Thermochimica Acta, 12 (1975) 57–63

THE DEHYDRATION OF $ZnSO_4 \cdot 7H_2O$ AND $NiSO_4 \cdot 6H_2O$

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(Received 13 December 1974)

ABSTRACT

Using differential scanning calorimetry (DSC) in combination with effluent analysis, differential thermal analysis (DTA), thermogravimetric analysis (TG) and X-ray analysis, the dehydration of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ was investigated and a few transition enthalpies were measured. The dehydration of both compounds showed a great analogy. For $NiSO_4 \cdot 6H_2O$ the α–β phase transition was studied.

The dehydration scheme of both hydrates can be given as follows:

$NiSO_4 \cdot 6H_2O$: $6\alpha \rightarrow 6\beta$ ($\Delta H = 1.56 \pm 0.04$ kcal mol^{-1}), $6\beta \rightarrow 4$, $4 \rightarrow 1$, $1 \rightarrow 0$.

($NiSO_4 \cdot 7H_2O$): ($7 \rightarrow 6\alpha$)

$ZnSO_4 \cdot 7H_2O$: $7 \rightarrow 6$ ($\Delta H = 3.68 \pm 0.06$ kcal mol^{-1}), $6 \rightarrow 4$, $4 \rightarrow 1$, $1 \rightarrow 0$.

INTRODUCTION

There is a good deal of literature about the dehydration of $NiSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 7H_2O$; in spite of several applied methods, viz. DTA and TG, the interpretations of the dehydration course are contradictory.

For $ZnSO_4 \cdot 7H_2O$ Vallet and Bassière[1] have found the hexahydrate and tetrahydrate as intermediates between hepta- and monohydrate by calculations on TG-curves; these intermediates were also shown, while the possibility of the existence of tri- or dihydrate was not excluded. Pannetier et al.[2] have found similar results. Using thermal analysis methods Demassieux and Fedoroff[3] have found hepta-, hexa- and monohydrate. On the basis of crystallization data Rohmer[4] has arrived at the conclusion that there are three stable (hepta-, hexa- and monohydrate) and two instable hydrates (tetra- and dihydrate).

Between hexa- and monohydrate Frost et al.[5] have found amorphous intermediates. This has also been given by Chihara and Seki[6], who have described the dehydration of $ZnSO_4 \cdot 7H_2O$ as: $7 \rightarrow 6$, $6 \rightarrow 6$ (phase transition of the hexahydrate), $6 \rightarrow 1$ and $1 \rightarrow 0$. Murgulescu and Segal[7] assume an intermediate tetrahydrate and Fruchart[8] gives the dehydration course as: $7 \rightarrow 6\beta$, $6\beta \rightarrow 6\alpha$, $6\alpha \rightarrow 5$, $5 \rightarrow 1$, $1 \rightarrow 0.75$, $0.75 \rightarrow 0$.

Finally, Berg and Pribylov[9] give hepta-, hexa-, di- and monohydrate as intermediates in the dehydration. Besides they give some transition enthalpies.

Analogous to zinc sulphate, Demassieux and Fedoroff[10] have found for nickel sulphate only the hepta-, hexa- and monohydrate, although they mention amorphous intermediates between hexa- and monohydrate. Chihara and Seki[6] give the following dehydration course: $7 \rightarrow 6\beta$, $6\beta \rightarrow 6\alpha$ (spontaneously), $6\alpha \rightarrow 6\gamma$ or $6\gamma'$ (below or above 100°C, respectively), 6γ or $6\gamma' \rightarrow 4$, $4 \rightarrow 1$, $1 \rightarrow 0$; they note that 6γ and $6\gamma'$may be the same. Lendormy[11] has found hepta- and monohydrate, Caillère and Pobeguin[12] give the dehydration as follows: $7 \rightarrow 6$, $6 \rightarrow 6$ (phase transition of the hexahydrate), $6 \rightarrow 4$, $4 \rightarrow 1$ (possibly via tri- or dihydrate), $1 \rightarrow 0$, while Pannetier et al.[13] confirm the conclusions of Caillère and Pobeguin.

