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INVESTIGATION OF THE PHASE DIAGRAM FOR THE SYSTEM $Ni(NO_3)_2$–H_2O AND EXAMINATION OF THE DECOMPOSITION OF $Ni(NO_3)_2 \cdot 6H_2O$ *

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ABSTRACT

The equilibrium relations of the $Ni(NO_3)_2$–H_2O system were determined by applying the DTA method. In addition to the hydrates [$Ni(NO_3)_2 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 4H_2O$] the compound $Ni(NO_3)_2 \cdot 2H_2O$ is also found to exist. The latter compound melts incongruently at 181° C. With the help of the quasi-isothermal–quasi-isobaric technique the boiling point curve of the system was also recorded. The decomposition mechanism of $Ni(NO_3)_2 \cdot 6H_2O$ was examined with the simultaneous TG, DTG, DTA and EGA measuring technique under conventional and quasi-isothermal–quasi-isobaric conditions (Derivatograph C). In the last period of the dehydration, hydropyrolytic reactions take place and intermediate basic salts [e.g., $Ni(NO_3)_2 \cdot Ni(OH)_2$] are formed. The anhydrous $Ni(NO_3)_2$ cannot be prepared thermally.

INTRODUCTION

There are differing opinions concerning the equilibrium relations of the $Ni(NO_3)_2$–H_2O system. In the literature [1–8] hydrates containing 9, 6, 4.5, 4, 3, 2 and 1.5 moles of water of crystallization are all mentioned. Sieverts and Schreiner [9] came nearest to reality: based on their solubility measurements they suggested that only hydrates with 9, 6, 4 and 2 water molecules exist. The results of their investigations are shown in Fig. 1. However, even this phase-diagram left several questions unanswered, e.g., the range above 100° C, which is characteristic of the equilibrium conditions for the dihydrate and the boiling point curve of the liquid phase. Other authors [2,4,5] have suggested the existence of the dihydrate, but it has not been proved by melting point examinations.

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* The authors are grateful of this opportunity to honour Professor W.W. Wendlandt on the occasion of his 60th birthday. We congratulate him on his distinguished career and express our appreciation for his many contributions and service to the field of thermal analysis. In addition we wish him a long life, good health and continued success in his endeavours.

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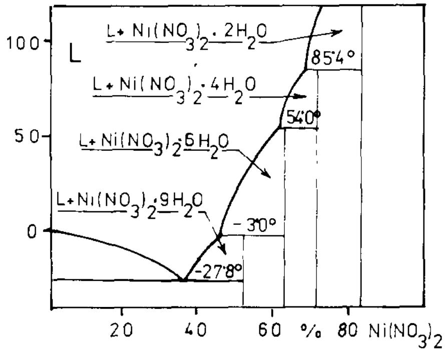

Fig. 1. Phase diagram of the $Ni(NO_3)_2$–H_2O system according to Sieverts and Schreiner [9].

Several contradictions can also be found in the literature with respect to the kinetics and mechanism of the decomposition of nickel nitrate hexahydrate. There are those [4,5,8,10–12] who think that the existence of an anhydrous nickel nitrate is possible while according to other authors [6,13] the anhydrous salt cannot be prepared. Furthermore, some authors [14–16] consider that nickel nitrate decomposes similarly to alkali and alkaline earth nitrates such that a transitional nickel nitrate is formed which decomposes only at higher temperatures. This theory, however, is rejected by most researchers. In general, the following questions could not be satisfactorily answered. To what extent do the processes of water departure and that of the gaseous decomposition products of nitrogen oxides overlap? How much is this overlap influenced by the experimental conditions? What intermediates [4,11,12] are formed during the course of the decomposition?

Based on earlier work it seemed that the first group of questions could be answered by DTA [17,18] studies performed with specially prepared samples of different compositions, while the response to the second group of questions could be found by simultaneous TG and EGA examinations [19–21] carried out under conventional and quasi-isothermal–quasi-isobaric conditions [19,22]. The results of these examinations are summarized in the present paper.

