

## DEHYDRATION/REHYDRATION PHENOMENA OF SURFACE LAYERS OF CRYSTAL HYDRATES

### Thermal aspects

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The study by thermal methods of the dehydration/rehydration phenomena of crystal hydrates shows that it is possible to separate the total heat of rehydration of previously dehydrated crystals into two contributions, attributed to surface and bulk, respectively. Values obtained for a number of salt hydrates are given and the ratio between the surface portion and the total heat is found to be of the order of 1%. Such findings are in agreement with results previously obtained by optical microscopy and are discussed in terms of recent views about the reversible reactions of crystalline solids.

A number of salt hydrates have recently been tested by optical microscopy [1] to generalize the results first obtained in dehydration/rehydration experiments on alums [2, 3]; the latter studies had evidenced a change in surface texture upon rehydration of a cleavage surface previously dehydrated to some extent. Because of the final aspect of the surface, the overall process was named "orange peel formation" [1, 3].

The texture change detected microscopically was found to extend over the whole surface, and this led to the conclusion that water elimination from the whole surface had also taken place. This in turn was regarded as proof that the function of nuclei was different from that hypothesized up to now [4], at least as concerns the reversible dehydration reactions.

Because of the thermicity of the dehydration/rehydration reactions ( $\Delta H \cong 55 \text{ kJ (mol H}_2\text{O)}^{-1}$ ), the above studies by optical microscopy were often complemented with investigations by thermal methods [1, 3]. In fact, even in the initial experiments [2], the thermal methods were of great help for the understanding of some particular features, such as the phase change leading to the formation of the circular halos surrounding the previously formed nuclei. The present report refers mainly to the information obtained from the thermal curves recorded during dehydration/rehydration experiments with the aim of gaining additional and possibly quantitative insight into the phenomena investigated.

## Experimental

The use of thermal methods was limited to cleaved crystals of sodium succinate hexahydrate, copper sulphate pentahydrate, manganese formate dihydrate, magnesium sulphate heptahydrate and potassium oxalate monohydrate. All these salts were also used in the experiments involving optical microscopy, and details concerning the preparation of single crystals and their cleavage are to be found in ref. [1].

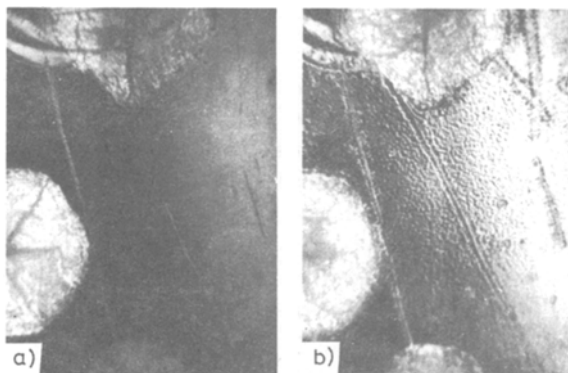
Dehydration/rehydration experiments were performed using a Mettler TA 2000 thermal analyzer equipped with a Watanabe SR 6255 recorder. With the exception of sodium succinate, which was dehydrated isothermally at room temperature (296 K) in a flow ( $30 \text{ cm}^3 \cdot \text{min}^{-1}$ ) of dry nitrogen [1], the dehydrations were performed with the temperature linearly increasing at a rate of  $2 \text{ deg} \cdot \text{min}^{-1}$  and with a flow of dry  $\text{N}_2$  of ca.  $12 \text{ cm}^3 \cdot \text{min}^{-1}$ . At the end of the complete dehydration the crystals were cooled to 296 K inside the thermal apparatus under the same flow of dry nitrogen. For every crystal hydrate some experiments were interrupted at this point and the crystals were taken from the apparatus to determine the extent of dehydration by weighing; otherwise, the isothermal rehydration experiments were started by allowing the same flow of nitrogen to reach the thermal apparatus after enrichment with a known partial pressure of water vapour by bubbling through aqueous solutions of sulphuric acid whose concentrations had been optimized in a number of preliminary experiments; in the end, four solutions were selected, viz. pure water, and 40%, 50% and 60% sulphuric acid, having the following water vapour pressures at 293 K: 2338.1, 1326.3, 826.5 and 382.6 Pa, respectively. The extent of rehydration was determined by weighing.

It is necessary to point out here that the rehydration experiments lasted for tens of hours, their duration obviously increasing with decrease of the partial pressure of water in the nitrogen flow.