On the basis of the contradictory literary data it seemed very interesting to investigate the dehydration of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ by an alternative method and consequently to investigate whether or not the hexahydrate of nickel sulphate shows a phase transition (crystal transition) during the dehydration.

EXPERIMENTAL

Materials

$NiSO_4 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$ and $TlNO_3$ were obtained from Merck; only p.a. reagentia were used. $NiSO_4 \cdot 7H_2O$ was obtained by crystallization from an aqueous solution of $NiSO_4 \cdot 6H_2O$ at room temperature.

Apparatus and procedures

Measurements were carried out by means of DSC-1B of Perkin-Elmer. Effusing crystal water was detected by a katharometer (effluent analysis). The pulvarized samples (5–15 mg) were placed in small aluminum pans. Experiments were done both with closed sample pans and with sample pans with a pin-hole of approximately 10–20 μm in diameter. X-ray photographs of powders of $NiSO_4 \cdot 6H_2O$ were made with a high temperature Guinier camera and a Debije–Scherrer camera. TG and DTA-scans were made of the powdered hydrates.

RESULTS

DSC

Figures 1 and 2 show DSC-scans of the dehydration of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ in closed sample pans as well as in sample pans with a pin-hole. Effluent analysis graphs are also drawn in these figures. From the fact that peaks 4 and 11 do not appear in scans with closed sample pans it was concluded that they are to be ascribed to the evaporization of liberated crystal water:

$$H_2O(l) \rightarrow H_2O(g)$$

Enthalpy changes (or in the case of closed sample pans, strictly speaking, heats of

dehydration) were measured for peaks 1 and 9. For other peaks no reliable values can be given because of complicating circumstances, inherent to the technique used, viz., solving the solid hydrate in liberated crystal water.

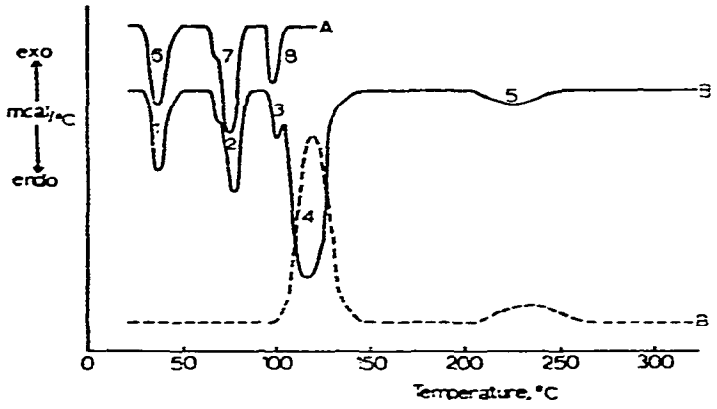

Fig. 1. DSC-scan of the dehydration of $ZnSO_4 \cdot 7H_2O$ in a closed sample pan (A) and in a sample pan with a pin-hole in combination with effluent analysis (B); 1, 6 = $ZnSO_4 \cdot 7H_2O(s) \rightarrow ZnSO_4 \cdot 6H_2O(s) + H_2O(l)$; 2, 7 = $ZnSO_4 \cdot 6H_2O(s) \rightarrow ZnSO_4 \cdot 4H_2O(s) + 2H_2O(l)$; 3, 8 = $ZnSO_4 \cdot 4H_2O(s) \rightarrow ZnSO_4 \cdot H_2O(s) + 3H_2O(l)$; 4 = $6H_2O(l) \rightarrow 6H_2O(g)$; 5 = $ZnSO_4 \cdot H_2O(s) \rightarrow ZnSO_4(s) + H_2O(g)$.

