THERMOGRAVIMETRIC INVESTIGATION OF THE DECOMPOSITION OF AQUO-ACIDO COMPLEXES UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS

I. EDTA CHELATES: $M_I M_{II} L.9H_2O$

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Authors investigated with the help of quasi-isothermal and quasi-isobaric thermogravimetry the dehydration process of the EDTA-chelates: $Mg_2L \cdot 9H_2O$, $Mn_2L \cdot 9H_2O$, $MgMnL \cdot 9H_2O$ and $MgCdL \cdot 9H_2O$ (where L^{4-} = EDTA anion). It was established that under the applied special conditions transitionally numerous intermediary products were formed whose existence could not be identified earlier with conventional thermoanalytical methods. Results of the investigations contain a great amount of information material regarding the mechanism, kinetics and equilibrium conditions of the processes.

The study of thermal properties of solid coordination compounds is of particular interest in those cases when the thermal transformation takes place without ligand destruction and can be described in terms of ligand substitution processes. Complexes with volatile ligands are the most convenient models for the investigation of the fundamental theoretical problems involved in the mechanisms of heterogeneous topochemical reactions.

A significant group among these compounds are the metal complexonates, complexes of chelate type with organic ligands, e.g. aminopolycarboxylic acids. They always crystallize from aqueous solutions as hydrates, with water molecules in both their inner and outer spheres. Due to dehydration, accompanied by intermolecular ligand substitution processes, the coordination numbers and the organic ligand dentity may change. Their thermal decompositions consist of various dehydration and anation processes with association or dissociation mechanism [1].

Different thermoanalytical equipments and methods are widely used for investigations in this field [2]. However it may occur that under the conventional experimental conditions it is impossible to separate the decomposition steps and to establish the existence of intermediates [3].

The recently developed methods of quasi-isothermal and quasi-isobaric thermogravimetry [4—7] offered new possibilities for the investigation of metal chelates. We therefore studied the dehydrations of the following compounds: $Mn_2L \cdot 9H_2O$, $Mg_2L \cdot 9H_2O$, $MgMnL \cdot 9H_2O$ and $MgCdL \cdot 9H_2O$ where L^{4-} is the anion of EDTA. These chelates had already been investigated [8—9] with conventional methods.

In our present paper we wish to report our results.

Experimental

Instrumental

The Q-Derivatograph (Hungarian Optical Works, Budapest) was used, which is suitable for thermoanalytical examinations under both conventional [10] and quasi-isothermal and quasi-isobaric conditions [4−7]. The operating principle of the latter measuring technique is that the temperature of the sample is increased so long as no weight changes occur in it, but at the moment a weight change begins a special control system establishes a minute difference between furnace and sample temperatures which ensures that the decomposition takes place at a strictly constant and very low rate (a weight change of about 0.5 mg/min). In the case of reactions leading to equilibrium the consequence of the above heating is the stabilization of the decomposition temperature; in other words, quasi-iso-thermal conditions are created.

Sample holders

The applied sample holders were of different types: a polyplate sample holder [10], a conventional crucible with and without lid, and a labyrinth sample holder [5−7]. The variation of these sample holders ensured that the partial pressure of the gaseous decomposition products, in contact with the solid sample changed in a broad interval. These values were determined experimentally [6, 7] according to the principle illustrated in Fig. 1. Curves 1−4 of this diagram demonstrate the course of the thermal decomposition of calcium carbonate in the four different kinds of sample holders under quasi-isothermal conditions. In the case of quasi-equilibrium, a strict causal correlation exists between the decomposition temperatures indicated by the curves and the values of the partial pressure of the decomposition products in contact with the solid phase. This is given by the relationship between decomposition pressure and temperature. This is also demonstrated in Fig. 1 by curve 5. On the basis of this latter curve it can be established that the decomposition temperature of 660, 710, 780 and 895° correspond to ca. $p_{CO_2} \sim 0.01$, 0.05, 0.2 and 1.0 atm. In the case of other gases (e.g. water vapour) these pressure values, with the exception of the last one, can show minute differences. However within the labyrinth crucible the pressure of the gases, independently of their nature will always be 1 atm.