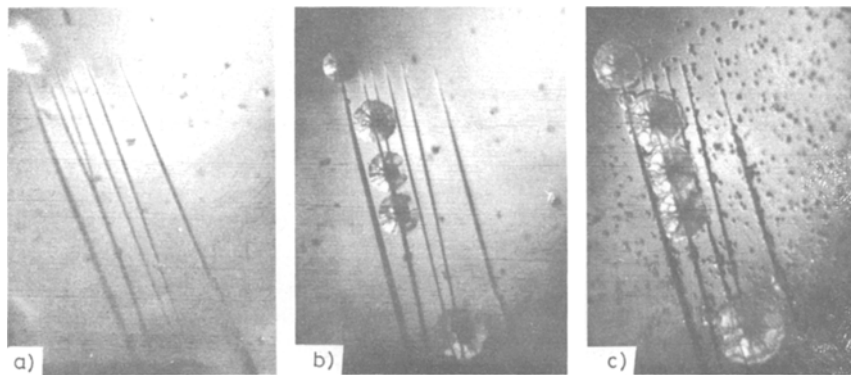
## Results and discussion

Besides the "orange peel" (Fig. 1), another more concealed change of the surface of a crystal hydrate due to dehydration had been evidenced by optical microscopy [1, 3], i.e. the formation of a great number of new nuclei upon renewed dehydration of an already rehydrated surface of some crystals not forming the orange peel (Fig. 2). Thus, both the orange peel and the enhanced nucleation phenomena clearly indicated as highly probable the formation, upon dehydration, of a dehydrated, strained layer over the whole surface of the crystal hydrate under study.

According to the results obtained, the relief of strain in such a layer can occur either by formation of the nuclei of a lower hydrate if the dehydration conditions are maintained, or by the two above phenomena upon rehydration. When the dehydration conditions are maintained, it is often observed that the nuclei form in correspondence to the points of emergence of dislocations [3, 5]. This is thought to support the view



**Fig. 1** A typical example of the change in surface texture (orange peel formation) taking place upon rehydration of a cleavage (111) surface of a crystal of common alum. a) before and b) after rehydration in a flow of  $N_2$  bubbled in water. Magn. X155



**Fig. 2** Enhanced nucleation on a cleavage (111) surface of a crystal of Chrome alum. a) before dehydration, b) during rehydration, c) at the beginnings of renewed dehydration. Magn. X155

that the nuclei are the sites where crystallization of the product is easier: indeed, particular geometric features are present at the dislocations as well as the availability of water (known to facilitate crystallization [6]), because of easy diffusion along the imperfections.

This being the new point of view about the nature and function of nuclei in reversible dehydrations of crystal hydrates, it follows that the actual site where the dehydration reaction takes place is not the boundary of the nucleus (i.e. the reactant/product interface), but any point on the surface of the hydrated crystal.

After the external layer is dehydrated, the progress of the reaction can be influenced only by the behaviour of the dehydrated part of the crystal, and the detachment of water molecules in further stages (the true reaction) can be studied only if the external layer does not interfere.

When the rehydration of a dehydrated crystal is taken into consideration, it is difficult to imagine that a single process takes place from the beginning up to complete rehydration. In view of the results obtained by microscopy, it is easier to think that initial rehydration of a superficial layer proceeds rather easily, while the subsequent (bulk) rehydration might be somewhat hindered by the presence of such an outer layer. If this were true, then the surface and bulk rehydrations should be separable. That this is so, is shown by the exothermic rehydrations of the crystals previously described. A typical rehydration curve is illustrated in Fig. 3, the asterisk indicating the point at which, when necessary, the water vapour pressure, the sensitivity of the apparatus and the chart speed were changed (vide infra).

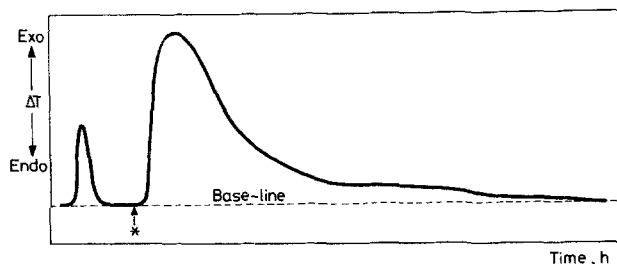


Fig. 3 1:2.7 reduction of the isothermal rehydration exotherm of the dehydration product of a cleaved single crystal of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . At the asterisk the sensitivity, initially  $10 \mu\text{V}$ , was reduced by a factor of 2 and the recorder chart speed, initially  $10 \text{ cm} \cdot \text{hr}^{-1}$ , by a factor of 4

The case of sodium succinate was a particularly lucky one; indeed, the separation of the first (surface) peak from the second (bulk) one is almost complete when nitrogen is bubbled through distilled water at room temperature. In general, to obtain the peak separation it was necessary, as expected, to reduce the water vapour pressure, making use of the sulphuric acid solutions described above. A typical change in shape of the first peak with the water pressure is shown schematically in Fig. 4. Because of the duration of the rehydration experiments, after the first (surface) peak was obtained the partial pressure of water was often increased to speed up the bulk rehydration. Also, to obtain curves of reasonable length, the chart speed was often drastically reduced between the two thermal events.

