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A NEW LOOK AT THE THERMAL PROPERTIES OF COPPER SULFATE 5-HYDRATE*

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ABSTRACT

The dehydration of $CuSO_4 \cdot 5H_2O$ was studied by sealed and open-tube DTA, QDTA, and by microreflectance and transmittance spectroscopy. By use of sealed-tube DTA, only two endothermic peaks were observed during the dehydration process; the first peak was due to the transition:

$$CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4 \cdot 3H_2O(s) + 2H_2O(l)$$

while the second was probably the transition of the

$$CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot 1H_2O$$

From QDTA, the heat of reaction of the first peak was found to be 12.9 ± 0.6 kcal/mole; for the second peak a ΔH of 6.3 ± 0.3 kcal/mole was found. The microreflectance and transmittance curves of single crystals of $CuSO_4 \cdot 5H_2O$ also showed the formation of the 3-hydrate at elevated temperatures.

INTRODUCTION AND DISCUSSION

The dehydration of $CuSO_4 \cdot 5H_2O$, as determined by various thermoanalytical techniques, has been the subject of numerous investigations. Using TG, Vallet[1] in 1934 investigated the effect of particle size, composition of the furnace atmosphere, and gas flow-rate over the sample, on the dehydration reactions. He showed that the presence of $CuSO_4 \cdot H_2O$ was not influenced by the gas flow-rate (in the range from 6.6 to 34.0 l/h) but that its formation was affected by the water vapor content of the furnace atmosphere. Using DTA, Taylor and Klug[2] in 1936 postulated the existence of $CuSO_4 \cdot 4H_2O$ on the basis that the double peak in the curve was due to the 5-hydrate to the 3-hydrate transition. Chemical analysis of the product after the first peak gave a copper–water ratio of 1:4. Further evidence for the 4-hydrate was reported by Ghosh[3] from TG data. Sidgwick[4] also reported the existence of the 4-hydrate citing the work previously reported[2].

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The dehydration reactions were elegantly elucidated by Borchardt and Daniels[5] in 1957 using DTA and X-ray diffraction techniques. They showed that the dehydration of $CuSO_4.5H_2O$ proceeded according to the reactions:

$$CuSO_4 \cdot 5H_2O \xrightarrow{90°} CuSO_4 \cdot 3H_2O(s) + 2H_2O(l) \quad (1)$$

$$2H_2O(l) \rightarrow 2H_2O(g) \quad (2)$$

$$CuSO_4 \cdot 3H_2O(s) \xrightarrow{130°} CuSO_4 \cdot H_2O(s) + 2H_2O(g) \quad (3)$$

$$CuSO_4 \cdot H_2O(s) \xrightarrow{250°} CuSO_4(s) + H_2O(g) \quad (4)$$

Although these reactions indicate that four peaks should occur in the DTA curve, the first two usually appear as a doublet in the 90–115°C temperature range. The first peak is greatly dependent on the ambient atmosphere water content and the pyrolysis condition of the sample. In many cases, it is absent from the curve completely, and only three DTA peaks are present in the curve.

A critical analysis of the DTA curve of $CuSO_4 \cdot 5H_2O$, as applied to the isobaric process, was described by Reisman and Karlak[6]. They showed that the dehydration process was a function of particle size, heating rate, nucleation rate, ambient aqueous tension, the vapor pressure–temperature curve of the hydrate system, the latent heats of hydration, the furnace geometry, sample packing, and so on. Using a sample of the 5-hydrate with a particle size of $<16>40$ mesh, a heating rate of 0.4°C/min, and an ambient aqueous tension of 11.5 min, only three peaks were observed in the DTA curve. They stated that an increase in heating rate to 1°/min caused a shift in the "dissociation temperature" by as much as 30°C. In none of the experiments were the molecular rotation heat effects, as previously reported by Taylor and Klug[2], observed. The latter authors were aware of the effect of particle size on the shape of the DTA curve but apparently applied a completely different interpretation to its effects.

In the more recent literature, $CuSO_4 \cdot 5H_2O$ is often used as a "standard" compound to test a new thermal technique, instrument or sample holder configuration. Mass-loss curves[7-15], DTA curves[16-25], simultaneous DTA–TG curves[26-30], and other curves[31-35], have been reported by various investigators. In almost all of the TG curves, plateaus were found for compounds with the compositions, $CuSO_4 \cdot 3H_2O$, $CuSO_4 \cdot H_2O$, and $CuSO_4$. In some cases, the plateau for the 3-hydrate was absent in curve due to the fast heating rate employed or the dehydration conditions. With DTA, generally only three endothermic peaks were observed. The first peak, reaction (1), is generally absent, even as a shoulder peak.