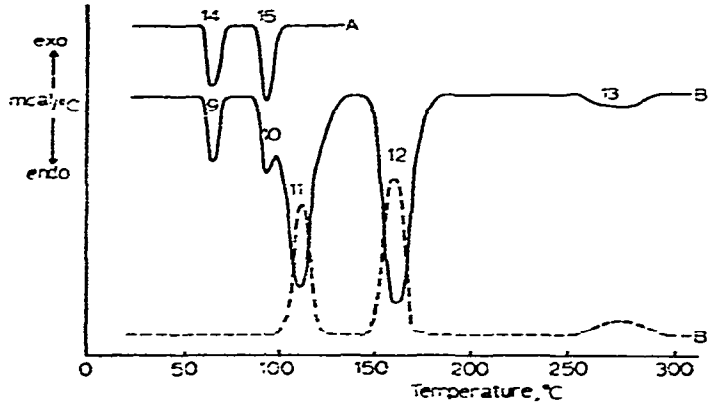

Fig. 2. DSC-scan of the dehydration of $NiSO_4 \cdot 6H_2O$ in a closed sample pan (A) and in a sample pan with a pin-hole in combination with effluent analysis (B); 9, 14 = $NiSO_4 \cdot 6H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6H_2O(s, \beta)$; 10, 15 = $NiSO_4 \cdot 6H_2O(s, \beta) \rightarrow NiSO_4 \cdot 4H_2O(s) + 2H_2O(l)$; 11 = $2H_2O(l) \rightarrow 2H_2O(g)$; 12 = $NiSO_4 \cdot 4H_2O(s) \rightarrow NiSO_4(s) + 3H_2O(g)$; 13 = $NiSO_4 \cdot H_2O(s) \rightarrow NiSO_4(s) + H_2O(g)$.

For the reaction at peak 1: $ZnSO_4 \cdot 7H_2O(s) \rightarrow ZnSO_4 \cdot 6H_2O(s) + H_2O(l)$, an enthalpy increase was found of 3.68 ± 0.06 kcal mol^{-1} (3.737 kcal mol^{-1} (ref. 14)).

Peak 9, which, as will be shown, is caused by the phase transition $NiSO_4 \cdot 6H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6H_2O(s, \beta)$, gives a ΔH-value of 1.56 ± 0.04 kcal mol^{-1}.

Determination of the quantity of crystal water

In order to determine whether the experiments had been started with $NiSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 7H_2O$, respectively, accurately weighed quantities of both materials were heated up to 400°C, then cooled down quickly and weighed immediately afterwards. The number of molecules of crystal water per molecule $NiSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 7H_2O$ were found to be 5.98 and 6.86, respectively.

Effluent analysis

Figures 1 and 2 show DSC-scans of $NiSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 7H_2O$ together with effluent analysis. For $ZnSO_4 \cdot 7H_2O$ the ratio of both effluent analysis peaks was 6:1; the three peaks of $NiSO_4 \cdot 6H_2O$ were in the proportion of 2:3:1.

Stability of $ZnSO_4 \cdot 4H_2O$

It appeared that $ZnSO_4 \cdot 7H_2O$, when exposed to air for a longer period, changes into $ZnSO_4 \cdot 4H_2O$. This was shown by DSC in combination with effluent analysis and by the determination of the quantity of crystal water (Fig. 3).

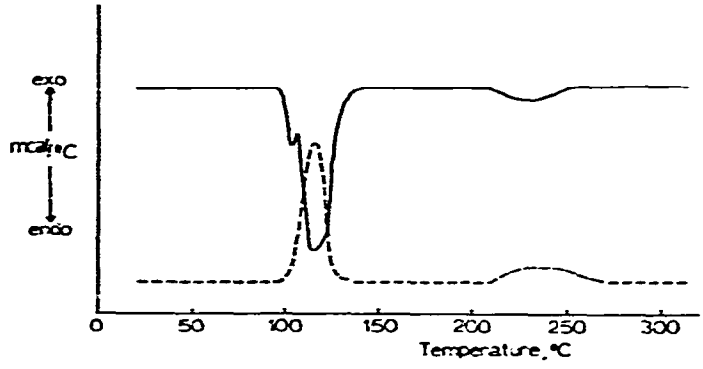

Fig. 3. DSC-scan of $ZnSO_4 \cdot 4H_2O$ in a sample pan with a pin-hole (solid curve) in combination with effluent analysis (dotted curve).

