

THERMOGRAVIMETRIC STUDY OF DEHYDRATION OF $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3 \text{H}_2\text{O}$ UNDER QUASI-ISOTHERMAL- QUASI-ISOBARIC CONDITIONS

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Conventional thermoanalytical curves provide little information on the thermal decomposition of $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3 \text{H}_2\text{O}$. In contrast from quasi-isothermal-quasi-isobaric thermogravimetric curves the mechanism can easily be interpreted. After the complex melts at 60°C, the solution formed is weight constant up to 135°C in the labyrinth crucible. The solution begins to boil at 135°C and gradually loses water, its boiling point increasing. The solution becomes saturated at 200°C. Thereafter, $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2$ separates out while the boiling point does not change. After the departure of the water, the $\text{CO}(\text{NH}_2)_2$ immediately decomposes and $\text{Ca}(\text{NO}_3)_2$ remains.

In an open crucible the above transformation is complicated by decomposition of type $AB_{(s)} = A_{(s)} + B_{(g)}$, solution "evaporation" "drying" of solid residue, surface crust formation, etc. In conventional thermoanalysis the latter processes accompany the above processes (melting-solution formation-loss of water during boiling) which hampers interpretation of the conventional curve.

The compound $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3 \text{H}_2\text{O}$ (abbreviated to C.U.3W.), a hydrated crystalline adduct of urea with an inorganic salt, has considerable potential as a fertilizer. It has the advantage of not being highly hygroscopic and its nitrogen content is 20.14%. Further, it remains active for a long time due to the favourable ratio of nitrate to amine nitrogen $N_{\text{NO}_3} : N_{\text{NH}_2} = 1:1$ [1, 2].

The solubility isotherms for the system C.U.W. at 0, 20, 40, 55 and 70° have been reported [3-5] and the crystallization range of C.U.3W. has partly been determined [2, 3, 4, 6]. We recently made measurements on this complex and obtained some previously missing data, by means of thermoanalytical methods [7].

The basic crystallographic data on C.U.3W. are available [4], its crystal structure is known [8], and the principal refractive indices have been measured [3]. The melting temperature measured by the capillary method is given as $60 \pm 1^\circ$ [6]. The thermal decomposition of C.U.3W. was earlier investigated by several researchers [9, 10], who reached similar conclusions to those that can be drawn from the simultaneous TG, DTG and DTA data in Fig. 1.

After melting, indicated by the 60° peak in the DTA curve, the sample gradually loses its water of crystallization (DTG: 150, 170, 190°). As soon as the loss of water is complete at 200°, the urea melts and subsequently decomposes (DTG: 240, 260°).

From a technological aspect, a detailed knowledge of the dehydration process is essential. The courses of the DTG and DTA curves indicate that the process is a complex one and the partial processes strongly overlap; this is why they have not yet been fully elucidated.

The separation of the partial processes was not possible with the conventional measuring techniques and the resolution could not be further increased. The use of quasi-isothermal—quasi-isobaric thermogravimetry (Q—TG) [11–13] has now led to some elucidation of such problems. Preliminary information about the dehydration of C.U.3W. was presented at a symposium [14].

Experimental

Method

It is characteristic of Q—TG [11–13] that processes accompanied by weight change take place at a strictly constant rate and are slower by one or two orders of magnitude ($0.2\text{--}1.0 \text{ mg min}^{-1}$) than transformations occurring conventional conditions.

The application of the labyrinth crucible is part of the essence of the method. Inside this crucible, immediately after the beginning of the decomposition, the partial pressure of the gaseous decomposition products reaches 100 kPa, and it remains constant up to the end of the process. If simple covered and uncovered crucibles and a multiplate sample holder are used [13], the gas product partial pressures are expected to reach ca. 20, 5 and 1 kPa, respectively [13]. Due to the constant decomposition rate, in these cases too the partial pressure remains practically constant until the process is completed. Under these conditions the temperature of the sample changes in a characteristic way, and the weight changes of the sample recorded as a function of temperature yield Q—TG curves of a characteristic shape, from which further conclusions can be drawn regarding the processes studied.

Materials

Pulverized singly crystals of C.U.3W. were examined. The single crystals were grown from aqueous solution by isothermal evaporation at room temperature [6].

Experimental conditions

Simultaneous TG, DTG and DTA (Fig. 1) and Q—TG examinations (Figs 2 and 3) were carried out with a Q-Derivatograph [13] (Hungarian Optical Works, Budapest).

Figure 1 illustrates simultaneous TG, DTG and DTA curves for C.U.3W. under dynamic heating conditions. The experiments were carried out with a 250 mg sample in an open crucible in the presence of air, with a heating rate of 5 degree min^{-1} .

