Studies of Crystalline Hydrates. II. Thermal Transition and Dehydration of Ni-, Fe-, Co-, Zn-, Mn-, and Mg-sulfate Hydrates

By Hideaki CHIHARA and Syûzô SEKI

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Introduction

The studies of the dehydration of crystal hydrates are of basic significance for clarifying the nature of the interaction between water and various materials on one side, and the mechanism of the typical hetero-phase reaction involving solids on another side, particularly in the cases in which atomic structures of the crystals are accurately known. Although numerous investigations have been made on the solubility of the hydrates for their successive degrees of hydration,(1) on the dissociation pressures and on the decomposition-reaction mechanisms,(2) there still remain much to be investigated from their atomistic and energetic points of view. Recently, the magnetic susceptibility measurement of hydrates containing paramagnetic ions and the nuclear magnetic resonance absorption studies of the crystal water have interested the physicists.(3) In these respects, it would be desirable to study the dehydration processes and the behavior of water molecules in hydrates in greater detail.

Although the method of the thermal analysis has been used by many investigators for the study of dehydration process, the detailed experiment in relation to the crystal structure, as far as the authors are aware, is only that of copper sulfate pentahydrate measured by Taylor and Klug.(4) We have applied the differential thermal analysis further to Ni sulfate hydrate, typical of known crystal structure, and other related hydrates under various conditions in order to elucidate their dehydration processes and also whether or not these crystals undergo transitions similar to those of $CuSO_4 \cdot 5H_2O$ which are considered to be attributed to the rotation of water molecules.

Experimental

Materials.—$NiSO_4 \cdot 7H_2O$.—The product of Kahlbaum Co. was recrystallized from an aqueous solution at about 0°C. and the excess water in the precipitate was removed by pressing it between filter paper and then dried in a desiccator containing the same hydrate partially dehydrated as a desiccating material. This procedure of drying was adopted for all of the samples mentioned below.

$ZnSO_4 \cdot 7H_2O$.—The product of Kahlbaum Co. was recrystallized from aqueous solution at about 0°C.

$MgSO_4 \cdot 7H_2O$.—The product of Merck Co. was recrystallized from aqueous solution at about 0°C.

$FeSO_4 \cdot 7H_2O$.—The product (extra pure) of Katayama Co. was recrystallized from slightly acidic solution at about 0°C.

$CoSO_4 \cdot 7H_2O$.—The product (extra pure) of Ishizu Co. was recrystallized from aqueous solution at about 0°C.

$MnSO_4 \cdot 7H_2O$.—The product (extra pure) of Ishizu Co. was recrystallized from an aqueous solution at about 0°C.

$NiSO_4 \cdot 6H_2O$.—The hexahydrate was prepared either by crystallizing from an aqueous solution

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(1) N. V. Tanzov, *J. Russian Phys.-Chem. Soc.* **55**, 335 (1924); A. Chretien and R. Rohmer, *Compt. rend.* **198**, 92 (1934); H. H. Ting and W. L. McCabe, *Ind. Eng. Chem.* **26**, 1207 (1934); R. Rohmer, *Compt. rend.* **210**, 669 (1940); J. H. Krepelka and B. Rejha, *Coll. Czechoslovak. Chem. Com.* **5**. 67 (1933); F. Fraenckel. Z. *anorg. Chem.* **55**, 223 (1939).

(2) "Chemical Reactions involving Solids", Discussions of the Faraday Society, 1938; E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.* **41**, 488 (1945).

(3) J. Wheatley and D. Halliday, *Phys. Rev.* **75**, 1412 (1949); G. E. Pake, *J. Chem. Phys.* **16**, 327 (1948).

(4) T. I. Taylor and H. P. Klug. *J. Chem. Phys.* **4**, 601 (1936).

at about 40°C. or dehydrating the heptahydrate. All these samples were stored in the desiccators during various periods of time to examine the aging effect.

