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

## II Results in a closed system: melting and solidification behaviour

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DTA, DSC and X-ray investigations of $Mg(NO_3)_2 \cdot 6H_2O$ revealed a lattice transformation at (71 ± 2) °C with $\Delta H$ = 12.5 J/g, and congruent melting at 90 °C with $\Delta H$ = 150.3 J/g. The results of the DTA investigations on different $Mg(NO_3)_2$–$H_2O$ samples are in good agreement with those of solubility investigations. The melting enthalpy of $Mg(NO_3)_2 \cdot 6H_2O$ is lowered considerably by deviation from the stoichiometric water content of the compound. The results allow conclusions as to the application of this salt hydrate as a latent heat-storage material.

In part I of this series on the thermal behaviour of $Mg(NO_3)_2 \cdot 6H_2O$, we reported on the mechanism of its thermal decomposition in an open system, with formation of MgO [1]. In addition to those investigations we studied the thermal behaviour of this salt hydrate in a closed system, i.e. with constant overall composition. The results obtained on the melting and solidification behaviour and on the melting enthalpy are interesting from the practical viewpoint of the usage of $Mg(NO_3)_2 \cdot 6H_2O$ as a latent heat-storage material. In most cases, the enthalpy difference of a solid-liquid phase transition (melting and solidification) is used for energy storage. In this connection, $Mg(NO_3)_2 \cdot 6H_2O$ has also been proposed, mainly by Lane [2, 3], for waste-heat storage.

In the present work, the thermal properties of the $Mg(NO_3)_2$–$H_2O$ system in the range of stability of $Mg(NO_3)_2 \cdot 6H_2O$ are described, and findings are reported on the behaviour of this compound under static storage conditions.

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## Experimental

For the investigations, $Mg(NO_3)_2\cdot 6H_2O$ p.a. was twice recrystallized from water and the water content was determined according to Karl Fischer [4].

DTA investigations were performed with small amounts of samples (in the milligram range) by means of a thermoanalyzer (Setaram, France + low-temperature equipment (cryostat, crucible holder suspensions with platinel thermocouples) in gastight titanium–palladium crucibles (EMO Ti–Pd 0.2) or glass ampoules. The chosen heating and cooling rates were 2 deg/min. DTA investigations were also performed with large samples (about 10 g) in glass ampoules, with a programmable liquid thermostat. The heating and cooling rates were 0.2 deg/min. In addition to the visual observation of the phase separation phenomena, a better transferability of the results to the conditions in static heat-storage units can be noted with large samples.

For investigation of the phase diagram, mixtures of the salt and water were melted in ampoules, homogenized by shaking, quenched in ice and tempered for about 24 hours at room temperature.

Figure 1 shows the results obtained in DTA investigations of $Mg(NO_3)_2\cdot 6H_2O$. Test results with modified ratios of salt and water in the concentration range

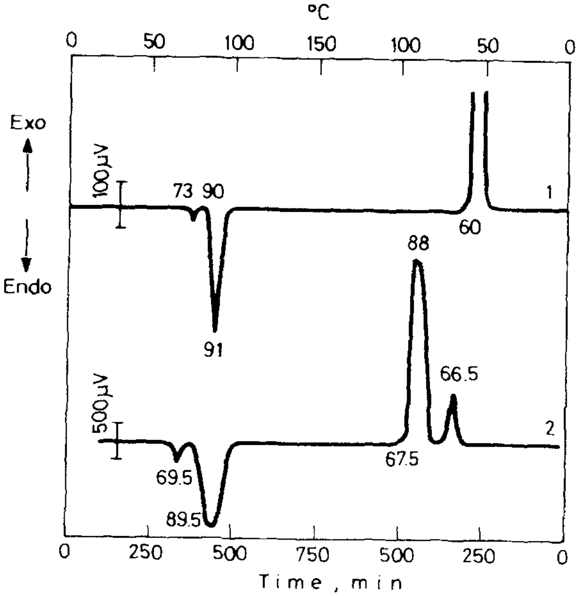

Fig. 1 DTA heating and cooling curves of $Mg(NO_3)_2\cdot 6.04H_2O$ using different sample weights. 1 – 0.0147 g; 2 – 7.83 g

