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

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An investigation was made of the thermal decomposition of $MgNH_4PO_4 \cdot 6H_2O$ under conventional and under quasi-isothermal—quasi-isobaric conditions. The experiments were carried out with a Derivatograph-suitable for simultaneous TG and EGA examinations. It was found that the thermal decomposition of $MgNH_4PO_4 \cdot 6H_2O$ consists of three, more or less overlapping partial processes. First 5 moles, then 1 mole of water of crystallization depart, and finally, strictly simultaneously and in an inseparable way, the departure of the ammonia and water of constitution takes place. The three processes can be separated best under quasi-isothermal and quasi-isobaric conditions.

The thermal decomposition of magnesium ammonium phosphate hexahydrate has been studied by many thermoanalysts [1–7], including ourselves [9–10]. We found that the course of the decomposition depends greatly on the experimental conditions. For example, the two-step decomposition process (curves 6 and 7 in Fig. 3) became a one-step process (curve 8 in Fig. 3) solely because the shape of the sample holder used was different [10]. However, only now have we succeeded in finding a reliable explanation of this phenomenon.

Our research was aimed at providing to the following questions:

Of what elementary partial reactions is the decomposition process composed?

What is the course of these partial reactions?

Why and how are these elementary processes influenced by the various experimental conditions?

The possibility of the following partial reactions has to be considered:

$$MgNH_4PO_4 \cdot 6H_2O = MgNH_4PO_4 \cdot (6\text{-}n)H_2O + n\,H_2O$$

where n may have any value from 1 – 6.

This process could be a one or more step reaction involving the possibility of many partial processes.

$$MgNH_4PO_4 = MgHPO_4 + NH_3$$

$$2\,MgHPO_4 = Mg_2P_2O_7 + H_2O$$

Experimental

To study the above questions it seemed appropriate to apply our thermo-gas-titrimetric method [11–14]. With the help of this technique the change in the amount of the different gaseous decomposition products evolved can be followed, i.e. the courses of the individual partial reactions can be determined separately. As Fig. 1 demonstrates, this is achieved in the following way.

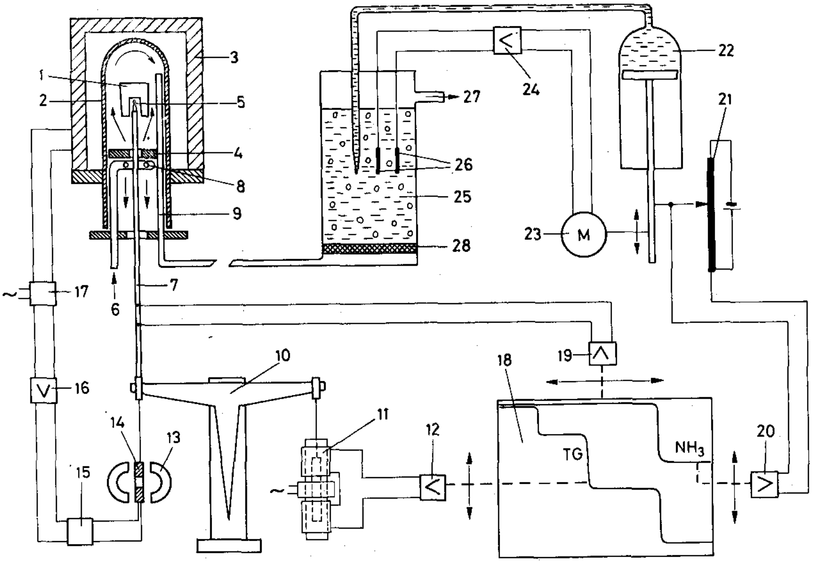

Fig. 1. *Derivatograph.* 1. sample; 2. quartz bulb; 3. furnace; 4. diaphragm; 5. thermocouple, 6. carrier-gas tube; 7. corundum tube; 8. carrier-gas inlet; 9. gas outlet; 10. balance; 11. differential transformer; 12. amplifier for TG-signal; 13. magnet; 14. coil; 15. sensor of DTG-signal; 16. amplifier-relay; 17. heating regulator; 18. recorder; 19. amplifier for T-signal; 20. amplifier for TGT-signal; 21. potentiometer; 22. automatic burette; 23. motor of the automatic burette; 24. pH-meter — amplifier; 25. absorber; 26. electrodes; 27. gas exhaust; 28. glass filter