EXPERIMENTAL

Figures 1 and 2 demonstrate the phase equilibrium conditions for the $Ni(NO_3)_2$–H_2O system. The former shows the result of the solubility studies of Sieverts and Schreiner [9] while the latter is a variation of it completed by the present authors.

In order to determine which of the salt hydrates really exist and which do not by DTA [17,18], samples of various water contents were prepared.

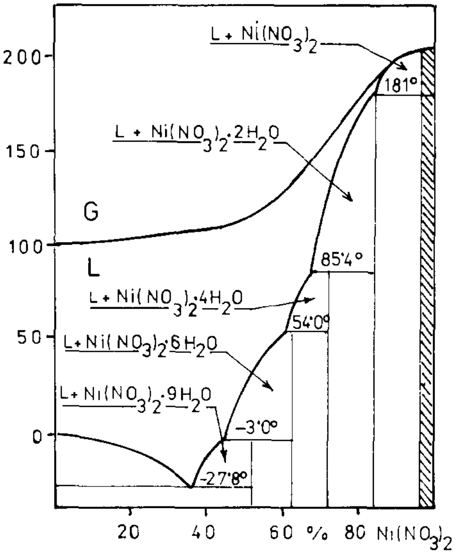

Fig. 2. Phase diagram for the $Ni(NO_3)_2$–H_2O system according to the present work.

Sample a. Before the DTA examination, 0.8 moles of water were added to the solid $Ni(NO_3) \cdot 6H_2O$ in the conical crucible.

Sample b. $Ni(NO_3)_2 \cdot 6H_2O$.

Samples c–s. $Ni(NO_3)_2 \cdot 6H_2O$ was heated in the conical crucible [22] by means of Derivatograph C [23,24] (Hungarian Optical Works, Budapest) with a quasi-isothermal heating technique [19,22]. With a weight decrease of 0.5 mg min^{-1}, water was slowly expelled so that the individual samples contained 5.5, 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.75, 1.5, 1.25, 1, 0.75, 0.50 and 0.25 moles of water, respectively. The evaporation was interrupted by sudden removal from the furnace at a set time. The samples were left in the closed crucibles and stored in a refrigerator until the DTA examinations.

The conical crucible [22] consists of a lower part and a tight-fitting cover (Fig. 3). The side wall of the crucible bears a spiral-shaped cavity of small diameter which forms a long channel when the tight-fitting lid is placed on the crucible. Due to this construction a "self generated" atmosphere is formed within the crucible. This sample holder was advantageous, because water could not evaporate from the incongruently melted sample solution during the lengthy DTA examination and water loss started only at the boiling point of the solution.

Figure 3 allows the usual interpretation of the phase diagram and the changes in the composition of the samples with respect to temperature. The nature of the processes which took place in the samples during their preparation and during the course of the DTA examinations could be determined.