**Table 1** D. s on the system $Mg(NO_3)_2$–$H_2O$

| % $H_2O$ by w | $Mg(NO_3)_2$–$H_2O$ | DTA effect (endothermic), °C | |
|---|---|---|---|
| 31 | 54.0$^{x}$ | | 79.0$^{x}$ |
| 36 | 49.5$^{\Delta}$ | 69.0$^{\Delta}$ | 76.0$^{\Delta}$ |
| | 54.0$^{x}$ | 71.0$^{x}$ | 85.0$^{x}$ |
| 37.5 | 49.5$^{\Delta}$ | 72.0$^{\Delta}$ | 87.0$^{\Delta}$ |
| 38.9 | 55.5$^{x}$ | 72.0$^{x}$ | 87.0$^{x}$ |
| 40.4 | 52$^{\Delta}$ | 72.0$^{\Delta}$ | 90.0$^{\Delta}$ |
| | 53$^{x}$ | 71$^{x}$ | 89.0$^{x}$ |
| 42.1 | | 71$^{\Delta}$ | 90$^{\Delta}$ |
| | | 71$^{x}$ | 90$^{x}$ |
| 45.9 | | 70.5$^{x}$ | 86.5$^{x}$ |
| 49 | | 70.5$^{x}$ | 79.0$^{x}$ |

$^{x}$ = large samples, $^{\Delta}$ = small samples.

between 31 and 49.3% $H_2O$ are listed in Table 1. The characteristic temperatures are plotted in the phase diagram of the system $Mg(NO_3)_2$–$H_2O$ (Fig. 2). X-ray investigations of the different $Mg(NO_3)_2 \cdot 6H_2O$ phases were carried out at 20° and 75° with a Philips PW 1050/70 X-ray diffractometer and graphite monochromator coupled with an HTK P–10 high-temperature attachment. Table 2 gives the results on $\beta$-$Mg(NO_3)_2 \cdot 6H_2O$.

Determination of the melting enthalpy of $Mg(NO_3)_2 \cdot 6H_2O$ with a DSC–2C

**Table 2** Results of X-ray investigations of $\beta$-$Mg(NO_3)_2 \cdot 6H_2O$

| $d_{obs}$/nm | $I/I_0$ | $hkl$ |
|---|---|---|
| 0.4285 | 100 | $20\bar{1}$ |
| 0.3071 | 40 | $12\bar{1}$ |
| 0.2768 | 13 | 221 |
| 0.2357 | 35 | $12\bar{2}$ |
| 0.2294 | 45 | 312 |
| 0.2135 | 30 | $42\bar{1}$ |
| 0.2088 | 40 | $10\bar{3}$ |
| 0.2024 | 22 | 412 |
| 0.1956 | 20 | 331 |
| 0.1849 | 15 | 521 |
| 0.1791 | 33 | $43\bar{1}$ |
| 0.1748 | 20 | 240 |
| 0.1689 | 40 | $24\bar{1}$ |
| 0.1655 | 20 | 340 |
| 0.1539 | 20 | 503 |

(Perkin–Elmer, USA) gave two endothermic peaks, with $\vartheta_{ON} = 74.1°$ ($\Delta H = 12.5$ J/g) and $\vartheta_{ON} = 92°$ ($\Delta H = 150.3$ J/g) above room temperature. The total enthalpy difference of 162.8 J/g served as a reference value for the determination of the melting enthalpy of $Mg(NO_3)_2$–$H_2O$ samples with different compositions. The dependence shown in Fig. 3 was obtained from the results of the quantitative DTA of large samples. In each case, the sums of the endothermic effects in the temperature range 70–89° were plotted as the mean values of 10 individual measurements.

## Discussion

On heating, $Mg(NO_3)_2 \cdot 6H_2O$ exhibited two endothermic effects, at $(71 \pm 2)°$ and $(89.5 \pm 0.5)°$ (Fig. 1). The lattice transformation effect found by Pouillen [5] at $(-13 \pm 2)°$ could not definitely be demonstrated.

The endothermic effect at 89–90° can obviously be attributed to the congruent melting of the salt hydrate. Even after several melting and solidification cycles, the melting temperature and melting enthalpy are reversible. The melting temperature corresponds very well with the literature value of 89.9° [6]. The melting enthalpy is 150.3 J/g. For comparison, Cantor [7] found 150.7 J/g.

As concerns the endothermic effect at 71°, different interpretations are to be found in the literature. Sidelnikov [8] reported on a phase transformation with noncoherent boundary lines. Cantor [7] referred to Pouillen [5], who found a polymorphic transformation in this temperature range. Nirsha et al. [9] mentioned in the list of references incongruent melting at 60° and congruent melting at 85–90°; in their own investigations, they observed incongruent melting at 80° with formation of $Mg(NO_3)_2 \cdot 2H_2O$. Finally, the maximum at about 70° in the $C_p$ vs. $T$ function was not discussed by Lane [2]. The $Mg(NO_3)_2 \cdot 6H_2O$ melting phenomena observed below 89° in the literature can most probably be ascribed to deviations from the stoichiometric water content throughout the whole sample or only in the surface regions, because the saturation curve in the phase diagram of the $Mg(NO_3)_2$–$H_2O$ system shows a sharp decrease in the range of $Mg(NO_3)_2 \cdot 6H_2O$.