Apparatus and Procedures.—The apparatus used for the differential thermal analysis was the same as that previously reported,⁽⁵⁾ so a brief comment may be given here. As shown in Fig. 1, A is a copper block with two drilled holes, in each of which a thinwalled glass tube is fitted: one contains NaCl as a standard material and the other the sample to be investigated. B and C are copper-constantan thermo-couples for the measurements of temperature of NaCl and of temperature difference between the sample and NaCl, respectively. In order to determine the water content of the samples, the capillary tubes D are used for collecting water vapor produced by decomposition. The water content at successive stages of dehydration is measured by the following procedure. After the completion of a stage of dehydration which is shown by the restoration of increased temperature difference to its normal steady state value, the heater is turned off and the cell system is pumped off slowly to condense the dehydrated water in a liquid air trap I. The temperature difference between the sample and NaCl is again on the increase by the self-cooling of the sample due to the evaporation of liberated water. As the amount of liberated water in the sample tube decreases, the deflection of the galvanometer for the differential thermocouple stops increasing and then begins to decrease. As soon as this decrease turns to increase again on account of the beginning of the next step of dehydration, the pumping is stopped and dry air is introduced into the whole system to prevent further dehydration. The collected water is then led to one of the capillary tubes D and the amount of water is weighed after the tube is fused off. As an example, data for $NiSO_4 \cdot 6H_2O$ are given in Table 1. In every run, the sample was heated at a constant rate of 0.6 to 1.5°C. per minute under atmospheric pressure, unless otherwise stated. The X-ray powder photographs were taken by copper $K\alpha$ radiation. To examine the structure change at the transition temperature, a high-temperature camera was employed.

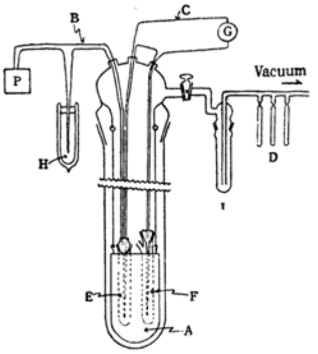

Fig. 1.—A schematic diagram of the apparatus for differential thermal analysis.
E: a reference cell containing NaCl;
F: a sample tube; G: a galvanometer;
H: the standard temperature (ice);
I: a liquid air trap; P: a potentiometer.

Table 1

Determination of Water Content of Nickel Sulfate Hydrates

Initial wt.	Loss of wt. at the transition or dehydration points.		
Room temp.	86°	110°	132°
0.829 g.	0.009 g.	0.115 g.	0.160 g.
	Loss of water. mole/mole of $NiSO_4$		
	≈0	2.09≈2	2.82≈3

Experimental Results.—(1) **Differential thermal analysis:**

One of the typical temperature-time curves is illustrated in Fig. 2. The whole results under different conditions for various samples are given in Figs. 3 to 8 in which the positions of the vertical lines represent the dehydration or transition temperatures and their length means an approximate value of the heat effect. The diffuse band stands for a transition or a dehydration ranging over a temperature interval. The downward band is for the evolution of heat. Ordinates show the temperature scale in t°C. (Fig. 2 corresponds to Fig. 3c). Dotted vertical lines show

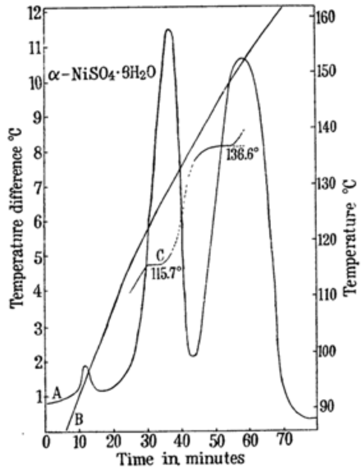

Fig. 2.—An example of differential thermal analysis.
A: Temperature difference between the sample and NaCl. (left scale)
B: Heating curve of NaCl. (right scale)
C: Heating curve of the sample which is drawn by subtracting A from B. (right scale).

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(5) I. Nitta, S. Seki, and H. Chihara, *J. Chem. Soc. Japan, Pure Chem. Sect.* **70**, 387 (1949).

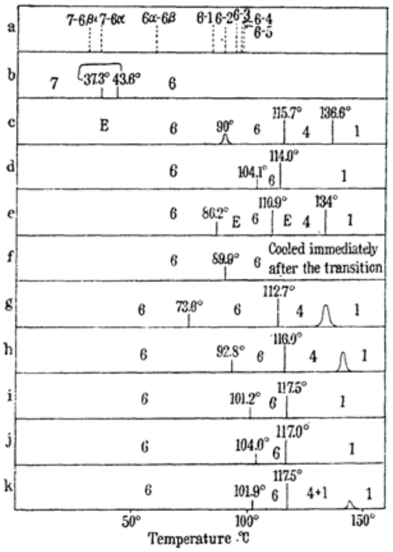

Fig. 3.—Differential thermal analyses of nickel sulfate hydrates. "E" stands for evacuation and admission of dry air. Time of storage of samples is as follows:

(b) 80 d. As to the two peaks, see in the text.
(c) 1 d. Continuation of (b).
(d, e, f) 13.5 m.
(g) Continuation of (f).
(h) 25 d. A week after grinding.
(i) 3.5 m. Immediately after grinding.
(j) 6 m. Unground sample.
(k) 6.5 m. Coarsely crushed sample.
(e, f, g, h) and (i, j, k) are two groups of specimens, each being parts of the same samples, respectively. d. = days, m. = months.

the transition or dehydration temperatures of hydrates in aqueous solutions determined from the solubility curves.(1) Fig. 3e corresponds to the experiment for determining the degrees of hydration given in Table 1.