The Derivatograph, modified for this purpose, measures in the conventional way the changes taking place in the temperature (T curve) and in the weight (TG-curve) of the sample. In order for the gaseous decomposition products to be collected quantitatively, the sample is surrounded by a silica bell (2). The gaseous decomposition products are transported with the aid of a carrier gas (6) into the absorption vessel (25). Here the gases, in the present case ammonia, are absorbed in water. A potential difference develops between the pH-measuring electrodes (26) dipping into the solution, and this actuates an automatic burette (22, 23). By means of this, the absorption liquid is continuously titrated with an appropriate reagent, in the present case hydrochloric acid solution. In the thermo-gas-titrimetric curve the changes in volume of titrant consumed are recorded by means of a potentiometer (21), an amplifier (20) and a recorder (18). Consequently, the curve shows the course of the partial reaction leading to the liberation of the gas in question.

In order to create very different experimental conditions, we used two kinds of heating programmes and four different types of sample holders.

Besides the application of the conventional dynamic heating rate of 10°/min (curves 5 – 8 in Fig. 3), the use of the quasi-isothermal heating [15 – 16] programme (curves 1 – 4 in Figs 3 – 5) proved especially successful.

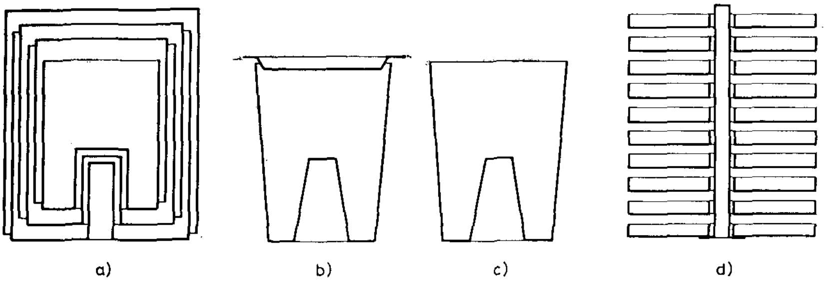

Fig. 2. *Sample holders*: a) labyrinth; b) crucible with lid; c) crucible without lid; d) polyplate

In this latter method the temperature of the furnace (3 in Fig. 1) is raised by the programme regulator (17) in the conventional way at a constant rate (3 – 10°/min) until the sample begins to decompose. In the case of even a minute variation in the rate of change of weight, the electric signal induced in the DTG coil (14) reaches a threshold value. Due to this the electric sensor (15) and amplifier-relay (16) immediately cut out the voltage of the heating current. As a consequence, the temperature decreases, the rate of the reaction is reduced, and the electric signal of the DTG coil drops under the threshold value, whereupon the heating starts again. The process described lasts only a few seconds and is repeated innumerable times until the end of the reaction.

In contrast with examinations carried out under conditions of a dynamic heating programme, the reactions in this case take place very slowly, without any acceleration, and at a strictly constant rate. Due to this, it was expected that the overlapping partial reactions could be better separated [16].

Furthermore, it was also expected that under conditions of a quasi-isothermal heating programme the reactions would take place at a constant temperature on condition that a) they are processes leading to equilibrium, b) the progress of the transformations is defined by the rate of the slow and constant heat transport and not by an even slower partial process (such as nucleus formation) [16], and c) the