Starting from $Ni(NO_3)_2 \cdot 6H_2O$ (sample b), during the preparation of

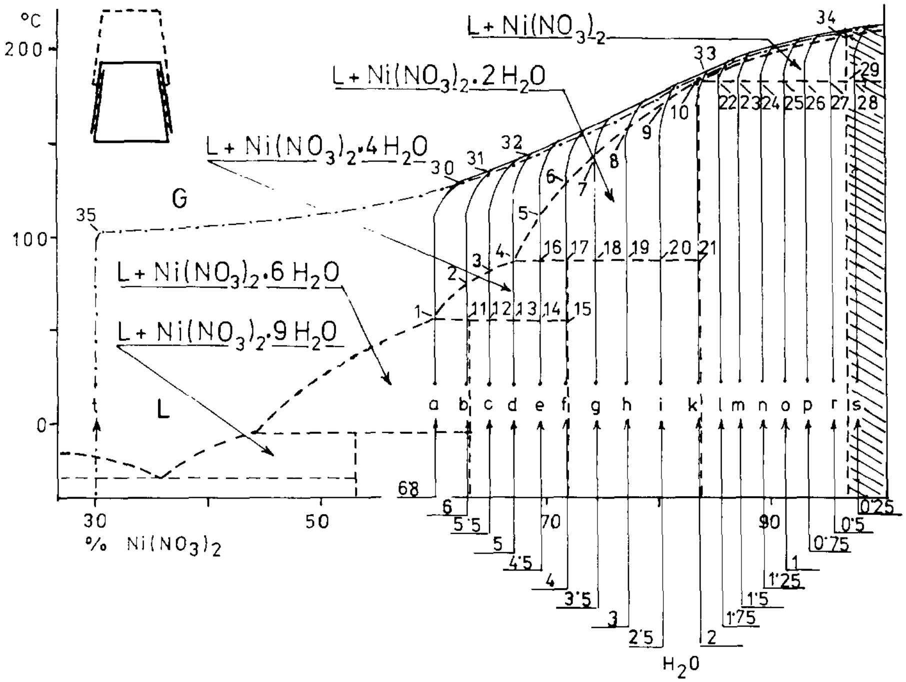

Fig. 3. Progress of dehydration during thermal production of $Ni(NO_3)_2$ preparations of various water contents illustrated on the phase diagram of the $Ni(NO_3)_2$–H_2O system.

$Ni(NO_3)_2 \cdot 5H_2O$ (sample d) the following occurred. $Ni(NO_3)_2 \cdot 6H_2O$ melted incongruently at 54 °C (point 11) and solid tetrahydrate and a saturated solution were formed. On heating to 77 °C (point 2) the tetrahydrate dissolved. The system did not lose water until the boiling point of the solution (138 °C, point 31) was reached. From the boiling solution, as controlled by the balance, 1 mole of water was expelled. Cooling of the solution was started at point 32. At 86 °C (point 4) the tetrahydrate began to separate, while at 54 °C, with the separation of the hexahydrate (point 13), the sample solidified. During the following DTA examination up to point 32 the reverse of the process, shown during the course of cooling, took place.

The DTA curves of samples a–g are shown in Fig. 4 while those of samples h–s are given in Fig. 5. These were obtained at a heating rate of 1 °C min^{-1}. Since the DTA examinations were also performed by means of Derivatograph C, it was possible to trace the DTG curves (curves a and h in Figs. 4 and 5, respectively).

The boiling point curve of the phase diagram (Figs. 2 and 3) was determined in the following way [17,18]. A solution containing 30% $Ni(NO_3)_2$ was placed into the labyrinth crucible [19,22] and heated with the quasi-isothermal heating technique [19,22] (evaporation rate 0.3 mg min^{-1}) while the weight changes of the solution were measured. Due to the good seal of the

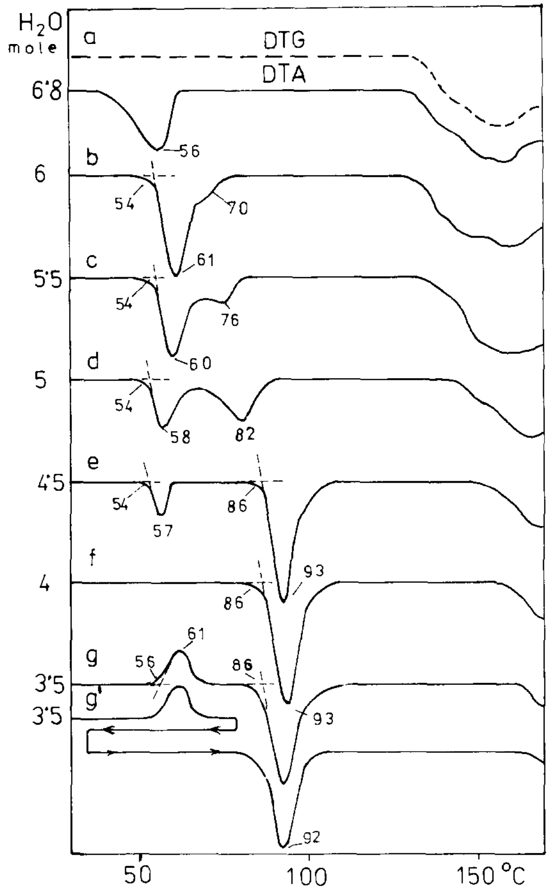

Fig. 4. DTA and DTG curves of $Ni(NO_3)_2$ preparations containing various amounts of water (6.8, 6, 5.5, 5, 4.5, 4 and 3.5 mol H_2O).

