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INVESTIGATION ON THE THERMAL BEHAVIOUR OF $Mg(NO_3)_2 \cdot 6H_2O$

I. THE DECOMPOSITION BEHAVIOUR

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The decomposition mechanism of $Mg(NO_3)_2 \cdot 6H_2O$ was studied by means of simultaneous TG, DTG and DTA method combined with EGA technique under conventional and quasi isothermal–quasi isobaric conditions. It has been found that $Mg(NO_3)_2 \cdot 6H_2O$ melts at 89 °C in a congruent way. The solution formed begins to boil at 147 °C. The water loss process of the salt hydrate and the decomposition process of the $Mg(NO_3)_2$ always overlap to some extent. Accordingly, $Mg(NO_3)_2$ of stoichiometric composition cannot be prepared thermally, because the compound always contains some basic salt. The last part of water departs in the vicinity of 270 °C with extreme rapidity. In contrast to expectations the compound decomposes in pure "self-generated" atmosphere at a temperature lower by about 80 °C than in the presence of air which contains a small amount of the gaseous decomposition product.

There are contradictory opinions about the mechanism of the thermal decomposition of $Mg(NO_3)_2 \cdot 6H_2O$ in the literature [1–11]. This question is reexamined in this paper.

Simultaneous TG, DTG, DTA and EGA measurements were performed under conventional [12, 13] and quasi isothermal–quasi isobaric conditions [12, 14, 15]. The purpose of the investigations was to answer the following main questions: Do the processes of water departure and of formation of nitrogen oxides overlap? In what way do the experimental conditions influence these processes and what is the mutual influence of the processes? Can anhydrous $Mg(NO_3)_2$ be prepared?

Experimental

The measurements were carried out with the latest model of derivatograph [17, 18] with microprocessor. Figures 1 and 2 are original diagrams. The TG, DTG and DTA curves in Fig. 1 were obtained under conventional circumstances. The sample

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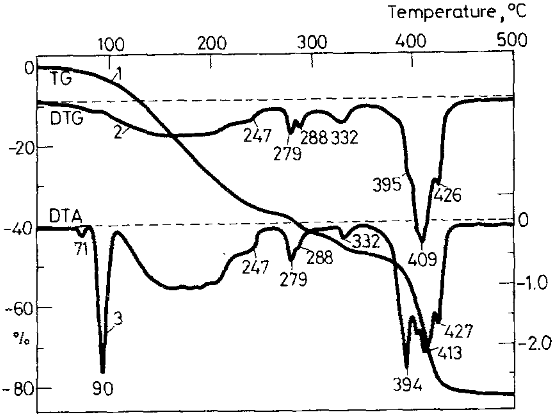

Fig. 1 Simultaneous TG, DTG and DTA curves of $Mg(NO_3)_2 \cdot 6H_2O$ obtained under conventional circumstances. Original chart traced by means of Derivatograph C

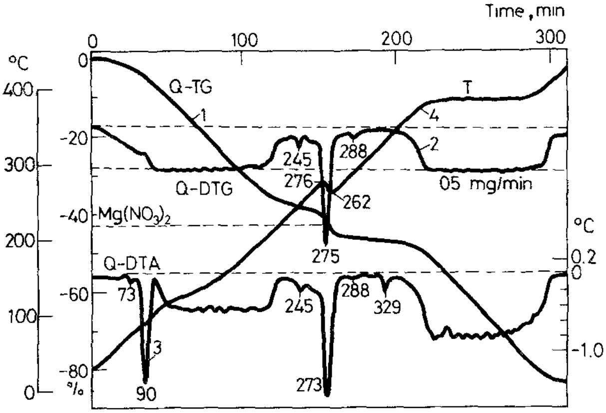

Fig. 2 Simultaneous Q–TG, Q–DTG and Q–DTA curves of $Mg(NO_3)_2 \cdot 6H_2O$ obtained under quasi isothermal–quasi isobaric conditions. Original chart traced by means of Derivatograph C

of cca 100 mg was placed in a platinum crucible and covered with a lid and heated at a rate of 5 deg min^{-1} in the presence of oxygen. Curves in Fig. 2 were obtained under the same conditions but by using the quasi isothermal heating technique [12, 14–16] (transformation rate: 0.5 mg min^{-1}).