There is no doubt that the thermal effect observed in the course of the heating process represents a lattice transformation of $Mg(NO_3)_2 \cdot 6H_2O$, which can also be observed on cooling at lower subcoolings in the DTA (Fig. 1). The more highly subcooled sample of low weight (curve 1) solidifies at 60°. In this case, the exothermic effect comprises the crystallization and lattice transformation enthalpy of $Mg(NO_3)_2 \cdot 6H_2O$. The measured enthalpy difference of 12.5 J/g for this effect, called the α → β transformation, is in very good agreement with the value of 12.1 J/g given by Cantor [7].

The thermal effect at (71 ± 2)° appears throughout the whole stability range of solid $Mg(NO_3)_2 \cdot 6H_2O$. As can be seen in Fig. 2, the DTA effects of the $Mg(NO_3)_2$–$H_2O$ samples (Table 1) reflect quite well the saturation curve known from solubility investigations [10]. Furthermore, the transformation at 71° is evident (Fig. 2).

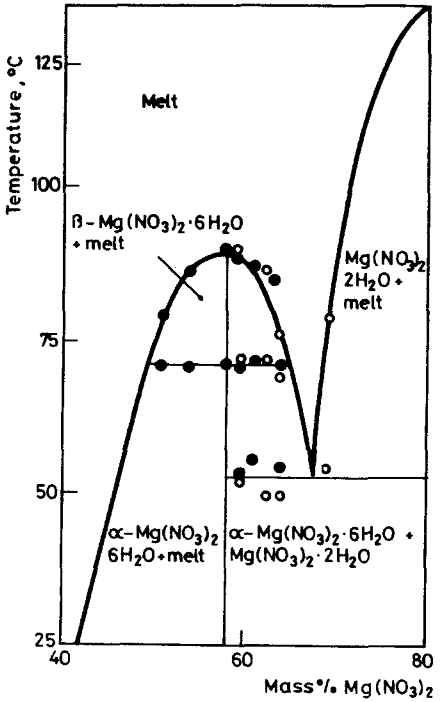

**Fig. 2** Parts of the phase diagram of the system $Mg(NO_3)_2$–$H_2O$ according to [10]. The plotted points show the results of the own investigations (Table 1)

The X-ray investigations on α-$Mg(NO_3)_2 \cdot 6H_2O$ at room temperature confirm the $Mg(NO_3)_2 \cdot 6H_2O$ lattice parameters found by Mazzi et al. [11] ($a_0 = 0.6194$ nm; $b_0 = 1.271$ nm; $c_0 = 0.66$ nm; $\beta = 93°$), which were used as the basis of the complete determination of the structure of this compound by Braibanti et al. [12]. By contrast, the characteristic interferences are not present in the X-ray diagram of a sample of α-$Mg(NO_3)_2 \cdot 6H_2O$ heated to 75°, but the line spectrum of the new phase, β-$Mg(NO_3)_2 \cdot 6H_2O$, can be observed (Table 2). In the angular domain 3–11.5°, conclusions on the presence of interferences of this phase by the halo of the cover film used for the preparation cannot be given. Indexing of the powder diagram by the trial and error program TREOR established by Werner [13] gave the best figure of merit for a lattice unit cell with $a_0 = 1.143$ nm; $b_0 = 0.735$ nm; $c_0 = 0.634$ nm; $\beta = 91.05°$. Thus, shrinkage in two space directions and an increase in the lattice parameters of the monoclinic cell occur during the transformation from α to $\beta$-$Mg(NO_3)_2 \cdot 6H_2O$. The changes in the lattice parameters became evident in the course of dilatometric measurements, with a resulting shrinkage of 0.3 to 0.4% [5].

As concerns the usage of $Mg(NO_3)_2 \cdot 6H_2O$ as a latent heat-storage material in static storage units, the results lead to the following conclusions:

— Owing to its congruent melting, $Mg(NO_3)_2 \cdot 6H_2O$ exhibits reversible melting and solidification behaviour.

— The melting enthalpy of 150.3 J/g is below the frequently cited calorimetric value of 159.9 J/g [14], which evidently also covers the lattice transformation of the salt hydrate at 70°. The lattice transformation enthalpy makes no contribution to the energy storage for a heat-storage unit with a narrow operation range, e.g. $\Delta\vartheta \simeq 10$ deg.

— Deviations of the water content of magnesium nitrate hexahydrate from stoichiometry, e.g. in the case of technical products, lead to a drastic decrease in the melting enthalpy. A deviation of 2% $H_2O$, corresponding to 0.5 mol $H_2O$/mol $Mg(NO_3)_2 \cdot 6H_2O$, results in a storage capacity loss of about 25% (Figure 3).

