

TG AND EGA INVESTIGATIONS OF THE DECOMPOSITION  
OF SOME METAL AMMONIUM PHOSPHATE MONOHYDRATES  
BY MEANS OF THE DERIVATOGRAPH UNDER CONVENTIONAL  
AND QUASI-ISOTHERMAL–QUASI-ISOBARIC CONDITIONS

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The thermal decomposition of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  were investigated under conventional and under quasi-isothermal–quasi-isobaric conditions. The experiments were carried out with a Derivatograph suitable for performing simultaneous TG and EGA examinations. It was found that the thermal decompositions of the four compounds each consist of two partial processes: the departure of the water of crystallization, and the subsequent inseparable escape of the ammonia and constitution water. Depending on the experimental conditions, the two processes more or less overlap. The relatively best separation of the two processes can be attained by using quasi-isothermal and quasi-isobaric conditions.

In our preceding paper on the decomposition of magnesium ammonium phosphate hexahydrate [1] it was mentioned that  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  is formed as an intermediate. With regard to the decomposition of this latter compound the following questions arose:

What partial reactions does this process include?

In what way are the individual partial reactions influenced by the experimental conditions?

In what way do the overlapping partial reactions change with the experimental conditions?

In what way do the overlapping partial reactions influence the shape of the TG curve?

For the sake of comparison examinations were made on not only  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  obtained in a thermal way, but also  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  prepared by precipitation, as well as  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ , the thermal decompositions of which were investigated earlier [3]. In the present paper the results of these investigations are reported.

### Experimental

The method, the equipment and the experimental conditions applied were described in detail in the preceding paper [1].

The thermal preparation of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  was performed by using the quasi-isothermal heating programme and the labyrinth sample holder, in which

$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  was heated up to  $150^\circ$ . The heating was then interrupted by the furnace being moved rapidly down, whereupon the reaction process stopped suddenly. Our earlier investigations showed (see curve 1 in Fig. 3 in [1]) that under these conditions the  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  yielded  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ , the weight of which remained quite stable between  $90$  and  $230^\circ$ . It was also shown that the compound lost ca. 5% of its ammonia content during the heating process. This ammonia loss was taken into consideration in the evaluation of the results.

The precipitation of  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  was carried out according to Winkler [2], with the difference that the solution was kept at the boiling point [3] during the process, instead of at  $70^\circ$ . The other three compounds investigated,  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ , were prepared in the same way.

Figs 1, 4, 6, 8 and 10 show the TG curves of the above compounds, obtained partly under quasi-isothermal conditions (curves 1–4), and partly with the conventional dynamic heating rate of  $10^\circ/\text{min}$  (curves 5–8). The experiments were carried out with four different kinds of sample holders: the labyrinth sample holder (curves 1 and 5), the conventional crucible of the Derivatograph with lid (curves 2 and 6), the same crucible without lid (curves 3 and 7) and the poly-plate sample holder (curves 4 and 8).

The  $\text{NH}_3$  curve recorded beside the TG curve in Fig. 2 shows how in the given case the amount of ammonia determined by thermo-gas-titration (TGT) changes as a function of temperature. All the other curves were obtained by calculation based upon the  $\text{NH}_3$  curve, assuming that, simultaneously with the departure of ammonia, water of crystallization ( $\text{H}_2\text{O}_{(\text{cr})}$ ) and water of constitution ( $\text{H}_2\text{O}_{(\text{co})}$ ) are also released. With the help of this Figure we wish to demonstrate that by calculation a curve can be found which is the most congruent with the TG curve. Of the many possibilities, only that complex process consisting of several partial reactions can be regarded as probable, the curve of which is congruent with the TG curve. Thus, for example, we could hardly obtain a curve which could be brought into accordance with the specially shaped TG curve of  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  (curve 1 in Fig. 11) if the water of crystallization, water of constitution and ammonia escaped in different amounts or in a different way from that shown by curve  $\text{NH}_3 + 0.1 \text{H}_2\text{O}_{(\text{cr})} + 0.5 \text{H}_2\text{O}_{(\text{co})}$  in Fig. 11.

In Figs 3, 5, 7, 9 and 11 the TG curves numbered 1, 4, 5 and 8 are shown along with the curve  $\text{NH}_3 + n \text{H}_2\text{O}_{(\text{cr})} + 0.5 \text{H}_2\text{O}_{(\text{co})}$  calculated on the basis of the amount of ammonia determined by thermo-gas-titrimetry (TGT), and the  $n \text{H}_2\text{O}_{(\text{cr})}$  curve constructed by difference calculation from the TG and TGT curves.