The ratio of the effluent analysis peaks was 3:1 in accordance with the supposition that $ZnSO_4 \cdot 4H_2O$ was present. Determination of the quantity of crystal water confirmed this.

Identification of peaks 9 and 10 (see Fig. 2)

The identification of peaks 9 and 10 gave rise to difficulties. In the literature[18,21], the existence of two different crystal modifications of $NiSO_4 \cdot 6H_2O$ is known: α-$NiSO_4 \cdot 6H_2O$, which is tetragonal and β-$NiSO_4 \cdot 6H_2O$, which is monoclinic. Further experimental work was done in order to confirm that the peaks are to be ascribed to:

$$NiSO_4 \cdot 6H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6H_2O(s, \beta) \text{ (peak 9)}$$

$$NiSO_4 \cdot 6H_2O(s, \beta) \rightarrow NiSO_4 \cdot 4H_2O + 2H_2O(l) \text{ (peak 10)}$$

The main difficulty was the coincidence of peaks 10 and 11 under various thermodynamic circumstances. In the following the results are stated briefly.

X-ray analysis

Powder photographs taken with a high temperature Guinier camera gave no definite results, mainly because of the instability of the supposed β-modification. However, there were some indications that the dehydration of $NiSO_4 \cdot 6H_2O$ proceeds via the 6α- and 6β-modifications and the tetrahydrate.

Reversibility

A way of determining whether peak 9 is caused by a crystal transition or by a dehydration would be to investigate the reversibility of the process. Therefore DSC-scans were made in sample pans with a pin-hole combined with the procedure of weighing the sample. It appeared that there was a loss of weight under isothermal circumstances near the transition temperature. No conclusion can be drawn from this experiment, as the assumption holds for both a dehydration and the instability of β-$NiSO_4 \cdot 6H_2O$.

DTA and TG

In these experiments peaks 9, 10 and 11 of the DSC-scans were found to coincide. Therefore it was concluded that the DTA-peak is caused by the overall reaction:

$$NiSO_4 \cdot 6H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 4H_2O(s) + 2H_2O(g)$$

The assumed instability of β-$NiSO_4 \cdot 6H_2O$ can account for this.

Dehydration of $NiSO_4 \cdot 7H_2O$

Figure 4 shows a DSC-scan of the dehydration of $NiSO_4 \cdot 7H_2O$ in a closed sample pan. Comparison with the dehydration of $NiSO_4 \cdot 6H_2O$ in a closed sample

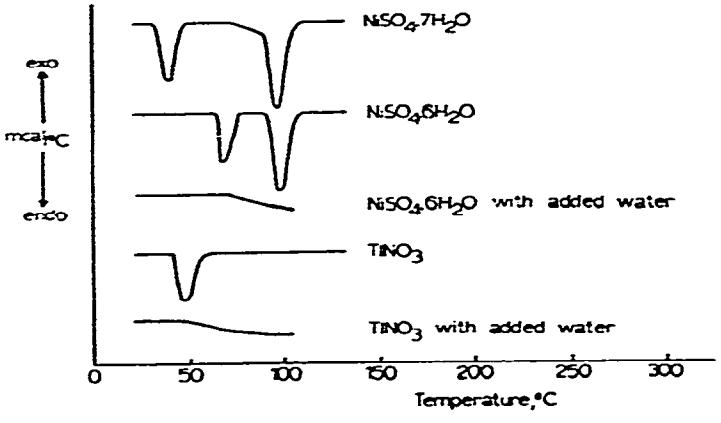

Fig. 4. DSC-scan of $NiSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$ and $TlNO_3$ in closed sample pans, showing the influence of added (liberated) water on the crystal transition.

pan clearly shows that crystal water, liberated from the transition 7→6 very strongly influences peak 9. The latter is deformed and shifted to a higher temperature, so that it partially coincides with peak 10. This experimental fact was used to distinguish between a crystal transition and a dehydration.