(2) **X-ray powder photographs:** Since the complete analysis of the crystal structure has been reported only for α-$NiSO_4 \cdot 6H_2O$ and $NiSO_4 \cdot 7H_2O$, we have applied the X-ray identification method only to these materials. The observed Debye line diagrams under various conditions are given in Fig. 9. Fig. 9e shows the reference positions calculated from the known crystal structure data of α-$NiSO_4 \cdot 6H_2O$ determined by Beevers and Lipson.(6)

Discussion of Results

(a) Comparison of the dehydration temperatures determined from the differential thermal analysis with those from the solubility curves.

It should be noted that the dehydration and the transition temperatures determined by these two methods have, in general, different meanings,

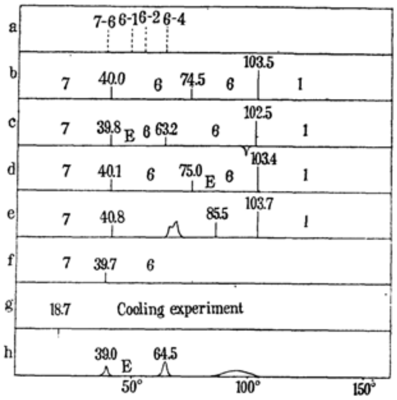

Fig. 4.—Differential thermal analysis of $ZnSO \cdot 7H_2O$.

(b) 15 m.
(c) 16.5 m. At 98°, a heat evolution is observed.
(d) 18.5 m. (e) 30.5 m. (f) 30.5 m.
(g) Continuation of (f), Cooling curve.
(h) Continuation of (g), A month after (g).

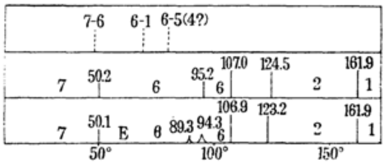

Fig. 5.—Differential thermal analysis of $MgSO_4 \cdot 7H_2O$.

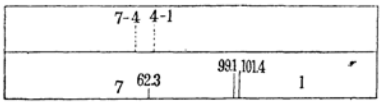

Fig. 6.—Differential thermal analysis of $FeSO_4 \cdot 7H_2O$.

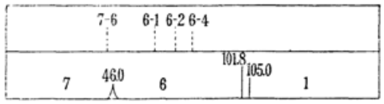

Fig. 7.—Differential thermal analysis of $CoSO_4 \cdot 7H_2O$.

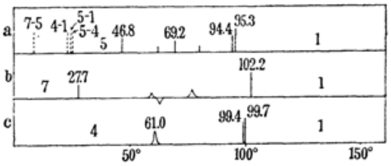

Fig. 8.—Differential thermal analysis of $MnSO_4$ hydrates.

a) Pentahydrate, b) Heptahydrate,
c) Tetrahydrate.

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(6) C. A. Beevers and H. Lipson, *Z. Krist.* **83**, 123 (1932).

i. e. the material subjected to the thermal analysis belongs to an open system, so that the existing phases are not absolutely in their equilibrium state, whereas in an aqueous solution the various phases in contact are in the true equilibrium state. Taking this situation into account, comparisons are now made of the transition temperatures in Figs. 3 to 8. In the case of Mn sulfate, none of the dehydration temperatures in the present study coincides with those obtained from the solubility curve, but in other hydrates the first step of dehydration (7−6) nearly agrees in both methods and this is particularly confirmed with Ni sulfate, in which case the dehydration temperature (43.6°C.) in the first run is shifted to lower temperature (37.3°C.) in the next repeated run, the second one being in perfect agreement with the dehydration temperature (heptahydrate→β-hexahydrate) in the aqueous solution (Fig. 3b). The solubility curve of hexahydrate, when temperature is raised, intersects with that of monohydrate first and then those of di-, tri-, tetra-, and penta-hydrates successively if they can exist. Hence, the lower hydrates are more stable than the higher ones in the aqueous systems (see, for instance, Fig. 3a). However, the situation is entirely different in an open system.* In raising temperature, the hexahydrates are dehydrated to form lower hydrates in just the opposite order from that in the open system. And none of the dehydration temperatures coincides in these two processes of dehydration. In aqueous solutions, the stable modification of nickel sulfate between 31.5 and 60°C. is the α-hexahydrate (6α), and it is this modification that first appears in the dehydration of the heptahydrate in the aqueous system. But in the dry system, as is shown in Fig. 3b, the transition from the heptahydrate to β-hexahydrate (6β) does take place first, which is evident by the coincidence of the dehydration temperatures in the dry and the wet systems at 37.3°C. A possible explanation of this apparent coincidence may be that a small amount of liberated liquid water causes a more or less similar situation to the wet system although the transformation to 6α from 6β is not admitted on account of the slow velocity of its nucleation. The fact that the unstable β-phase appears first is already reported by Simon and Knauer(7) and is also ascertained by our X-ray photographs. This fact, together with the phenomenon that the unstable dehydration products appear in reverse order in comparison with the result obtained from the solubility studies, may be explained by the so-called "rule of successive transformation(8)."