The thermogravimetric curves in Figs 3 and 4 are the results obtained with four different types of sample holders (labyrinth, covered, uncovered crucibles and multiplate sample holder) [12, 15]. Otherwise the experimental conditions were identical with those described in the case of Figs 1 and 2.

Curves 5 and 6 in Fig. 4 are the results of special examinations carried out by applying the quasi isothermal heating technique. In the case of curve 5 the examination was started by using the labyrinth crucible. However, the heating was interrupted at the point when according to calculations the sample had lost its whole water content. By lifting the furnace the sample was rapidly cooled down to

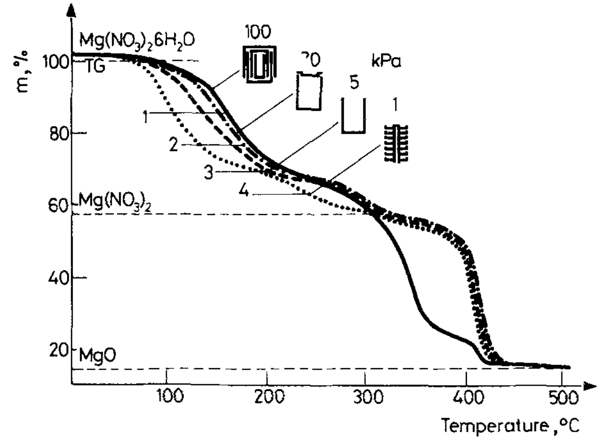

Fig. 3 TG curves of $Mg(NO_3)_2 \cdot 6H_2O$ obtained under conventional circumstances using the labyrinth (1), covered (2), uncovered (3) crucibles and multi plate sample holder (4) resp.

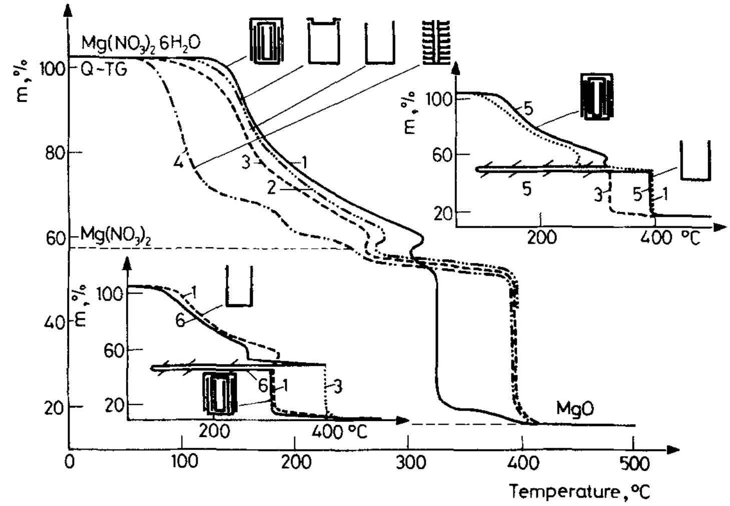

Fig. 4 Q-TG curves of $Mg(NO_3)_2 \cdot 6H_2O$ obtained under quasi isothermal-quasi isobaric conditions using the labyrinth (1 and 5), covered (2), uncovered (3 and 6) crucibles and multi plate sample holder resp. In the case of curves 5 and 6 the heating was interrupted after the dehydration and the sample holder was exchanged

room temperature, and after the removal of the covering parts of the crucible the examination of the material in the open crucible was started again. In the case of curve 6 the situation was the reverse. The measurement was started by using the open crucible and ended by applying the closed labyrinth crucible. According to Fig. 4 the first half of curve 5 became similar to curve 1, while its second half to curve 3. In the case of curve 6 a reverse situation was observed showing that the mechanism of the decomposition changed with the variation of the applied sample holder. It changed according to the partial pressure of the sample contacting gaseous decomposition product.

