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THE ROLE OF LIQUID WATER IN CRYSTALLINE HYDRATE DEHYDRATION

Copper sulphate pentahydrate

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Abstract

Simultaneous Differential Thermal Analysis/Thermogravimetric experiments carried out on one large single crystal, several small single crystals and powdered crystals of pentahydrate copper sulphate have been used to demonstrate the role that retained liquid water plays in maintaining crystal morphology during dehydration. Measured activation energies for stepwise dehydration in the system show the presence of solution-based transformations provide lower energy paths for the dehydration steps and stress relieving mechanisms. Skeletal anhydrous crystals from large-sized pentahydrate copper sulphate have the same morphology as the starting crystal on complete dehydration at controlled heating rates as long as a solution phase is maintained within the crystal during decomposition. The athermal activation energies, in this work, are in agreement with those obtained by isothermal methods as long as coincident reaction paths for the two techniques are maintained. The literature has been reviewed in the light of this work and a three-stage process is presented to rationalise the conflicting information obtained by workers using a variety of different experimental techniques.

Keywords: activation energies, copper sulphate, dehydration

Introduction

Well-crystallised, pentahydrate copper sulphate ($CuSO_4{\cdot}5H_2O_{(c)}$) is a material used to test and sometimes calibrate Differential Thermal Analysis/Thermogravimetric (DTA/TG) instruments. On reviewing the literature this is perhaps not surprising because from the nineteen thirties [1] to date, the dehydration of copper sulphate has been a continuous subject of study. The problem has been approached from as diverse directions as fine focus X-ray diffraction using topotactic methods [2]; gas chromatographic detection of

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evolved water as a function of heating rate [3]; electrical conductivity determination [4–7]; open pan and closed pan DTA and/or TG [8–10]; infrared measurements [11]; thermochemical measurements [12, 13]; the role of particle size; heating rate and gas atmosphere effects [14]. This diversity has lead to conflicting suggestions for the reaction mechanism and has produced energy data that is not always coincident. Some confusion arises from the apparent insulated way that separate groups have done their work. Effort over such a long time tends to foster the belief that the peak positions in a DTA analysis of the process and the enthalpy of the reactions are well established. Indeed, since we were at the time investigating drug-water and clay dehydration reactions we assumed at an early stage that the enthalpy associated with the removal of one water molecule from $CuSO_4{\cdot}5H_2O$ is a fifth of the value for the overall process as quoted by earlier workers. In the end this was not such a bad decision, but, because calibrations involving the first, that is lowest temperature, DTA peak and associated mass loss, gave more inconsistent results, than for the other two peaks on the thermal analysis trace, we were encouraged to consult the literature more fully. The findings of the search resulted in us performing a series of thermal analysis experiments using large, several small and powdered crystals of $CuSO_4{\cdot}5H_2O_{(c)}$.

Arguably the key work in the very diverse earlier reports appears to be the combined electrical conductivity-thermogravimetric and DTA work of Wendtlandt and his group [4–7] using both unsealed and sealed crucibles containing copper sulphate crystals. It is against these results and the detailed study of the effect of different crucible geometry of Paulik *et al.* [9], that the contradictions of other work can be rationalised in terms of whether or not equilibrium is established with water vapour pressure above the decomposing hydrate. The dominant role of the water vapour pressure and the extent to which water transport is impeded through channels of molecular dimensions was the focus of some of the earliest work with hydrates, such as $CuSO_4{\cdot}5H_2O$ [15]. It was shown that dehydration usually leads to structural degradation except in strong covalent network systems, such as zeolites. Structural collapse leads to impedance of water removal from the system, which probably produces some of the variations in reported literature data. From the resultant amorphous phase a variety of nucleation processes precede the appearance of a new phase. Nucleation in the sub-surface regions produces characteristic shapes related to the original crystalline phase. It follows from this that a number of reaction paths relating to evaporation of water from within hydrates exposed to increasing temperatures have been proposed [9, 10].

The fact is usually overlooked that some large crystals maintain their morphology through extremely large volume decreases. The anhydrous material is much smaller but a close copy of the original hydrate. Hence reaction path and related rate proposals must encompass satisfactory stress relief mechanisms. This work proposes mechanisms that might produce the stress relief.

Proposed reaction paths

From a review of the literature we propose the following overall view of the process in a series of reaction steps. In closed crucible conditions the process can be described by the following five stages as the temperature increases:

Stage 1, the dehydration of the pentahydrate

$$CuSO_4{\cdot}5H_2O_{(c)} \rightarrow CuSO_4{\cdot}3H_2O_{(c)}+2H_2O_{(l)} \tag{1}$$

This produces an endothermic event on DTA/TG examination with minimal mass loss by evaporation from the system.

