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THE DEHYDRATION OF NICKEL SULFATE

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ABSTRACT

Nickel sulfate was recrystallized to obtain the 7 H_2O, β6 H_2O and various habits of α6 H_2O. Dehydration and phase transitions were studied using X-ray analysis and DSC with effluent gas analysis. $NiSO_4 \cdot 7\,H_2O$ dehydrates spontaneously via $7 \rightarrow 6\beta \rightarrow 6\alpha$ at room temperature, while the dehydration pathway of $NiSO_4$ α6 H_2O is $6\alpha \rightarrow 6\gamma \rightarrow 4 \rightarrow 1$. The effect of time and storage on the 6α—6β phase transition was investigated.

INTRODUCTION

Literature reports concerning the dehydration of $NiSO_4 \cdot 7\,H_2O$ and $NiSO_4 \cdot 6\,H_2O$ are contradictory. Rabbering et al. [1] reviewed these reports and, using differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and X-ray analysis, attempted to clarify the dehydration pathway and confirm whether the hexahydrate shows a phase transition.

We have prepared the α and β polymorphs of $NiSO_4 \cdot 6\,H_2O$ together with various habits of the α form. The effects of time and storage conditions on the α—β transition were investigated. Our interpretation of the dehydration pathway and phase transition differs substantially from that of Rabbering et al.

EXPERIMENTAL

Nickel sulfate (certified A.C.S., Fisher Scientific Company) was recrystallized from water above 38° to obtain $NiSO_4 \cdot \alpha 6\,H_2O$ and at room temperature or in a refrigerator to obtain $NiSO_4 \cdot 7\,H_2O$. Crystals of a tetragonal bipyramidal habit of $NiSO_4 \cdot \alpha 6\,H_2O$ were grown in a fluidized-bed crystallizer by Phillips and Epstein [2]. Recrystallization above 38° in the presence of traces of gelatin resulted in the growth of a platy crystalline habit of $NiSO_4 \cdot \alpha 6\,H_2O$. Dehydration of the heptahydrate at room temperature in a desiccator gave rise to an acicular habit of $NiSO_4 \cdot \alpha 6\,H_2O$. Details concerning the preparation and properties of the various habit modifications are reported elsewhere (Burt and Mitchell [3]).

Crystals of $NiSO_4 \cdot \beta 6\,H_2O$ were recrystallized from aqueous solution at 58° followed by storage at 58° in a tightly closed bottle to prevent dehydration.

Thermal analysis was performed using a Perkin-Elmer differential scanning calorimeter (DSC-1B) equipped for effluent gas analysis. Crystals were ground in a glass pestle and mortar and 1—5 mg samples were weighed using a Cahn Gram electrobalance directly into aluminum volatile sample pans. Scans were made at 10° min^{-1} using closed pans and pans with a 0.1—0.2 mm pinhole. Vaporization of the water of crystallization from the pans with a pinhole was detected using the effluent gas analyzer and was estimated quantitatively by weighing the pan after each endothermic peak.

X-Ray diffraction patterns were determined by placing about 300 mg of ground material into a sample slide and exposing to $CuK\alpha$ radiation in a Philips wide angle X-ray diffractometer. The location and intensity of peaks at different values of 2θ were studied.

RESULTS AND DISCUSSION

Table 1 shows the X-ray and DSC results for the various crystal samples. The X-ray powder diffraction patterns of the A.C.S., bipyramidal, platy and acicular crystals were characteristic of $NiSO_4 \cdot \alpha 6\,H_2O$, (Selected Powder Diffraction Data [4]). The temperatures are mean values of the peak maxima for a number of DSC scans. However, the sequence of peaks is of more significance than the actual temperature of transition, dehydration or vaporization since the desolvation of solvates is highly dependent on the experimental conditions. Peaks 1 and 2 are internal transitions since they occurred using both closed pans which prevent water loss, and pans with a pinhole when there was no evidence of vaporization. Peaks 3 and 4 include both simultaneous dehydration and vaporization. Vaporization was confirmed qualitatively by effluent analysis and quantitatively by the weight loss. Peaks 5 and 6 also indicate both dehydration and vaporization reactions but an independent determination of dehydration was not possible, in most cases, since the vapor pressure was sufficient to distort or explode the closed pans. The overall water loss obtained on heating each sample to about 500° confirmed that each crystal sample was initially the hexahydrate.