In the case of the labyrinth crucible [5−7] the gases evolved are forced to leave through a long and narrow channel, and due to this the decomposition takes place in a self-generated atmosphere, i.e. under quasi-isobaric conditions.

Experimental conditions

Curves 1−4 in Figs 2−5 were obtained by applying the quase-isothermal heating programme and the four different types of sample holders. For the sake of comparison, the diagrams also include the TG curves (curves 5 drawn with

dotted lines), which were traced in the conventional way, i.e. by using the open crucible and a heating rate of 5°/min. The TG, DTG and DTA curves in Fig. 6, representing the whole decomposition of the samples up to 1000°, were similarly

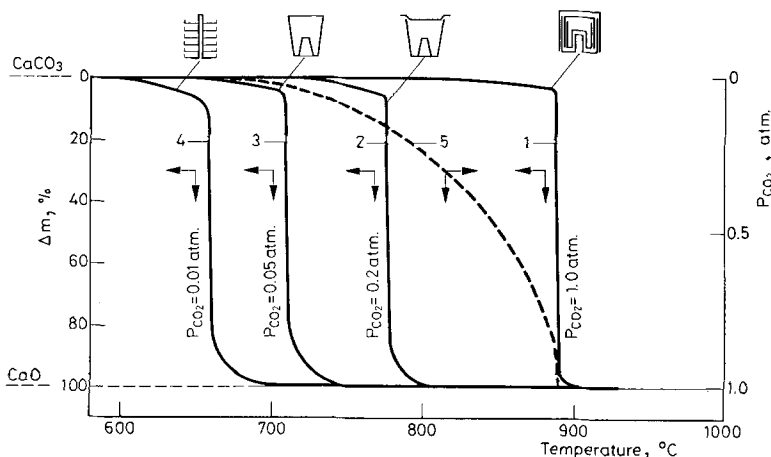Fig. 1. *Relationship between the decomposition temperature of* $CaCO_3$ *and the partial pressure of* CO_2. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1—4: quasi-isothermal. Decomposition rate: curves 1—4: 0.5 mg/min. Relationship between decomposition pressure and temperature: curve 5
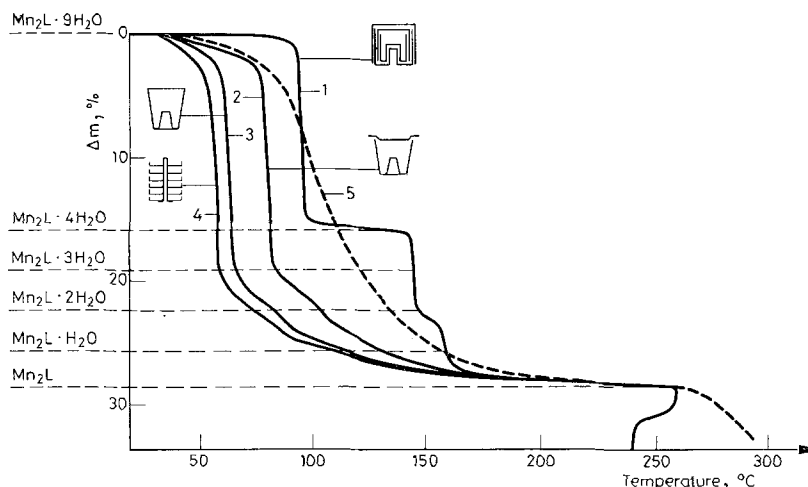

Fig. 2. *Dehydration of* EDTA *chelate* $[Mn(H_2O)_6]$ $[MnL(H_2O)].2H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1—4: quasi-isothermal; decomposition rate: 0.5 mg/min; curve 5: dynamic; heating rate: 5°/min. Weight of sample: ca. 280 mg. Atmosphere: air