Stage 2, the formation of localised pockets of saturated solution from the liberated water

Where the released water is in contact with $CuSO_4{\cdot}5H_2O_{(c)}$ and also now $CuSO_4{\cdot}3H_2O_{(c)}$, both are highly soluble salts and a simple physical dissolution reaction can take place:

$$H_2O_{(l)}+CuSO_4{\cdot}xH_2O_{(c)} \rightarrow (\text{saturated solution})_{(l)} \tag{2}$$

The saturated solution is at localised points within the crystal and little mass change occurs by evaporation from the surface. The heat of solution for these processes causes some uncertainty in the determination of the overall enthalpy change.

Stage 3, formation of the trihydrate

$$(\text{Saturated solution})_{(l)} \rightarrow H_2O_{(g)}+CuSO_4{\cdot}3H_2O_{(c)} \tag{3}$$

This stage produces a very strong endothermic effect with of course a loss of mass from the reaction pan.

When these three stages occur in open pan conditions it is common that only one endothermic effect is observed, with on occasion a shoulder on the curve, dependent on the heating rate, as localised conditions lead to a partial separation of the stages. Topotactic X-ray experiments [2] concerning nucleation of this stage were done without the any admitted pre-knowledge of these consecutive solution–evaporation reactions and so no crystal structure relationship was found. Furthermore reports in the literature of an amorphous transition from penta to monohydrate are to some extent understandable. The peak maximum temperature for this stage of the decomposition process in open pan conditions will be affected by several factors other than just the heating rate, for example sample size and impedance to water flow, as suggested by Topley [16], which will determine the period during which liquid water is retained as part of the system.

Stage 4, formation of the monohydrate

$$CuSO_4{\cdot}3H_2O_{(c)} \rightarrow CuSO_4{\cdot}H_2O_{(c)}+2H_2O_{(g)} \tag{4}$$

This endothermic reaction leads to further mass loss from the open pan with a heating rate dependent, peak maximum in a DTA analysis.

Stage 5, the production of the anhydrous sulphate

$$CuSO_4{\cdot}H_2O_{(c)} \rightarrow CuSO_{4(c)}+H_2O_{(g)} \tag{5}$$

This is the final stage and gives a clear third DTA peak in an open pan experiment or a fourth peak in a closed pan DTA experiment.

Separation of the consecutive dehydration steps in a DTA/TG experiment will be closely related to the heating rate and whether open or closed pan conditions are prevailing. However, it should be stressed that the position of all peak maxima are variable depending on the heating rate itself and this fact can be exploited to determine the activation energies associated with the various stages in the dehydration process. For example the work of Kissinger [17] and Ozawa [18] give Arrhenius-type relationships between the reciprocal of the peak maximum temperatures in degrees Kelvin and natural logarithm of the heating rate, which allow estimation of activation energies. For a DTA process an Ozawa plot [18], based on the work of Kissinger [17], measures the slope of a graph of the reciprocal peak temperature, $1/T_p$, *vs.* the natural logarithm of the heating rate, α. This gives the activation energy, Q, divided by the Universal Gas Constant, R, from the expression:

$$\ln\alpha=-\frac{mQ}{nRT_p}+C \tag{6}$$

In this equation m and n are constants which characterise various nucleation and growth mechanisms.

Kissinger [17] developed Eq. (6) and did verification work on re-crystallisation of glass. Thus the method relates best to processes which involve an amorphous to crystal transition. If Topley [16] and subsequent workers are correct, a vitally important stage in the dehydration of ionic hydrates is the change from an amorphous near surface layer to a crystalline product and so it was decided that Kissinger's analysis of the effect of the heating rate on the DTA endothermic peak positions could be a relevant way to investigate the dehydration process further. Temperature gradients in the specimen are a possible source of error when using this method and the recorded temperature will not always be the mean specimen temperature. Since the difference would depend upon the heating rate, which is the variable used in the method, it was decided to minimise this problem by limiting the heating rates used to those between 2 and 20°C min^{-1}. This produced peak maximum temperature changes of up to 50°C.

Following the literature review it was decided that the purpose of this experimental work was to establish activation energies for the separate steps in the dehydration process in open pan conditions, using three forms of $CuSO_4{\cdot}5H_2O_{(c)}$ in order to test and extend the current picture of the reaction mechanism.