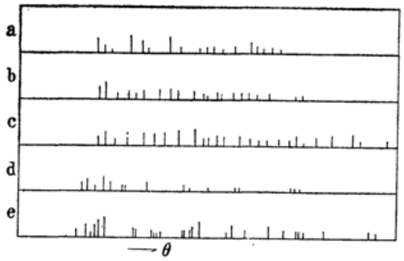

Fig. 9.—Debye photographs of nickel sulfate hydrates.

a) heptahydrate, b) α-hexahydrate,
c) β-hexahydrate (green part of the specimen formed by the dehydration of the heptahydrate),
d) γ-hexahydrate at 100°C. (Fig. 3h),
e) α-hexahydrate (Ref. 6).

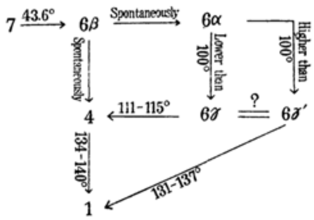

Fig. 10.—A schematic diagram correlating various modifications of nickel sulfate hydrates.

(b) **Dehydration stages and the phase transitions without accompanying dehydration.**

As mentioned above, prior to its first dehydration, $CuSO_45H_2O$ undergoes phase transitions which may be attributed to the rotation of water molecules according to Taylor and Klug.(4) As expected, similar transitions were found in the present investigation in some of the hydrates examined. The present discussion, with reference to its dehydration process, will be mainly concerned with the case of nickel sulfate which was studied in greatest detail. The β-form of hexahydrate produced by the first decomposition of heptahydrate changes spontaneously and slowly to 6α and circumstantially to tetrahydrate, so that the product initially obtained by heating heptahydrate, consisting of a mixture of 6β and heptahydrate, changes to a mixture of 6β, 6α and tetrahydrate even at a constant temperature as the decomposition proceeds. Fig. 9a corresponds to the mixture of heptahydrate and 6β containing possibly minute amount of 6α. Fig. 9c contains no heptahydrate and consists of 6β and a trace of 6α, while Fig. 9b consists mainly of 6α and a small amount of 6β. Thus, these three figures are considered to represent the main features of the successively transformed products of the heptahydrate, respectively. Although there remains a possibility that the last two figures contain traces of tetrahydrate, it was not ascertained on account of the difficulty of taking a Debye photograph of pure tetrahydrate. Further heating of the hexahydrate leads to a phase

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* It may be noticed that water produced in the first step of dehydration would dissolve a part of the hexahydrate, and lower hydrate than hexahydrate would be present before the second step of dehydration takes place.

(7) A. Simon and H. Knauer, *Z. anorg. allg. Chem.* **242**, 375 (1939).

(8) R. S. Bradley, *Quarterly Rev.* **5**, 323 (1951).

transition accompanying no dehydration.* This transition temperature varies very sensitively depending on the external conditions as well as on the history of the sample; that is, these temperatures range from 70.5 to 117°C. as shown in Fig. 3. Althongh a similar state of affairs is also reported in the case of $CuSO_4\cdot5H_2O$, detailed conditions governing it are not clearly described.(4) It is confirmed by the Debye photograph at about 100°C. that 6α changes its crystal structure at the transition point (Fig. 9 d). And it was also found that this transition is completely reversible by both the X-ray method and the differential thermal analysis (Fig. 3 f, g). It is interesting to note here that when 6α was coarsely crushed or was stored long (longer than a few months), the transition temperature is always a few degrees higher than 100°C. and on top of that the stage of tetrahydrate does not appear (see Fig. 3 d, i, j). On the other hand, the sample, finely powdered or not stored long, undergoes transition at a lower temperature and always goes through the stage of tetrahydrate (see Fig. 3 c, e, g, h). In Fig.3 k, is given the intermediate case between these two. The reason for such behavior is not yet clear, but it is very plausible to assume that a trace of tetrahydrate which may be present after grinding or short-time storing acts as a self-catalyst for the growth of the phase of tetrahydrate. Fig. 10 illustrates schematically the various phases of nickel sulfate hydrates, in which 6γ (or $6\gamma'$) denotes the phase found by the present study which is formed by the transition below (or above) 100°C. These two phases, 6γ and $6\gamma'$, may be identical with each other although there is no direct proof about it.*

