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Thermochimica Acta 269/270 (1995) 79–88

thermochimica  
acta

## Thermal investigation of the role of outer surfaces in the decomposition of crystalline solids<sup>☆</sup>

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Received 16 September 1994; accepted 16 June 1995

### Abstract

Recent studies have evidenced different decomposition behaviour between stored and freshly recrystallized samples of both  $\text{NaHCO}_3$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ . To verify whether the above findings could be a general property of crystalline materials undergoing thermal decomposition we compared the thermal behaviour of aged and freshly recrystallized samples of a number of crystal hydrates of different nature (e.g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , etc.) The results suggest that the compounds examined can be divided into three main classes namely: i) those for which fresh surfaces retard the decomposition; ii) those for which the decomposition remains unaltered; iii) those for which fresh surfaces enhance the reactivity. It appears that the three classes can be characterized by different kinetic behaviour also. These findings can be interpreted in terms of a three-stage mechanism recently proposed for the dehydration of tetragonal nickel sulphate hexahydrate.

*Keywords:* Ageing of samples; Crystalline solids; DSC; Outer surface; Thermal analysis; Thermal decomposition

### 1. Introduction

Recently [1], examining together the results of a number of different experiments [2–5], we proposed a three stage mechanism (3SM) to explain the peculiar behaviour of the dehydration of  $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$  (NISH). This mechanism, which proved to account also for the dehydration of common and chrome alums [6], places relevant importance

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<sup>☆</sup> Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September, 1994.

in the nature and properties of the outer boundaries of the reactant crystals. To verify whether the mechanism could be applied also to other systems we undertook the study of the dehydration of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  [7] and of the decomposition of  $\text{NaHCO}_3$  [8], the latter reputed of particular interest being not a simple dehydration. Both systems showed the peculiar feature of giving different thermal curves for aged or freshly prepared crystals. In particular the thermal curves of fresh materials were somewhat delayed and steeper. This result could be interpreted by the 3SM in terms of the hindrance due to the relative perfection of the fresh surfaces leading to difficult crystallization of the product.

There is little new in these findings, in fact fresh (as well as recently cleaved) surfaces of good perfection are the complete opposite of aged (full of defects caused by, e.g., reciprocal scratching of crystals during storage) ones; indeed the practice of speeding up a reaction by “infecting” the surfaces of the reactant by rubbing them with the product or with an abrasive has been known for long time [9, 10]. So it could be expected that the decomposition of crystals limited by fresh surfaces of relatively high perfection was somewhat delayed with respect to that of aged crystals of the same material. The interesting point is that, by thermal methods and using the 3SM, it is possible to reveal such behaviour and understand the reasons for it.

The present study was undertaken to verify if this kind of dependence on surface perfection was a general property of decomposing crystals. Hence we reconsidered in this light a number of already studied decompositions executing new experiments on materials of different nature.

## 2. Experimental

The present experiments were performed using aged and fresh crystals of sodium citrate dihydrate (NACD), [11], tetragonal nickel sulphate hexahydrate (NISH), [1], oxalic acid dihydrate (OAD), [12, 13], copper sulphate pentahydrate (CUSP), [14], cobalt sulphate heptahydrate (COSH), [15] and nickel acetate tetrahydrate (NIAT), [16, 17].

With the exception of NISH (*vide infra*), crystalline powders of high purity commercial products (Table 1) were used as aged materials. Fresh crystals were obtained from

Table 1  
List of the hydrated compounds examined

Compound	Origin	Symbol	Recrystallization procedure (see text)	Sieving 425–300 $\mu\text{m}$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Carlo Erba RPE ACS	CUSP	i), ii), iii)	Yes
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	Merck PA	NACD	i)	No
$\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	Carlo Erba RPE	NIAT	i)	Yes
$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	Riedel FA	OAD	i)	No
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	Carlo Erba RPE	COSH	i), iii)	Yes

aqueous solutions of the same materials: i) by evaporation at room temperature (or 65°C for NACD); ii) by adding ethanol to the solutions; iii) allowing warm saturated solutions to cool under magnetic agitation. In the case of NISH the aged material consisted of powders prepared in previous work [4] sieved to collect the 420–300  $\mu\text{m}$  fraction. The fresh samples were prepared either by lightly grinding the > 420  $\mu\text{m}$  fraction of the same powder or by heavily grinding large (cm size) single crystals (also from previous work [2, 3]); in both cases the same 420–300  $\mu\text{m}$  fraction was collected.

