

## THERMOGRAVIMETRIC ANALYSIS OF HEXA- AND HEPTAHYDRATE CRYSTALS AND PACKED POWDER OF NICKEL SULFATE

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### ABSTRACT

The sequence of the deaquation of hexa- and heptahydrates of nickel sulfate crystals, pellets and packed powder was studied by thermogravimetry. Crystals were grown at 12.5 and 40°C. It was observed that crystals grown at 12.5°C show the presence of seven molecules of water of crystallization irrespective of whether the starting material is hexa or hepta, whereas crystals grown at 40°C behave as hexahydrate irrespective of the starting material. The sequence of the deaquation steps in  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  crystals is given as 1 mole, 3 moles, 2 moles and 1 mole, and the corresponding DTG minima occur at 130, 190, 210 and 380°C. Crystals grown at 40°C show deaquation steps as 1 mole, 2 moles, 2 moles and 1 mole, and the DTG dips corresponding to this occur at 129, 187, 214 and 390°C. Pellets and packed powder show deaquation steps as 2 moles, 3 moles and 1 mole, and the corresponding DTG minima occur at 134, 178 and 345°C irrespective of whether they are hepta- or hexahydrate.

### INTRODUCTION

The sequence of deaquation steps in many polyhydrated metal sulfates as reported by Ben-Dor and Margalith<sup>1</sup> consists of two definite steps. First, all but one molecule of water are evolved at relatively low temperatures (beginning at 60°C) then after a significant rise in temperature the last molecule is evolved. Tanabe and co-workers<sup>2</sup> used X-ray, IR, ESR and NMR techniques in their investigations of nickel sulfate monohydrate because of the special interest in catalytic activity. Fruchart and Michel<sup>3</sup> detected intermediate compounds when  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  was heated and ascribed their success to the slow heating rate of  $0.6^\circ\text{C min}^{-1}$ . The sequence of deaquation steps of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  was given by Fruchart and Michel<sup>3</sup> as 1 mol, 2 moles, 3 moles and 1 mole. Sarig<sup>4</sup>, from simultaneous TG, DTG and DTA analysis, suggested the deaquation steps in  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  as 1 mole, 3 moles, 2 moles and 1 mole at temperatures 60, 110, 130 and 330°C, respectively. The scheme of Sarig for the heptahydrate is quite different from that of Fruchart and Michel. It has been pointed out by Sarig that both Ben-Dor and Margalith and Tanabe and

co-workers list  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  as the starting material but report results concerning  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  only.

It is reported<sup>5</sup> that above room temperature ( $30^\circ\text{C}$ ),  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  is always transformed into  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ; even if the sample is kept in a closed vessel, it slowly loses one molecule of water of crystallization. Paulik et al.<sup>6</sup>, in their extensive study on the effect of experimental conditions on the reproducibility and selectivity of thermal analysis results, stressed the importance of sample packing and layer thickness.

Different workers have mentioned different temperatures for the same deaquation steps. More stress has generally been given to the deaquation steps rather than to the deaquation temperatures though actually the deaquation steps are determined by the distinct deaquation temperatures. In view of the facts that (i)  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  is transformed into  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , (ii) thermal analysis results are susceptible to sample packing, and (iii) experiments carried out on different samples under different experimental conditions give different results for the same deaquation process, it was thought fit to reinvestigate the deaquation steps in both  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  independently using freshly prepared samples. Thus  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  have been procured and their crystals have been grown at two different temperatures,  $12.5$  and  $40^\circ\text{C}$ , at which one is definitely hepta and the other a hexa crystal. Thermogravimetric studies of these crystals along with their pellets and packed powder are presented in this paper.  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  crystals show the same scheme of deaquation as was suggested by Sarig<sup>4</sup> but  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  has a different scheme.

## EXPERIMENTAL

### *Nature of the samples*

Nickel sulfate hexa- and heptahydrate powders of purity greater than 99.5% were obtained from Sarabhai Chemicals and BDH chemicals, respectively. The powders were ground to  $104\ \mu\text{m}$  size and pellets were prepared by pressing the powder in a hydraulic press to a pressure of  $5000\ \text{kg cm}^{-2}$ . The powder and the pellets were then used for thermogravimetry measurements. Also, crystals were grown from the aqueous solutions of these two sulfates by a slow evaporation process at  $40$  and  $12.5^\circ\text{C}$  respectively.