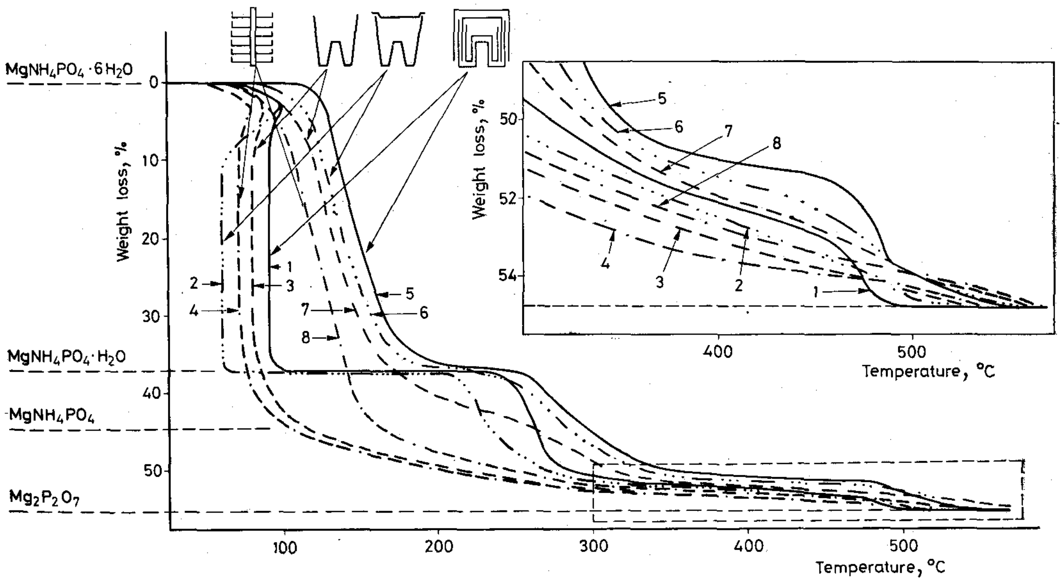

Fig. 3. *TG curves of* $MgNH_4PO_4 \cdot \sigma H_2O$ recorded with quasi-isothermal (1—4) and dynamic (5—8) heating using labyrinth (1 and 5), covered crucible (2 and 6), uncovered crucible (3 and 7) and polyplate (4 and 8) sample holders

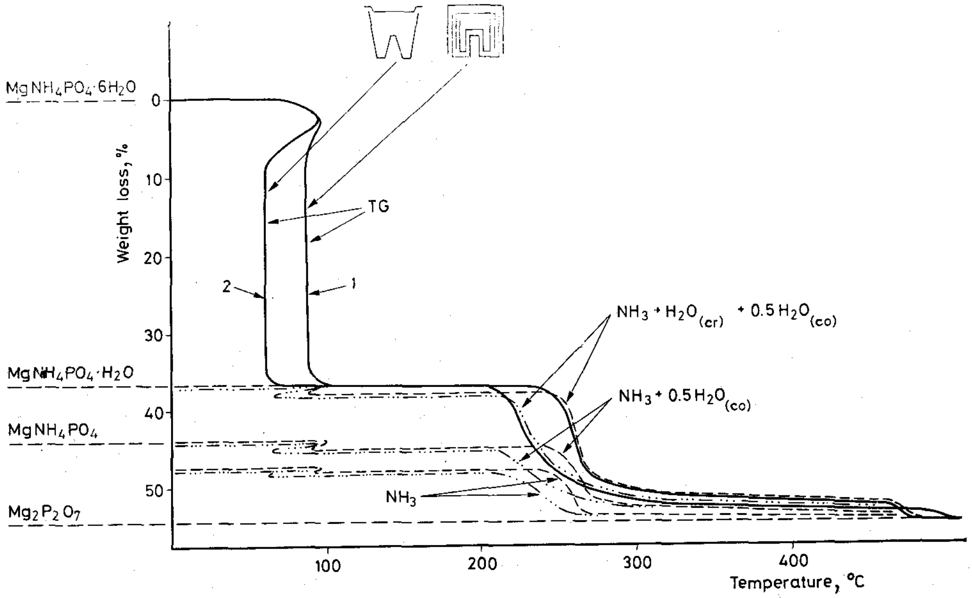

Fig. 4. *TG and TGT curves of* $MgNH_4PO_4 \cdot \sigma H_2O$ recorded with quasi-isothermal heating using labyrinth sample holder (1) and covered crucible (2). The titration curve of NH_3 shows the course of the release of ammonia. The calculated $NH_3 + 0.5\ H_2O_{(co)}$ and $NH_3 + H_2O_{(cr)} +$ $+ 0.5\ H_2O_{(co)}$ curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitution water

partial pressure of the gaseous decomposition products in contact with the solid sample does not change during the examination [16].