In the TG curves of Figs 4 and 5 a weight loss of about 1.5% can be observed in the vicinity of  $100^\circ$ , which indicates that the compound also contained  $\text{MgNH}_4\text{PO}_4 \cdot n + 1 \text{H}_2\text{O}$  as a slight contamination.

### Results and discussion

First of all it can be established that the thermal decompositions of each of the five compounds are of the same character. In the decomposition processes of these compounds two main periods could be distinguished (Figs 1, 4, 6, 8 and 10). In every case investigated the first period of the decomposition, in contrast to the second one, took place without significant changes in the temperature, about 50–80% of the volatile components being lost. The decomposition always began with the departure of the water of crystallization.

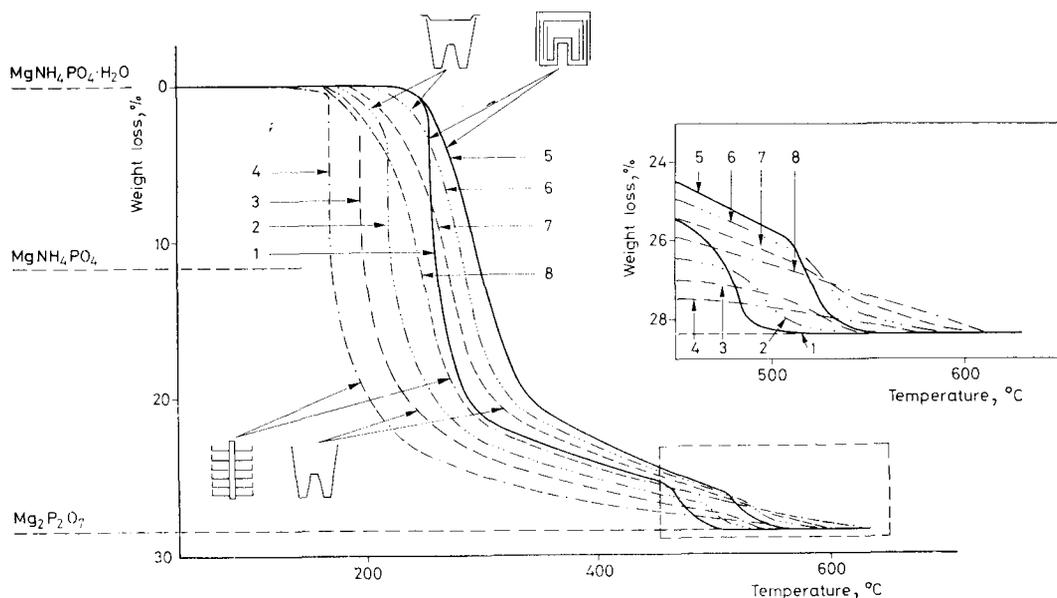


Fig. 1. TG curves of  $MgNH_4PO_4 \cdot H_2O$  prepared by heating recorded with quasi-isothermal (1–4) and dynamic (5–8) heating, using labyrinth (1 and 5), covered crucible (2 and 6), uncovered crucible (3 and 7) and polyplate (4 and 8) sample holders

The second period of the decomposition took place in a broad temperature interval extending over several hundred degrees. For this period the departure of ammonia and water of constitution is characteristic.

It was observed that the first period of the decomposition took place in a shorter temperature interval if not the dynamic (curves 5–8), but the quasi-isothermal heating (curves 1–4) programme was applied.

The same relationship was found in every case between the transformation temperature and the shape of the sample holder, i.e. the composition of the gaseous atmosphere in the vicinity of the sample. The sequences of the transformation temperatures, depending on the experimental conditions, are as follows for the