$TlNO_3$ and $NiSO_4 \cdot 6H_2O$ with water

It is known[15] that $TlNO_3$ shows a crystal transition at about 43 °C. A DSC-scan of this transition is shown in Fig. 4. In the same figure the DSC-scans of $TlNO_3$ with water, of $NiSO_4 \cdot 6H_2O$ (with and without water) and of $NiSO_4 \cdot 7H_2O$ (all in closed sample pans) are given. Solubility data being known[15], the quantities of water, added to $TlNO_3$ and $NiSO_4 \cdot 6H_2O$, were comparable. For practical reasons it was impossible to add an amount of water comparable to the quantity of crystal water that effuses at the transition 7→6 of $NiSO_4 \cdot 7H_2O$.

However, it is clear from Fig. 4 that addition of water has the same effect on peak 9 of $NiSO_4 \cdot 6H_2O$ as on the phase transition of $TlNO_3$. This gives strong evidence for a phase transition of $NiSO_4 \cdot 6H_2O$.

$ZnSO_4 \cdot 7H_2O$

From Fig. 2 it can be seen that the dehydration peaks 6→4 and 4→1 are not influenced by crystal water, liberated during a previous dehydration (7→6).

DISCUSSION

On the basis of the experimental results, the dehydration of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ was established as follows:

$$ZnSO_4 \cdot 7H_2O(s) \rightarrow ZnSO_4 \cdot 6H_2O(s) + H_2O(l); \quad \Delta H = (3.68 \pm 0.06) \text{ kcal mol}^{-1}$$
$$ZnSO_4 \cdot 6H_2O(s) \rightarrow ZnSO_4 \cdot 4H_2O(s) + 2H_2O(l)$$
$$ZnSO_4 \cdot 4H_2O(s) \rightarrow ZnSO_4 \cdot H_2O(s) + 3H_2O(l)$$
$$6H_2O(l) \rightarrow 6H_2O(g)^*$$
$$ZnSO_4 \cdot H_2O(s) \rightarrow ZnSO_4(s) + H_2O(g)^*$$

$$NiSO_4 \cdot 6H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6H_2O(s, \beta); \quad \Delta H = (1.56 \pm 0.04) \text{ kcal mol}^{-1}$$
$$NiSO_4 \cdot 6H_2O(s, \beta) \rightarrow NiSO_4 \cdot 4H_2O(s) + 2H_2O(l)$$
$$2H_2O(l) \rightarrow 2H_2O(g)^*$$
$$NiSO_4 \cdot 4H_2O(s) \rightarrow NiSO_4 \cdot H_2O(s) + 3H_2O(g)^*$$
$$NiSO_4 \cdot H_2O(s) \rightarrow NiSO_4(s) + H_2O(g)^*$$

When starting from $NiSO_4 \cdot 7H_2O$, the following transition is also present:

$$NiSO_4 \cdot 7H_2O(s) \rightarrow NiSO_4 \cdot 6H_2O(s, \alpha) + H_2O(l).$$

*These transitions only occur when starting with sample pans with a pin-hole.

The dehydration course of $ZnSO_4 \cdot 7H_2O$ agrees with the findings of Pannetier et al.[2]. The transition of $ZnSO_4 \cdot 6H_2O$ to $ZnSO_4 \cdot 4H_2O$ shows a shoulder peak (Fig. 1), giving some indication for a crystal transition, analogous to $NiSO_4 \cdot 6H_2O$. However, this could not be confirmed.