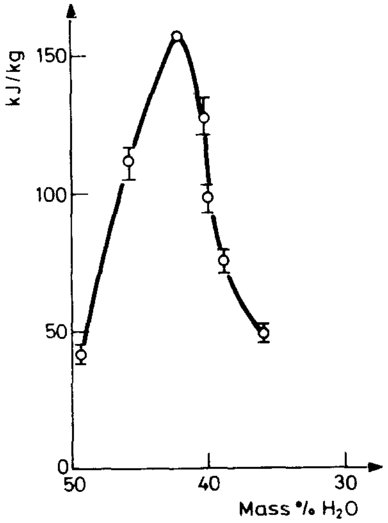

**Fig. 3** Sum of the melting and lattice transformation enthalpy in the stability range of the $\beta$-$Mg(NO_3)_2 \cdot 6H_2O$

— Subcooling of $Mg(NO_3)_2 \cdot 6H_2O$ decreases with increasing sample weight. The nucleation efficiency of magnesium hydroxide or magnesium oxide [15] is confirmed.

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## References

1 F. Paulik, J. Paulik, M. Arnold and R. Naumann, J. Thermal Anal., (in press).

2 A. Lane, Int. J. Ambient Energy, 1, (1980) 155.

3 J. H. Swisher and W. A. Frier, United Department of Energy, Thermal Energy Storage Program DOE/RL/O1830–T 6 Report.

4 W. Poethke and W. Kupferschmied, Praktikum der Maßanalyse, VEB Gustav Fischer Verlag. Jena, 1979.

5 P. Pouillen, C. R. Acad. Sci., 250 (1960) 3318.

6 D. F. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, U.S. Govt. Printing Office, Washington D.C., 1952.

7 S. Cantor, Thermochim. Acta, 33 (1979) 69.

8 A. A. Sidelnikov, A. P. Chupakin and V. V. Boldyrev, Dokl. Akad. Nauk. SSSR, 266 (1982) 1181.

9 B. M. Nirsha, A. A. Fakeev, A. N. Knyazeva, B. W. Schbanov, Y. W. Ovosnenko, G. R. Allachwerbov and I. A. Poljakova, Neorg. Mater., 16 (1980) 1597.

10 A. N. Kirginzev, L. N. Trushnikova and V. G. Lavrenteva, Rastvorinost neorganiceskich vecestv v vode, Isdatelstvo Chimia, 1972, p. 152.

11 R. L. Mazzi and W. R. Bekebrede, Acta Cryst., 14 (1961) 1296.

12 A. Braibanti, A. Triripicchio, A. M. M. Lanfredi and F. Bigoli, Acta Cryst., B 25 (1969) 354.

13 P. E. Werner, Z. Krist., 120 (1964) 375.

14 E. H. Riesenfeld and C. Milchsack, Z. Anorg. Chem., 85 (1914) 424.

15 US–PS 4271029.

**Zusammenfassung** — DTA-, DSC- und röntgenographische Untersuchungen von $Mg(NO_3)_2 \cdot 6H_2O$ zeigten die Existenz einer Gitterumwandlung bei (71 ± 2) °C mit $\Delta H$ = 12.5 J/g und ein kongruentes Schmelzen bei 90 °C mit $\Delta H$ = 150.3 J/g. Die Ergebnisse der DTA-Untersuchungen an verschiedenen $Mg(NO_3)_2$–$H_2O$ Proben stehen in guter Übereinstimmung mit denen von Löslichkeitsuntersuchungen. Durch ein Abweichen vom stöchiometrischen Wassergehalt der Verbindung wird die Schmelzenthalpie von $Mg(NO_3)_2 \cdot 6H_2O$ beträchtlich vermindert. Die Ergebnisse ermöglichen Aussagen zur Anwendbarkeit dieses Salzhydrates als Wärmespeichermedium.

**Резюме** — ДТА, ДСК и рентгеноструктурные исследования гексагидрата нитрата магния показали превращение его решетки при 71 ± 2° с $\Delta H$ = 12,5 дж · г̂$^{1}$ и его конгруэнтное плавление при 90° с $\Delta H$ = 150,3 дж · г$^{-1}$. Результаты ДТА исследований с различными образцами $Mg(NO_3)_2$–$H_2O$ хорошо согласуются с результатами по их растворимости. Энтальпия плавления гексагидрата нитрата магния значительно понижается при отклонении содержания воды от стехиометрического. Результаты проведенных исследований позволили сделать заключение о потенциальном применении этой соли в качестве теплового аккумулятора.