### *Thermogravimetric analysis*

TG study was carried out using a special TG assembly fabricated in the laboratory. The details of the assembly have already been reported in previous communications. The measurements of loss in mass of  $\text{NiSO}_4$  hexa- and heptahydrate crystals, pellets and loosely packed powder samples were carried out in the temperature range  $30$ – $450^\circ\text{C}$ . The samples were heated at a constant rate of  $5^\circ\text{C min}^{-1}$ . The loss in mass and time were measured at an interval of  $5^\circ\text{C}$ . The values of  $\Delta m/\Delta t$ , i.e. the rate of change of mass ( $\text{mg min}^{-1}$ ) were calculated at different temperatures. Graphs were

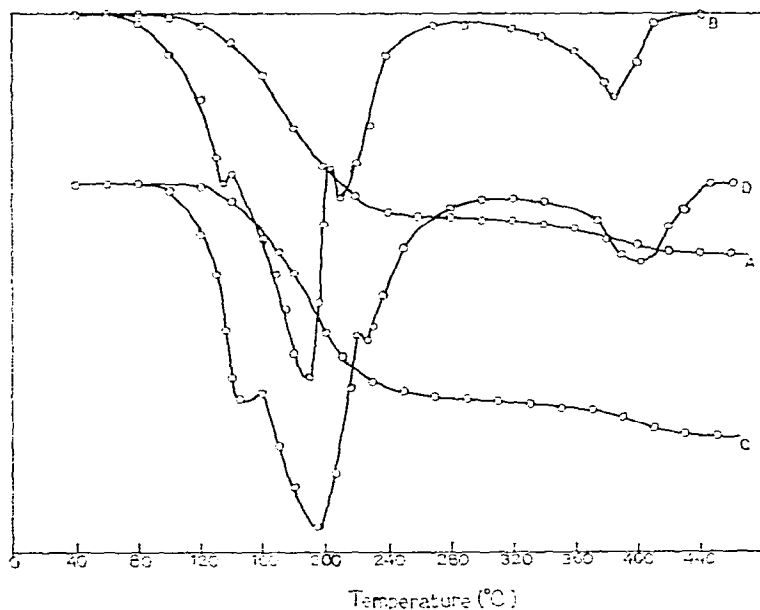


Fig. 1. TG curves for  $\text{NiSO}_4$  crystal grown at  $12.5^\circ\text{C}$ . A and B, the respective TG and DTG curves for crystals grown from  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  powder. C and D, the respective TG and DTG curves for crystals grown from  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  powder.

plotted of the change in mass vs. corresponding temperatures (TG) and rate of change of mass vs. corresponding temperatures (DTG).

#### RESULTS AND DISCUSSION

Figure 1 gives a representative set for the sequence of deaquation steps in nickel sulfate hepta- and hexahydrate crystals grown at  $12.5^\circ\text{C}$ . The crystals grown from both the samples show four different DTG minima at the respective mean temperatures 136, 190, 210 and  $384^\circ\text{C}$  giving the sequence of deaquation steps as 1 mole, 3 moles, 2 moles and 1 mole. Such a sequence of deaquation steps has been reported by Sarig in the case of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . The mean temperatures have been determined from five sets of observations taken for each crystal. The graph shows one of the representative sets.

Crystals grown at  $40^\circ\text{C}$  from both the samples show four minima in the DTG curve (Fig. 2) at the respective mean temperatures 129, 187, 214 and  $390^\circ\text{C}$ . The results indicate the sequence of deaquation-steps as 1 mole, 2 moles, 2 moles and 1 mole.

Powder and pellets from both the samples show the presence of three distinct minima in the DTG curves (Figs. 3 and 4) at the mean temperatures 134, 178, and  $345^\circ\text{C}$ . The corresponding deaquation steps are 2 moles, 3 moles and 1 mole. In some cases, however, the single step of three molecules splits further into two different steps of 1 mole and 2 moles, making the deaquation steps 2 moles, 1 mole, 2 moles and 1 mole.