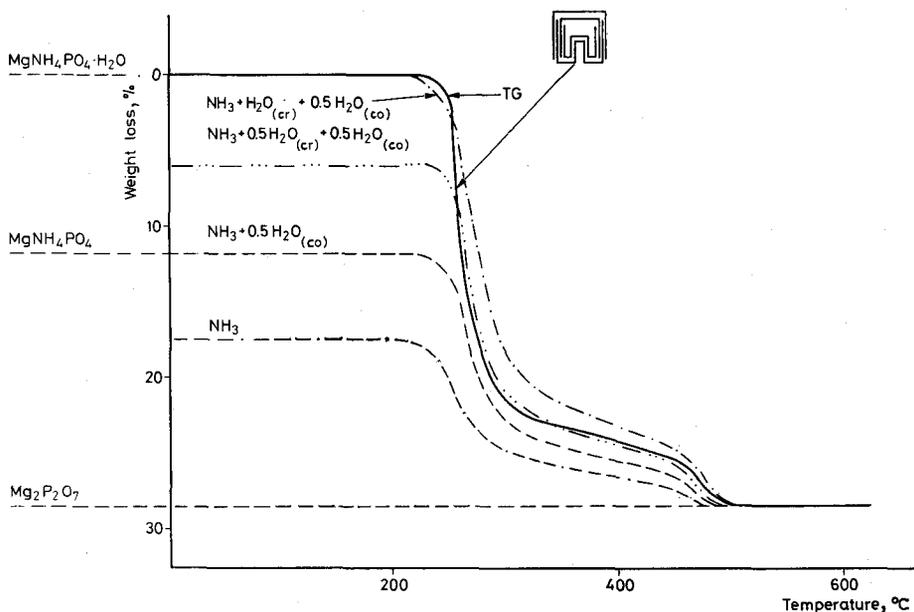


Fig. 2. TG and TGT curves of  $MgNH_4PO_4 \cdot H_2O$  prepared by heating recorded with quasi-isothermal heating and labyrinth sample holder. The titration curve of  $NH_3$  shows the course of the release of ammonia. The calculated  $NH_3 + 0.5 H_2O_{(co)}$  and  $NH_3 + n H_2O_{(cr)} + 0.5 H_2O_{(co)}$  curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitution water

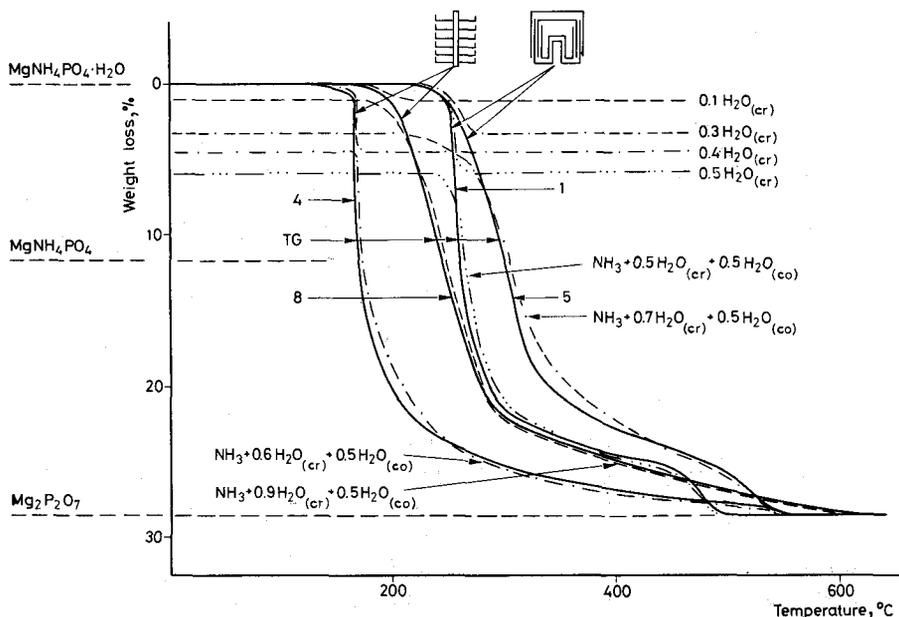


Fig. 3. TG and TGT curves of  $MgNH_4PO_4 \cdot H_2O$  prepared by heating recorded with quasi-isothermal (1 and 4) and dynamic (5 and 8) heating, using labyrinth (1 and 5) and polyplate (4 and 8) sample holders. The calculated  $n H_2O_{(cr)}$  curves show the course of the release of crystal water. The  $NH_3 + n H_2O_{(cr)} + 0.5 H_2O_{(co)}$  curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitution water