In addition to the TG, DTG and DTA examinations also the so-called thermogastitrimetric measurement, which can be classified among the EGA methods, was in every case simultaneously performed as well under the conventional [12, 13] (TGT) as under the quasi isothermal–quasi isobaric (Q–TGT) conditions [12, 15, 16]. Of these curves in Fig. 5 those curves are illustrated (curves 2, 4, 6 and 8) which are the representatives of the two borderline cases, i.e. the results obtained of samples located in the labyrinth crucible and on the multiplate sample holder.

The Q–TG curve obtained by using the labyrinth crucible and the quasi isothermal heating technique (curve 1 in Fig. 4) is also demonstrated [15] in the phase diagram of the $Mg(NO_3)_2$–H_2O system [19, 20]. This is curve 1 (points a, b, c,

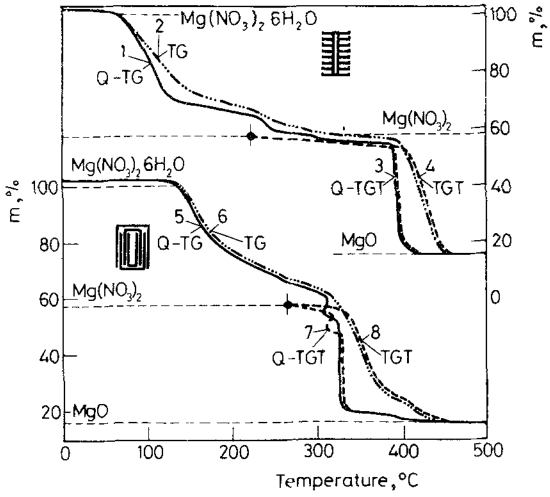

Fig. 5 TG, Q–TG, TGT and Q–TGT′ curves of $Mg(NO_3)_2 \cdot 6H_2O$ under conventional (2, 4, 6 and 8) and quasi isothermal–quasi isobaric conditions using the labyrinth (5–8) and multi plate sample holder (1–4)

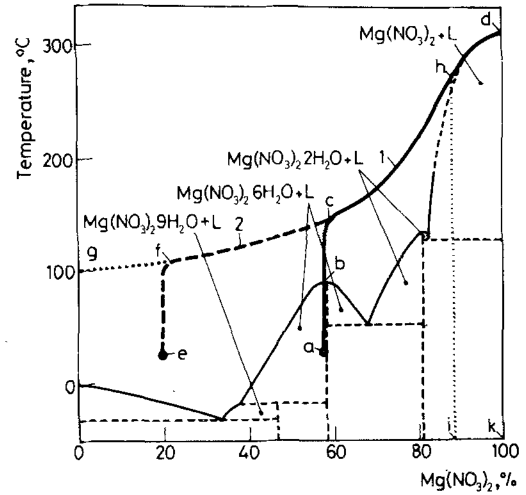

Fig. 6 Phase diagram of $Mg(NO_3)_2 \cdot H_2O$ system. Curves 1 and 2 show the changes in the composition in function of temperature during the Q–TG examination of $Mg(NO_3)_2 \cdot 6H_2O$ (1) and of the solution containing 20% of $Mg(NO_3)_2$ (2)

d) in Fig. 6. Curve 2 (points e, f, c, d) in the same figure is a transformed Q–TG curve too. It was obtained by the examination of a solution containing 20% $Mg(NO_3)_2$. Also in this case, the labyrinth crucible and the quasi isothermal heating technique were used.

Discussion

From several points of view, the results illustrated in Figs 1–6 put the mechanism of the thermal decomposition of $Mg(NO_3)_2 \cdot 6H_2O$ in new light.