Experimental

Copper sulphate crystals of AnalaR grade manufactured by BDH Chemicals, Poole, U. K., were dissolved in double distilled water, placed in a flat bottomed evaporating dish which was covered by a filter paper and allowed to stand undisturbed until the crystals appeared. The copper sulphate was recrystallised as some of the original crystals did not have the full five waters of crystallisation. Single crystals of about 0.5 to 5 mm crystal edge length were grown and fine crystalline powder was obtained by grinding the smaller crystals. A large crystal about 5 mm along the longest edge, or five to seven small crystals of about 0.5 mm, or a fine powder was placed in the specimen pan of the DTA, and dry nitrogen gas passed at 40 ml min^{-1} through the equipment and over the specimen. Various heating rates were used from 2.0 to 20.0°C min^{-1} from room temperature up to a maximum temperature of 300°C. Continuous readings were taken of the temperature, enthalpy and mass changes. All experiments were performed with open pans. The DTA/TG used was a Stanton Redcroft STA 780.

All the crystals used were examined in an Olympus BH2-UMA optical microscope and micrographs were printed on a UP-3000P Mavigraph. Some were re-examined after the heating cycle.

The experiments were performed by two workers independently. Practically identical results were obtained by both workers except for the large, single crystal experiments. In the latter the heat transfer between the pan and crystal is not as good as with the powders and small crystals and is very dependent upon the area of contact between the pan and the surface of the large crystal.

Results and discussion

The experiments showed that the large single crystals of pentahydrate copper sulphate could be completely dehydrated without distorting the template of the original crystal but just uniformly shrinking it (Fig. 1). Further microscopic examination of the dehydrated single crystals showed a series of features (Fig. 2). The question is raised as to what these are?

In Garner's book [15] similar pictures are shown facing page 219 to those of Figs 1and 2 and the text describes them as subsurface nuclei. They may have been in that case but in this work they come from a completely dehydrated sample, not a partially dehydrated one like that shown by Garner. One must assume that the nuclei here will have become part of the new anhydrous crystalline phase and therefore the features are more likely places where water left the crystal and so they are aggregations of molecular channels through which water has travelled. Indeed some non-random arrangement might just be seen in Fig. 2. These molecular-sized channels would provide the impedance needed to establish liquid water environments within the crystal.

Several of the micrographs shown in Garner's [15] text could be interpreted as etched dislocation pits. The craters here could also be such etched pits with the etchant being water. Nuclei tend to have sharp features which mirror the topography of the parent crystal. The pits shown in Fig. 2 and those shown by Garner, are spherical with fibrous projections. This feature may be indicating some degree of liquid water interaction with the nuclei or surface traces of the emergent tunnels.

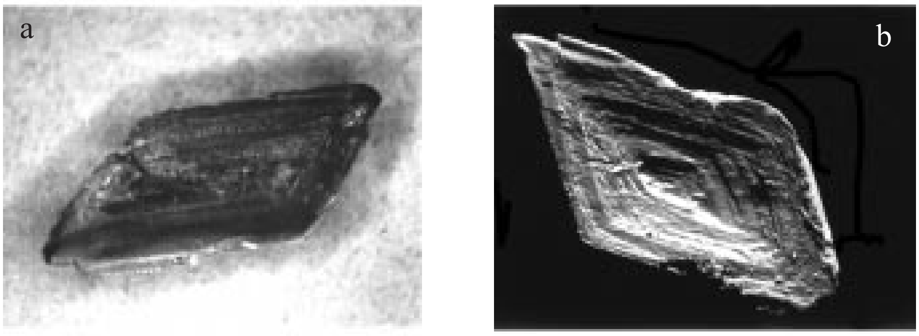

Fig. 1 A single crystal of $CuSO_4 \cdot 5H_2O_{(c)}$ before heating (a); Crystal after complete dehydration (b). Mag. ×20 for both

Hence one suggestion is that the water left the system along well-defined crystallographic paths which were related in $CuSO_4 \cdot 5H_2O_{(c)}$ and the final product $CuSO_{4(c)}$. This suggestion is not contradictory to the study of Zagray *et al.* [2] where the effect of water removal was investigated both microscopically and by fine focus X-rays. In their work rapid removal of water vapour into high vacuum showed x-shaped nuclei of $CuSO_{4(c)}$ as vapour left the solid from $CuSO_4 \cdot 5H_2O_{(c)}$. Less rapid water removal produced elliptical nuclei as the $CuSO_4 \cdot 3H_2O_{(c)}$ phase was presumed to crystallise from local pockets of saturated solution. Even though a solution was