The DTG of the crystals grown at  $12.5^\circ\text{C}$  from both the hexa and hepta samples

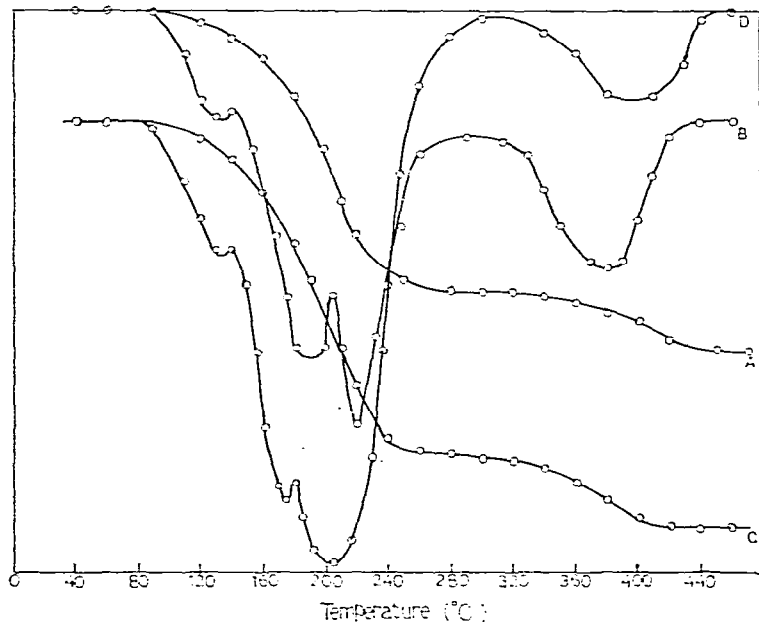


Fig. 2. TG curves for  $\text{NiSO}_4$  crystals grown at  $40^\circ\text{C}$ . A and B, the respective TG and DTG curves for crystals grown from  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  powder. C and D, the respective TG and DTG curves for crystals grown from  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  powder.

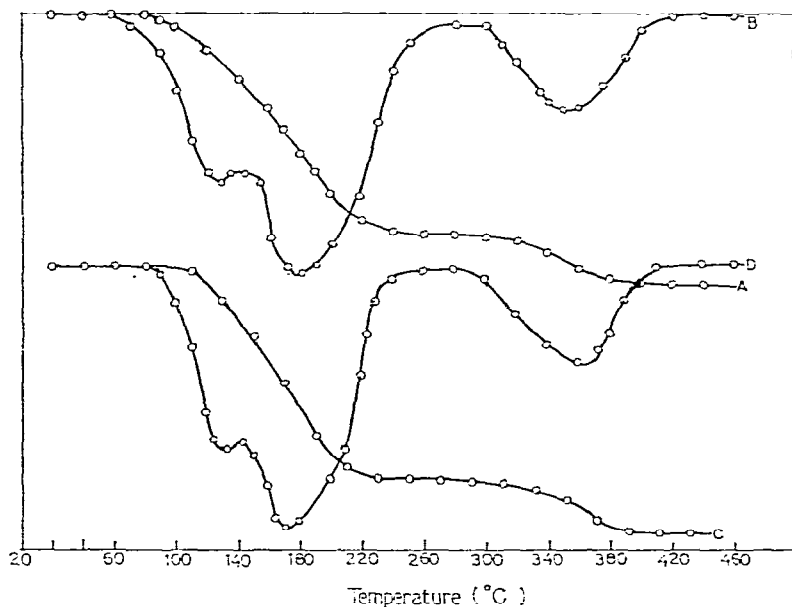


Fig. 3. TG and DTG curves for  $\text{NiSO}_4$  powder pack ( $104 \mu$  size). A and B, curves for powder pack from  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . C and D, curves for powder pack from  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .

indicates that the crystals formed are heptahydrate in nature irrespective of the starting materials. Sarig<sup>4</sup> reports the deaquation temperatures for  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  as 60, 110, 130 and  $330^\circ\text{C}$  using DTA and DTG techniques, and claims that the first water molecule shows its existence in both DTA and DTG peaks. The occurrence

