der Verlauf der Dampfdruckkurve des Phasendiagramms wurde durch Untersuchung von unterschiedliche Wassermengen enthaltenden Systemen bestimmt.

Резюме – Фазовая диаграмма системы $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 - \text{H}_2\text{O}$ (в дальнейшем обозначена как К.М.-В.) неизвестна в областях, содержащих меньше 25% воды, так как традиционные определения растворимости неприемлемы для определения равновесной растворимости между очень концентрированным и вязким раствором, а также между твердым

К.М. С помощью термоаналитических методов была определена неизвестная область фазовой диаграммы. ДТА исследования показали, что К.М.ЗВ. выделяется из растворов, содержащих 7–21% воды, тогда как безводная К.М. выделяется из более концентрированных растворов. К.М.ЗВ. и К.М. образуют эвтектическую смесь состава 36:64% и с точкой кипения 28 °С квазиизотермическая—квазиизобарная термогравиметрия показала, что точка кипения раствора, насыщенного по отношению к К.М. (состава К.М.:В. = 97:3%), равна 200 °С. Путем исследования систем с различным количеством воды, был определен ход кривой натяжения фазовой диаграммы.