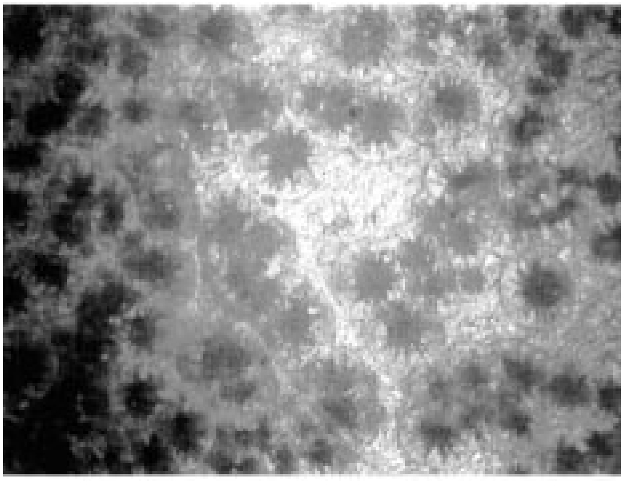

Fig. 2 Micrograph of the surface of the crystal. Dark spots are craters where water has left the sample

thought to be involved, the crystal axes of $CuSO_4{\cdot}3H_2O_{(c)}$ were closely related to those of $CuSO_4{\cdot}5H_2O_{(c)}$ indicating some topotactic process control. This topotactic control may be a reason why the general shape of the crystal is maintained as shown in Fig. 1 and the presence of liquid solutions would provide stress-relieving mechanisms. This is why stages 1 and 2 (above), where solutions are formed prior to water loss, were included in the overall mechanism.

A more detail explanation on a localised model which leaves the crystal essentially intact while implying differences in behaviour between hydrates obtained by decomposition or by addition of water is:

Stage [A]

$$CuSO_4{\cdot}5H_2O_{(c)} \rightarrow \begin{bmatrix} CuSO_4{\cdot}3H_2O_{(dec)(c)} \\ + \\ H_2O_{(1)} \end{bmatrix} \rightarrow \begin{bmatrix} \text{saturated} \\ \text{solution} \\ \text{pockets} \end{bmatrix} \rightarrow \begin{bmatrix} xCuSO_4{\cdot}3H_2O_{(c)} \\ (1-x)CuSO_4{\cdot}3H_2O_{(dec)(c)} \\ yH_2O_{(l)}+(2-y)H_2O_{(g)} \end{bmatrix}$$

The materials in the square brackets are not in equilibrium and x and y can be quite variable depending on heating rate and size of crystal. Note that (dec) means that the material in the sample holder used for subsequent heat treatment was obtained by decomposition of the previous higher hydrate.

Stage [B]

$$\begin{tikzcd} & \text{Fast heating}\quad CuSO_4{\cdot}H_2O_{(dec)(c)}+2H_2O_{(g)} \\ CuSO_4{\cdot}3H_2O_{(c)} \arrow[ur] \arrow[dr] & \\ & \text{Slow heating}\begin{bmatrix} CuSO_4{\cdot}H_2O_{(dec)(c)}+zH_2O_{(g)} \\ \text{concurrent with} \\ CuSO_4{\cdot}H_2O_{(dec)(c)}+(2-z)H_2O_{(l)} \end{bmatrix} \end{tikzcd}$$

Again, as in stage A, z is variable and difficult to measure experimentally.

Stage [C]

$$CuSO_4{\cdot}H_2O_{(c)} \rightarrow CuSO_{4(c)}+H_2O_{(g)}$$

These stages are most strongly supported by the work in Wendlandt's group [4–7] whose combined DTA and electrical conductivity measurements definitely show the presence of liquid water to beyond 102°C at slow heating rates for initial decomposition of $CuSO_4{\cdot}5H_2O$. A quadruple point $CuSO_4{\cdot}5H_2O$, $CuSO_4{\cdot}3H_2O$, liquid water and water vapour with a partial pressure less than one atmosphere was identified. In subsequent experiments these workers showed that the presence of liquid water depended on the heating rate and whether or not the sample was wrapped in a tight fitting Teflon cover. This is the reason we have introduced stage B. The proposed scheme is supported by the detailed thermogravimetric analysis of Paulik and co-workers [9, 10]. In their work fast heating rates gave ambiguous evidence for the presence of liquid water but wrapped crystals always produced this evidence. Hence hindering the diffusion of water vapour will allow liquid water to collect in the crystal, and since reactions inside relatively large crystals are ‘wrapped’, different reaction activation energies should come from experiments involving substantially different particle sized material.