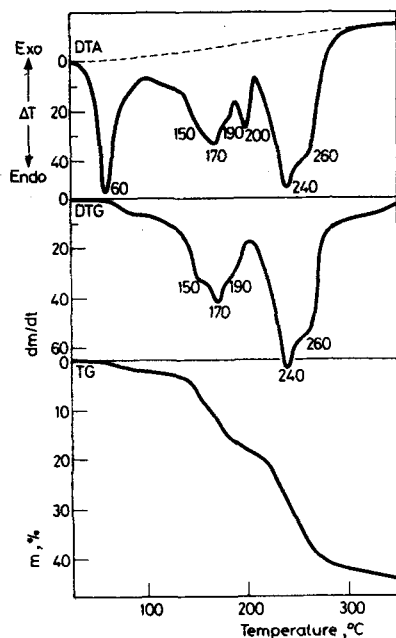


Fig. 1 Simultaneous TG, DTG and DTA curves of the $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ complex

Figure 2 illustrates Q-TG curves of C.U.3W. A sample size of about 500 mg was used and the selected transformation rate was 0.5 mg min^{-1} for 100 mg total weight change. Four different types of sample holders were employed: a labyrinth crucible (curve 1), a covered crucible (curve 2), an uncovered crucible (curve 3) and a multiplate sample holder (curve 4). The experiments were carried out under a nitrogen atmosphere to ensure that the urea was not oxidized.

In Fig. 3 Q-TG curves are shown for C.U.3W. (curves 1 and 4), $\text{Ca}(\text{NO}_3)_2$ and $\text{CO}(\text{NH}_2)_2$ mixed in a 1:1 mole ratio (curves 2 and 5), and pure $\text{CO}(\text{NH}_2)_2$ (curves 3 and 6). A multiplate sample holder (curves 1-3) and a labyrinth crucible (curves 4-6) were used. These curves were obtained in N_2 atmosphere at a transformation rate of 0.5 mg min^{-1} .

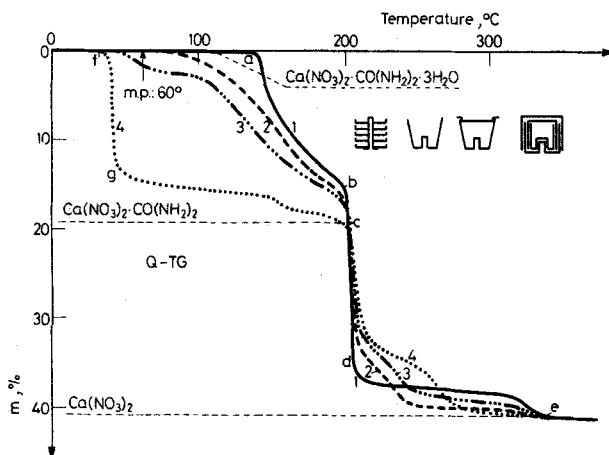


Fig. 2 Q-TG curves of the $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ complex traced by using the labyrinth (1) a covered (2) an uncovered (3) and a polyplate sample holder

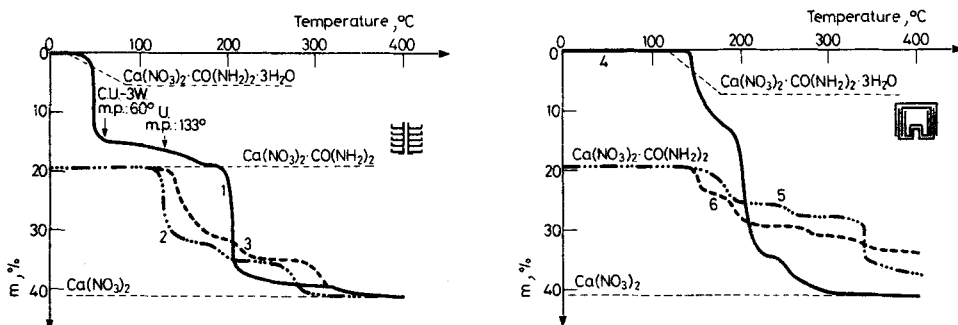


Fig. 3 Q-TG curves of $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2$ (1, 4) of $\text{CO}(\text{NH}_2)_2$ (2, 5) and of the mixture of $\text{CO}(\text{NH}_2)_2$ and $\text{Ca}(\text{NO}_3)_2$ (3, 6) investigated in N_2 atm., with multiplate sample holder (1, 2, 3) and with labyrinth crucible (4, 5, 6)

Discussion

In the interpretation of the Q-TG curves in Fig. 2, the starting point is that the C.U.3W. melted at 60° and a saturated solution was formed [15]; as the temperature increased, this solution became unsaturated. Curve 1 shows that the weight of material in the labyrinth crucible remained constant up to 135° (point a). At this temperature the unsaturated solution reached its boiling point. Thereafter (curve section a-b), the solution gradually lost water, its concentration increasing, and thus the boiling

point of the solution also rose. At 200° the solution became saturated again (point *b*). From then on (curve section *b-c*) water was lost quasi-isothermally, with parallel separation of the corresponding amount of anhydrous solid C.U. Hence, the concentration of the solution remained constant and the boiling point did not change further. The water loss was completed at point *c*. It may be presumed that the anhydrous C.U. — first melted and immediately afterwards underwent disproportionation. The urea then began to decompose. The temperature of the sample hardly changed (section *c-d*), while its weight decreased to nearly the calculated value. Under the given conditions the decomposition of urea ended at about 350° (point *e*). The residue was calcium nitrate.