The most reliable survey over the causal correlation between the mechanism of water loss and the course of the Q–TG curves is offered by curve 1 in Fig. 6. This curve is originally identical with curve 1 of Fig. 4 but illustrated on the phase diagram of $Mg(NO_3)_2$–H_2O system. The solid $Mg(NO_3)_2 \cdot 6H_2O$ placed in the labyrinth crucible and heated with the quasi isothermal heating technique melts in a congruent way at 89° (point *b*) (see also DTA peak at 90° in Figs 1 and 2) and a saturated homogeneous solution is being formed which becomes unsaturated with increasing temperature. The solution begins to boil at 147° (point *c*). Below this temperature the sample does not lose water since the partial pressure of water vapor within the labyrinth crucible reaches the atmospheric pressure only at the boiling point and so the water vapor can depart from the crucible only at a pressure higher than atmospheric. Between 147 and 320° (section *c–d*) the solution keeps boiling while it becomes gradually more and more concentrated and the temperature of the boiling point increases continuously. Accordingly, the *c–d* section of curve 1 can be identified by the corresponding section of the boiling point curve of the $Mg(NO_3)_2$–H_2O system [15]. Starting from a solution containing 20% of $Mg(NO_3)_2$ (curve 2 in Fig. 6) the *c–f* section of the boiling point curve could also be determined in the above way. The *f–g* section of the boiling point curve is extrapolated. It is worth to be mentioned that the boiling point curve of the $Mg(NO_3)_2$–H_2O system was sofar unknown.

In the case of the TG and Q–TG curves resp. obtained by using the covered and uncovered crucibles, and the multiplate sample holder (curves 2–4 in Figs 3 and 4) the departure of water is a far more complicated process. Namely, in these cases there is no unanimous phase change between liquid-vapor leading to eqilibrium, since crust formation [5, 15, 21] on the surface of the melt and complicated drying processes [15, 21] can also take place. However, in every case, the course of the curves changes corresponding to the partial pressure of the water vapor (1–100 kP).

Figures 1 and 2 also give some further informations. According to the DTA curves (Figs 1 and 2) in $Mg(NO_3)_2 \cdot 6H_2O$ before its melting (90°), a modification change [23] takes place at 71°. The course of the curves is remarkable in Fig. 2 in the temperature domain between 220 and 350°. Reaching 270° the weight loss process transitionally accelerates and on the Q–DTG, and simultaneously also on the Q–DTA curve, sharp peaks (275, 273°) are formed. Closely thereafter the temperature of the sample drops from 276° to 262° (curve 4) in a sudden spontaneous way. It seems that these rapid weight, enthalpy, and temperature changes indicate a critical point in the mechanism of the decomposition reaction. On the basis of both stoichiometric calculations and the results of thermogastitrimetric examinations (TGT curve in Fig. 5) it is very likely that in this temperature range the loss of water terminates and the decomposition of the waterfree $Mg(NO_3)_2$ starts. It seems also to be probable that the sample retains the last traces of water with quite large forces, since after the release of the rest of water, the temperature, characteristic of the energy content of the sample, drops spontaneously by 14°.

The interpretation of the maxima of the DTG and DTA curves at 245° and 288°, respectively, and the maximum at 329° appearing only in the DTA curve should have required further thorough investigations. As far as these peaks are concerned it can be stated that every maximum is reproducible and appeared even under the altered conditions of dynamic heating (Fig. 1).

By thermogravimetric investigations, it was shown that under the conventional as well as under quasi isothermal–quasi isobaric heating conditions the release of nitrogen oxides started (although very slowly) on the multiplate sample holder at about 200° (curves 3 and 4 in Fig. 5) and in the labyrinth crucible at about 270° (curves 7 and 8). However, this process became intensive at 390° in the former and at 320° in the latter case. The processes of water release and the following departure of nitrogen oxides overlapped in temperature intervals of 200° if the multiplate sample holder was used. This interval extended only over 50° if the labyrinth crucible was applied. In both cases in this interval only a minute amount of N_2O_5 departed. This observation agrees with earlier opinions [11] according to which $Mg(NO_3)_2$ in totally waterfree form cannot be produced in thermal way but a product contaminated with a small amount of the basic salt. From the course of curves 5 and 7 the conclusion can also be drawn that systems, containing more than about 85% $Mg(NO_3)_2$ due to decomposition, cannot be prepared in thermal way, because the evolution of nitrogen oxides starts already at about 270°. The system above the mentioned concentration is a multicomponent system, and so, the domain between points *d*, *h*, *i* and *k* in the phase diagram (Fig. 6) can not be interpreted. It is remarkable that independently of the sample holder type used the decomposition of the waterfree $Mg(NO_3)_2$ took place always in isothermal way if the quasi isothermal heating technique was applied.