Fig. 3. *Dehydration of* EDTA *chelate* $[Mg(H_2O)_6]$ $[MgL(H_2O)].2H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1—4: quasi-isothermal; decomposition rate: 0.5 mg/min; curve 5; dynamic; heating rate: 5°/min. Weight of sample: ca. 250 mg. Atmosphere: air
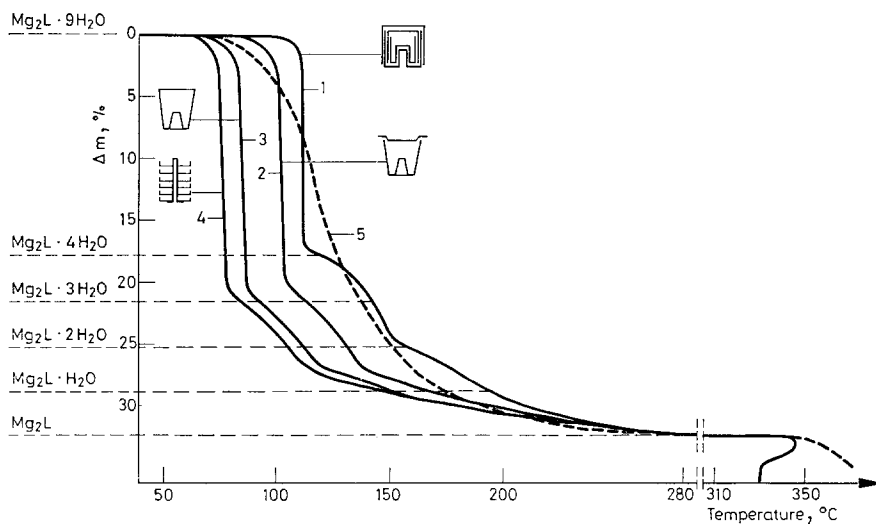

Fig. 4. *Dehydration of* EDTA *chelate* $[Mg(H_2O)_6]$ $[MnL(H_2O].2H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1—4: quasi-isothermal; decomposition rate: 0.5 mg/min; curve 5: dynamic; heating rate: 5°/min. Weight of sample: ca. 250 mg. Atmosphere: air
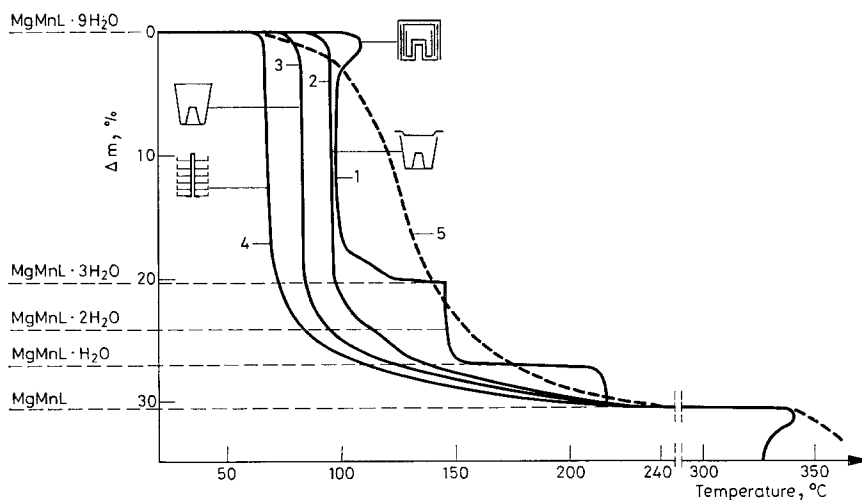
traced under the conventional experimental conditions. All experiments were carried out in the presence of air.
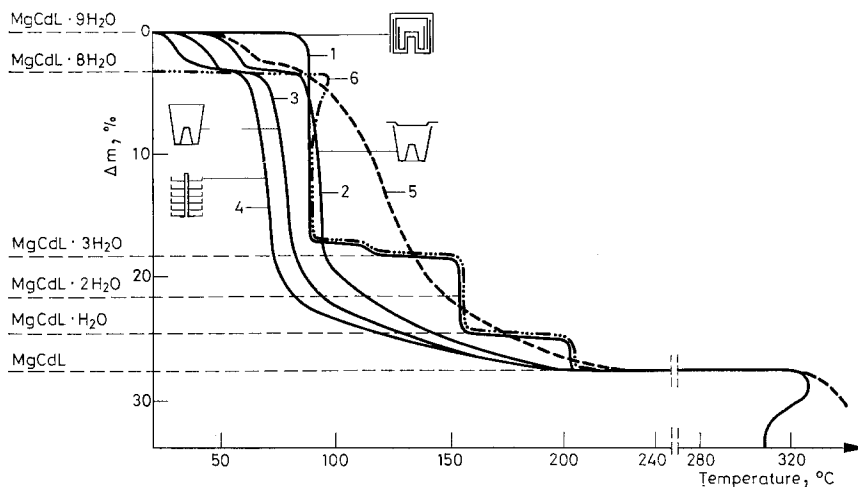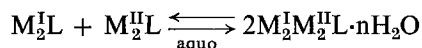