In order for condition to be satisfied, application of the labyrinth sample holder [16, 17] proved indispensable. This sample holder, as shown in Fig. 2, consists of 4–6 specially-shaped crucibles fitting into one another in such a way that a long, narrow, channel-like system is formed. The gaseous decomposition products, streaming outwards from the sample through this labyrinth, impede the diffusion of air in the opposite direction. Accordingly, the construction of the sample holder makes it possible for the decomposition reactions always to occur in a self-generated atmosphere, i.e. under quasi-isobaric conditions [16].

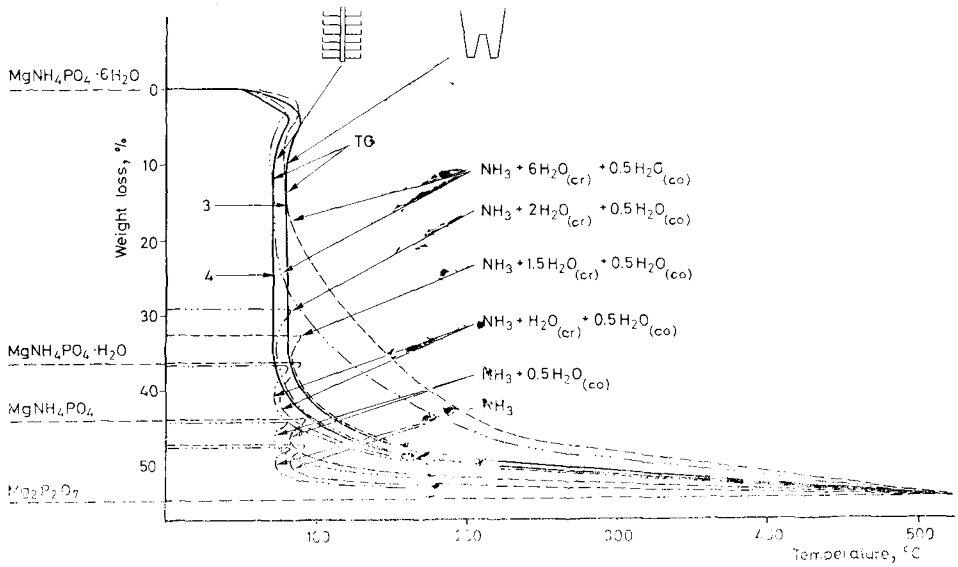

Fig. 5. *TG and TGT curves of* $MgNH_4PO_4 \cdot \sigma H_2O$ recorded with quasi-isothermal heating using uncovered crucible (3) and polyplate sample holder (4). The titration curve of NH_3 shows the course of the release of ammonia. The calculated $NH_3 + 0.5\ H_2O_{(co)}$ and $NH_3 + n \cdot H_2O_{(cr)} + 0.5\ H_2O_{(co)}$ curves demonstrate the course of the simultaneous departure of ammonia, crystal and constitution water

The labyrinth sample holder combined with the quasi-isothermal heating programme may create experimental conditions such that in ideal cases, i.e. when the progress of the transformation is governed by heat transport as the slowest process, the transformations leading to equilibrium will take place at known, physicochemically well-defined temperatures, attained by the system only if the solid phase is in contact with its pure gaseous decomposition products at 1 atm [16].