labyrinth crucible the weight of the sample did not change (section t–35 of curve t in Fig. 3) until the temperature of the solution attained the boiling point corresponding to the composition of the solution (point 35) and the partial pressure of the water vapour reached 100 kPa inside the crucible (self-generated atmosphere). Thereafter water vapour departed from the crucible while the temperature of the solution gradually increased according to its composition (section 35–33 of curve t in Fig. 3). The course of the boiling point curve determined in the way described was almost in agreement with the changes in boiling point in the course of preparing samples a–k for the DTA examination.

The essence of the quasi-isothermal–quasi-isobaric measuring technique [19,22] lies in a special heating controller, incorporated in the derivatograph. This automatically maintains the difference between the sample and furnace temperatures such that the transformations take place at a strictly constant 2

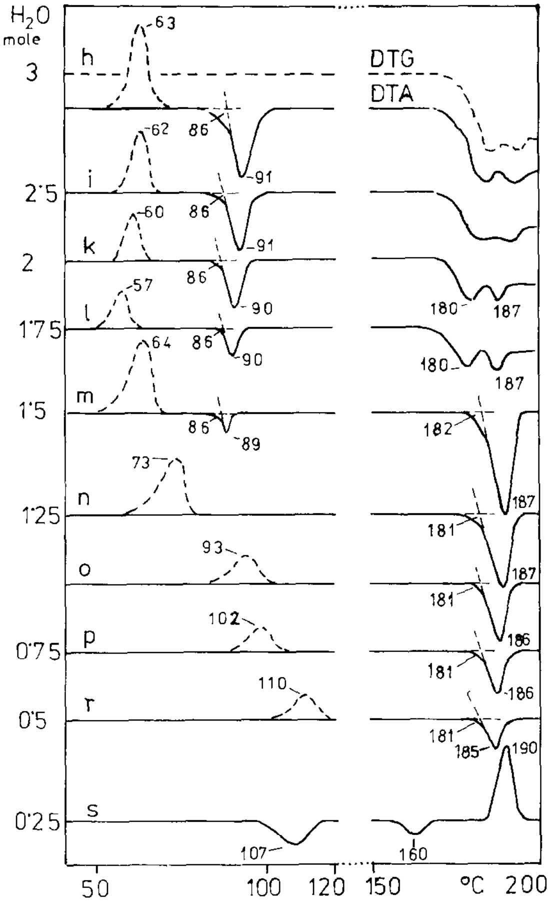

Fig. 5. DTA and DTG curves of $Ni(NO_3)_2$ preparations containing various amounts of water (3, 2.5, 2, 1.75, 1.5, 1.25, 1, 0.75, 0.5 and 0.25 mol H_2O).

orders of magnitude lower rate (0.1–0.5 mg min^{-1} weight change) than in the case of the conventional dynamic heating technique. The result of this special heating technique is that transformations (boiling, decomposition) always take place at a temperature corresponding to the actual quasi-equilibrium determined by the existing conditions (partial pressure of water vapour and gaseous products).

Figure 6 illustrates the conventional simultaneous TG, DTG and DTA curves. The curves were obtained by means of Derivatograph C in air using an open crucible and applying a heating rate of 5 °C min^{-1}. The weight of the sample was ~ 100 mg.