The thermal behaviour of the crystal samples in Table 1 falls into two groups; the scans of the bipyramids are identical with the original A.C.S. material but differ significantly from the platy and acicular habits. In pans with a pinhole, all crystals show transition peaks 1 and 2 with peak 2 as the major peak. In closed pans, peak 1 becomes the major transition for the bipyramids and A.C.S. crystals with peak 2 missing, whereas with the platy and acicular habits the situation is reversed and the only transition corresponds to peak 2.

Further differences between the two groups of crystals are apparent on comparing peaks 3 and 4. The A.C.S. and bipyramidal crystals undergo dehydration between 113 and 119° (peak 3) with the simultaneous vaporization of 2 H_2O. The platy and acicular habits undergo these reactions between

TABLE 1

Thermal analysis and X-ray diffraction

		Endothermic peak maxima (°C) (moles H_2O vaporized per mole $NiSO_4$)[a]						X-Ray
		1	2	3	4	5	6	
A.C.S.	C[b]	90		119				$\alpha 6H_2O$
	P[b]	96[c]	103	112 (2)		173 (5)	> 400 (6)	
Bipyramid	C	97		118				$\alpha 6H_2O$
	P	98[c]	103	118 (2)		174 (5)	>420 (6)	
Platy	C		106	118[d]	128			$\alpha 6H_2O$
	P	96[c]	108	118[d]	128 (2)	159 (5)	>450 (6)	
Acicular	C		107		126			$\alpha 6H_2O$
	P	96	110	120[d]	128 (2)	162 (5)	>400 (6)	
$NiSO_4 \cdot 7H_2O$	P	97[c]	107	122[d]	131	160	>450	$7H_2O \rightarrow \beta 6H_2O \rightarrow \alpha 6H_2O$

[a] Values in parentheses are to the nearest stoichiometric ratio.

[b] C = closed pan; P = closed pan with pinhole.

[c] Small peak.

[d] Shoulder.

126 and 128° (peak 4) with only a shoulder at about 118° to indicate some dehydration at this temperature.

Boldyrev [5] has shown that the rate-controlling step in the dehydration of $ZnSO_4 \cdot 6\ H_2O$ depends on the external conditions. When carried out in vacuum or at low partial pressures of water vapor, the reaction is controlled by the gaseous reaction product, i.e. by the water vapor pressure, but when the vapor pressure is increased, catalysis by the solid product of the dehydration reaction becomes predominant.

Isothermal losses of water vapor at various temperatures below the transition temperature in pans with a pinhole showed that the bipyramidal crystals lost water more rapidly than the platy or acicular habits. Hence it seems likely that the differences in the dehydration reaction, peaks 3 and 4, are due to the effect of a difference in vapor pressure between the various habits.