A Perkin–Elmer DSC7 differential scanning calorimeter was used to record the thermal curves at various scan rates,  $\beta$ , in the range 0.5–16  $\text{K min}^{-1}$  using sample masses of the order of 10 mg. Weighing was performed in standard aluminum pans before and after the runs, lids being invariably employed to cover both sample and reference containers loosely. A 16  $\text{ml.min}^{-1}$  flow of dry nitrogen was always used to purge the sample holder cell of the apparatus. Comparisons of the thermal curves recorded under the same conditions for aged and fresh samples as well as the enthalpic evaluations were performed by the built in Perkin–Elmer software that was also used for the kinetic analysis of the DSC output; the latter results were, however, also checked by a differential method [18] already successfully employed [1, 6].

### 3. Results

The main findings of the present research are reported below salt by salt.

#### 3.1. NIAT

The four water molecules are lost in a single thermal event; comparison of the thermal curves for samples of aged and fresh crystalline powders of comparable mass are reported in Fig. 1. The dehydration of the fresh material is delayed. The mean value of heat of reaction is:  $\Delta_{\text{d}}H = 204.4 \pm 7.5 \text{ kJ mol}^{-1}$ . First order kinetics are found to give the best fit ( $n = 1.25 \pm 0.3$ ) with  $E_{\text{a}} = 146 \pm 11 \text{ kJ mol}^{-1}$  and  $\ln(A/\text{s}^{-1}) = 40.3 \pm 5.1$ .

#### 3.2. NACD

The two water molecules are lost in a single step (Fig. 2) but some retention is evidenced by the high temperature tails of the curves. Again the dehydration is delayed for fresh material.  $\Delta_{\text{d}}H = 24 \pm 9 \text{ kJ mol}^{-1}$ . Second (or higher) order kinetics result in the best fit ( $n = 2.85 \pm 1.3$ ) but the unreasonably high and probably unreliable values deduced for both  $E_{\text{a}}$  and  $\ln(A)$  prompt us to further work on this compound.

#### 3.3. NISH

Approximately four of the six water molecules are lost but for this salt the comparison is not strictly between aged and fresh materials but merely between unaltered aged powders and poorly or heavily ground materials; the results are collected in Fig. 3. It appears that light grinding causes some delay of dehydration

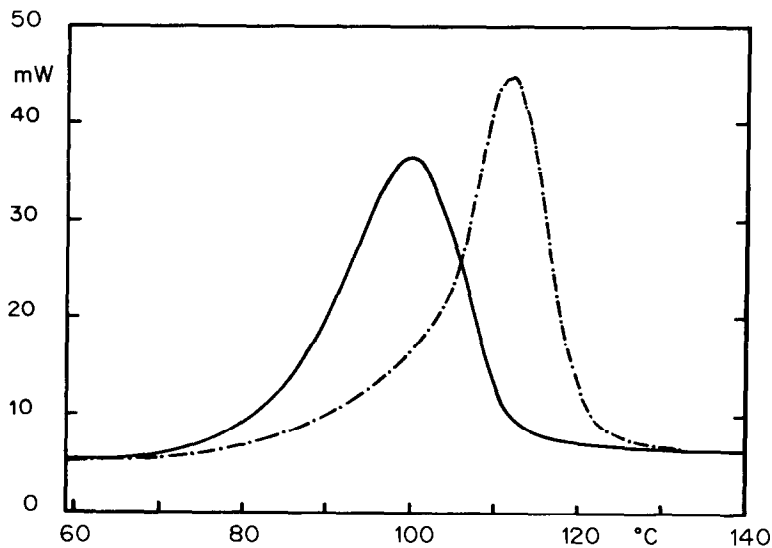


Fig. 1. Comparison of DSC dehydration curves of samples of fresh and aged NIAT. ( $\beta = 4 \text{ K min}^{-1}$ ). a) — aged 10.31 mg; b) -·-·- fresh 10.85 mg.

