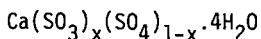


STUDIES ON ALKALINE EARTH SULFITES - VI. THERMAL DEHYDRATION OF



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ABSTRACT

Samples of calcium sulfite-calcium sulfate tetrahydrate,  $\text{Ca}(\text{SO}_3)_x(\text{SO}_4)_{1-x} \cdot 4\text{H}_2\text{O}$ , where  $1/3 \leq x \leq 1$ , were investigated by thermogravimetric analysis and differential scanning calorimetry. For compositions near  $x=2/3$ , the sample is thermally stable at room temperature and dehydrates at 80°-160°C to an anhydrous mixed salt, which passes through an exothermic transition at about 340°C. Samples of higher sulfite or sulfate content are unstable and decompose partially to lower hydrates,  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  respectively. Temperatures and heats of dehydration and recrystallization of the various samples are presented and the variations in stability are explained by structural considerations.

INTRODUCTION

Previous studies have shown the possibility of preparing a highly hydrated calcium sulfite,  $\text{CaSO}_3 \cdot 4\text{H}_2\text{O}$ , from calcium chloride and sodium sulfite solutions, by addition of small amounts of additives like sodium citrate (ref.1). The tetrahydrate is also obtained when part of the sulfite is replaced by sulfate (ref.2); in the latter case the product is the double salt  $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$  or a solid solution  $\text{Ca}(\text{SO}_3)_x(\text{SO}_4)_{1-x} \cdot 4\text{H}_2\text{O}$ . This work presents the results of thermal analysis studies on these products.

EXPERIMENTAL

Sample preparation

Samples were prepared at 3-5°C. Aqueous solutions of  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{SO}_4$  in various ratios, with a total concentration of 1M, were stirred into equal amounts of 1M aqueous solution of  $\text{CaCl}_2$ . All samples used were of analytical purity. The samples were washed with  $\text{O}_2$  free distilled water at 3°C, dried between filter paper and kept at 0°C for characterization. Samples with the following values of  $x = \text{SO}_3^{2-} / \text{Ca}^{2+}$  were prepared: A, 1.00; B, 0.74; C, 0.71; D, 0.67; E, 0.62; F, 0.57; G, 0.50; H, 0.33.

Thermal analysis

The following instruments were used: DuPont 1090 Thermal Analysis Data System, with DuPont 910 Differential Scanning Calorimeter and 951 Thermogravimetric

Analyzer. Both TGA and DSC experiments were performed at a heating rate of 5°C/min. DSC curves were obtained for both open sample vessels with dry nitrogen flow and closed sample vessels (under water vapour pressure).

## RESULTS

### Thermogravimetric analysis

TGA results are shown in Table 1. It can be calculated that the weight losses in samples C-F correspond, within the experimental error, to four water molecules per Ca atom. In samples B, G and H, they are slightly lower. In sample A, the weight losses correspond to a two-step dehydration,  $\text{CaSO}_3 \cdot 4\text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_3$ .

TABLE 1

Dehydration temperatures (°C) and weight losses(%) of  $\text{Ca}(\text{SO}_3)_x(\text{SO}_4)_{1-x} \cdot 4\text{H}_2\text{O}$

Sample	T <sub>1</sub>	T <sub>2</sub>	Weight loss	T <sub>3</sub>	T <sub>4</sub>	Weight loss
A	30	60	32.82	365	382	4.69
B	75	103	35.46			
C	77	106	36.52			
D	81	114	36.44			
E	81	106	36.31			
F	80	102	35.82			
G	80	100	34.42			
H	74	99	32.28			

T<sub>1</sub>, T<sub>3</sub>: extrapolated onset temperature (intersection of the slope and base lines)  
T<sub>2</sub>, T<sub>4</sub>: peak temperature

### Differential scanning calorimetry

DSC results are shown in Table 2. For sample B, DSC curves obtained with open and closed sample vessels are shown in Fig. 1.

TABLE 2

Transition temperatures (°C) and heats of transition (J/g) of  $\text{Ca}(\text{SO}_3)_x(\text{SO}_4)_{1-x} \cdot 4\text{H}_2\text{O}$  (op. = open vessel, cl. = closed vessel)

Sample	T <sub>1</sub>		T <sub>2</sub>		ΔH <sub>1</sub> <sup>a</sup>	T <sub>3</sub>		T <sub>4</sub>		ΔH <sub>2</sub> <sup>a</sup>
	op.	cl.	op.	cl.		op.	cl.	op.	cl.	
A	28		54		-88	365		381		-450
B	64	{ 81 98	94	{ 72 115	-880(-760) <sup>b</sup>	343	370	352	383	+50(-63) <sup>b</sup>
C	65	122	102	149	-900	347		359		+46
D	66	126	107	152	-920	334		351		+45
E	65	126	108	153	-880	338		358		+48
F	65	124	102	154	-860	330		351		+44

T<sub>1</sub>, T<sub>3</sub> Extrapolated onset temperature; T<sub>2</sub>, T<sub>4</sub> peak temperature

<sup>a</sup> ΔH>0 exothermic, ΔH<0 endothermic transition

<sup>b</sup> in parentheses, ΔH for closed sample vessel; in other samples, no significant difference was found.

