Journal of Thermal Analysis, Vol. 36 (1990) 915-922

ON THE THERMAL DECOMPOSITION OF $NiSO_4.nH_2O$ (n = 7, 6, 4, 1) AND OF THEIR DEUTERATED ANALOGS

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(Received May 2, 1989)

The DTA method has been used in studying the thermal dehydration and decomposition of $NiSO_4.nH_2O$, accordingly of $NiSO_4.nD_2O$, (at n = 7, 6, 4, 1) in a temperature interval of 20 to 900°C, at a heating rate of 10 deg/min. The endoeffects observed show in all cases partial dehydration to monohydrate and evolution of the last molecule of hydrate water at a high temperature T_{max} ~ 360°C for the hydrates and T_{max} ~ 360-335°C for the deuterates. At $NiSO_4.6H_2O$ ($6D_2O$) and $NiSO_4.4D_2O$ there occurs stepwise dehydration before the monohydrate as well. Decomposition of the anhydrous $NiSO_4$ takes place at higher temperature which depends on whether it had been obtained from the respective deuterate ordinary hydrate. The one obtained from the deuterate undergoes decomposition at relatively lower temperature.

Pertinent literature contains data about the thermal decomposition of $NiSO_4.7H_2O$ and $NiSO_4.6H_2O$, which are contradictory as regards the stages of the dehydration process. For instance, according to [1], hexahydrate and monohydrate are obtained as intermediates, while according to [2] monohydrate is obtained directly from the heptahydrate. E. Fruchard and A. Michel [3] assume that $NiSO_4.7H_2O$ is dehydrated at several steps, the first to be obtained being $NiSO_4.6H_2O$ which undergoes allotropic conversion and is then dehydrated to tetra-, tri-, di-, mono- and anhydrous $NiSO_4$. The obtaining of tetra- and dihydrate is judged only by a change in the mass of the sample, without any isolation or identification of these phases. The same is with the stages of dehydration in [4] as well, the difference being that the authors assume the existence not of two but of four polymorphous modifications of $NiSO_4.6H_2O$, without offering proof for them.

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By investigating the influence of the water-vapour pressure on the process of thermal dehydration in [5], the obtaining of $NiSO_4.4H_2O$ is proved as an intermediate phase, analogous to the dehydration of the heptahydrates of cobaltic and magnesium sulphate. Tetrahydrate has also been proved in [6, 7], and the authors of these studies assume that the initial $NiSO_4.7H_2O$ undergoes direct dehydration to it. The assumption in [8] is that, in addition to $NiSO_4.4H_2O$, an intermediate hydrate is obtained between the tetrahydrate and the monohydrate, for which no chemical formula has been offered.

A study has presented in [9] of the isothermal decomposition of $NiSO_4.7H_2O$ at several temperatures in the 100-200° interval, and it proves stepwise dehydration via 5-, 4-, 3-, 2-, and 1-hydrates.

Other authors [10] have investigated the dehydration of $NiSO_4.7H_2O$ in a flow of dry air in the temperature range of 20-100°. Under these conditions the process takes place at two stages - analogous to [1].

The aim of the present study was, by using the DTA method, to investigate the thermal dehydration and decomposition of the hydrates of $NiSO_4$ ($NiSO_4.nH_2O$, n = 7, 6, 4, 1) and their deuterated analogs, with a view to comparing their behaviours and temperatures of phase transitions.

Experimental

The initial hydrates were obtained by the following methods: $NiSO_4.7H_2O$ by recrystallization from aqueous solution at 20°C; $NiSO_4.6H_2O$ and $NiSO_4.4H_2O$ - by a method described in [11], whereby the respective monoclinic modifications are obtained; and $NiSO_4.H_2O$ was obtained by heating $NiSO_4.7H_2O$ at 290° to a constant weight [12]. The last hydrate is slightly hygroscopic, that is why it is kept in inert medium. The initial $NiSO_4.7D_2O$ was isolated by twofold recrystallization from heavy water at 20°. The lower hydrates - deuterites were obtained from it by methods analogous to the ordinary ones.

The compounds investigated were identified by the methods of quantitative analysis: Ni - complexometrically [13]; SO_4^{2-} - by weight [14]; water - after Fischer and thermogravimetrically. The thermal curves of all of them were taken in the 20-900° range at a heating rate of 10 deg/min, with equal mass of the sample and with open ceramic crucibles, using MOM type derivatograph.