Fig. 5. *Dehydration of* EDTA *chelate* $[Mg(H_2O)_6]$ $[CdL(H_2O)].2H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1—4: quasi-isothermal; decomposition rate: 0.5 mg/min; curve 5: dynamic; heating rate: 5°/min. Weight of sample ca. 290 mg. Atmosphere: air. Curve 6: the conditions of this separate experiment are described in detail in the text

Chemicals

The EDTA chelates were prepared as described earlier [11, 12] by the reactions:

$$H_4L + 2MCO_3 \xrightarrow[\text{aquo}]{} M_2L \cdot nH_2O + 2CO_2 + 2H_2O$$

$$M_2^IL + M_2^{II}L \underset{\text{aquo}}{\overset{}{\rightleftharpoons}} 2M_2^IM_2^{II}L \cdot nH_2O$$

The precipitates obtained upon the simple mixing of the reagents were filtered off, washed with small amounts of water and methanol and dried at room temperature.

Results and discussion

The EDTA chelates $Mg_2L \cdot 9H_2O$, $Mn_2L \cdot 9H_2O$, $MgMnL \cdot 9H_2O$ and $MgCdL \cdot 9H_2O$ are isostructural. They involve two independent coordination spheres:

$$[M_I(H_2O)_6][M_{II}L(H_2O] \cdot 2H_2O$$

Binuclear chelates $M_I L M_{II}$ can be formed only in the course of dehydration. The coordination number of M_{II} is 7.

The identical structures of these chelates mean that their dehydration processes have many common features, but there are also a good many differences between them.
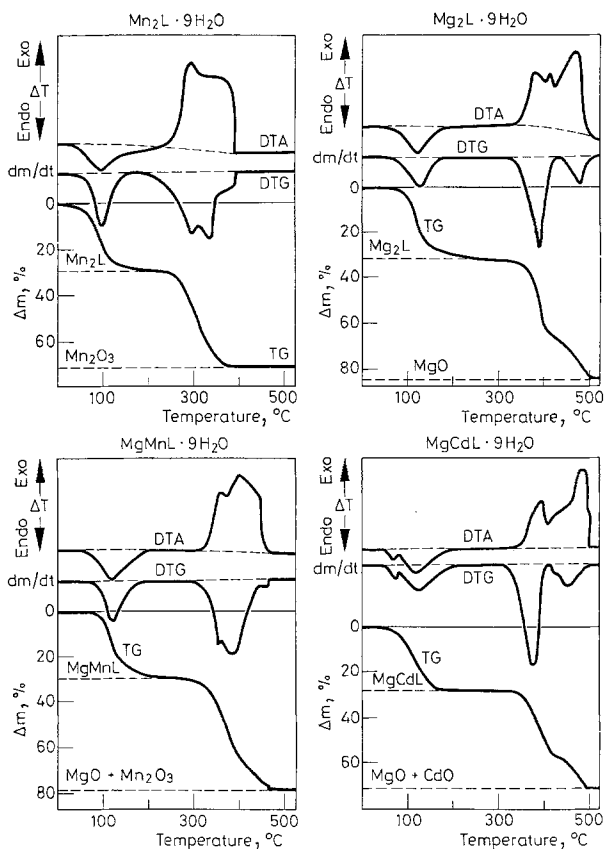