The curves shown in Figs 3, 4 and 5 were recorded partly under the abovementioned quasi-isothermal and quasi-isobaric, and partly under conventional conditions. These curves represent the weight changes (TG) of the sample and the changes in the amount of ammonia evolved (NH_3) as a function of temperature. From the latter curve, calculation gave the curves representing the changes in the amount of 1 mole ammonia + 0.5 mole water of constitution (curve: NH_3 + 0.5 mole $H_2O_{(co)}$) and 1 mole ammonia + n moles water of crystallization + 0.5 mole water of constitution (curve: $NH_3 + n\,H_2O_{(cr)} + 0.5\,H_2O_{(co)}$). These curves were constructed in order to decide which of them would best correspond to the TG curve, i.e. which of the many possible processes is the most probable.

In contrast to the labyrinth sample holder, with the help of the polyplate sample holder (Fig. 2/d) a reverse effect can be attained. In the vicinity of the sample, which is spread out in a thin layer on the high surface area of the plates, the gaseous decomposition products cannot accumulate, and due to this the transformation takes place as if under an atmospheric depression of about 5 – 10 torr [14, 16]. The conventional crucible of the Derivatograph in its covered (Fig. 2/b) and uncovered (Fig. 2/c) forms can be considered a transition between the two described sample holders from the point of view of the extent of accumulation of the evolved gaseous products inside the sample in the spaces unfilled by grains.

By variation of the sample holders, the partial pressure of the gaseous decomposition products in contact with the solid phase could be changed in four different degrees. Conclusions regarding the composition of these gaseous atmospheres could be drawn from the results of our earlier investigations [16]. It was then found that the thermal decomposition of $CaCO_3$ took place under quasi-isothermal conditions at 660, 710, 780 and 897° on a polyplate sample holder, a conventional crucible in uncovered and covered form, and a labyrinth sample holder respectively. However, from the relationship between decomposition pressure and temperature it follows that $CaCO_3$ could decompose at these temperatures only if the partial pressure of the CO_2 gas in contact with the solid sample was 0.01, 0.04, 0.15 and 1 atm. respectively. It should also be noted that owing to the constant decomposition rate, in the case of the quasi-isothermal heating programme the composition of the gaseous atmosphere, established in the above-mentioned way, remained constant during the whole transformation process (quasi-isobaric), while due to the acceleration of the thermal decomposition in the case of the dynamic heating programme, it changed in an uncontrollable way.

The $MgNH_4PO_4 \cdot 6H_2O$ used was prepared according to Winkler [18].

Results and discussion

Considering the forms of the TG curves, it can be stated that the thermal decomposition of magnesium ammonium phosphate hexahydrate in certain cases can be divided into two, and in other cases into three sections. In essence, however, the thermal decomposition consists of three consecutive partial reactions which, depending on the experimental conditions, more or less overlap. First 5 moles then 1 mole of water of crystallization depart, and finally in an inseparable way the ammonia and water of constitution.

As already mentioned, the decomposition of magnesium ammonium phosphate hexahydrate always commences with the release of 5 moles of water of crystallization. This is clearly demonstrated in curves 1 and 2 of Fig. 3. Here due to the special experimental conditions applied, the two closely-following partial processes could be separated to such an extent that the weight of the transitionally formed $MgNH_4PO_4 \cdot H_2O$ remained quite constant in a temperature interval extending over 170°.

The departure of the 5 moles of water of crystallization took place in a single step in every case investigated. Up to the level corresponding to the composition of $MgNH_4PO_4 \cdot H_2O$ no break point can be found in the TG curve of Fig. 3, indicating a several-step process.

This finding is not contradicted by the fact that in the case of curves $1-4$ in Fig. 3, i.e. under quasi-isothermal conditions, after the beginning of the decomposition the temperature of the sample spontaneously dropped to some extent. This can be explained by the supposition that, under the given circumstances, nucleus formation could begin only with a delay; at higher temperatures and at the moment when a sufficient number of nuclei had been formed for the reaction to continue with the appropriate rate, the temperature of the sample spontaneously dropped to the value corresponding to quasi-equilibrium. Thereafter the temperature remained constant.