Experimental data and discussion

The data from the thermal analysis are collected in the Table, while the respective DTA and TG curves are shown in the Figure.

The DTA curve of the heptahydrate (Fig., curve a for $NiSO_4.7H_2O$ (1) and curve a' for $NiSO_4.7D_2O$ (1')) show three distinct endoeffects. The first one is quite large and split, with T_{max} = 140 and 200° for 1 and T_{max} = 160 and 200° for 1'. A noteworthy feature is that the intensity of the two maximums changes in the ordinary and deuterated hydrates, i. e. in 1 the second maximum is larger than the first, whereas this is the opposite in 1'. The change in the TG curve (Table), corresponding to the first maximum, is used to determine the change in the mass of the sample $\Delta m_{exp.}$ = 37.8 % (for 1) at $\Delta m_{calc.}$ = 38.5 %, which corresponds to the evolution of six molecules of crystalline water and to obtaining monohydrate - $NiSO_4.H_2O$. Analogous is the change of the TG curve in the same region for 1' as well, but to $\Delta m_{exp.}$ = 42.7 % corresponds $\Delta m_{calc.}$ = 40.8 % i. e. the experimentally determined decrease in the mass of the sample is by about 2 % larger than the calculated one. This fact, observed in the deuterated hydrate, can be explained by the further course of the dehydration process, i. e. the beginning of the evolution of the last molecule of hydrate water. By way of corroboration for that assumption is also the smaller intensity of the second endoeffect in the DTA curve of 1', compared to the same one for 1. The maximum temperature of that effect for 1 and 1' is one and the same, T = 360°, and it corresponds to the data given in the literature [1-4].

The character of the examined first endoeffect in the DTA curves of $NiSO_4.7H_2O$ and of $NiSO_4.7D_2O$, respectively, shows that the dehydration to monohydrate proceeds stepwise, but from the data obtained it is not possible to give an accurate reply as to which these steps are. Ensuing from the structure of 1 [15, 16, 17] it follows that it possesses five types of aqueous molecules with different ambience. Their difference, from the point of view of energy, is not large (with the exception of one of them), since splitting of the effect is to be observed only in DTA, and it is not possible to record a change in the course of the TG curve. Quite different is the behaviour of the last water molecule, with the endoeffect having T_{max} = 360° corresponding to its evolution (Fig., curves a and a'). Such a high temperature of dehydration is a very rare phenomenon in hydrates. The anhydrous nickel sulphate is stable within a broad temperature range (Table).

The last endoeffect observed in the DTA of 1 has T_{max} = 860°, while for 1' it is at T_{max} = 820°. It corresponds to decomposition of the anhydrous

Table 1 Data from DTA and TG-curves for $NiSO_4.nH_2O$, accordingly $NiSO_4.nD_2O$ (n = 7, 6, 4, 1)

Transitions	H				D			
	Δm, %		Temp. interval,	T_{max},	Δm, %		Temp. interval.	T_{max},
	Calc.	Exper.	°C	°C	Calc.	Exper.	°C	°C
$NiSO_4.7H_2O \rightarrow NiSO_4.H_2O + 6H_2O$	38.5	37.8	80-290	140 & 200	40.8	42.7	100-340	160 & 200
$NiSO_4.H_2O \rightarrow NiSO_4 + H_2O$	6.4	6.6	320-480	360	6.8	5	340-480	360
$NiSO_4$ – stable (after TG)	-	-	480-740	-	-	-	480-700	-
$NiSO_4 \rightarrow NiO + SO_3$	28.5	27.9	740-900	860	27.1	26.8	700-860	820
$NiSO_4.6H_2O \rightarrow NiSO_4.4H_2O + 2H_2O$	13.7	13.2	80-150	120	14.5	14.5	80-150	120
$NiSO_4.4H_2O \rightarrow NiSO_4.H_2O + 3H_2O$	20.5	21	150-310	180	21.5	20.5	150-325	170
$NiSO_4.H_2O \rightarrow NiSO_4 + H_2O$	6.9	6.6	310-480	360	7.3	7.3	325-430	345
$NiSO_4$. – stable (after TG)	-	-	480-740	-	-	-	430-680	-
$NiSO_4 \rightarrow NiO + SO_3$	30.5	30.3	740-865	840	29.1	28.5	680-865	810
$NiSO_4.4H_2O \rightarrow NiSO_4.H_2O + 3H_2O$	23.8	23.7	105-300	170	25.6	28.3	80-290	120 & 165
$NiSO_4.H_2O \rightarrow NiSO_4 + H_2O$	8	7.9	300-460	360	8.5	4.7	290-420	345
$NiSO_4$ – stable (after TG)	-	-	460-700	-	-	-	420-640	-
$NiSO_4 \rightarrow NiO + SO_3$	35.2	34.8	700-865	840	34.1	33.5	640-860	810
$NiSO_4.H_2O \rightarrow NiSO_4 + H_2O$	10.4	10.8	280-540	360	11.4	12.3	260-450	335
$NiSO_4$ – stable (after TG)	-	-	500-700	-	-	-	460-700	-
$NiSO_4 \rightarrow NiO + SO_3$	46.3	45.8	650-860	840	45.8	45.2	700-860	810