Differences in vapor pressure may also explain the differences in the internal transitions, peaks 1 and 2 for the various habits when compared in closed pans and pans with a pinhole. Although the $6\ H_2O \rightarrow 4\ H_2O$ dehydration (peaks 3 or 4) occurs at temperatures greater than the transition temperatures, the hexahydrate will lose water at any temperature provided the vapor pressure of water surrounding the solid is less than the equilibrium vapor pressure at that temperature. Thus on heating a pan with a pinhole, vapor loss will occur although the rate will become appreciable only when the vapor pressure within the pan is equal to the atmospheric pressure. On the other hand, water vapor cannot escape from a closed pan and the vapor pressure increases with increase in temperature. It is suggested that the lower transition temperature for the bipyramidal and A.C.S. crystals in a closed pan is related to the higher vapor pressure of these habits. This observation is supported by the fact that when the effect of vapor pressure is reduced by using a pan with a pinhole, both transition peaks 1 and 2 appear in the thermograms of all habits with peak 2 becoming the major peak in each case. Chihara and Seki [6] found similar transitions above and below 100° using DTA and postulated the existence of two phases 6γ and $6\gamma'$, although they noted that these may be the same. Rabbering et al. found no indication of the existence of a γ phase or phases. Our results support Chihara and Seki but show that the transitions occur below 100°, above 100° or both, depending on whether the system is closed or open, and on the crystal habit. Hence it is necessary to postulate the existence of only one 6γ phase.

The transition and dehydration reactions for the two groups of crystals are summarized below.

$NiSO_4 \cdot 6\ H_2O$. A.C.S. and bipyramidal

$NiSO_4 \cdot 6\ H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6\ H_2O(s, \gamma)$	Peak 1
$NiSO_4 \cdot 6\ H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6\ H_2O(s, \gamma)$	Peak 2 *
$NiSO_4 \cdot 6\ H_2O(s, \gamma) \rightarrow NiSO_4 \cdot 4\ H_2O(s) + 2\ H_2O(l)$	Peak 3
$2\ H_2O(l) \rightarrow 2\ H_2O(g)$	Peak 3 *
$NiSO_4 \cdot 4\ H_2O(s) \rightarrow NiSO_4 \cdot H_2O(s) + 3\ H_2O(g)$	Peak 5 **

$NiSO_4 \cdot H_2O(s) \rightarrow NiSO_4 + H_2O(g)$	Peak 6 **

$NiSO_4 \cdot 6\ H_2O$. Platy and acicular

$NiSO_4 \cdot 6\ H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6\ H_2O(s, \gamma)$	Peak 1 *
$NiSO_4 \cdot 6\ H_2O(s, \alpha) \rightarrow NiSO_4 \cdot 6\ H_2O(s, \gamma)$	Peak 2
$NiSO_4 \cdot 6\ H_2O(s, \gamma) \rightarrow NiSO_4 \cdot 4\ H_2O(s) + 2\ H_2O(l)$	Shoulder 3
$NiSO_4 \cdot 6\ H_2O(s, \gamma) \rightarrow NiSO_4 \cdot 4\ H_2O(s) + 2\ H_2O(g)$	Peak 4
$2\ H_2O(l) \rightarrow 2\ H_2O(g)$	Peak 4 *
$NiSO_4 \cdot 4\ H_2O(s) \rightarrow NiSO_4 \cdot H_2O(s) + 3\ H_2O(g)$	Peak 5 **
$NiSO_4 \cdot H_2O(s) \rightarrow NiSO_4 + H_2O(g)$	Peak 6 **

Table 1 includes results for $NiSO_4 \cdot 7\ H_2O$. The heptahydrate rapidly lost weight after grinding prior to X-ray analysis and DSC. Comparison of successive X-ray scans with the published *d* values of nickel sulfate [4] showed that the heptahydrate dehydrates rapidly to $NiSO_4 \cdot \beta 6\ H_2O$ which then undergoes transition to $NiSO_4 \cdot \alpha 6\ H_2O$ within one hour. The DSC scan was the same as that of the acicular habit, i.e. the dehydrated heptahydrate.