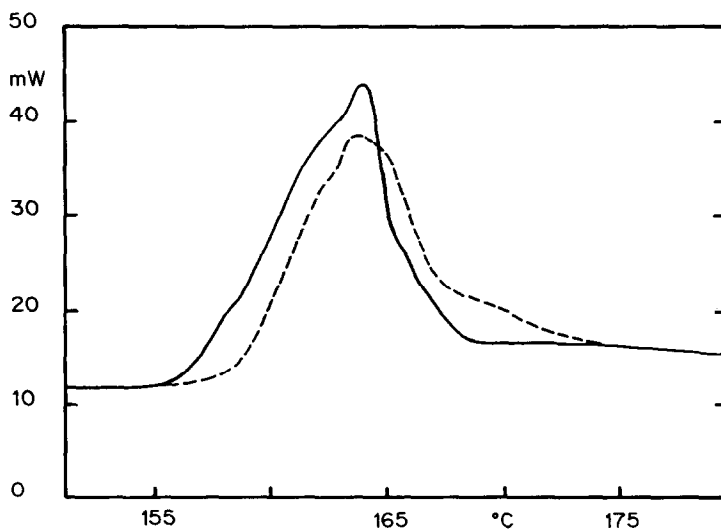


Fig. 2. Comparison of the dehydration curves of fresh and aged NACD. ( $\beta = 2 \text{ K min}^{-1}$ ). a) — aged 12.10 mg; b) - - - - fresh 12.53 mg.

while heavy crushing leaves things almost unaltered. On the whole the behaviour of NISH can be classified as intermediate between that of the preceding materials and that of the following compound. The kinetic law and the values obtained for  $\Delta_d H$ ,  $E_a$  and  $\ln A$  match those reported in Ref. [1] for low  $\beta$  ( $\leq 2 \text{ K min}^{-1}$ )

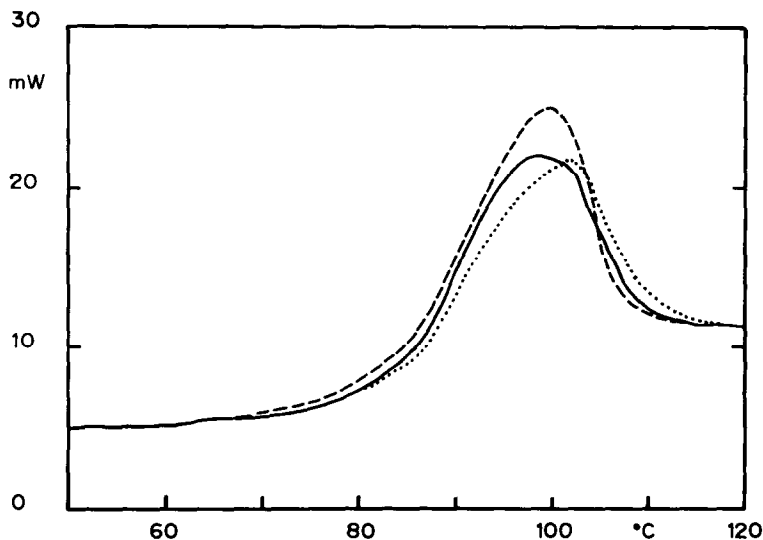


Fig. 3. Thermal curves of the dehydration of aged, poorly or heavily crushed samples of NISH ( $\beta = 2 \text{ K min}^{-1}$ ). a) — aged 10.23 mg; b) ---- heavy ground 10.44 mg; c) ..... light ground 10.50 mg.

### 3.4. OAD

The two water molecules are lost in a single step. Fig. 4 shows that this material is not particularly affected by ageing, differences being due only to mass disparity between the two samples.  $\Delta_d H = 103.4 \pm 2.8 \text{ kJ mol}^{-1}$ . Contracting circle kinetics ( $\bar{n} = 0.42 \pm 0.09$ ) with  $E_a = 81.8 \pm 2.4 \text{ kJ mol}^{-1}$  and  $\ln(A/s^{-1}) = 19.3 \pm 1.2$ .