In covered and uncovered crucibles the water loss from the unsaturated solution had a different character (curves 2 and 3). This process will be called "evaporation" [15]. In this case, in the relatively more open systems the partial pressure of the water vapour in contact with the solution was significantly lower than in the labyrinth crucible. The rate of evaporation was found to be strongly dependent on the experimental conditions. Since the solutions were viscous, it may be presumed that a thin solid crust was formed on the surface, which affected the course of the curves. Therefore, curves 2 and 3 cannot be regarded as characteristic.

In the multiplate sample holder, the sample was spread out in thin layers over a large surface area and lost two-thirds of the crystal water content (section *f-g*) at a temperature as low as 40° , i.e. appreciably before melting. The residual water was lost between 40 and 200° . The phase diagram for the system C.U.W. indicates that in the given composition range C.U. and the solution phase are in equilibrium with one another. On analogy with similar systems [15] we may suppose that on the surface of the mixture of the solid anhydrous salt and the very viscous concentrated solution a compact crust of solid anhydrous salt may be formed. Consequently, the process of loss of water from the system cannot be described as either boiling or evaporation. To distinguish this process from the other two, we have called it "drying" [15].

The decomposition of urea in an exceedingly complicated process, which depends strongly on the experimental conditions. Therefore, no attempt has been made to interpret the shape of the four curves beyond point *c*. It can be stated, however, that water stabilizes the complex. All four curves in Fig. 2 indicate that the urea began to decompose at 200° , only after the last traces of water had departed.

The same is demonstrated by the courses of the curves in Fig. 3. The decomposition of pure $\text{CO}(\text{NH}_2)_2$ (curves 3 and 6) and that of water-free mixture of $\text{Ca}(\text{NO}_3)_2$ and $\text{CO}(\text{NH}_2)_2$ (curves 2 and 5) begins at a much lower temperature and ends earlier than for the decomposition of the anhydrous salt (formed after the departure of water) of identical composition (curves 1 and 4).

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Zusammenfassung – Herkömmliche thermoanalytische Kurven liefern wenig Informationen über die thermische Zersetzung von $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$. Quasi-isotherme/quasi-isobare thermogravimetrische Kurven dagegen ermöglichen leicht eine Interpretation des Mechanismus. Nach dem Schmelzen des Komplexes bei 60°C bleibt das Gewicht der Lösung im Labyrinthtiegel bis 135°C konstant. Die Lösung beginnt bei 135°C zu sieden und verliert zunehmend an Wasser, wobei der Siedepunkt ansteigt. Die Lösung erreicht den Sättigungspunkt bei 200°C. Danach scheidet sich $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2$ ohne weitere Veränderung des Siedepunktes ab. Nach Entfernung des Wassers zersetzt sich das $\text{CO}(\text{NH}_2)_2$ sofort und $\text{Ca}(\text{NO}_3)_2$ bleibt zurück.

In einem offenen Tiegel wird die obige Umwandlung durch Zersetzung des Types $AB(s) = A(s) + B(g)$, durch "Verdampfung" der Lösung, durch "Trocknung des festen Rückstandes", durch Oberflächenverkrustung usw. kompliziert. Diese Prozesse begleiten bei der herkömmlichen Thermoanalyse die oben erwähnten Vorgänge (Schmelzen—Lösungsbildung—Wasserverlust durch Sieden), wodurch die Interpretation der herkömmlichen Kurven erschwert wird.

Резюме — Обычные термоаналитические кривые термического разложения аддукта $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ мало информативны. Наоборот, на основе квазиизотермических и квазиизобарных термогравиметрических кривых, механизм разложения может быть легко интерпретирован. После плавления комплекса при 60°C образующийся в тигле лабиринтного типа раствор остается постоянным по весу до 135°C. Раствор начинает кипеть при 135°C и по мере потери воды увеличивается точка кипения. Раствор становится насыщенным при 200°C. С этого времени, $\text{Ca}(\text{NO}_3)_2 \cdot \text{CO}(\text{NH}_2)_2$ отделяется при неизменной точке кипения. После отделения воды, мочеви́на разлагается и остается только нитрат

кальция. В открытой тигле, вышеприведенное превращение осложняется разложением типа $AB_{\text{раств.}} = A_{\text{раств.}} + B_{\text{раств.}}$, "выпариванием" раствора, "высушиванием" твердого остатка, образованием поверхностной корки и т.п. При обычном термоанализе последние процессы сопровождаются вышеприведенными процессами: плавление — образование раствора — потеря воды во время кипения, что затрудняет интерпретацию традиционной кривой.