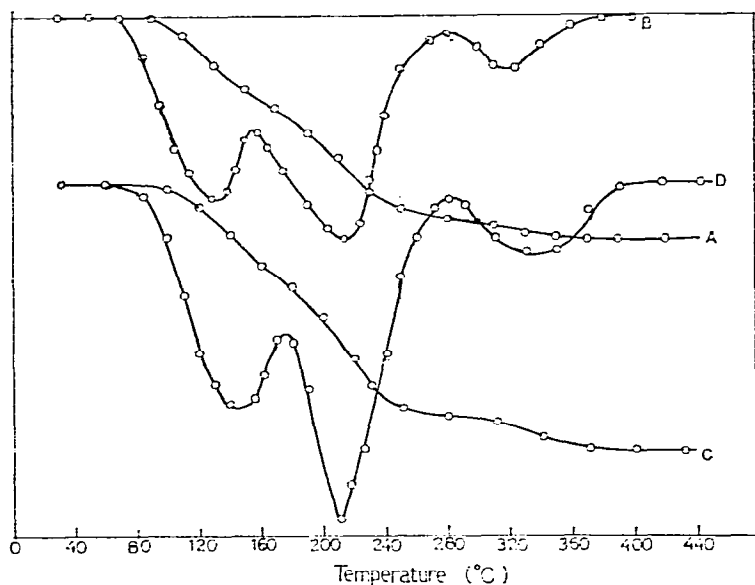


Fig. 4. TG and DTG curves for  $\text{NiSO}_4$  pellets ( $104 \mu$  size). A and B, curves for pellets from  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . C and D, curves for pellets from  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .

of the DTG peak at  $60^\circ\text{C}$ , however, appears to be erroneous because it has been reported<sup>7-10</sup> that  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  melts in its own water of crystallization at  $88^\circ\text{C}$  and the water then boils off at  $102\text{--}105^\circ\text{C}$ . This means that the first molecule of water of crystallization which comes out of the crystal lattice at  $60^\circ\text{C}$  remains partly within the crystal and partly on its surface, dissolving some of the nickel sulfate in it. This water then boils off. It indicates that although the water molecule comes out of the crystal lattice, it does not leave the crystal and therefore there should not be any weight loss in the process.

Also, when a crystal of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  of mass 709 mg was maintained at  $70^\circ\text{C}$  for 1 h, a change of only 1 mg was observed in its mass though actually a change of 45 mg was expected for the release of the first water molecule deaquating at  $60^\circ\text{C}$ , clearly indicating that there cannot be any DTG minimum at  $60^\circ\text{C}$ . DTA may, however, show an exothermic peak for such a change. The melting and boiling of the first molecule of water of crystallization is very well demonstrated in the conductivity measurements on  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  (results of the conductivity and dielectric measurements are being communicated separately). The conductivity increases abruptly at  $65^\circ\text{C}$  by seven orders of magnitude and remains at this value upto about  $125^\circ\text{C}$ , beyond which it again abruptly decreases to the original value. The direct observation of the crystal surface also reveals the presence of water. On removal of the surface water, the crystal loses its transparent nature due to the formation of a thin layer of nickel sulfate.

In the case of crystals grown at  $40^\circ\text{C}$ , it is observed that, irrespective of the starting materials, the crystals obtained are transparent and hexahydrate in nature. It may be noted that the crystals grown at  $12.5^\circ\text{C}$  have a habit of growing in plates,