Fig. 6. TG, DTG and DTA *curves of* EDTA *chelates.* Sample holder: crucible without lid. Heating programme: dynamic, 5°/min. Weight of sample: ca. 250 mg. Atmosphere: air

$Mn_2L \cdot 9H_2O$ and $Mg_2L \cdot 9H_2O$

According to curve 1 in Fig. 2, which was obtained by using the quasi-isothermal heating programme and the labyrinth crucible, the decomposition of $Mn_2L \cdot 9H_2O$ occurred in three steps. The first dehydration period took place at 95°, when about 5 moles of water escaped without any change in the temperature. Subsequently, two and then a further two moles of water departed at 145 and 160° respectively, the temperature again not changing significantly.

The decomposition of the sample in the other three sample holders (curves 2, 3 and 4) similarly took place in three steps, but with the differences that the decomposition temperatures decreased in accordance with the lower partial pressure of the solid phase in contact with the gaseous decomposition products, and that the second and third periods of the decomposition did not take place at a constant temperature but in a rather broad temperature interval.

From such and similar changes in the decomposition temperatures, conclusions can be drawn regarding the kinetics and mechanism of the transformation [7]. The Q-Derivatograph does not establish a constant temperature during the examination, but ensures only that the reaction should take place at a very low and constant rate by creating a minute temperature difference between sample and furnace, so that the decomposition rate is governed by the heat transport.

Consequently, if the temperature of the sample spontaneously becomes constant under the conditions mentioned, this means that the transformation takes place during the whole process at the temperature corresponding to the actual pressure of the gaseous products, the decomposition process occurs free from all other side-reactions and under quasi-equilibrium conditions, and finally the composition of the starting material and residue are uniform and well-defined.

However, the stabilization of the temperature also means that the reaction rate is governed only by the heat transport, i.e. a physical process independent of changes occurring in the concentration of the sample, and therefore the reaction is of zero order. For the sake of simplicity, this type of decomposition process will henceforth be called a zero-order reaction.

If the temperature does not become constant, this may have several causes. It may be that the reaction rate is governed by another, concentration-dependent and slower physical process than the heat transport (e.g. nucleus formation, nucleus growth, gas diffusion within the grains, etc.). The transformation also takes place at a non-constant temperature but in a more or less broad temperature interval in the following cases:

when the transformation is the resultant of two or more partly overlapping reactions leading to equilibrium;

when the intermediate is unstable under the given conditions; and
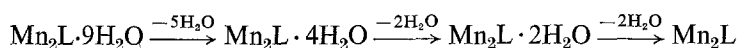
when the reaction does not lead to equilibrium.

Consequently, the processes mentioned cannot be qualified as zero-order reactions.

Returning to the analysis of Fig. 2, it can be stated that on the above basis the first period of the decomposition took place with zero order, since the temperature of the sample stayed strictly (curve 1) or practically (curves 2−4) constant. However, the second and third periods of the decomposition took place with zero order only in the labyrinth crucible (curve 1). In the case of the three other sample holders the reaction order differed from zero since the reactions took place in a broad temperature interval, probably because the intermediates were not stable under the given conditions.
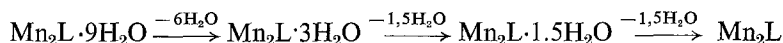
However, there is not only a difference between curve 1 and curves 2, 3 and 4

