Thermochimica Acta, 41 (1980) 241—245
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THERMOGRAVIMETRIC ANALYSIS OF COBALT SULFATE

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(Received 5 February 1980)

Cobalt sulfate exists in two forms. Crystals grown below 40.6°C are heptahydrate and those grown above this temperature are hexahydrate in nature [1,2]. It is found that the dehydration of the heptahydrate readily occurs to form hexahydrate by exposure to dry air [3,4]. It is reported that the heptahydrate is completely dehydrated at 250°C and at 100°C gives monohydrate. It is also reported that the complete dehydration occurs between 300 and 420°C [5]. The sequence of dehydration steps as given by Ben Dor and Margalith [6] for many polyhydrated metal sulfates consists of two steps. All except one molecule of water are released at low temperature and the last one is evolved after a significant rise in temperature. Nickel sulfate, which is isomorphous with cobalt sulfate, was investigated by many workers [7—9] but Sarig [10] pointed out that, though these workers reported the dehydration of $NiSO_4 \cdot 7\,H_2O$, the substance must be $NiSO_4 \cdot 6\,H_2O$. We have studied [11] the dehydration steps in nickel sulfate hexahydrate and heptahydrate crystals grown at two different temperatures at which the crystals are either hexahydrate or heptahydrate. Looking into the fact that different workers have mentioned different temperatures and dehydration steps for the same substance and that very little data showing a distinction between cobalt sulfate hexahydrate and heptahydrate are available, it was thought fit to investigate the dehydration steps in $CoSO_4 \cdot 6\,H_2O$ and $CoSO_4 \cdot 7\,H_2O$ independently using freshly prepared crystals. Cobalt sulfate crystals were grown at three different temperatures, 12.5, 40 and 50°C. Crystals grown at 12.5 and 40°C were heptahydrate and those grown at 50°C were hexahydrate. Thermogravimetric studies of these crystals along with their pellets and packed powders are reported in this paper.

EXPERIMENTAL

Cobalt sulfate of purity greater than 99.9% was obtained from B.D.H. The crystals of cobalt sulfate were grown at 12.5, 40 and 50°C by slow evaporation of an aqueous solution. The crystals were ground to 104 μm and pellets

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prepared by pressing the powder in a hydraulic press to a pressure of 5000 kg cm^{-2}.

The measurement of the mass loss of cobalt sulfate crystals, pellets and loosely packed powder samples was carried out in the temperature range 30—450°C. The samples were heated at a constant rate of 5°C min^{-1}. The loss in mass and time were measured at intervals of 5°C. The value of $\Delta m/\Delta t$, i.e. the rate of change of mass (mg min^{-1}) was calculated at different temperatures. Curves were plotted of the change in mass versus temperature (TG) and the rate of change of mass versus temperature (DTG).

RESULTS AND DISCUSSION

It was observed that crystals of cobalt sulfate have a habit of prismatic growth up to 50°C. The habit is similar to that observed in the case of nickel sulfate grown at 40°C.

Figure 1 gives representative sets for the sequence of dehydration steps in cobalt sulfate crystals grown at 12.4, 40 and 50°C, respectively. DTG curves for these crystals show four different dehydration steps. Crystals grown at 12.5 and 40°C show four different DTG peaks at the mean temperatures 119.6, 161.7, 184.7 and 294.5°C giving the sequence of dehydration steps as 1 mole, 3 moles, 2 moles and 1 mole. The temperatures are the means corresponding to all the samples grown at 12.5 and 40°C. The mean temperatures have been determined from five sets of observations taken for each crystal.