It is easy to see that in the case of curves $1-4$ in Fig. 3 the spontaneous stabilization of the sample temperature indicates the set-in of the quasi-equilibrium corresponding to the given conditions (the magnitude and stability of the partial pressures of the gaseous products, etc.). In the case of the quasi-isothermal heating programme the heating regulator ensures not the stability of the furnace temperature, but its regulation in such a way that a temperature difference be formed between sample and furnace; i.e. the rate of heat absorption of the sample, necessary for the continuation of the reaction, is such that the reaction takes place at a preselected very low and strictly constant rate.

Consequently, it can be stated that the first period of the decomposition is a process leading to equilibrium. This is further proved by the fact that the departure of the first 5 moles of water of crystallization took place in every case in accordance with the vapour concentration in contact with the sample and depending on the shape of the sample holder applied. The only exception is curve 2, with its seemingly anomalous course; this will be discussed later. In order of decreasing decomposition temperatures, the curve sequences are as follows $5 > 6 > 7 > 8$ and $1 > 3 > 4 > 2$.

From the fact that besides the stability in the rate of weight-change the sample temperature also became constant, it follows that, apart from the nucleus formation process, the course of the reaction is governed by the heat transfer as the slowest process, i.e. by a physical process, and consequently the reaction is of zero order.

The significant differences between the course of curves 1 – 4 in Fig. 3 indicate that $MgNH_4PO_4 \cdot H_2O$ was formed only if the partial pressure of the vapour in the reaction space attained a definite value which, according to curve 2, could be ensured by covering the crucible (Fig. 2/b). As curve 3 proves, in the uncovered crucible $MgNH_4PO_4 \cdot H_2O$ was not formed. As a reminder it should be mentioned here that in the case of $CaCO_3$ the covering of the crucible changed the partial pressure of CO_2 from about 0.05 atm to about 0.2 atm.

From the above phenomenon it follows quite clearly that the thermal decomposition of $MgNH_4PO_4 \cdot H_2O$ is similarly a process leading to equilibrium.

Further, the decomposition of the material took place according as to whether $MgNH_4PO_4 \cdot H_2O$ was formed as intermediate, or not. Let us examine the first case (curves 1 and 2 in Fig. 4).

In the second period of the decomposition the transitionally-formed $MgNH_4PO_4 \cdot H_2O$ apparently lost its crystal water, ammonia and water of constitution in a single step. This conclusion could be drawn from the fact that the curve $NH_3 + H_2O_{(cr)} + 0.5\,H_2O_{(co)}$ can be brought into accordance with the TG curve in an apparently acceptable way.

However, a more accurate and detailed examination showed that this process consists of two overlapping partial reactions. First mostly water of crystallization escapes, while later the inseparable departure of ammonia and water of constitution comes increasingly into prominence. The results of our investigations concerning this question will be dealt with in detail in the following paper in this issue.

The 70 – 100° section of the thermo-gas-titrimetric curve shows the very same temperature drop as was observed in the TG curve and brought into connection with the nucleus formation. This indicates that though very slowly, the formation of ammonia began at the very beginning of thermal decomposition, simultaneously with the departure of the 5 moles of water of crystallization, about 5% of the total ammonia content being lost. This is why the TG and $NH_3 + H_2O_{(cr)} + 0.5\,H_2O_{(co)}$ curves are not congruent in the temperature interval 100 – 200°.

In contrast with the decompositions of $MgNH_4PO_4 \cdot 6H_2O$ and $MgNH_4PO_4 \cdot H_2O$, that of $MgNH_4PO_4$ does not lead to equilibrium. After the first period of the decomposition was over, the temperature changed, continuously, even under quasi-isothermal conditions (curves 1 – 4 in Fig. 3). The decomposition was unusually protracted, over a temperature interval of several hundred degrees. One of the possible explanations of this may be that the new solid phase of $Mg_2P_2O_7$ is not of a porous but of a compact and glassy structure, through which the diffusion of the gaseous decomposition products is hindered. But it may also be that the equilibrium cannot be established because the decomposition, as has already been shown with the help of other methods, is a rather complicated polycondensation process.