in the course of the decomposition but also in the composition of the intermediates. Curve 1 unambiguously proves the formation of $Mn_2L \cdot 4H_2O$ and $Mn_2L \cdot 2H_2O$ as intermediates, while curves 2, 3 and 4 uniformly show two inflexion points corresponding to the compositions $Mn_2L \cdot 3H_2O$ and $Mn_2L \cdot 1,5H_2O$. This can be explained by the variation of the sample holders used since the pressure of the water vapour decreased below $p_{H_2O} = 1$ atm, in the case of curves $2-4$ and due to this the mechanism of decomposition of the chelate probably changed too. The two possible modes of thermal decomposition may be indicated by the formation of the following intermediates:

if $p_{H_2O} = 1$ atm (curve 1):

$$Mn_2L \cdot 9H_2O \xrightarrow{-5H_2O} Mn_2L \cdot 4H_2O \xrightarrow{-2H_2O} Mn_2L \cdot 2H_2O \xrightarrow{-2H_2O} Mn_2L$$

if $p_{H_2O} < 1$ atm (curves 2, 3 and 4):

$$Mn_2L \cdot 9H_2O \xrightarrow{-6H_2O} Mn_2L \cdot 3H_2O \xrightarrow{-1,5H_2O} Mn_2L \cdot 1.5H_2O \xrightarrow{-1,5H_2O} Mn_2L$$

The decomposition of $Mg_2L \cdot 9H_2O$ (Fig. 3) was analogous in every respect with that of $Mn_2L \cdot 9H_2O$, with the only exception that the temperatures of the second and third periods did not stabilize even when the labyrinth crucible was used. The possible explanation of this phenomenon is that the intermediates $Mg_2L \cdot 4H_2O$ and $Mg_2L \cdot 2H_2O$ are not stable even in a water vapour atmosphere of $p_{H_2O} = 1$ atm, their decomposition beginning immediately after their formation.

$MgMnL \cdot 9H_2O$ and $MgCdL \cdot 9H_2O$

Curve 1 in Fig. 4 shows that under the given conditions the original substance decomposed at 105°; the intermediate $MgMnL.3H_2O$ decomposed at 150° and $MgMnL.H_2O$ at 220°. All three processes led to equilibrium and were reactions of zero order, since except for the initial period of the decomposition the temperature of the sample did not change during the decomposition processes. It was unusual that in the present case the substance first overheated to 115° and subsequently cooled down slowly to 105°. This phenomenon can probably be explained by delayed nucleus formation [7, 8]. No signs can be found in curves 2, 3 and 4 which would indicate the formation of the above-mentioned intermediates.

According to curve 1 in Fig. 5, this chelate too decomposed in three successive zero-order reactions leading to equilibrium while $MgCdL \cdot 3H_2O$ and $MgCdL \cdot H_2O$ were formed. The decompositions took place at 90, 160 and 210° respectively. However, in this case curves 2, 3 and 4 also deserve special attention. As these curves demonstrate, in a water vapour atmosphere lower than 1 atm, the decomposition took place in a different way. First $MgCdL \cdot 8H_2O$ was formed as intermediate, which started to decompose at a temperature higher by about 25°. While the temperature increased slowly, 5 moles of water departed. The release

of the last 3 moles of water was protracted over a temperature interval of about 100°. Accordingly, the decomposition mechanisms were different in the cases of curve 1 and curves 2, 3 and 4. This can perhaps explain the strange contradiction that in the first period of the decomposition the sample temperature assumed a lower value in the labyrinth crucible, in spite of the higher partial pressure of the water vapour (curve 1) than in the covered crucible (curve 2). However, this contradiction is only an apparent one since, if a decomposition process may take place in different ways, with the formation of different intermediates, then it is quite justified that the decomposition temperatures should also differ from one another. We have encountered similar phenomena earlier.