The balance of our work and other reports, see below, leads us to reverse the role played by the heating rate in stage B, from that previously suggested by considering electrical conductivity measurements. Such a technique cannot easily distinguish between water on the surface and water trapped in pockets within the crystal. Hence confusion can arise as to where the water is situated, which in turn may lead to faulty interpretation as to the effect of heating rate on the decomposition.

The mechanism involving stages A and B could explain the variable shapes of the first two peaks in the DTA trace and the appearance of a skeleton $CuSO_{4(c)}$ from the original hydrate. The presence of the pockets of saturated solution provides a mechanism for stress relief, which presumably is why the crystal remains intact. The picture in Fig. 2 suggests that water diffusion and loss can be controlled by crystallinity. In fact the large crystal is a ‘perfect, wrapped experiment’. The smaller values for decomposition activation energies of all three stages, obtained when using the large crystals, suggest solution mechanisms assist in overcoming energy barriers in dehydration.

Experiments to assess the activation energy for such processes were focused on measuring the DTA peak-maximum temperature as a function of heating rate. From the above scheme more consistent results from the high temperature reaction, described as stage C, might be expected, with some inconsistency in data from stage A, and to a lesser extent stage B. This is because solution enthalpies are involved in step A and may be in stage B.

Ozawa [18] plots are shown for one large crystal, Fig. 3, for 5–7 medium sized crystals, Fig. 4 and for powders Fig. 5, for the 3 peaks occurring when open pan experiments are performed. The associated activation energies are given in Table 1. In each case distinct linear plots for peaks conforming to stages A, B and C in the model are obtained which implies that the heating rates used are not in a range sufficient to distinguish the two subsections of step B. It is stressed that all the results are from an open pan configuration, with dry flowing nitrogen gas to remove the water vapour. Good correlation coefficients were common for the experiments involving powder and the collection of small crystals, but more variance was apparent in the single crystal data. The results suggest that as far as stages A and B are concerned the physical form of the specimens are sufficiently close as not to produce significant differences, but the physical form does affect stage C. In all stages the trend in activation energy values indicate that processes are assisted by the retention of a crystal structure, decrease in surface area and the presence of liquid water.