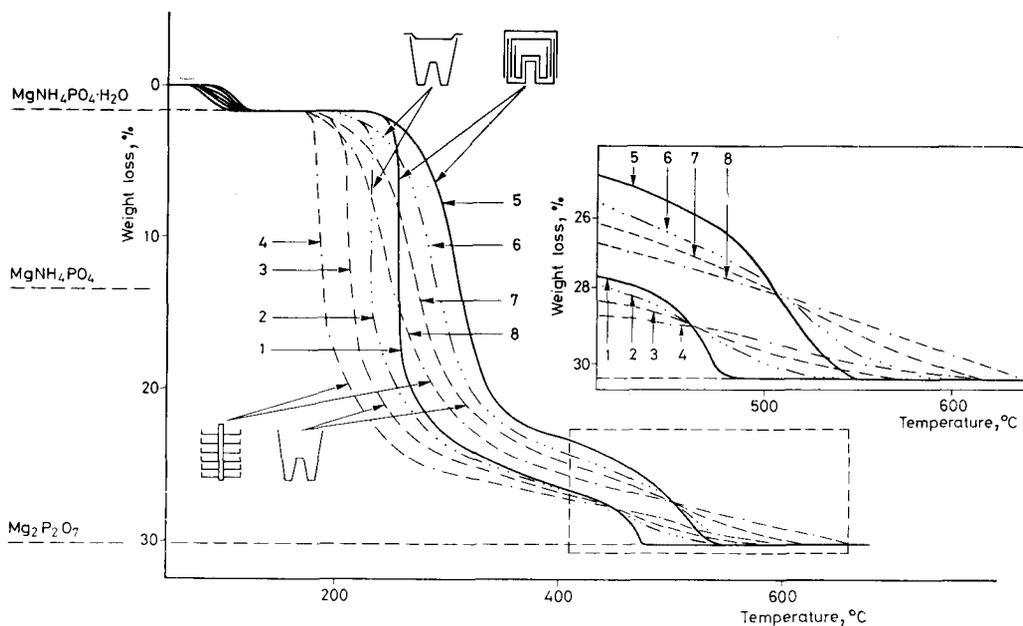


Fig. 4. TG curves of  $MgNH_4PO_4 \cdot H_2O$  prepared by precipitation recorded with quasi-isothermal (1–4) and dynamic (5–8) heating, using labyrinth (1 and 5), covered crucible (2 and 6), uncovered crucible (3 and 7) and polyplate (4 and 8) sample holders

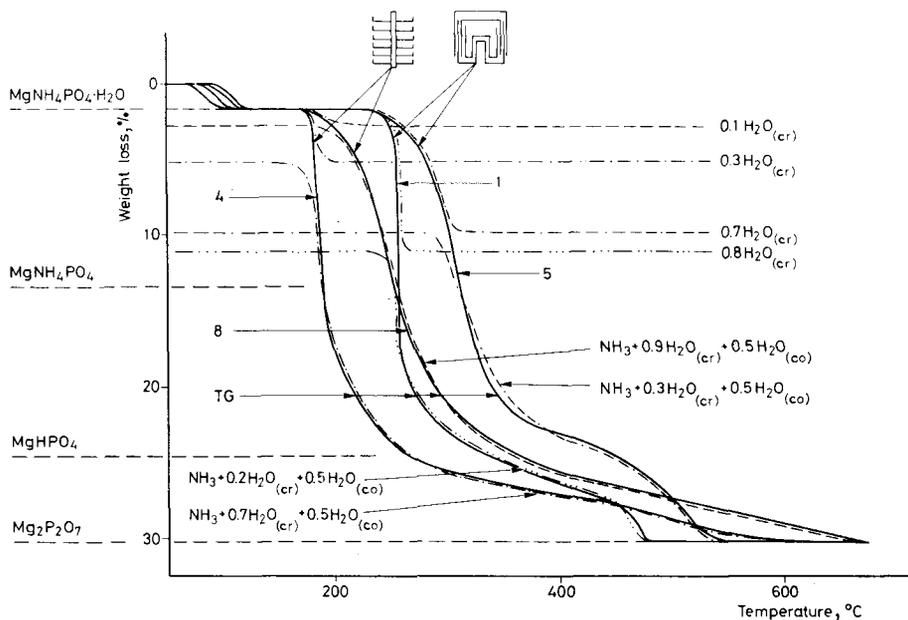


Fig. 5. TG and TGT curves of  $MgNH_4PO_4 \cdot H_2O$  prepared by precipitation recorded with quasi-isothermal (1 and 4) and dynamic (5 and 8) heating, using labyrinth (1 and 5) and polyplate (4 and 8) sample holders. The calculated  $n H_2O_{(cr)}$  curves show the course of the release of crystal water. The  $NH_3 + n H_2O_{(cr)} + 0.5 H_2O_{(co)}$  curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitution water