Figure 7 shows the Q-TG curves of $Ni(NO_3)_2 \cdot 6H_2O$ which were traced using the quasi-isothermal heating technique. In order to determine whether the changes in the partial pressure of the gaseous decomposition products surrounding the sample would influence the process of transformation,

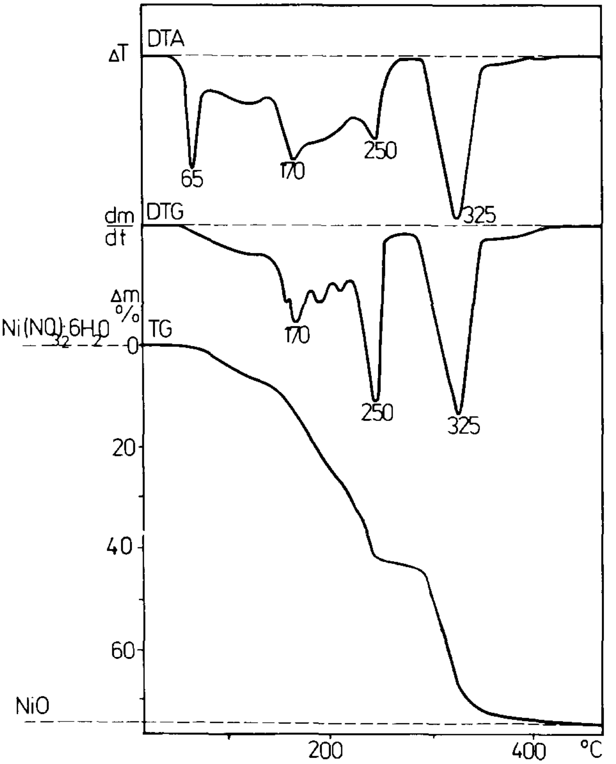

Fig. 6. Simultaneous TG, DTG and DTA curves of $Ni(NO_3)_2 \cdot 6H_2O$ recorded in the conventional way.

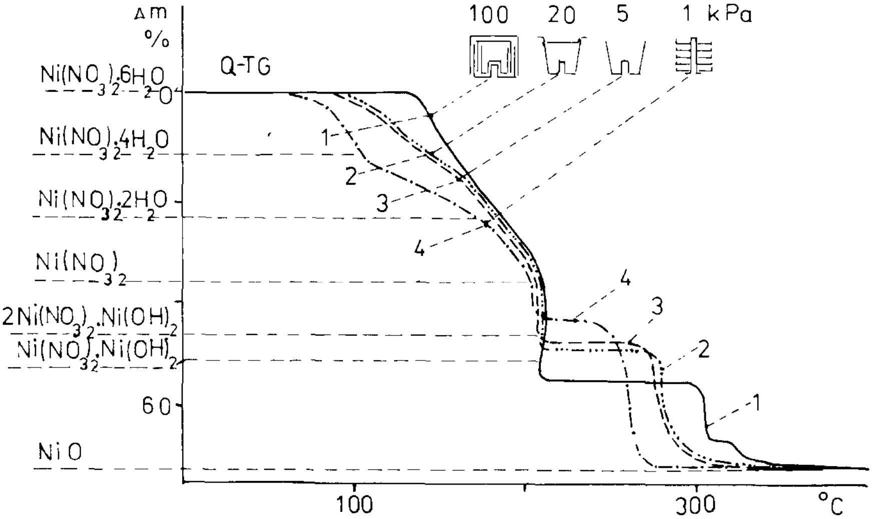

Fig. 7. Q-TG curves of $Ni(NO_3)_2 \cdot 6H_2O$ recorded with the quasi-isothermal–quasi-isobaric measuring technique using various kinds of sample holders (labyrinth, open and covered crucibles, multi-plate sample holder).