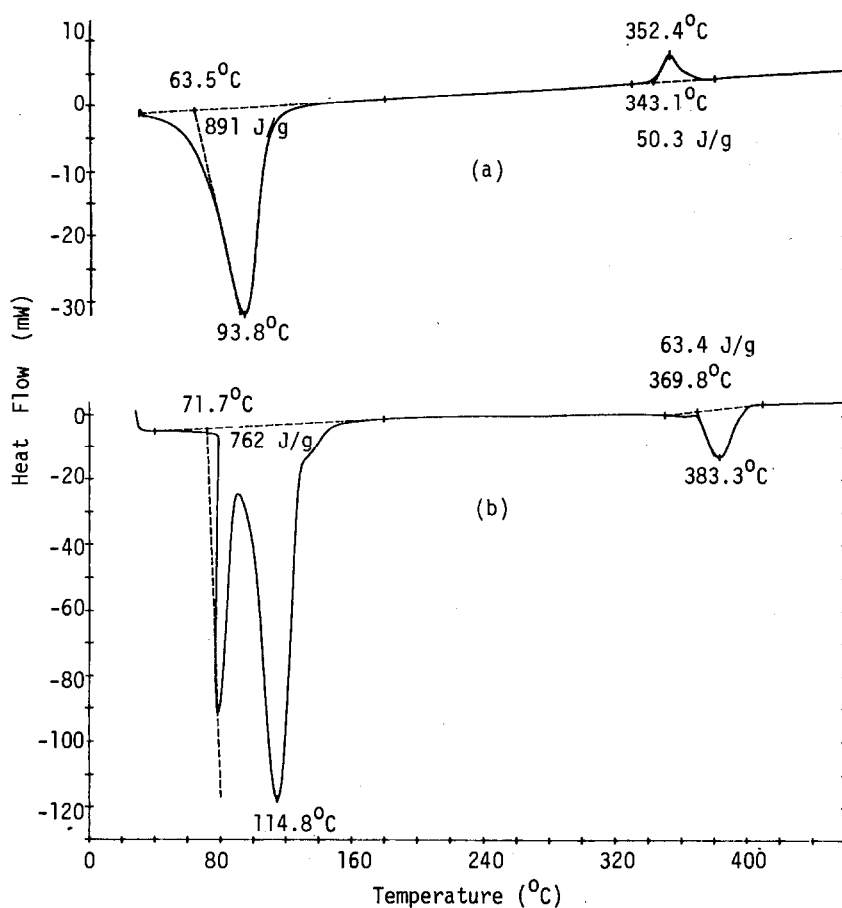


Fig. 1. Differential scanning calorimetry of sample B. (a) open vessel. (b) closed vessel.

It can be seen that the dehydration temperatures in TGA and open-vessel DSC are very similar, but in closed vessel DSC much higher. Heats of dehydration are much higher in samples B-F than in sample A. The exothermic peak in samples C-F and also in open-vessel B should be noted. Of special interest is the double dehydration peak in closed-vessel B.

#### DISCUSSION

The crystalline structures of  $\text{CaSO}_3 \cdot 4\text{H}_2\text{O}$  (ref.3) and  $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$  (ref.2) have been established by X-ray diffraction studies. It was shown that

2 types of sulfite ions exist in  $\text{CaSO}_3 \cdot 4\text{H}_2\text{O} : \text{S}(1)\text{O}_3^{2-}$ , where the oxygen atoms are coordinated to the calcium ions, and  $\text{S}(2)\text{O}_3^{2-}$ , where the oxygen atoms participate in hydrogen bonds with the water molecules (ref.4). In the double salt  $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{S}(2)\text{O}_3^{2-}$  is replaced by  $\text{S}(2)\text{O}_4^{2-}$ , the extent of hydrogen bonding is significantly increased and the disorder of the oxygen atoms strongly decreased. This explains the high stability of the double salt, or solid solutions with  $x$  near  $2/3$ , compared to the pure sulfite (sample A), as evidenced by the large differences in  $T_1$ ,  $T_2$  and  $\Delta H_1$ . When  $x=1$ , the stable form even at room temperature is  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , which dehydrates at about  $380^\circ\text{C}$ . For  $x=0.74$  (sample B), there is competition between the dehydration mechanism of  $\text{CaSO}_3 \cdot 4\text{H}_2\text{O}$  and that of  $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ ; under dry conditions (open vessel) the latter mainly prevails, but under increased vapour pressure of water (closed vessel) part of the sulfite first dehydrates to  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ . This dehydration accounts for the first part of the double endothermic peak in fig. 1 b), while the dehydration of the remaining double salt, occurring at a lower than usual temperature for a closed vessel sample, is expressed in the second part of the double peak.

Powder X-ray diffraction shows the dehydrated samples C-G to be amorphous up to about  $350^\circ$  (ref.5); the exothermic peak  $T_3$ - $T_4$  therefore expresses the recrystallization of anhydrous  $\text{Ca}(\text{SO}_3)_x(\text{SO}_4)_{1-x}$ . This is obscured in sample B, closed vessel DSC, by the endothermic dehydration peak of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  at  $330^\circ\text{C}$ . Also, powder X-ray diffraction of the hydrated samples G-H shows gradual changes in their crystalline structure upon standing at room temperature, with the emergence of lines characteristic of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (ref.5). This may account for the fact that these samples show a slightly lower water content than calculated for tetrahydrate. The decrease in stability of the crystalline structure in samples G-H, as compared to  $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ , may be attributed to the increased oxygen/hydrogen ratio, which decreases the amount of hydrogen bonds available to each oxygen (ref.5).

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