### 3.5. COSH

Approximately five ( $5.08 \pm 0.21$  over 26 experiments) water molecules are lost in the first endotherm. In Fig. 5 a number of experimental findings are collected together, namely: 1) the usual comparison between aged and fresh material (curve e in respect of any of the others); 2) the comparison between recrystallized materials as soon as dried and four days later (curves a vs. b and c vs. d); 3) the comparison between materials washed with acetone or not (curves a vs. c and b vs. d). It is evident that recrystallization enhances the reactivity. The behaviour of freshly recrystallized material, evident in Fig. 5, shows no further changes on longer (weeks) ageing:  $\Delta_d H = 242.4 \pm 4.9 \text{ kJ mol}^{-1}$ . First order kinetics ( $\bar{n} = 1.08 \pm 0.22$ ) with  $E_a = 149.2 \pm 14.8 \text{ kJ mol}^{-1}$  and  $\ln(A/s^{-1}) = 42.1 \pm 5.3$ . It is to be noted that, in a number of experiments in which samples of any kind were taken to  $400^\circ\text{C}$  for complete dehydration, weighing revealed that the amount of water lost was never stoichiometric, corresponding usually to something less than 6.8 molecules. Part of this discrepancy can probably be attributed

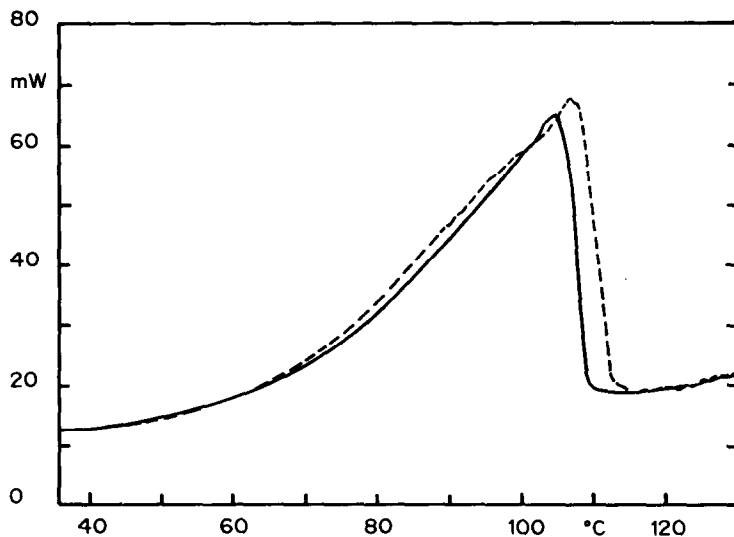


Fig. 4. Dehydration curves recorded with samples of fresh and aged OAD. ( $\beta = 8 \text{ K min}^{-1}$ ). a) — aged 10.42 mg; b) ---- fresh 11.96 mg.

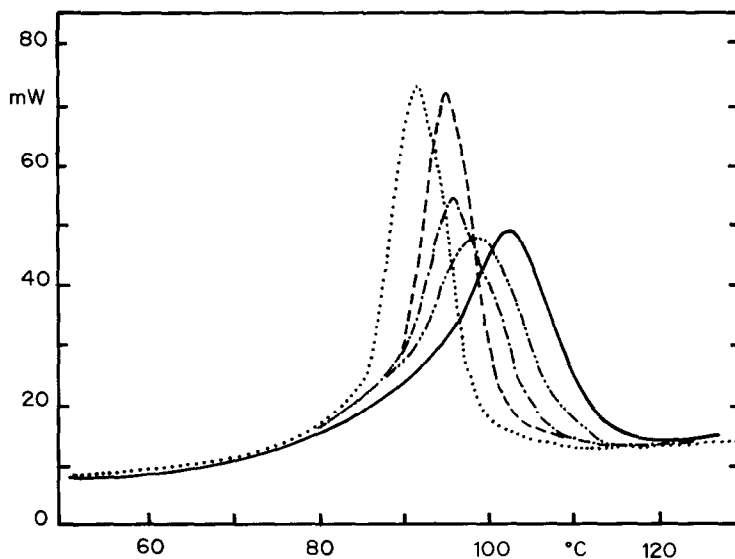


Fig. 5. Comparative plot of the initial dehydration peaks recorded ( $\beta = 4 \text{ K min}^{-1}$ ) using samples of COSH of various nature (see text). a) ..... fresh, washed with acetone 10.72 mg; b) ---- fresh + 4d, washed with acetone 10.61 mg; c) - · - · - fresh 10.20 mg; d) - · - · - fresh + 4d. 10.73 mg; e) — aged 10.91 mg.

to some retention, however visual observation (colour change from dark red to reddish pale brown) and preliminary optical microscopy experiments indicate that crystal surfaces as grown and as generated by cleavage do not last for long in air at room temperature, probably forming a layer of a lower hydrate [19].