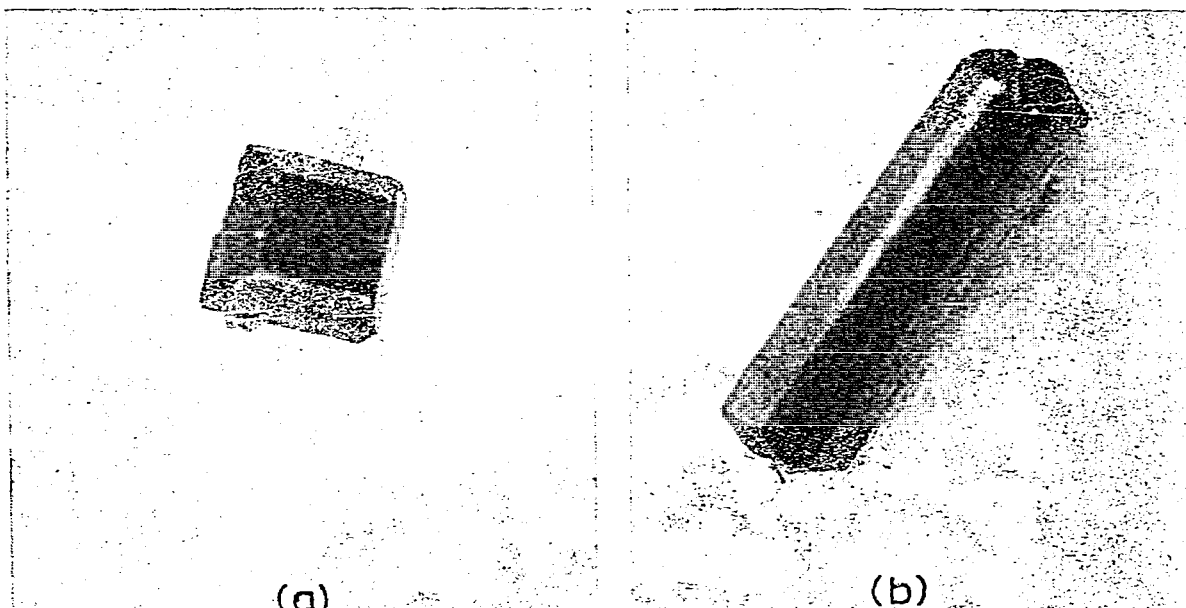


Fig. 5. Photograph of the crystal grown at (a) 40 °C and (b) 12.5 °C.

whereas the crystals grown at 40 °C have a different habit (prismatic). Figure 5(a, b) shows the crystals grown at 40 and 12.5 °C, respectively.

The TG study of powder and pellet shows that  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  is converted into  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  at room temperature and shows similar deaquation steps as shown by  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ . In the case of crystals, it is observed that the first minimum in the DTG curve always occurs at about 134 °C irrespective of whether the crystal is heptahydrate or hexahydrate. It appears, therefore, that in the case of heptahydrate crystals, although the first water molecule is weakly bound and is released at a sufficiently low temperature (60 °C), it does not lead to loss in mass of the sample as it is retained in the sample upto about 110 °C. On the other hand, in the case of hexahydrate crystals, the first water molecule is bound more strongly. Its release occurs at a relatively higher temperature and this release is followed by a loss in mass of the sample. After the removal of the first water molecule from the heptahydrate, the next three water molecules do not behave in a similar manner as the first three molecules of the hexahydrate crystal, probably due to the difference in their binding strengths. When the heptahydrate crystal is gradually converted into hexahydrate at room temperature, after the removal of the first water molecule the remaining water molecules rearrange in such a way that the second deaquation step comprising of three water molecules is split into two different steps of 1 mole and 2 moles. The release of this molecule is responsible for the occurrence of a minimum at 134 °C.

Evans<sup>11</sup> has made a clear distinction between the crystals containing six and seven water molecules.  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  has been listed as containing only coordinating water molecules whereas  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  has been listed as containing coordinating as well as structural water. However, the TG study shows that whether the sample is a hexa- or a heptahydrate, the last water molecule comes out at the same high tempera-

ture (385°C) and its deaquation is spread over a wide temperature range. Hence the last water molecule appears to behave like structural water in both hepta- and hexahydrates.

## CONCLUSIONS

It may be concluded from the study that the degree of crystal perfection appreciably affects the deaquation steps and the deaquation temperatures. At room temperature, both the hexa- and heptahydrate samples behave as hexahydrate only. Only freshly prepared crystals grown at low temperatures show the presence of seven molecules of water of crystallization. The first deaquation step occurring at 60°C shows its presence in DTA and conductivity measurements but not in TG.

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