It may be also of interest to note that in the labyrinth crucible the decomposition of the waterfree $Mg(NO_3)_2$ took place at a temperature value lower by about 80° than in the other three sample holders (curves 1–4 in Fig. 2) since just the reverse phenomenon could have been expected. Namely, the accumulated nitrogen oxides in the labyrinth crucible should have shifted the equilibrium of the dissociation in the direction of higher temperatures. This apparent contradiction can probably be resolved by assuming changes in the reaction mechanism caused by the different experimental conditions. It was an early observation [11] that in the course of the dehydration of $Mg(NO_3)_2 \cdot 6H_2O$ by heating, depending on the applied experimental conditions, more or less basic salt was always formed. In contrast to this, other authors [22] showed that if simultaneously waterfree gas of nitric acid is introduced into the melt, no basic salt would be formed. Thus, it can be supposed that, since in the present case the labyrinth crucible hindered the departure of the gaseous decomposition products and it increased its partial pressure, no basic salt could be formed and so dissociation took place directly. In contrast to this, in the case of the other sample holders, the gaseous decomposition products could easily depart from the neighbourhood of the sample and the decomposition took place indirectly under the formation of basic salt as an intermediate. This change in the reaction mechanism is expressed also in the shift of the decomposition temperature. The fact that in the present case the reaction mechanism—and along with this the behaviour of the reaction with changing temperature—depend indeed on the partial pressure of the gaseous decomposition products is convincingly proved by curves 5 and 6 in Fig. 4. These curves were obtained so that the dissociation reaction of the waterfree $Mg(NO_3)_2$ was quenched and by opening or closing the crucible the measurements were continued. The result of this procedure was that the course of the curves continued in such a way as if the examination had been started by using the sample holder later applied. Thus, there is a strict causal correlation between the shape of the sample holder and the mechanism of the reaction.

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Zusammenfassung — Mittels simultaner TG-, DTG- und DTA-Methoden kombiniert mit EGA-Techniken unter herkömmlichen und quasi-isothermen bzw. quasi-isobaren Bedingungen wurde der Zersetzungsmechanismus von $Mg(NO_3)_2 \cdot 6H_2O$ untersucht. Den Autoren nach schmilzt $Mg(NO_3)_2 \cdot 6H_2O$ stets bei 89 °C. Die entstehende Lösung fängt bei 147 °C an zu kochen. Die Prozesse von Wasserverlust der hydrierten Salze und Zersetzung von $Mg(NO_3)_2$ überschneiden sich in gewissem Maße. Demzufolge kann $Mg(NO_3)_2$ stöchiometrischer Zusammensetzung nicht thermisch hergestellt werden, da die Verbindung immer Ausgangssalz enthält. Der letzte Wasseranteil wird bei etwa 270 °C schnell abgegeben. Entgegen der Erwartungen zersetzt sich die Verbindung in reiner „selbstgenerierter" Atmosphäre schon bei einer Temperatur, die etwa 80 °C unter der Zersetzungstemperatur an Luft mit geringen Anteilen der gasförmigen Zersetzungsprodukte liegt.

Резюме — Совмещенным методом ТГ, ДТГ и ДТА в комбинации с АВГ изучен механизм термического разложения гексагидрата нитрата магния в обычных и квази-изотермических, квази-изобарных условиях. Установлено, что соединение плавится конгруэнтно при температуре 89°, а кипение начинается при 147°. Процессы потери воды и разложения частично перекрываются. В связи с этим, нитрат магния стехиометрического состава не может быть получен термическим путем, поскольку при этом всегда содержится основная соль. Оставшаяся часть воды чрезвычайно быстро выделяется при температуре около 270°. Вопреки ожидаемому, соединение в чистой «самогенерируемой» атмосфере разлагается при температуье на 80° ниже, чем в атмосфере воздуха, содержащем небольшое количество газообразного продукта разложения.