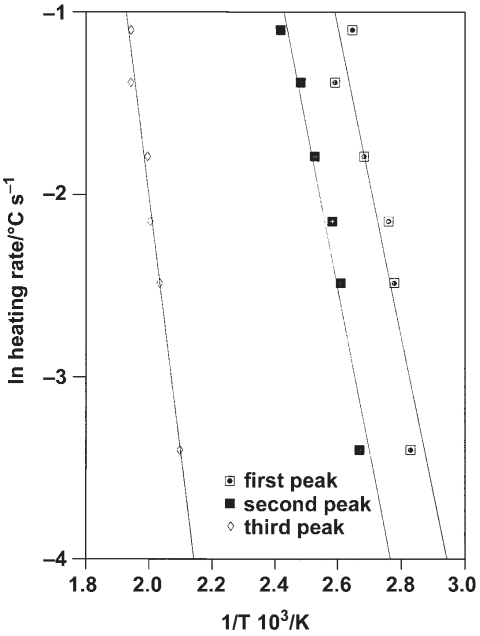

Fig. 3 Ozawa plot for single crystals of $CuSO_4 \cdot 5H_2O$

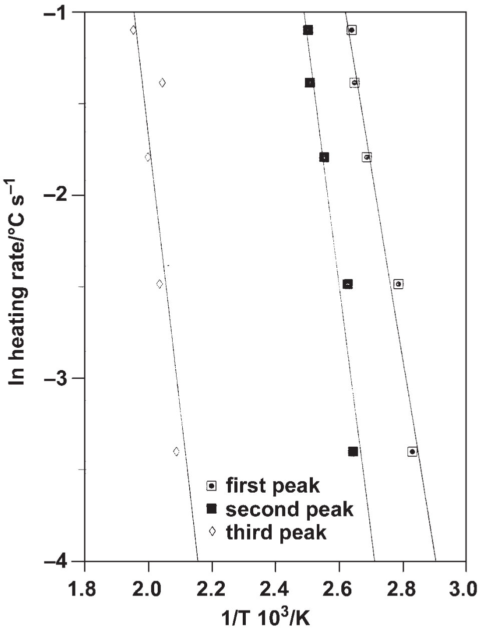

Fig. 4 Ozawa plot for several small crystals of $CuSO_4 \cdot 5H_2O$

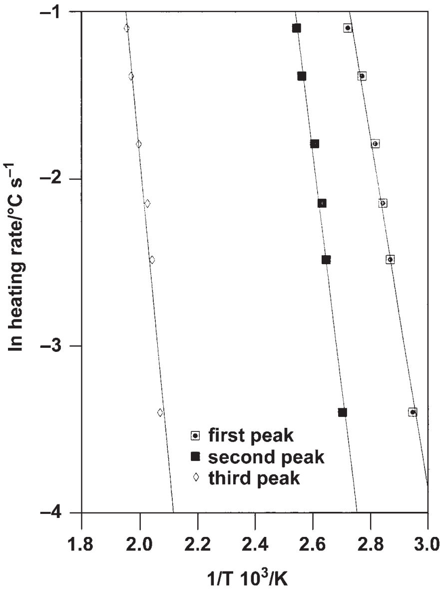

Fig. 5 Ozawa plot for powdered crystals of $CuSO_4 \cdot 5H_2O$

Table 1 Activation energies for dehydration of copper sulphate crystals

Reaction path	Peak 1/kJ mol^{-1}	Peak 2/kJ mol^{-1}	Peak 3/kJ mol^{-1}
	A	B	C
Type of specimen			
Powder	88.2	119.0	155
Small crystals	87.4	114.0	135
One large crystal	70.2	73.5	116

Sedlak and Beebe [3] used a temperature programmed desorption method that measured water in the gas phase as the sample is purged with helium gas. The samples were collections of small crystals with maximum edge lengths of 0.5 mm. From plots of temperature *vs*. concentration of water in the gas stream, at several heating rates, they were able to make temperature of water evolution peak maxima against square root of heating rate graphs, to obtain dehydration activation enthalpies. The method of analysis showed a different heating rate dependence above and below 8.15°C min^{-1}. Lines of different slope were obtained giving a difference of up to 80% in the activation enthalpy change. Their interpretation was the intervention of a crystalline to amorphous phase change. From the data presented in their paper we have calculated activation energies from their experiments, using the Ozawa [18] technique. Values of 68.4, 83.7 and 125 kJ mol^{-1} for the three stages A, B and C as defined here are obtained. These results are closest to the activation energy values for the large crystals we examined here. We were not able to detect in their results [3] any affect of heating rate above and below 8.15°C min^{-1}.

Marcu and Segal [19] used athermal thermogravimetric analysis from a constant slow heating rate, to establish activation energies for what would be stages A and B using powdered samples of $CuSO_4 \cdot 5H_2O$. Their activation energies are 115.5 and 135.5 kJ mol^{-1}, respectively. These are higher values than the data for our powdered samples, as shown in Table 1, and this probably reflects the very slow heating rate they used allowing a longer time period for equilibrium to be achieved and so, as Paulik [10] explains, the decomposition does not involve liquid water but is the process described by:

$$CuSO_4 \cdot 5H_2O_{(c)} \rightarrow CuSO_4 \cdot 3H_2O_{(c)} + H_2O_{(g)} \quad (7)$$

This is in agreement with our work, which suggests that liquid water, and solution evaporation mechanisms assist the process.

Pope and Sutton [14] used $CuSO_4 \cdot 5H_2O_{(c)}$ in seven size fractions, ranging from –14+18 to –100+150 BS mesh. They proposed three distinct endothermic processes contributing to the observed endothermic peaks for the decomposition to the monohydrate. Interestingly one of these is a liquid water to water vapour transition. With the largest particles (–14+18 BS mesh), the first stage of decomposition occurs comparatively slowly, due to the small surface/mass ratio and the time taken for the evolved water to diffuse to the particle surfaces. The corresponding endothermic peaks tend to merge, as liquid water is present throughout the process. Samples in the range –52+72 BS mesh show three distinct peaks corresponding to the three distinct endothermic processes. When using samples with the widest size range three peaks always are observed. This seems to support the importance of water removal paths, which are size and time dependent.