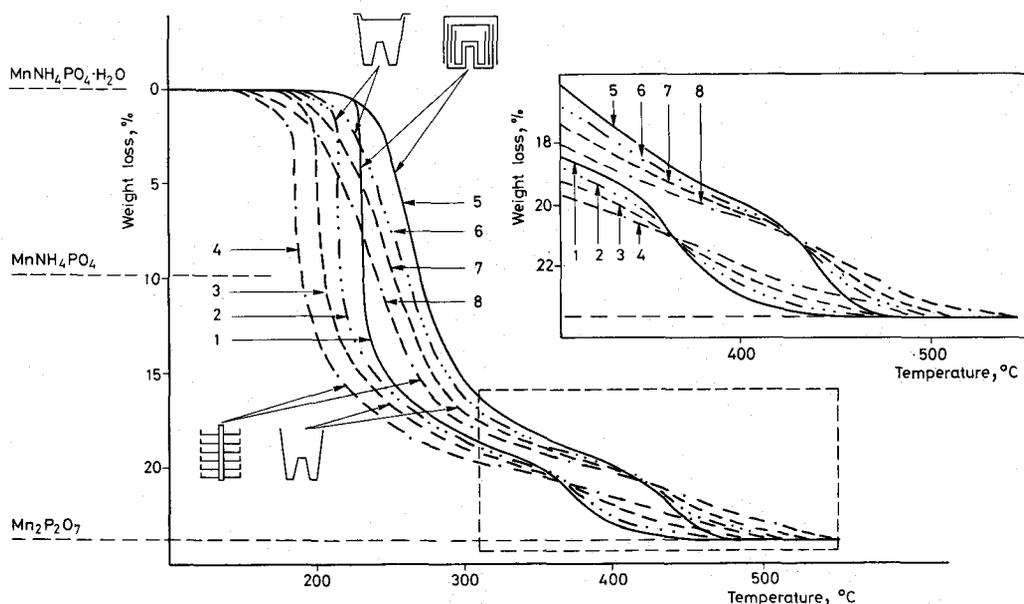


Fig. 6. TG curves of  $MnNH_4PO_4 \cdot H_2O$  recorded with quasi-isothermal (1–4) and dynamic (5–8) heating, using labyrinth (1 and 5), covered crucible (2 and 6), uncovered crucible (3 and 7) and polyplate (4 and 8) sample holders

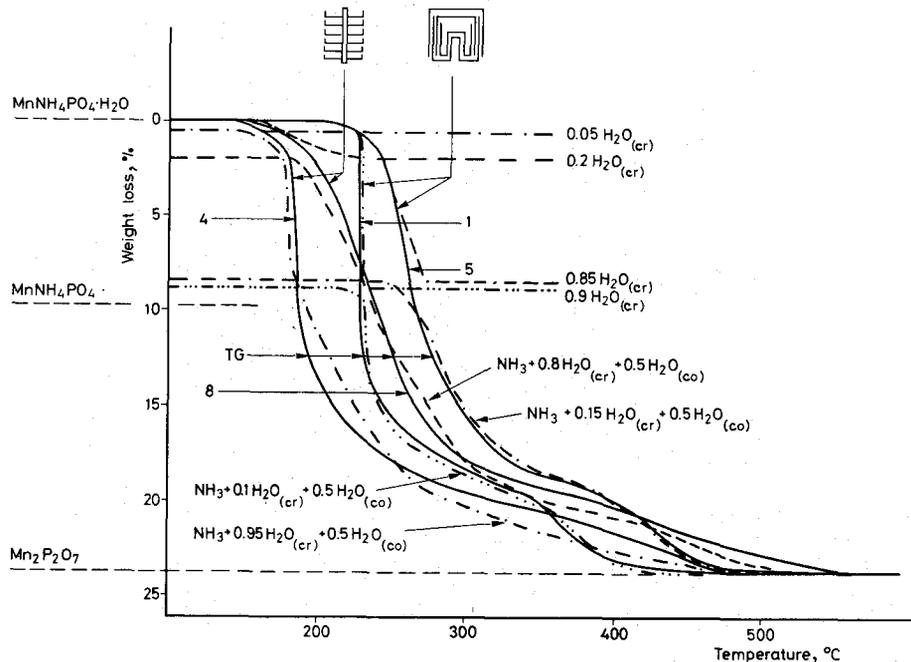


Fig. 7. TG and TGT curves of  $MnNH_4PO_4 \cdot H_2O$  recorded with quasi-isothermal (1 and 4) and dynamic (5 and 8) heating, using labyrinth (1 and 5) and polyplate (4 and 8) sample holders. The calculated  $n H_2O_{(cr)}$  curves show the course of the release of crystal water. The  $NH_3 + n H_2O_{(cr)} + 0.5 H_2O_{(co)}$  curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitutional water