In the cases of other hydrates, phase transitions without dehydration were also found at 62—85° for $ZnSO_4$, 89—95° for $MgSO_4$, and 60—85° for $MnSO_4$. In every case, these temperatures are sensitively influenced by the external conditions and the sample's history similarly to that of Ni salt. These results together with the dehydration stages are given in Figs. 4 to 8. It is of interest to note that there exists the dihydrate of magnesium sulfate which has hitherto been unknown at least in an open system. In all cases the final stages of hydration at the highest temperature examined are monohydrates.

(c) Effect of evacuation, heat evolution, rehydration and aging effect.

The effect of evacuation was also examined upon the dehydration and transition temperatures as well as upon the velocity of transition from an amorphous to a crystalline state. Generally, the temperature of dehydration is not so influenced by this treatment as the transition temperature. The heat evolution effect, which may be due to transformation of an amorphous, unstable, skeleton formed after dehydration to stable crystalline state, has recently been remarked by several investigators in the cases of $CuSO_4\cdot5H_2O$, $ZnSO_4\cdot7H_2O$, and $MnSO_4\cdot4H_2O$ by Khomyakov,(9) Mn-oxalate dihydrate by Volmer and Seydel,(10) and $ZnSO_4\cdot6H_2O$ and $CuSO_4\cdot5H_2O$ by Frost, et al.(11) Similar effects have been found in the present investigation in $ZnSO_4\cdot7H_2O$ at about 100°C. and in $MnSO_4\cdot7H_2O$ at about 65°C., the latter of which occurs even without previous evacuation (Fig. 8 b). It may be worthwhile to note that in the case of $ZnSO_4\cdot7H_2O$ the effect of evacuation which gives rise to evolution of heat is revealed at the temperature just below the second dehydration point after the transition (63.2°C.) is over, prior to which it has been evacuated (see Fig. 4 c).* Finally, a brief comment may be given on the experiment of rehydration for $ZnSO_4\cdot7H_2O$. When this substance is heated up to about 40°C. and then cooled, the evolution of heat is observed, which is attributed to the rehydration (Fig. 4 f, g). This may be explained either by the reaction

$$ZnSO_4\cdot6H_2O+H_2O=ZnSO_4\cdot7H_2O$$

or by the reaction

$$6(ZnSO_4\cdot6H_2O)=5(ZnSO_4\cdot7H_2O)+ZnSO_4\cdot H_2O$$

which can be predicted from the measurements of dissociation pressures.(12) The authors are for the latter interpretation since repeated heating and cooling procedure across this dehydration point results in the dehydration of more than one mole of water per mole of the heptahydrate (Fig. 4 h). The aging effect due to storing the sample for a long time is very complicated. Although, to date, no definite conclusion can be drawn about it, it may be said that the transition temperatures are much more influenced than the dehydration temperatures.

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Department of Chemistry, Faculty of Science, Osaka University, Osaka

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* The evidence of no dehydration at the transition point is given in Table 1.

** The shift of the transition temperature of Fig. 3 j to Fig, 3 k and the simultaneous appearance of the small hump indicating the existence of the tetrahydrate may be regarded as a proof of this identity.

(9) K. C. Khomyakov, *J. Phys. Chem.* (*U. S. S. R.*) **11**, 805 (1938).

(10) M. Volmer and G. Seydel, *Z. physik. Chem.* A **179**, 153 (1936).

(11) G. B. Frost, K. A. Moon and E. H. Tompkins, *Can. J. Chem.* **29**, 604 (1951).

(12) L. C. Copeland and O. A. Short, *J. Am. Chem. Soc.* **62**, 3285 (1940); See also R. E. Barieau and W. E. Giauque, ibid. **72**, 5676 (1950).

* It is known that in the case of $ZnSO_4\cdot6H_2O$ the velocity of transformation from amophous to crystalline state depends on the water vapor pressure and has a maximum around pressure of 0.95 mm.Hg (Ref. 11).