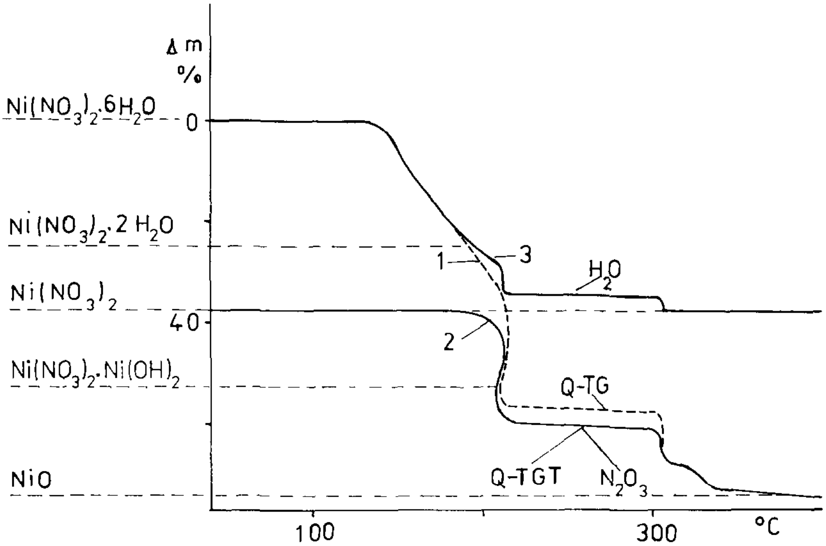

Fig. 8. Q-TG and Q-TGT curves of $Ni(NO_3)_2{\cdot}6H_2O$ recorded under quasi-isothermal and quasi-isobaric conditions using the simultaneous TG and EGA (thermogastitrimetry, TGT) technique.

sample holders of various shapes were used. According to the literature [19,22], the partial pressure of the surrounding gaseous decomposition products changed from about 100 to 20, 5 and 1 kPa, respectively, depending on whether a labyrinth, a covered or uncovered crucible or a multi-plate sample holder were used for the examination. The weight of the sample was ~ 100 mg, the rate of the transformation was 0.3 mg min^{-1} and the examinations were carried out in air.

The course of the departure of gaseous products, such as water vapour (H_2O curve in Fig. 8) and nitrogen oxides (N_2O_5 curve), was also examined using the simultaneous Q-TG and Q-TGT technique [19–22,24].

In this case the Derivatograph C measured, under quasi-isothermal–quasi-isobaric conditions, not only the weight changes of the sample (Q-TG curve) but also the amount of nitrogen oxides evolving at the same time (N_2O_5 curve). According to the measuring principle of the TGT method the equipment quantitatively collects the evolving gases (N_2O_5, N_2O_3, N_2O_4, NO) and transports them by a carrier gas (oxygen) into an absorber vessel where the nitrogen oxides are absorbed by water. The nitric acid formed changes the pH of the solution activating an automatic burette that continuously titrates, in a pH-stat manner, the acid with sodium hydroxide. In this way it is possible to determine the course of the departure of nitrogen oxides directly, while the departure of water vapour is determined indirectly by difference calculations of Q-TG and Q-TGT curves (Fig. 8).

The curves in Fig. 8 were made using the labyrinth crucible. In order to hinder the decomposition of the nitrogen oxides to N_2O and N_2 [17], which cannot be transformed to HNO_3, the examination was carried out in an oxygen atmosphere. Similar examinations were carried out using covered and uncovered crucibles and the multi-plate sample holder. Since the courses of the Q-TGT and Q-TG curves obtained were very similar to one another, they are not illustrated here.

DISCUSSION

It seems that our earlier knowledge concerning the phase equilibrium of the $Ni(NO_3)_2$–H_2O system requires some correction.

The course of the DTA curves in Figs. 4 and 5 prove that beside $Ni(NO_3)_2 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 2H_2O$ also exists, but not $Ni(NO_3)_2 \cdot 5H_2O$, $Ni(NO_3)_2 \cdot 3H_2O$ or $Ni(NO_3)_2 \cdot 1.5H_2O$. These suggestions agree with the findings of Sieverts and Schreiner [9] as well as those of Wheeler and Frost [2].

According to both the literature [9] and the "onset" temperature of the peaks of curves b–e in Fig. 4, $Ni(NO_3)_2 \cdot 6H_2O$ melts incongruently at 54.0 ° C (Fig. 3, points 1 and 11–15). The incongruent melting of $Ni(NO_3)_2 \cdot 4H_2O$ at 85.4 ° C (points 4 and 16–21 in Fig. 3) is also supported by the peaks of the curves e–m with the "onset" temperature at 86 ° C (Figs. 4 and 5).