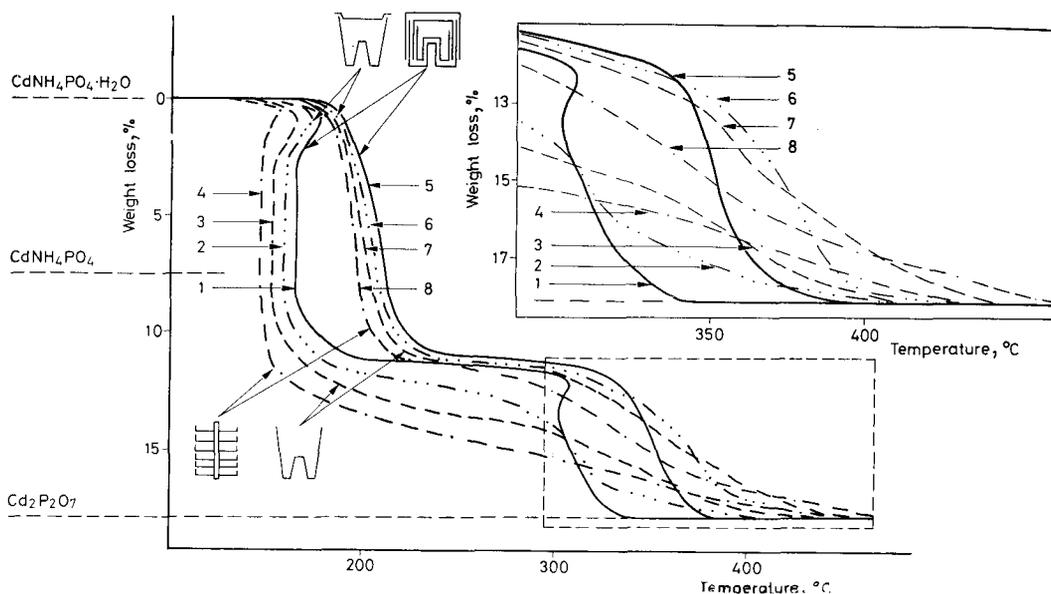


Fig. 8. TG curves of  $CdNH_4PO_4 \cdot H_2O$  recorded with quasi-isothermal (1–4) and dynamic (5–8) heating, using labyrinth (1 and 5), covered crucible (2 and 6), uncovered crucible (3 and 7) and polyplate (4 and 8) sample holders

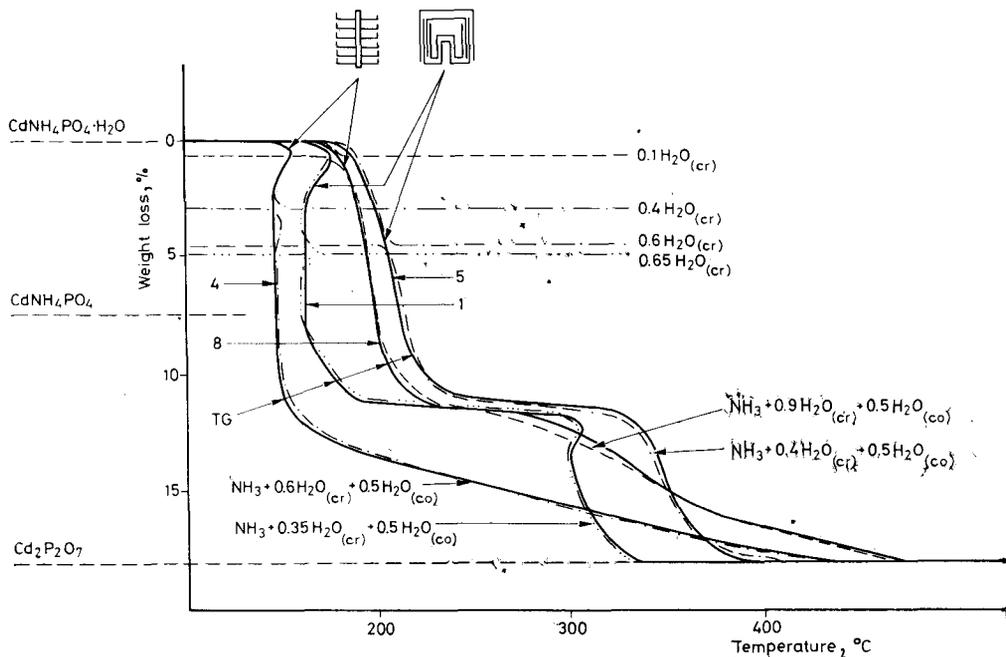


Fig. 9. TG and TGT curves of  $CdNH_4PO_4 \cdot H_2O$  recorded with quasi-isothermal (1 and 4) and dynamic (5 and 8) heating, using labyrinth (1 and 5) and polyplate (4 and 8) sample holders. The calculated  $n H_2O_{(cr)}$  curves show the course of the release of crystal water. The  $NH_3 + n H_2O_{(cr)} + 0.5 H_2O_{(co)}$  curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitutional water

various curves:  $1 > 2 > 3 > 4$  and  $5 > 6 > 7 > 8$ . Hence, the transformation temperature decreased in accordance with the decrease of the partial pressure of the gaseous decomposition products. From this it follows that the dehydration of the monohydrate is a process leading to equilibrium.