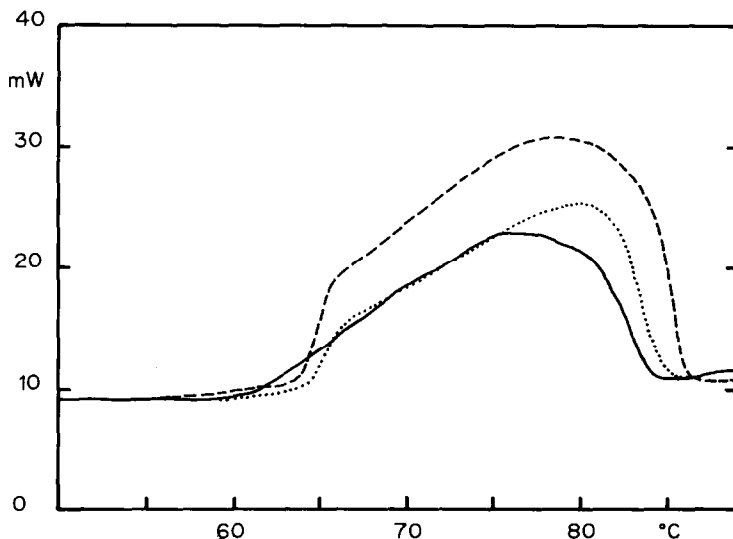


Fig. 6. Thermal curves of the first dehydration peaks recorded ( $B = 2 \text{ K min}^{-1}$ ) using samples of CUSP aged, fresh or crystallized by addition of ethanol to the aqueous solutions. a) — aged 11.65 mg; b) ..... fresh 11.01 mg; c) ----- fresh EtOH 11.71 mg.

### 3.6. CUSP

The amount of water lost in the first endotherm depends on sample preparation, therefore enthalpic changes are given per mol of water and kinetic parameters refer to samples losing ca. 2 water molecules (i.e. samples in which the dehydration proceeds through the trihydrate).  $\Delta_a H = 51.97 \pm 4.6 \text{ kJ (mol H}_2\text{O)}^{-1}$ . Contracting sphere kinetics ( $\bar{n} = 0.71 \pm 0.12$ ) with  $E_a = 146 \pm 23 \text{ kJ mol}^{-1}$  and  $\ln(A/\text{s}^{-1}) = 43.6 \pm 8.3$ . The behaviour of CUSP is intermediate between those of OAD and COSH; in fact, while the initial portions of the dehydration are clearly accelerated by recrystallization, the subsequent evolution parallels that of the aged material (Fig. 6, curves a,b). A particular behaviour is shown by the samples recrystallized by addition of ethanol to the aqueous solutions (Fig. 6, curve c): again there is a relevant initial enhancement of rate and the subsequent evolution is regular but the heat evolved is much higher as this kind of CUSP is known [9, 14] to decompose directly to the monohydrate without formation of the trihydrate. This latter compound is formed in reduced amounts also during the decomposition of CUSP precipitated under magnetic agitation, in this case the initial peak shows composite shape coupled with water losses  $> 3\text{H}_2\text{O}$ .

## 4. Discussion

A word of warning is necessary at this point: the systems studied in the present research show high sensitivity to changes in the experimental conditions; our experi-

ence on some systems [1, 3, 6] indicates that variation of the scanning rate can afford relevant changes in the kinetics and mechanisms of the decompositions; changes in the atmosphere prevailing over the sample can, of course, also be very effective in this sense. So the results given above and what follows are both reputed significant only within the limits of the experimental conditions given.

The experiments described and previous findings on other compounds [7, 8] indicate that the decompositions of crystalline materials can be divided roughly into three main classes namely: a) those which are delayed by the presence of fresh surfaces; b) those which are insensitive to surface modifications; c) those which are enhanced by the presence of freshly recrystallized surfaces. This classification is perhaps too rigid as, even in the present report, compounds showing behaviour intermediate between classes (NISH, CUSP) are evidenced; it is however, useful for discussing the results.