The melting point of $Ni(NO_3)_2 \cdot 2H_2O$ has not been determined previously (Fig. 1). Based on the course of curves m–r in Fig. 5 we were able to state that the dihydrate also melts incongruently (points 10 and 22–27 in Fig. 3) and that the melting occurs at 181 ° C.

From curves a–s in Figs. 4 and 5 further information can also been found.

Curve a in Fig. 4 indicates an enthalpy change beginning at room temperature with a maximum temperature of 56 ° C. This is due to the gradual dissolution of the solid $Ni(NO_3)_2 \cdot 6H_2O$ that is present in the saturated solution (section between points a–1 in Fig. 3).

The maxima at 70, 75 and 82 ° C of curves b–d in Fig. 4 are also the result of gradual dissolution. In this case, the tetrahydrate intermediate dissolves gradually with increasing temperature (sections 11–2, 12–3 and 13–4 in Fig. 3).

The sections of the DTA curves (points a–i in Figs. 4 and 5) above 130 ° C are connected with the departure of water from the boiling liquid phase (points 30–33 in Fig. 3), as also proved by the DTG curves of samples a and h.

The course of this section of the DTA curves obtained for samples m–r, containing 1.5 moles or less water, completely changes. The specific course of the DTA curves, characteristic of boiling, fails to occur and instead a large endothermic peak with an "onset" temperature of 181° C appears (curves m–r in Fig. 5) which indicates the incongruent melting of the dihydrate.

The DTA curves k and l form a borderline between the two former types. These still indicate the boiling of the solution (max. 180° C) and already the incongruent melting of the dihydrate (max. 187° C).

Accordingly, in the case of sample m only the heat effect associated with melting appears and that indicating boiling does not occur. It can be concluded that for the composition $Ni(NO_3)_2 \cdot 1.75H_2O$ the liquid (L) mono-phase ceases to exist. Accordingly, only the section between points 30 and 33 of the boiling point curves indicates the real changes in the boiling point of the solution phase (L). In the section between points 33 and 34 the water departs from the system by a slow and simple evaporation without giving any indication of an eventual boiling process. But in this case one has to suppose that beyond the boiling point of the dihydrate, in the domain falling between points 10, 33, 34 and 27, a binary system is present which consists of a saturated solution phase (L) and of solid $Ni(NO_3)_2$ (in Fig. 3).

From the barely interpretable course of the DTA curve marked s in Fig. 5, one could draw the conclusion that by heating samples containing less than 0.5 mol H_2O, solid intermediate decomposition products appear due to hydropyrolysis through which the sample ceases to be a two-component system and becomes a multi-component system for which different equilibrium rules are valid.

In curves g–r an exothermic peak can also be seen. The existence of this can probably be explained as follows. On preparation of the samples the dehydration process was interrupted by lifting from the furnace and due to rapid cooling, the crystalline phase corresponding to the equilibrium composition could not be developed. However, in the course of DTA examinations of the sample, when the sample temperature was again increased, the structure of the meta-stable amorphous substance was rearranged in the temperature interval indicated by the exothermic peaks and the equilibrium crystalline phase was again developed.

This is proved by the experiment carried out with sample g. If the sample after the exothermic peak was cooled very slowly to room temperature and reheated during the DTA examination, the exothermic peak did not appear (curve g′ in Fig. 4) because the substance was already crystalline. Nor did the exothermic peak occur in those cases when the sample was cooled down extremely slowly (0.5° C min^{-1}) to room temperature after removal of the appropriate amount of water. We also observed that if the water content of the sample was lower, we have to raise the temperature of the sample in order to achieve rearrangement of the crystal structure (curves m–r in Fig. 5).

It seems to be a contradiction that still in the case of samples l and m the peak at 86° C appears, characteristic of the tetrahydrate, despite the theoretical evidence with that given composition that the tetrahydrate should not separate. Wheeler and Frost [2] in their X-ray diffraction measurements also observed this phenomenon and explained it by supposing that the crystallization of the tetrahydrate is more rapid than that of the dihydrate.