The kinetics of the dehydration reaction have been investigated[14,23,36]. Using Kissinger's method[37], Ishii *et al.*[23] found E_a values of 45.0 kcal/mole for reactions (1+2). Pavlyuchenko and Borisenko[36] and Kaliaguine[14] reported that the E_a and preexponential values were both pressure dependent. At a pressure of 10 mm Hg, apparent E_a-values of 45.2, 29.5, and 28.5 kcal/mole, were found for reactions (1+2), (3), and (4), respectively[14]. On increasing the pressure to 500 mm Hg, the values were 125.4, 80.4, and 46 kcal/mole, respectively. The reactions were said to be zero order. In view of the comments by Clarke *et al.*[38], the reaction order is perhaps misleading if not meaningless to use.

From the previous TG studies, it is apparent that the compound, $CuSO_4 \cdot 4H_2O$, does not exist. However, Larson and Hepler[39] recently reported the standard heat of solution of the compound as −1.31 kcal/mole. They stated that there was some disagreement in the literature on whether the 4-hydrate was a mixture of the 5- and 3-hydrate or a stoichiometric compound. The disagreement was not resolved by their data.

The electrical conductivity of the dehydration reaction was studied by Berg and Burmistova[40] and others[34,35]. Wendlandt[34] found that this technique could be used to detect the quadruple point of the hydrate system, as described by Eqns. (1) and (2). The evolution of liquid water in Eqn. (1) caused a large increase in the conductivity of the sample. As the water vaporized, the electrical conductivity decreased. No such changes were observed for reactions (3) and (4) although David[35] reported their presence using an applied potential of 0 V.

We have found that reaction (1) can be isolated if the dehydration reaction is studied by sealed-tube DTA. Also, by use of quantitative differential thermal analysis, QDTA, the ΔH of this reaction can be determined. The dehydration reactions of single crystals and of the powdered compound were studied by microreflectance and transmittance techniques.

EXPERIMENTAL

The $CuSO_4 \cdot 5H_2O$ used was obtained from the J. T. Baker Chemical Co., Phillipsburg, Pa. The water content was determined by mass-loss on the thermobalance. A typical TG curve, showing the presence of the 3-hydrate plateau, is illustrated in Fig. 1. The final product in the curve illustrated is $CuSO_4 \cdot H_2O$.

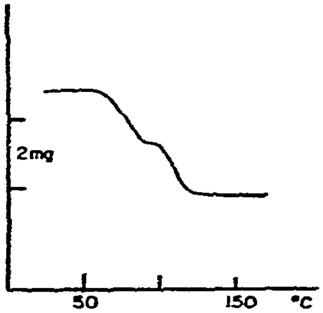

Fig. 1. TG of $CuSO_4 \cdot 5H_2O$ in air at 10°C/min.

Sealed-tube DTA apparatus

A schematic diagram of the sealed-tube DTA furnace and sample holder assembly is illustrated in Fig. 2.

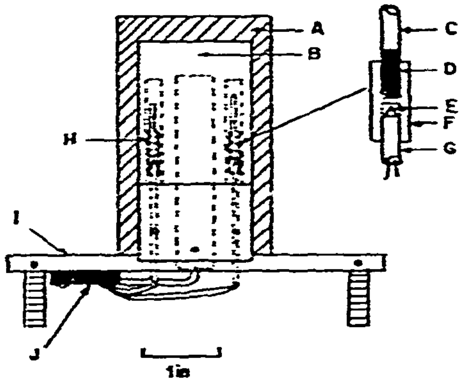

Fig. 2. Schematic diagram of sealed-tube DTA furnace and sample chamber; A, insulated cover; B, aluminum block; C, glass capillary tube; D, sample; E, sample thermocouple; F, aluminum heat transfer sleeve; G, ceramic insulator tube; H, reference chamber; I, transite platform; J, terminal strip.

The furnace consisted of an aluminum cylinder, B, 5.0 cm in diameter by 8.0 cm in length. Two cylindrical cavities, H, were used for the sample and reference compartments. The sample was contained in a 0.9–1.1-mm ID diameter glass capillary melting-point tube, C, (Kimax No. 34507), which was placed in an aluminum heat transfer sleeve, F. An identical empty tube was used in the reference chamber. The furnace block was heated by a stainless-steel heater cartridge of 210-W capacity. The d. c. microvolt amplifier, temperature programmer, and X–Y recorder have been described elsewhere[18].