The question may arise as to how the intermediate $MgCdL \cdot 8H_2O$ would decompose, if it were further investigated in the labyrinth crucible and under quasi-isothermal heating conditions. To settle this problem we heated the sample up to 60° in the open crucible, when according to curve 3 the material lost 1 mole of water. The heating was then stopped and by lifting the furnace the reaction was frozen. Thereafter the cold material was brought into the labyrinth sample holder and was further investigated as in the case of curve 1. As a result of our examination we obtained curve 6. According to this curve the sample was transiently overheated to 110° and thereafter gradually cooled down to 90° while about 2 moles of water escaped. From this point on, the courses of curves 1 and 6 were identical. Consequently, the decomposition of $MgCdL \cdot 8H_2O$, except for the initial period, took place in the same way as if we had started from $MgCdL \cdot 9H_2O$. The temperature overheating of the sample cannot be explained here by nucleus formation, since its inner structure was no longer intact, but rather by the supposition that a structural rearrangement took place gradually within the sample. A structure was formed which corresponded to the changed conditions, namely to the presence of water vapour at 1 atm, and which is in accordance with the structure formed from $MgCdL \cdot 9H_2O$ when this attained this degree of thermal decomposition. Thus it is understandable that subsequently the two curves coincided.

Curves 5 in Figs. 2–5 were obtained in the conventional way, and it can be seen that none of the many aspects and changes described above could be guessed on their basis.

The TG, DTG and DTA curves in Fig. 6 demonstrate the complete decomposition processes of the investigated compounds. According to these curves the decomposition of the EDTA anions of these chelates, similarly as for other complex organic materials, is a very involved process which is difficult to interpret; e. g. the exothermic peaks of the DTA curve indicate beside the decomposition oxidation and combustion processes too. The weight changes up to 550° and the end-products of the decomposition were always in accordance with our expectations.

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RÉSUMÉ — On a étudié par thermogravimétrie quasi-isotherme/quasi-isobare le processus de la déshydratation des chélates suivants de l'EDTA: $Mg_2L \cdot 9H_2O$, $Mn_2L \cdot 9H_2O$, $MgMnL \cdot 9H_2O$ et $MgCdL \cdot 9H_2O$ ($L^{-4} =$ l'anion EDTA). Les conditions spéciales utilisées ici établissent que de nombreux produits intermédiaires se forment transitoirement. Leur existence n'avait pu être identifiée auparavant par les méthodes thermoanalytiques conventionnelles. Les résultats de la présente étude constituent une source importante de renseignements sur le mécanisme, la cinétique et les conditions d'équilibre des processus étudiés.

ZUSAMMENFASSUNG — Der Dehydratationsvorgang der ÄDTA-Chelate $Mg_2L \cdot 9H_2O$, $Mn_2L \cdot 9H_2O$, $MgMnL \cdot 9H_2O$ und $MgCdL \cdot 9H_2O$ ($L^{-4} =$ ÄDTA-Anion) wurde mit Hilfe der quasi isothermen — quasi isobaren thermogravimetrischen Methode untersucht. Es wurde gefunden, dass unter den angewandten speziellen Versuchsbedingungen vorübergehend Intermediäre entstehen, deren Existenz mit den konventionellen thermoanalytischen Methoden nicht nachgewiesen werden konnte. Die Versuchsergebnisse bilden ein bedeutendes Informationsmaterial in bezug auf Mechanismus, Kinetik und Gleichgewichtsverhältnisse der untersuchten Vorgänge.

Резюме — С помощью квази-изотермической и квази-изобарной термогравиметрии, авторы исследовали процесс дегидратации ЕДТА-хелатов: $Mg_2L \cdot 9H_2O$, $Mn_2L \cdot 9H_2O$, $MgMnL \cdot 9H_2O$ и $MgCoL \cdot 9H_2O$ (где $L^{-4} =$ анион ЕДТА). Было установлено, что при использовании специальных условий образовывались многочисленные переходные промежуточные продукты, существование которых ранее не было идентифицировано обычными термоаналитическими методами. Результаты исследований содержат большое количество информационного материала относительно механизма, кинетики и равновесий этого процесса.