It is very probable that the misleading and barely interpretable variations in the shape of the TG curve, representing the resultant of the three partial reactions can be attributed to the above circumstance. The different experimental conditions inevitably strongly influence the courses of the two partial reactions leading to equilibrium, while they do not (or only indirectly) influence the third reaction which does not lead to equilibrium. An indirect effect can be exerted, for example, if the first two reactions are shifted in the direction of higher temperatures, whereupon the third one will also begin at a higher temperature since it cannot precede the first two processes.

Passing to the other case (curves 3 and 4 in Fig. 5), it can be established that by using the uncovered crucible and the polyplate sample holder, respectively, the three partial reactions, though partly overlapping, do not take place simultaneously. This follows from the fact that the TG and $NH_3 + 6\,H_2O_{(cr)} + 0.5\,H_2O_{(co)}$ curves are not congruent. However, the curves $NH_3 + 2\,H_2O_{(cr)} + 0.5\,H_2O_{(co)}$ and $NH_3 + 1.5\,H_2O_{(co)} + 0.5\,H_2O_{(co)}$ can be brought into accordance with the corresponding TG curves. In both original and the constructed thermo-gas-titrimetric curves the same temperature drop can be seen in the vicinity of 70–90° as in the TG curves. This proves again that, though very slowly, the release of ammonia began immediately at the beginning of the decomposition.

Finally, let us return to the contradictory phenomenon observed in curves 2 and 3 of Fig. 3. The former curve was recorded using the covered crucible, and the latter by using the uncovered one. In spite of this, the first period of the decomposition took place at a lower temperature (70°) in the first case than in the second one (80°). This can probably be explained by the fact that in the case of curve 2 only the first partial process took place, while in the case of curve 3 the other two, whose transformation temperatures are higher, also began. The average transformation temperature of the latter three processes became higher, even at the lower partial pressure of the gaseous products than the temperature of the first process alone at a higher partial pressure.

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Résumé — Les auteurs ont étudié la décomposition thermique de $MgNH_4PO_4 \cdot 6H_2O$ dans les conditions conventionelles ainsi que dans des conditions presque isothermes et presque isobares. On a effectué les expériences à l'aide d'un "Derivatograph" qui se prête aux études simultanées par TG et AGE. Dans les conditions conventionnelles, la décomposition thermique de $MgNH_4PO_4 \cdot 6H_2O$ s'effectue en trois processus élémentaires qui se recouvrent plus ou moins. Le départ de 5 puis d'une molécule d'eau de cristallisation est suivi de celui d'ammoniac et d'eau de constitution, celui-ci étant strictement simultané et indissociable. Ces trois processus peuvent être mieux séparés si l'on opère dans des conditions voisines du régime isotherme et isobare.

Zusammenfassung — Die Autoren untersuchten die thermische Zersetzung von $MgNH_4PO_4 \cdot 6H_2O$ unter konventionellen und quasi isothermischen — quasi isobaren Bedingungen. Die Versuche wurden mit einem zur TG- und EGA-Analyse geeigneten Derivatograph-Typ durchgeführt. Die Autoren fanden, daß die thermische Zersetzung von $MgNH_4PO_4 \cdot 6H_2O$ aus drei mehr oder weniger überlappenden Teilvorgängen besteht. Zuerst werden 5, dann 1 Mol Kristallwasser entfernt, das Konstitutionswasser und Ammoniak werden streng simultan und von einander untrennbar entfernt. Die drei Vorgänge können am besten unter quasi isothermischen und quasi isobaren Bedingungen von einander getrennt werden.

Резюме — Авторы исследовали термическое разложение $MgNH_4PO_4 \cdot 6H_2O$ при условных и квази-изотермических и квази-изобарных условиях. Эксперименты были выполнены с помощью дериватографа, приспособленного для одновременного выполнения TG и GA исследований. Авторы нашли, что термическое разложение $MgNH_4PO_4 \cdot 6H_2O$ состоит из трех более или менее перекрывающихся частичных процессов. Сначала выделяются первые пять молей воды, затем один моль воды, а в конце строго одновременно и совместно происходит выделение аммиака и воды. Эти три процесса могут быть наилучше разделены при квази-изотермических и квази-изобарных условиях.