Ideas regarding the decomposition mechanism of $Ni(NO_3)_2 \cdot 6H_2O$ also need modification. The two earlier views, according to which anhydrous $Ni(NO_3)_2$ exists and can be prepared, and that the decomposition of $Ni(NO_3)_2$ is a gradual process due to the formation of an intermediate nickel nitrite, must be disregarded. These two erroneous conclusions were probably based on the circumstance that at about 260 °C the sample temporarily maintains a constant weight as shown by the TG, DTG and DTA curves in Fig. 6.

With the help of simultaneous Q-TG and Q-TGT (thermogastitrimetric) examination (Fig. 8) it can be stated that the gradual decomposition is due to hydropyrolytic reactions causing the formation of basic nickel nitrates [$2Ni(NO_3)_2 \cdot Ni(OH)_2$, $Ni(NO_3)_2 \cdot Ni(OH)_2$] (eqn. 1). In the present case (Fig. 8) these intermediates maintained a constant weight between 210 and 300 °C but above 300 °C they decomposed (eqn. 2).

$$2Ni(NO_3)_2 + H_2O = Ni(NO_3)_2 \cdot Ni(OH)_2 + N_2O_5 \tag{1}$$

$$Ni(NO_3)_2 \cdot Ni(OH)_2 = Ni(NO_3)_2 \cdot NiO + H_2O \tag{2}$$

$$Ni(NO_3)_2 \cdot NiO = 2NiO + N_2O_5 \tag{3}$$

$$Ni(NO_3)_2 = NiO + N_2O_5 \tag{4}$$

$$2Ni(NO_3)_2 = Ni(NO_3)_2 \cdot NiO + N_2O_5 \tag{5}$$

The conclusion regarding the formation of basic nickel nitrate was based on the following.

The liberation of N_2O_5 (eqn. 1) from the system began at 180 °C, containing 2 moles of water (curve 2 in Fig. 8). The N_2O_5 departed in two well-defined steps (eqn. 1 and eqns. 2 and 3, respectively). Between 210 and 300 °C no N_2O_5 was liberated (curve 2 in Fig. 8). Between 210 and 300 °C some water (0.5 mol) was retained (eqn. 1). However, above 300 °C (curve 3 in Fig. 8) the remaining water also escaped (eqn. 2).

Between the amounts of water retained (eqn. 2), and N_2O_5 liberated below 210 °C (eqn. 1), a correlation corresponding to their molecular weights could be found (curves 2 and 3 in Fig. 8). This proportionality between the amounts of H_2O and N_2O_5 could always be detected regardless of the experimental conditions applied, i.e., the various sample holders used and whether the measurements were carried out under dynamic or quasi-isothermal heating regimes. The amount of transitionally formed basic salt changed according to the experimental conditions. In this respect conclusions could be drawn not only from the amount of N_2O_5 (eqn. 1) departing in the first step (curve 2 in Fig. 8), but also from the magnitude of the weight changes of the sample measured up to its constant weight period (TG curve in Fig. 6, curves 1–4 in Fig. 7).

The course of the TG (Fig. 6) and Q-TG (Fig. 7) curves shows that if the partial pressure of the sample in contact with water vapour within the crucible was higher, the amount of basic salt formed would be greater. If the hydropyrolytic reaction went further, the amount of material decomposed through simple dissociation (eqn. 4) would be less.

Although the idea that the stepwise decomposition of $Ni(NO_3)_2$ (eqn. 5) occurred in parallel with the hydropyrolytic reaction cannot be fully excluded, its extent must have been less significant under the conditions applied.

The partial pressure of the gaseous products (N_2O_5) was higher if the temperature at which the intermediate basic salt (eqn. 3) and the still present $Ni(NO_3)_2$ (eqn. 4) decomposed (Fig. 7) was higher. Accordingly, these processes lead to equilibrium.

Moreover if, according to the earlier suggestion, the stepwise course of the TG curve was caused by the formation of anhydrous $Ni(NO_3)_2$, the constant weight section of the curve must have appeared at the height of the calculated level of $Ni(NO_3)_2$.

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