In addition to the formation of $NiSO_4 \cdot \beta 6\ H_2O$ on dehydration of the heptahydrate, the β form recrystallizes from aqueous solution above 53° (Nicholls [7]). Crystals formed in this work at 58° were an emerald green colour, characteristic of the β form but the X-ray diffraction pattern taken immediately after crystallization was characteristic of the α form with only a trace of β crystals. The DSC scan, Table 2, however, was different from any of the α forms in Table 1 and showed a $6\ H_2O \rightarrow 1\ H_2O$ dehydration at 129°. On storage in an oven at 58° for two days the DSC scan changed to give a thermogram typical of the α form but the X-ray pattern became mainly that of the β form with some α form present. After five days at 58°, transition peaks 1 and 2 disappeared while the X-ray pattern remained mainly that of the β form. It is apparent that, although the material crystallizing above 53° has the appearance of the β form, several days storage above the transition temperature were required before the crystals became this form as characterized by X-ray and DSC. Unlike the α form, the β crystals do not undergo internal transition prior to dehydration.

The dehydration reactions are

$NiSO_4 \cdot 6\ H_2O(s, \beta) \rightarrow NiSO_4 \cdot 4\ H_2O(s) + 2\ H_2O(g)$	peak 3
$NiSO_4 \cdot 4\ H_2O(s) \rightarrow NiSO_4 \cdot H_2O(s) + H_2O(g)$	peak 5

On removal from the oven, the crystals turned blue-green within a day, the X-ray pattern reverted to mainly α, and a transition endotherm reappeared in the thermogram at 98°.

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* Only when using pans with a pinhole.

** Distortion of the closed pan usually prevents measurement of dehydration temperature.

TABLE 2

Changes in thermograms and X-ray diffraction of emerald green crystals on storage at 58°C

Days		Endothermic peak maxima (°C) (moles H_2O vaporized per mole $NiSO_4$)[a]						X-Ray
		1	2	3	4	5	6	
0	P[b]	98[c]		117[d]	129 (5)		>400 (6)	Mainly α; some β
2	C[b]		100	119		168		
	P	94[c]	100	116 (2)		171 (5)	>400 (6)	
4	C	86		116		168		Mainly β; some α
	P	86[c]	90[c]	117 (2)		171 (5)		
5	P			114 (2)		171 (5)		
8	C			113		174		Mainly β; some α
	P			110 (2)		170 (5)		

[a] Values in parentheses are to the nearest stoichiometric ratio.

[b] C = closed pan; P = closed pan with pinhole.

[c] Small peak.

[d] Shoulder.

TABLE 3

Changes in thermograms and X-ray diffraction of emerald green crystals on storage at room temperature

Days		Endothermic peak maxima (°C) (moles H_2O vaporized per mole $NiSO_4$) [a]					X-Ray
		1	2	3	4	5	
0	P	98 [c]		117 [d]	129 (5)		Mainly α; some β
5 hours [e]	P	94 [c]	106	121 [d]	129 (5)		
5	C		102	120 [d]	126	158	
	P	94 [c]	105	119 [d]	129 (3—4)	156(5)	α
12	P	94 [c]	104	114 [d]	126	165(5)	
28	C		101	120		164	α
	P	95 [c]	105	123 (2)		160 (5)	

[a] Values in parentheses are to the nearest stoichiometric ratio.

[b] C = closed pan; P = closed pan with pinhole.

[c] Small peak.

[d] Shoulder.

[e] Emerald green → blue green within 5 h.

If, after recrystallization and drying at 58°, the resulting emerald green crystals were removed from the oven and stored at room temperature, then the crystals turned blue-green within 5 h. According to X-ray analysis, the crystals were mainly the α form with some β form initially present, but about 28 days storage at room temperature was necessary before the thermogram became characteristic of the α form (Table 3). For up to about 12 days, the major dehydration—vaporization reaction was $6s \rightarrow 1s$, but with increasing evidence of the $6s \rightarrow 4s \rightarrow 1s$ pathway. Effluent gas analysis and weighing the sample pans after each endotherm were indispensable techniques in distinguishing this $6\,H_2O \rightarrow 1\,H_2O$ dehydration from the $6\,H_2O \rightarrow 4\,H_2O$ dehydration of the platy and acicular crystals since in each case the endotherms occurred between 126 and 129° (peak 4).