The thermal results obtained in the dehydration/rehydration experiments for the various salts examined are summarized in Table 1, where  $\Delta H$  values are reported for the dehydration ( $\Delta H_d$ ), the surface rehydration ( $\Delta H_r^s$ ) and the overall (surface + bulk) rehydration ( $\Delta H_r^t$ ). The absolute values of  $\Delta H$  for each water molecule in dehydration and in rehydration processes always match within the experimental error, due mainly to changes in thermal contact (enhanced by the use of single crystals) because of sample deformation during the dehydration/rehydration processes. In the last column of Table 1 the percentages of the surface with respect to the total (surface + bulk)

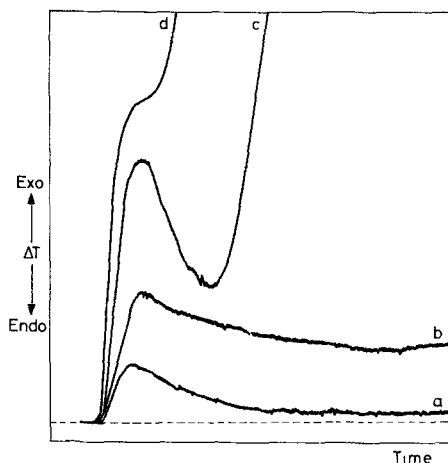


Fig. 4 Diagrammatic representation of the first rehydration peak changing shape according to the different water contents of the  $N_2$  gas bubbled through solutions of a) 60%  $H_2SO_4$ , b) 50%  $H_2SO_4$ , c) 40%  $H_2SO_4$  and d) pure water. The curves refer to the rehydration of dehydrated  $MgSO_4 \cdot 7 H_2O$

rehydration heats are reported. It appears that the surface heat of rehydration is generally about 1% of the total.

The fact that the separation between surface and bulk rehydration peaks is common to all the salt hydrates investigated tends to indicate this thermal behaviour as a general one, just like the orange peel formation. However, even if both phenomena depend on the rehydration of a certain external layer of the material under study, up to now we have no definite proof that they are two aspects of the same phenomenon. In fact, in the case of the orange peel, the layer considered is the external one of a cleaved single-crystal only partially dehydrated (but for nuclei, the surface examined has to remain microscopically unaltered before rehydration), while in the case of "thermal separation" the layer considered is the external one of an aggregate having the same shape as the original crystal, but formed by extremely small crystallites of the product and thus having a very high surface area.

We believe that the possibility of separating the "surface" rehydration from the "bulk" rehydration by thermal methods is due to the simultaneous and favourable action of two factors, viz. the great extension of the surface of the product and the relatively high rate of hydration of the external layer.

## Conclusion

The process of rehydration of cleaved single crystals of various crystal hydrates which lose their water molecules reversibly is shown by thermal methods to take place in two steps, one of which is identified with the rehydration of a surface layer, while