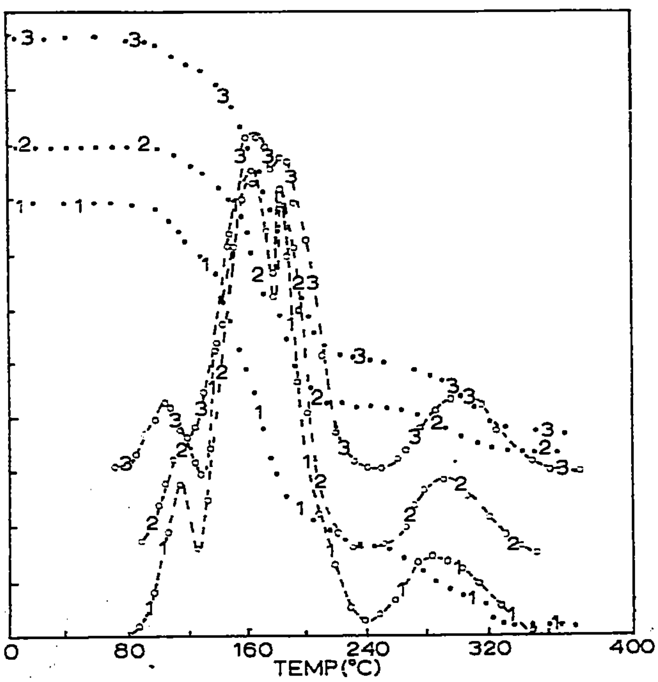

Fig. 1. TG (· · · · · ·) and DTG (o———o) curves for crystals of cobalt sulfate grown at 1, 12.5°C; 2, 40°C; and 3, 50°C.

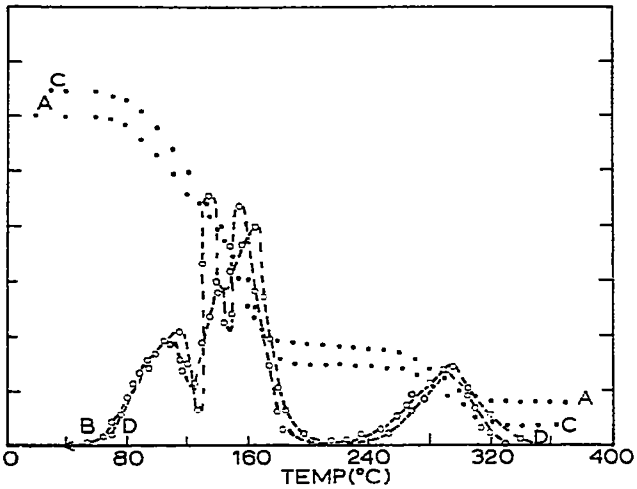

Fig. 2. TG (A, C) and DTG (B, D) curves for pellet and packed powder from crystals grown at 12.5°C.

Crystals grown at 50°C show four peaks in the DTG curve at the respective mean temperatures 108.8, 161.7, 187 and 301.6°C. The results indicate the sequence of dehydration steps as 1 mole, 2 moles, 2 moles and 1 mole.

Thus the crystals grown at 12.5 and 40°C are heptahydrate, whereas those grown at 50°C are hexahydrate in nature.

Figures 2 and 3 give the TG and DTG curves for pellets and loosely packed powders obtained after crushing the crystals grown at 12.5, and 50°C, respectively. Except for the powdered sample from the 40°C crystal, the DTG curves show the occurrence of four peaks at the mean temperatures 113.3, 138.6, 159.1 and 296°C and give the sequence of dehydration steps as 1 mole, 2 moles, 2 moles and 1 mole. The powder pack for the 40°C crys-