The dehydration of $NiSO_4 \cdot 6H_2O$ has also been given by Caillère and Pobeguin[12] and by Pannetier et al.[13]. No indications have been found of other crystal modifications of $NiSO_4 \cdot 6H_2O$ as given by Chihara and Seki[6].

Of major importance for all experiments with DSC were the thermodynamic circumstances. As soon as the experimental circumstances were changed, as for example was the case with DTA, TG and X-ray analysis, the dehydration course was different from that established by DSC and effluent analysis.

This was most evident in the transition $6\alpha \rightarrow 6\beta$ for $NiSO_4 \cdot 6H_2O$. This peak coincided with the dehydration $6 \rightarrow 4$ because of the instability of β-$NiSO_4 \cdot 6H_2O$.

The strong resemblance in dehydration between $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ is striking; the transition temperatures of the dehydrations, which are higher for nickel sulphate, constitute the main difference. It is known that hepta-, tetra- and monohydrate of nickel- and zincsulphate are isomorphous[13,16–18]. It is equally well known that the hydrates $FeSO_4 \cdot 6H_2O$, $MnSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 6H_2O$ etc., are isomorphous with those of nickel- and zincsulphate [16–20]. It is reasonable to suppose that these hydrates will show a behaviour, analogous to the dehydration of $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$.

REFERENCES

1 P. Valiet and M. Bassière, *Bull. Soc. Chim. Fr.*, 5 (1938) 546.
2 G. Pannetier, A. Michel, J.-M. Brégeault and G. Djega-Mariadassou, *Bull. Soc. Chim. Fr.*, (1963) 1204.
3 N. Demassieux and B. Fedoroff, *C.R. Acad. Sci.*, 205 (1937) 457.
4 R. Rohmer, *C.R. Acad. Sci.*, 210 (1940) 669.
5 G. Frost, K. Moon and E. Tompkins, *Can. J. Chem.*, 29 (1951) 604.
6 H. Chihara and S. Seki, *J. Chem. Soc. Japan*, 26 (1953) 88.
7 I. Murgulescu and E. Segal, *Anal. Univ. Bucarest*, 22 (1959) 75.
8 E. Fruchart, *Thesis*, Lille, 1959.
9 G. Berg and K. Pribylov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 7 (1964) 535; and 9 (1966) 6.
10 N. Demassieux and B. Fedoroff, *C.R. Acad. Sci.*, 206 (1938) 1649.
11 N. Lendormy, *Chim. Anal.*, 44 (1962) 255.
12 S. Caillère and Th. Pobeguin, *Bull. Soc. Chim. Fr., Miner. Crist.*, 85 (1962) 48.
13 G. Pannetier, J.-M. Brégeault, C. Lecouturier and G. Djega-Mariadassou, *Bull. Soc. Chim. Fr.*, (1964) 3141.
14 R. Barieau and W. Giauque, *J. Am. Chem. Soc.*, 72 (1950) 5676.
15 *Handbook of Physics and Chemistry*, Chem. Rubber Publishing Co., Cleveland, 52nd ed., 1971/1972.
16 Y. le Fur, J. Coing-Boyat and G. Bassi, *C.R. Acad. Sci., Ser. C*, 262 (1966) 632.
17 G. Pannetier, J.-M. Brégeault and M. Tardy, *Bull. Soc. Chim. Fr.*, (1966) 324.
18 R. Wijckoff, *Crystal Structures*, Vol. 3, Interscience Publishers, New York, 1965.
19 H. Oswald, *Helv. Chim. Acta*, 48 (1965) 590.
20 B. O'Connor and D. Dale, *Acta Crystallogr.*, 21 (1966) 705.
21 D. Sutor, *Acta Crystallogr.*, 12 (1959) 72.