Langfelderova *et al.* [13] also used athermal thermogravimetry to find activation energies for what would be stages A, B and C here but introduced a significant change by making measurements on freshly prepared $CuSO_4 \cdot 3H_2O_{(c)}$ and $CuSO_4 \cdot H_2O_{(c)}$ crystals. They compared the data from these fresh crystals to that obtained from a step-wise decomposition of $CuSO_4 \cdot 5H_2O_{(c)}$ down to anhydrous copper sulphate. The results show that a well defined, freshly prepared, crystalline sample has a much lower activation energy at the final stage, C, and a lower activation energy for the B stage, in contrast to anhydrous $CuSO_4$ produced by three decomposition stages. This data highlights the role that sample crystallinity plays in the mechanism of dehydration. The progress from penta to anhydrate by decomposition:

$$CuSO_4 \cdot 5H_2O_{(c)} \rightarrow CuSO_4 \cdot 3H_2O_{(dec)(c)} \rightarrow CuSO_4 \cdot H_2O_{(dec)(c)} \rightarrow CuSO_4$$

has an activation energy of 216.9 kJ mol^{-1} for the final step, while the activation energy to obtain $CuSO_{4(c)}$ from fresh crystalline $CuSO_4 \cdot H_2O_{(c)}$ is only 126.8 kJ mol^{-1}. These results are summarised in Table 2 and are useful to compare with the activation energies for the large single crystals we measured, which maintained their morphology. Our average value for both large and small crystals is 126 kJ mol^{-1}. From this it could be argued that fresh $CuSO_4 \cdot 3H_2O_{(c)}$ crystals are formed from crystallisation from the solution prior to the decomposition leading to stage C. Thus, experiments performed at a rate able to maintain crystal morphology throughout, have a mechanism which reflects closed container conditions that allow a solution – recrystallisation route. This observation fits well with Pope and Sutton's work [14] on the effect of particle size.

Table 2 Activation energies from Langfelderova *et al.*, 1980 [13]

Reaction[*]	Reaction path as Langfelderova *et al.*, 1980	Activation energy/ kJ mol^{-1}	Notes
A	$CuSO_4\cdot 5H_2O_{(c)}$ $\downarrow$ $CuSO_4\cdot 3H_2O_{(dec)}$	124.9	Langfelderova *et al.* has soln → (*c*) + (*g*) here we have (*c*) → (*c*)+(*l*)+(*g*)
	$CuSO_4\cdot 3H_2O_{(c)}$ $\downarrow$ $CuSO_4\cdot H_2O_{(dec)}$	198.8	(*c*) → (*c*)+(*g*)
	$CuSO_4\cdot H_2O_{(c)}$ $\downarrow$ $CuSO_{4(dec)}$	126.8	(*c*) → (*c*)+(*g*)
B	$CuSO_4\cdot 3H_2O_{(dec)}$ $\downarrow$ $CuSO_4\cdot H_2O_{(dec)}$	235.4	
C	$CuSO_4\cdot H_2O_{(dec)(dec)}$ $\downarrow$ $CuSO_{4(dec)}$	216.9	The (*dec*)(*dec*) notation shows that originally this was $CuSO_4\cdot 5H_2O$

[*] Refers to the reactions pathways described in the text.

To a lesser extent Langfelderova *et al.*'s [13] data show the crystal structure effect; when the reaction:

$$CuSO_4\cdot 3H_2O_{(c)} \rightarrow CuSO_4\cdot H_2O_{(dec)(c)}$$

is compared to:

$$CuSO_4\cdot 3H_2O_{(dec)(c)} \rightarrow CuSO_4\cdot H_2O_{(dec)(c)}$$

which sequence is stage B in the above scheme but approached from different sample histories, the decomposition of freshly prepared $CuSO_4\cdot 3H_2O_{(c)}$ gave a lower activation energy value at 198.8 kJ mol^{-1} than the 235 kJ mol^{-1} for the $CuSO_4\cdot 3H_2O_{(dec)(c)} \rightarrow CuSO_4\cdot H_2O_{(dec)(c)}$ measured in this work. The same reaction for the small crystals we used gave activation energies around 114 kJ mol^{-1}, which is significantly below Langfelderova *et al.*'s [13] value. We suggest that this reflects the presence of newly crystallised $CuSO_4\cdot 3H_2O_{(c)}$ from the saturated solution pockets that are present up to 120°C. Crystals, which maintain coherence, give easier passage of water to the atmosphere and it seems that Langfelderova *et al.*'s [13] results and those obtained here agree over this point. The overall implication is that activation energies can be dominated by the presence of liquid water within the crystal, crystal perfection, particle size and the passage of water to the atmosphere.

Tanaka [12] using powdered, well crystallised $CuSO_4{\cdot}5H_2O_{(c)}$ measured activation energies for the three stages of decomposition occurring at 52, 77 and 200 °C using both isothermal and athermal thermogravimetric methods. His values for the activation energies are 72.9, 106.5 and 157.1 kJ mol^{-1}, which are in good agreement with our data in Table 1 for powdered samples. Thus the use of DTA peak temperatures and the Ozawa analysis in a variable heating rate experiment gives data close to that obtained from accepted, isothermal methods for $CuSO_4{\cdot}5H_2O_{(c)}$ dehydration. This would seem to support our original view that a method developed for amorphous to crystalline transitions would work.