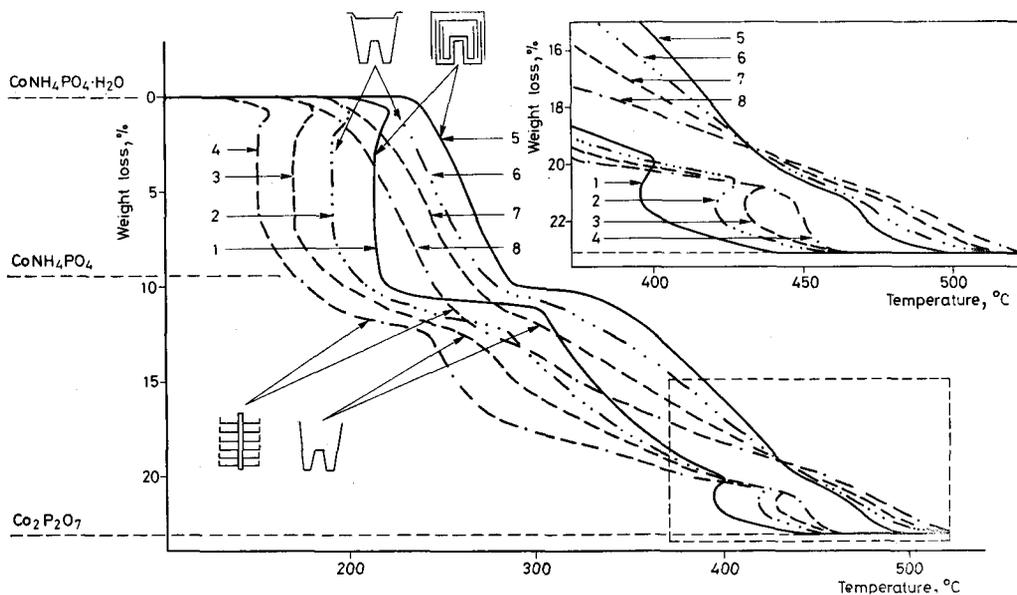


Fig. 10. TG curves of  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  recorded with quasi-isothermal (1–4) and dynamic (5–8) heating, using labyrinth (1 and 5), covered crucible (2 and 6), uncovered crucible (3 and 7) and polyplate (4 and 8) sample holders

The conclusion that the decomposition begins with the departure of the water of crystallization is supported by the good agreement of the TG and  $\text{NH}_3 + n \text{H}_2\text{O}_{(\text{cl})} + 0.5 \text{H}_2\text{O}_{(\text{co})}$  curves (Figs 2, 3, 5, 7, 9 and 11), i.e. by the  $n \text{H}_2\text{O}_{(\text{cr})}$  curve constructed as difference between the above two curves.

On comparison of these curves it can be observed that the two decomposition periods, i.e. the departure of the water of crystallization and the simultaneous release of ammonia and water of constitution, can be better separated under the conditions of the quasi-isothermal, than under the dynamic heating programme, and a better separation can similarly be attained, by using the labyrinth instead of the polyplate sample holder.

Passing to the interpretation of the second period of the decomposition (Figs 1, 4, 6, 8, and 10), it can be established that the process resulting in the release of ammonia and water of constitution, does not lead to equilibrium. The cause of this, as already discussed [1], may be either that the different metal pyro-