It is apparent that, when the crystals are stored at 58° until transition to the β form is complete (about 5 days), then the $\beta \rightarrow \alpha$ transition occurs very rapidly at room temperature (<1 day). If, however, the transition to the β form is incomplete before removal from the oven, then the transition to the α form takes up to 28 days at room temperature.

Various workers have reported that the hexahydrate formed on the dehydration of $NiSO_4 \cdot 7\,H_2O$ undergoes a phase transition (Caillère and Pobeguin [8], Pannetier et al. [9]) or transitions (Chihara and Seki [6]) prior to further dehydration. Starting with $NiSO_4 \cdot \alpha 6\,H_2O$, Rabbering et al. attributed peak 1 in a DSC scan to an $\alpha \rightarrow \beta$ transition followed by the $6 \rightarrow 4$ dehydration of the β form, peak 2, and vaporization of the liberated water, peak 3. However, even if peaks 1 were due to the $\alpha \rightarrow \beta$ transition, rather than the $\alpha \rightarrow \gamma$ transition, peaks 2 and 3 cannot be due to the consecutive dehydration and vaporization of the β form since the thermograms of $NiSO_4 \cdot \beta 6\,H_2O$ show that dehydration and vaporization occur simultaneously (peak 3, Table 2).

CONCLUSIONS

The dehydration pathway of $NiSO_4 \cdot \alpha 6\ H_2O$ is $6\alpha \rightarrow 6\gamma$, $6\gamma \rightarrow 4$, $4 \rightarrow 1$, $1 \rightarrow 0$.

$NiSO_4 \cdot \alpha 6\ H_2O$ can be recrystallized in various habits which exhibit one of two distinctive thermograms as determined by DSC. The difference in the DSC scans of the various habits is attributed to a difference in water vapor pressure.

$NiSO_4 \cdot 7\ H_2O$ undergoes a spontaneous dehydration at room temperature $7 \rightarrow 6\beta$, $6\beta \rightarrow 6\alpha$.

Emerald green crystals of the hexahydrate recrystallized at 58° take about 5 days at 58° to become established as the 6β form as characterized by X-ray and DSC, but when once established undergo rapid transition to the blue-green 6α form at room temperature.

The emerald green crystals stored at room temperature before the 6β form is established rapidly change colour to the blue-green of the 6α form. However, about 28 days elapse before the thermogram corresponds to that of the 6α form even though the X-ray diffraction pattern corresponds to pure 6α within a few days.

The dehydration pathway of the β hexahydrate is $6\beta \rightarrow 4$, $4 \rightarrow 1$, $1 \rightarrow 0$.

The occurrence of at least three polymorphic forms, three hydrates and different crystalline habits and the complex effect of time and storage conditions on the 6α—6β enantiotropic transition are most probably responsible for the contradictory reports in the literature concerning the transitions and dehydration of nickel sulfate.

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REFERENCES

1 G. Rabbering, J. Wanrooy and A. Schniff, Thermochim. Acta, 12 (1975) 57.
2 V.R. Phillips and N. Epstein, Am. Inst. Chem. Eng., 20 (1974) 678.
3 H.M. Burt and A.G. Mitchell, Int. J. Pharm., in press.
4 Selected Powder Diffraction Data for Minerals. Data Book, Joint Committee on Powder Diffraction Standards, Pennsylvania, 1974, 1st edn.
5 V.V. Boldyrev, J. Therm. Anal., 8 (1975) 175.
6 H. Chihara and S. Seki, J. Chem. Soc. Jpn., 26 (1963) 88.
7 D. Nicholls, Comprehensive Inorganic Chemistry, Vol. 3, Pergamon Press, Oxford, 1973.
8 S. Caillère and Th. Pobeguin, Bull. Soc. Fr. Mineral. Cristallogr., 85 (1962) 48.
9 G. Pannetier, J.M. Bregeault, C. Lecouturier and G. Djega-Mariadassou, Bull. Soc. Chim. Fr., (1964) 3141.