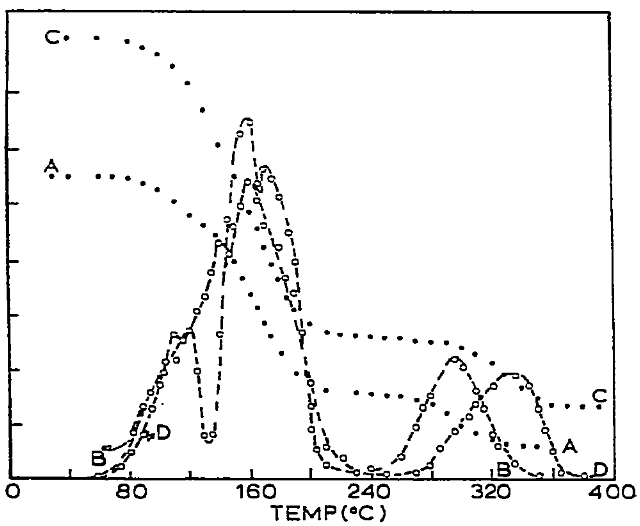

Fig. 3. TG (A, C) and DTG (B, D) curves for pellet and packed powder from crystals grown at 50°C.

TABLE 1

Dehydration temperatures from TG studies

Step	T_m* [K(°C)]	Δm * (K)	%S * (K)
$CoSO_4$ crystal grown at 12.5 °C			
1	391 (118)	2.66	0.68
2	433 (160)	5.77	1.33
3	454.6 (181.6)	5	1.09
4	564.6 (291.6)	6.33	1.12
$CoSO_4$ crystals grown at 40°C			
1	394.2 (121.2)	2.24	0.56
2	436.1 (163.1)	3.5	0.80
3	460.8 (187.8)	6.5	1.41
4	570.3 (297.3)	4	0.70
$CoSO_4$ crystals grown at 50°C			
1	381.8 (108.8)	1.44	0.37
2	434.7 (161.7)	5.35	1.23
3	460 (187)	5.6	1.21
4	574.6 (301.6)	12.32	2.14
$CoSO_4$ pellet			
1	383.8 (110.8)	7.8	2.03
2	406.7 (133.7)	6.8	1.69
3	431.8 (158.8)	8.12	1.88
4	573.5 (300.5)	9.83	1.71
$CoSO_4$ powder			
1	390.8 (117.8)	4.7	1.20
2	415.5 (142.5)	6.25	1.50
3	439.5 (166.5)	6.57	2.72
4	604.1 (331.1)	5.20	0.86

* T_m = mean temperature, Δm = mean deviation and %S = percentage error in temperature.

tal shows the sequence of dehydration as 1 mole, 4 moles and 1 mole. This suggests that, irrespective of whether the powder is prepared after crushing a 12.5, 40 or 50°C crystal, it always shows the presence of six water molecules. This also shows that the first water molecule in $CoSO_4 \cdot 7\ H_2O$ is weakly bound and can be very easily removed. This is also verified from the fact that if a heptahydrate crystal is kept in the open atmosphere for some days, it loses its transparent nature due to loss of one molecule of water. The study shows that the bonding between the water molecules and cobalt and sulfate ions for a particular step is nearly the same whether the crystal is hexahydrate or heptahydrate. However, the strength of the bond is different for different steps, even for the same crystal. The electrical conductivity study (to be reported separately) further strengthens the argument. The result of the study shows that the activation energy needed in each step for the heptahydrate and hexahydrate is nearly the same.

Cobalt sulfate shows a close resemblance to nickel sulfate as regards its thermal and electrical properties. Both these substances form heptahydrate crystals at 12.5°C and hexahydrate crystals above 40°C. The sequence of deaquation steps for the heptahydrate and hexahydrate is the same for both substances. The fact that cobalt sulfate is isomorphous with nickel sulfate shows that a similar model to that suggested in the case of nickel sulfate [11] may be assumed to explain the dehydration of different water molecules at different temperatures.

CONCLUSION

The study gives the sequence of dehydration in $CoSO_4 \cdot 7\ H_2O$ as 1 mole, 3 moles, 2 moles and 1 mole at 119.6, 161.7, 184.7 and 294.5°C and in $CoSO_4 \cdot 6\ H_2O$ as 1 mole, 2 moles, 2 moles and 1 mole at 108.8, 161.7, 187 and 301.6°C. From the study, it may be concluded that, by and large, the dehydration temperatures for heptahydrate and hexahydrate remain the same. However, the dehydration steps are different for the two hydrates.

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