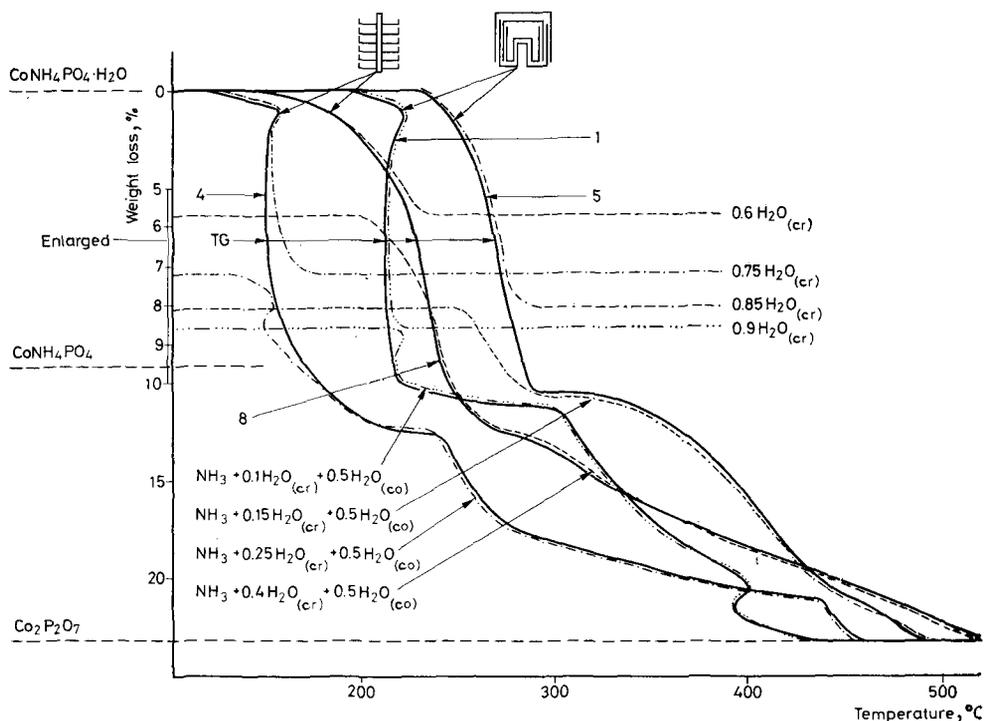


Fig. 11. TG and TGT curves of  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  recorded with quasi-isothermal (1 and 4) and dynamic (5 and 8) heating, using labyrinth (1 and 5) and polyplate (4 and 8) sample holders. The calculated  $n \text{H}_2\text{O}_{(\text{cr})}$  curves show the course of the release of crystal water. The  $\text{NH}_3 + n \text{H}_2\text{O}_{(\text{cr})} + 0.5 \text{H}_2\text{O}_{(\text{co})}$  curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitutional water

phosphates, similarly to  $\text{Mg}_2\text{P}_2\text{O}_7$ , are of a glassy structure and form a phase through which the gases can scarcely diffuse, or that this partial reaction is in itself a complex polycondensation process.

Figs 1, 4, 6, 8 and 10 show that depending on the partial pressure of the gaseous products, the sequence in the course of the TG curves, not only discontinues shortly before the end of the decomposition but, after the intersection of the curves, takes a reverse turn without exception. So far no acceptable explanation of this extraordinary phenomenon has been found.

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RÉSUMÉ — Les auteurs ont étudié la décomposition thermique de  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  et  $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  dans les conditions conventionnelles ainsi que dans des conditions presque isothermes et presque isobares. Les expériences ont été effectuées à l'aide d'un "Derivatograph" qui se prête aux études simultanées par TG et AGE. La décomposition thermique des quatre composés s'effectue en deux processus élémentaires à savoir le départ de l'eau de cristallisation auquel succède l'élimination de l'ammoniac et de l'eau de constitution, simultanée et indissociable. Suivant les conditions expérimentales, ces deux processus se recouvrent plus ou moins. C'est en opérant dans des conditions presque isothermes et presque isobares que l'on parvient à séparer relativement bien les deux processus.

ZUSAMMENFASSUNG — Die Autoren untersuchten die thermische Zersetzung von  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  und  $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  unter konventionellen und quasi isothermischen—quasi-isobaren Bedingungen. Die Versuche wurden in einem zur simultanen Ausführung von TG- und EGA-Prüfungen geeigneten Derivatograph-Typ durchgeführt. Die Autoren fanden, daß die thermische Zersetzung der vier Verbindungen aus zwei Teilvorgängen besteht, und zwar aus dem Abspalten des Kristallisationswassers und dem nachfolgenden untrennbaren Entweichen des Ammoniaks und des Konstitutionswassers. Den Versuchsbedingungen entsprechend überlappen einander die beiden Vorgänge mehr oder weniger. Die verhältnismäßig beste Trennung der beiden Vorgänge kann durch quasi isothermische und quasi isobare Bedingungen erzielt werden.

Резюме — Авторы исследовали термическое разложение  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  и  $\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  при условных и квази-изотермических и квази-изобарных условиях. Эксперименты были выполнены с помощью дериватографа, приспособленного для одновременного выполнения TG и ГА исследований. Авторы нашли, что термическое разложение этих четырех соединений состоит из двух процессов, а именно: выделение кристаллизационной воды и последующее совместное выделение аммиака и воды. Согласно экспериментальным условиям эти два процесса более или менее перекрываются. Относительно наилучшее разделение этих двух процессов может быть достигнуто использованием квази-изотермических и квази-изобарных условий.