Table 1 Heats of transformation for some dehydration/rehydration reactions

Dehydration/rehydration reactions	weight change, % calc.	weight change, % exp.	$\Delta H_d$	$\Delta H_d/w$	$\Delta H_f^s$	$\Delta H_f^t$	$\Delta H_f^t/r/w$	$\Delta H_f^s/\Delta H_f^t, \%$
$\text{Na}_2(\text{C}_4\text{H}_4\text{O}_4) \cdot 6 \text{H}_2\text{O} \rightarrow$ $\text{Na}_2(\text{C}_4\text{H}_4\text{O}_4) + 6 \text{H}_2\text{O}$	-39.98	-39.6 ± 0.4	312 ± 10	52 ± 2				
$\text{Na}_2(\text{C}_4\text{H}_4\text{O}_4) + 6 \text{H}_2\text{O} \rightarrow$ $\text{Na}_2(\text{C}_4\text{H}_4\text{O}_4) \cdot 6 \text{H}_2\text{O}$	66.60	66.4 ± 0.4			-1.4 ± 0.7	-305 ± 19	-53 ± 1	ca. 0.5
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4 \text{H}_2\text{O}$	-28.84	-28.7 ± 0.2	218 ± 4	55 ± 1				
$\text{CuSO}_4 \cdot \text{H}_2\text{O} + 2 \text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$	20.26	20.4 ± 0.3			-1.4 ± 0.5	-113 ± 2	-57 ± 1	ca. 1.2
$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O} \rightarrow \text{MgSO}_4 + 7 \text{H}_2\text{O}$	-51.12	-50.7 ± 0.6	316 ± 6	51 ± 2				
$\text{MgSO}_4 + 6 \text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$	89.64	89.6 ± 0.6			-6 ± 3	-308 ± 4	-51 ± 1	ca. 1.9
$\text{Mn}(\text{HCOO})_2 \cdot 2 \text{H}_2\text{O} \rightarrow$ $\text{Mn}(\text{HCOO})_2 + 2 \text{H}_2\text{O}$	-19.89	-19.7 ± 0.2	116 ± 4	58 ± 2				
$\text{Mn}(\text{HCOO})_2 + 2 \text{H}_2\text{O} \rightarrow$ $\text{Mn}(\text{HCOO})_2 \cdot 2 \text{H}_2\text{O}$	24.83	24.4 ± 0.3			-0.9 ± 0.1	-118 ± 2	-59 ± 1	ca. 0.8
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$	-9.77	-9.9 ± 0.4	59 ± 2	59 ± 2				
$\text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	10.83	10.4 ± 0.4			-0.19 ± 0.07	-58 ± 1	-58 ± 1	ca. 0.3

$\Delta H_d$  = heat of dehydration,  $\Delta H_d/w$  = heat of dehydration per mole  $\text{H}_2\text{O}$ ;  $\Delta H_f^s$  = surface heat of rehydration;  $\Delta H_f^t$  = total heat of rehydration;  $\Delta H_f^t/w$  = total heat of rehydration per mole  $\text{H}_2\text{O}$ .

the second is connected to the bulk rehydration. Thus, studies of the rehydration process both by optical microscopy and by thermal methods converge in pointing out the formation in the materials employed of external layers having unforeseen properties. While some interesting consequences (e.g. about the nature and function of nuclei) have already been drawn in the case of the orange peel layer, a deeper interpretative hypothesis about the "surface" thermal peak needs the support of, for instance thermogravimetric and surface area determinations, which are now in progress.

## References

- 1 G. G. T. Guarini and L. Dei, *J. Chem. Soc. Faraday I*, 79 (1983) 1599.
- 2 G. G. T. Guarini, R. Spinicci and A. K. Galwey, *Proc Journées de Calorimétrie et d'Analyse Thermique*, Turin, 28–30 June 1978, B12–89.
- 3 A. K. Galwey, R. Spinicci and G. G. T. Guarini, *Proc. Roy. Soc. London Ser. A*, 378 (1981) 477.
- 4 W. E. Garner, *Chemistry of the Solid State*, Butterworths, London, 1955.
- 5 J. M. Thomas, *Advances in Catalysis*, 19 (1969) 293.
- 6 M. Volmer and G. Seydel, *Z. Phys. Chem.*, 179 (1937) 153.

**Zusammenfassung** – Die Untersuchung der Dehydratisierung-/Rehydratisierungsphänomene von Kristallhydraten durch thermische Methoden zeigt, daß es möglich ist, die totale Rehydratisierungswärme in zwei Komponenten zu zerlegen, die der Oberfläche bzw. der Gesamtmasse zugeschrieben werden. Es werden Werte für eine Anzahl von Salzhydraten angegeben. Der Oberflächenanteil liegt in der Größenordnung von 1% der Gesamtwärme. Diese Befunde stimmen mit früheren, durch optische Mikroskopie erhaltenen Ergebnissen überein und werden auf der Basis moderner Ansichten über die reversiblen Reaktionen kristalliner Feststoffe diskutiert.

**Резюме** – Изучение термическими методами явлений дегидратации и обратной гидратации кристаллогидратов показало, что общая теплота обратной гидратации может быть разделена на две компоненты, отнесенные к гидратации на поверхности и во всей массе кристалла. Для ряда кристаллогидратов приведены эти значения и найдено, что отношение теплоты гидратации на поверхности к общей теплоте должно быть порядка 1%. Полученные данные согласуются с результатами, ранее полученными методом оптической микроскопии. Обсуждение результатов проведено на основе недавно принятых взглядов на обратимые реакции кристаллических твердых тел.