Paulik *et al.* [9] and Arthur and Redfern [8] sounded a warning that care should be taken in the interpretation and significance of TG curves when studying dehydration. They did experiments using $CuSO_4{\cdot}5H_2O_{(c)}$ in open and closed pan conditions and their data confirms the importance of water diffusion in determining values of the activation energies and reaction enthalpies.

Table 3 Thermodynamic and derived properties of the hydrates of copper sulphate

Compound	ΔH_f^o/ kJ mol^{-1}	Dehydration enthalpy/kJ mol^{-1}	ΔH per mol H_2O/ kJ mol^{-1}	Crystal symmetry
$CuSO_4{\cdot}5H_2O$	–2277.4	1506.9	301.4	triclinic
$CuSO_4{\cdot}3H_2O$	–1688.7			monoclinic
$CuSO_4{\cdot}H_2O$	–1084.4			monoclinic
$CuSO_4$	–770.4			rhombohedral
$1H_2O$–$CuSO_4$		313.5	313.5	m–r
$3H_2O$–$1H_2O$		597.0	298.5	m–m
$3H_2O$–$CuSO_4$		912.5	304.2	m–r
$5H_2O$–$3H_2O$		594.4	297.2	t–m

If a large single crystal is used, can the reaction enthalpy data be used to distinguish between different forms of H_2O to ion bond within the crystal? Several spectroscopic and above all X-ray crystal structure determination studies, have shown that all the water in the copper sulphate crystal is co-ordinated and none is free. However four water molecules are associated with the Cu^{2+} ion and one with the SO_4^{2-} ion. Overall the total dehydration enthalpy for the removal of five water molecules is, from Table 3, 1506.9 kJ mol^{-1} which gives an average dehydration enthalpy per mol of water of 301.4 kJ. A closer examination of data in Table 3 indicates an enthalpy change for removal of the last water as 313.5 kJ mol^{-1}. Does this reflect the different bonding state or the presence of liquid water in the earlier dehydration steps? It is hard to decide because at least two crystallographic transformations are involved. Enthalpies of formation of the various copper sulphate hydrates are given in Table 3, along with some crystallographic information. From this data the value of 301.4 kJ (mol of water $)^{-1}$ of water removed is sometimes used to calibrate thermal analysis peaks using copper sulphates as a standard. This approach smoothes over the fact that four of the water molecules are co-ordinated to the Cu^{2+} ion, one is co-ordinated to SO_4^{2-} ion and two crystallographic changes are involved in sequential water removal. Using the data for $CuSO_4{\cdot}3H_2O$ dehydrating to $CuSO_4{\cdot}H_2O$ involves no crystal structure change and only the breaking of Cu^{2+}–H_2O bonds which gives an average value of 298.5 kJ $(mol\ H_2O)^{-1}$. Considering the 5 to 3 H_2O dehydration alongside the 3 to 1 H_2O, an estimate of 2.6 kJ mol^{-1} is arrived at for the triclinic to monoclinic conversion. An estimate for the different binding energy between H_2O–Cu^{2+} and H_2O–SO_4^{2-} comes from the $CuSO_4{\cdot}H_2O \rightarrow CuSO_4$ and $CuSO_4{\cdot}3H_2O \rightarrow CuSO_4$ reactions, which have a difference in $\Delta H/H_2O$ removal of 9.3 kJ $(mol\ H_2O)^{-1}$. This implies a 4.7 kJ mol^{-1} difference in binding water to cupric ion. Removal of the last water of crystallisation involves a monoclinic to rhombohedral transformation and breaking of a H_2O to SO_4^{2-} bond, a process involving 313.5 kJ $(mol\ H_2O)^{-1}$. This is some 4% different from the average value frequently used. For our subsequent work on drug–water reactions and clay hydrations the calibration peak used was that from Stage C using the value 313.5 kJ because it is not involved with a liquid water stage at any heating rate used.

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Nomenclature

α is the heating rate in °C min^{-1} also °C s^{-1}	
C is a constant	
ΔH_f^o is the heat of formation at 25°C	kJ mol^{-1}
Q is the activation energy	kJ mol^{-1}
R is the universal gas constant	kJ mol^{-1} K^{-1}
T_p is the maximum temperature of the enthalpy peak	K

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