sulphate to nickel oxide. Noteworthy is the lower (by 40°) temperature of decomposition of $NiSO_4$ obtained from $NiSO_4.7D_2O$, compared to that obtained from $NiSO_4.7H_2O$. This effect has also been observed in other hydrates investigated by us.

Curves b and b' of the Figure show the thermal curves of $NiSO_4.6H_2O$ (2) and $NiSO_4.6D_2O$ (2') - monoclinic modifications. They differ from those of the heptahydrate in the character of the first endoeffect and in its corresponding TG curve, as well as in the temperature of their phase transitions. This is something to be expected, having in mind the difference in their crystalline structures. A stepwise dehydration is clearly to be differentiated here, along both the DTA and TG curves, in the following diagram:

$$NiSO_4.6H_2O \xrightarrow{-2\,H_2O} NiSO_4.4H_2O \xrightarrow{-3\,H_2O} NiSO_4.H_2O$$

analogous in the case of the deuterate as well. Consequently, at the thermal decomposition of the hexahydrate it is possible to record the obtaining of $NiSO_4.4H_2O$, or $NiSO_4.4D_2O$, respectively, but the region of their stability is very small, and on that account their isolation and accurate identification is impossible at the thermal analysis. This behaviour of the monoclinic hexahydrate can be explained by the data about its crystalline structure [18, 19]. According to it, the water molecules coordinated around Ni - despite the different ambience obtained through hydrogen bonds with the structural groups surrounding them - behave differently upon thermal decomposition. Two of them, probably those with tetrahedral ambience determining a more essential weakening of the coordination bond, are the first to separate, and $NiSO_4.4H_2O$ ($4D_2O$) is obtained as an intermediate phase. The next moment the dehydration process continues, the remaining three molecules of hydrate water are evolved (they differ slightly from the first ones), and only after that the last water molecule is evolved at T_{max} = 360° for 2 and T_{max} = 345° for 2' (curves b and b' of the Figure), i. e. the temperature of its evolution differs essentially from that of the other ones, as in the case of the heptahydrates. Unlike the latter, it is different for the hexahydrates: for the deuterated hydrate it is by 15° lower than that of the ordinary one, this being in correlation with the data about the parameters of the crystalline lattice of the monoclinic modifications of the hexahydrates [20].

For the purpose of comparison, the thermal curves of $NiSO_4.4H_2O$ (3) and of $NiSO_4.4D_2O$ (3') are given in the Figure (c, c') immediately below those of the hepta- and hexahydrates. It is interesting to note that at 3' the first endoeffect is manifested split to a considerable extent, while the TG

curve clearly shows the respective step corresponding to the transition $NiSO_4.4D_2O \rightarrow NiSO_4.3D_2O$. Under the same conditions the thermal curves of 3 does not permit the recording of stepwise evolution of the hydrate water. The further dehydration of the monohydrate obtained takes place at the same temperature as in the case of the heptahydrate and hexahydrate. The last endoeffect of curves c and c' corresponds to decomposition of the anhydrous $NiSO_4$, the difference in the T_{max} for 4 and 4' remaining the same.