The present research had been undertaken with the aim of verifying if the delayed reactivity of recrystallized samples observed for some compounds was a general property of decomposing systems. So we expected that all the decompositions considered belonged to class a). We were only partly right, in fact several systems (to which we might almost safely add common and chrome alums [6]) pertain to this class; these are therefore easily understandable, in terms of our 3SM [1], as systems in which the outer crystal zones form a reacted layer opposing the migration of the gaseous products up to its own crystallization. Also the almost unexpected class b) systems however can be easily accounted for by the 3SM as those for which conversion of the dehydrated layer into the product (crystallization) is easy at least on some surfaces; as a consequence the reacted layer is rendered almost immediately discontinuous and easily permeable to the gaseous product. What we did not expect was the behaviour of COSH, class c), indeed the explanation we offer here, based on considerations concerning the incomplete weight loss and on some preliminary observations by optical microscopy, is to be considered just temporary; indeed further studies on this compound have already been undertaken to gain deeper insight. Microscopic observation of cleavage surfaces indicates that they do not keep their flatness for long but undergo retexturing in some tens of minutes. This information coupled with the non-stoichiometric weight loss suggests that COSH undergoes some superficial dehydration even in the laboratory atmosphere at room temperature. So the surfaces of the investigated materials are probably not those of the proper heptahydrate but those of some lower (hexa?) hydrate [19]. Anyway, whatever the nature of the outer surface, the fact that recrystallization enhances the reactivity remains. On the grounds of the 3SM we suggest that, in this case, long permanence of the crystals in air favours a stabilizing reconstruction of the outer surfaces forming a more or less continuous film of a lower hydrate; in contrast relatively fresh surfaces, which become (optical microscopy) full of crossing steps and defects conducive to easy layer crystallization, enable rapid escape of the gaseous product. The best fitting kinetic law suggests that reaction may take place generating cracks in the parent lattice so to bring it to collapse. Some support in this sense was obtained from optical microscopy observations but further studies are necessary.

Taking now into consideration the systems showing behaviour intermediate between classes, the case of NISH is reputed to validate our point of view. In fact light



grinding is considered necessary to produce fresh cleavage surfaces but insufficient to scratch them while heavy crushing produces also this second effect making the crystallization of the surface layer easy so that the decomposition becomes unhindered. Accordingly the thermal dehydration curves result slightly delayed (light grinding) or not (heavy grinding).

Coming to CUSP, we recall that this salt was reported [20] as showing “nearly all peculiarities that make the process of dehydration so specifically complicated”. Again its behaviour is rather puzzling; it is in fact found that for fresh materials the evolution of the transformation is somewhat affected only at the very beginning which takes place suddenly in comparison with that of aged materials. Careful observation of Fig. 6, however, reveals that the sudden start of the transformation of fresh samples is somewhat delayed relative to the regular beginning of the aged ones. This induces us to believe (in agreement with the existence of the Smith–Topley effect for this salt [21–23]) that, after the first part of the transformation forming the dehydrated surface layer, the third step of the 3SM, namely the crystallization of the lower hydrate, is particularly slow. When eventually the first microcrystal forms, the crystallization of the whole layer may be very rapid (a sort of release of supersaturation). Correspondingly, the reaction rate (no longer hindered by the continuous layer preventing the escape of the gaseous product) rapidly reaches the value corresponding to the higher temperature. From this point on the evolution of the system is regular and the contracting kinetics supports our point of view. Confirming the complex nature of CUSP dehydration the shape of the thermal curves places this system between classes b and c but the interpretation just given suggests that its place is midway between classes a and b.

## 5. Conclusions

Previous and present results confirm that the thermal decompositions of crystalline materials are strongly dependent on the status of the outer surfaces and that thermal methods can be used to reveal such dependence.

The comparison of the thermal decomposition curves of aged and fresh samples, recorded under identical conditions, reveals that the decompositions can be retarded (class a), can remain unaltered (class b) or can be accelerated (class c) by the presence of fresh surfaces. For the time being the only system pertaining to class c is COSH for which, however, some surface damage has been ascertained.

With some uncertainty for class c, to be reconsidered after further studies, the 3SM accounts for the results reported. This underlines once more its generality.

## Acknowledgements

The authors feel indebted to Mr. Paolo Parri for his careful preparation of the illustrative material. Financial support from M.U.R.S.T. (60%) is acknowledged.

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