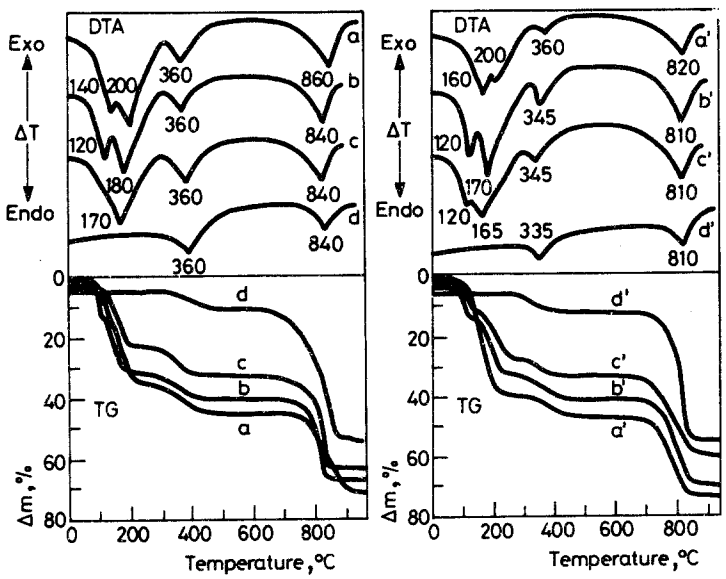

Fig. 1 TG and DTA curves of: $NiSO_4.7H_2O$ (a); $NiSO_4.7D_2O$ (a'); $NiSO_4.6H_2O$ (b); $NiSO_4.6D_2O$ (b'); $NiSO_4.4H_2O$ (c); $NiSO_4.4D_2O$ (c'); $NiSO_4.H_2O$ (d); $NiSO_4.D_2O$ (d')

The thermal curves of the monohydrates (curves d and d' on the Figure) are quite interesting and unexpected. The one water molecule is evolved at a temperature unusually high for monohydrates, $T_{max} = 360^{\circ}$ for 4 and $T_{max} = 335^{\circ}$ for 4', though its value is close to the temperature at which it is evolved in the higher hydrates. This fact suggests that this is a case of a water molecule from a structural group participating in the formation of the various hydrates investigated.

There are no data on this matter in the literature, because the authors studying these problems investigate the structures and the behaviours of single-type hydrates (hepta-, hexa-, tetra-, and monohydrates) of several dif-

ferent bivalent metals [1-10, 16, 17, 21], whereas this is a case of comparing the thermal curves of the different hydrates of one and the same element, and the relevant interpretations are made on the basis of them and of the structural data.

The last endoeffect (curves d and d' on the Figure) corresponds to $NiSO_4$ decomposition, and its maximum temperatures coincide accordingly with those of b, b' and c, c'.

A comparison of the initial temperatures of decomposition of $NiSO_4$ obtained from the various hydrates (n = 7, 6, 4, 1), ordinary and deuterated (Figure), shows that in all cases it is lower for samples obtained from the respective deuterates, compared to those obtained from the hydrates.

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Zusammenfassung — Mittels DTA wurde im Temperaturbereich von 20 bis 900°C die thermische Dehydratation und Zersetzung von $NiSO_4.nH_2O$ sowie $NiSO_4.nD_2O$ (mit n=7,6,4,1) bei einer Aufheizgeschwindigkeit von 10 deg/min untersucht. Ende-Effekte weisen in allen Fällen auf eine teilweise Dehydratation zum Monohydrat hin. Das letzte Molekül Kristallwasser wird bei einer höheren Temperatur, im Falle der Hydrate bei T_{max} 360°C, im Falle der Deuterate bei T_{max} 360-335°C abgegeben. Bei den Verbindungen $NiSO_46H_2O$ ($6D_2O$) sowie $NiSO_4.4D_2O$ verläuft auch eine stufenweise Dehydratation vor Erreichen der Monohydratstufe. Die Zersetzung von wasserfreiem $NiSO_4$ verläuft bei höheren Temperaturen, deren Wert davon abhängt, ob die Verbindung aus Deuterat oder Hydrat

entstand. Das aus Deuteraten erhaltene zersetzt sich schon bei relativ geringeren Temperaturen.