The procedure for a sealed-tube run was as follows: from 5–7 mg of the powdered $CuSO_4 \cdot 5H_2O$ sample was placed in the capillary tube and gently tamped in place at the bottom of the tube. The tube was then sealed off, using a small oxygen-gas flame, to a length of about 20 mm. The sealed tube was then placed in the sample holder and heated at a heating rate of 7°/min. For quantitative DTA measurements, an external strip-chart recorder was connected in parallel to the Y-axis of the X–Y recorder. The QDTA system was calibrated over the 40–150°C temperature range with benzophenone, azobenzene, napthalene, catechol, benzoic acid, ammonium nitrate, and cinnamic acid. Peak area measurements were obtained by use of a planimeter. An average of three area determinations was taken for each measurement. The precision of the ΔH measurements was about ±3% with an accuracy of about ±5%.

Microreflectance and transmittance spectroscopy apparatus

This apparatus has been described elsewhere[41]. The microreflectance and transmittance curves of single crystals and of powdered samples of $CuSO_4 \cdot 5H_2O$ were determined at ambient and at elevated temperatures. The powdered samples were studied in sealed and in open capillary tubes. All measurements were made in monochromatic light at a wavelength of 450 nm.

RESULTS AND DISCUSSION

DTA results

The open and sealed-tube DTA curves of $CuSO_4 \cdot 5H_2O$ are shown in Fig. 3.

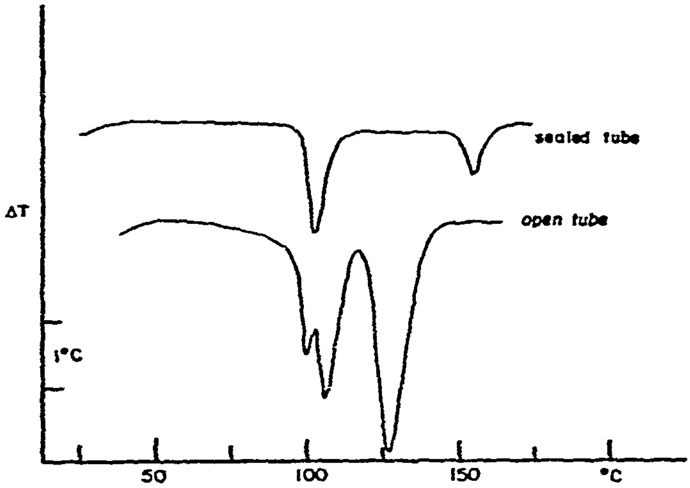

Fig. 3. Open and sealed-tube DTA curves of $CuSO_4 \cdot 5H_2O$. Heating rate of 7 °C/min.

In the open-tube DTA curve, the peaks are due to reactions (1), (2), and (3). Reaction (4) did not take place because of the temperature limitations of the curve. Peak minimum temperatures, ΔT_{min}, observed were 100, 105, and 127 °C, respectively. For the sealed-tube curve, only two endothermic peaks were recorded, with ΔT_{min} values of 101 and 153 °C, respectively. The 101 °C peak is well defined and is due to reaction (1). The origin of the 153 °C is not definitely known; it is probably due to the transition:

$$CuSO_4 \cdot 3H_2O(s) \rightarrow CuSO_4 \cdot H_2O(s) + 2H_2O(l) \qquad (5)$$

Using a sealed-tube sample holder, the endothermic peak for reaction (1) is well resolved and does not show up as a shoulder peak as is the case with the open-tube DTA curve.

Using QDTA, the ΔH for the reaction:

$$CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4 \cdot H_2O(s) + 4H_2O(g) \qquad (6)$$

was found to be 56.8 ± 3 kcal/mole. This value is in fair agreement with the value of 54.2 kcal/mole found by Hioki and Mori[20]. However, with the sealed-tube sample, the ΔH for the first peak was 12.9 ± 0.6 kcal/mole and the second was 6.3 ± 0.3 kcal/mole. If the second peak is due to reaction (5), then the ΔH for the reaction,

$$CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4 \cdot H_2O(s) + 4H_2O(l) \qquad (7)$$

is 19.2 ± 1.0 kcal/mole. All of the values reported here are uncorrected for the change in C_p of the products with temperature.

Microreflectance and transmittance studies

The scanning microreflectance curves (SMR) of a single crystal of $CuSO_4 \cdot 5H_2O$ are shown in Fig. 4.

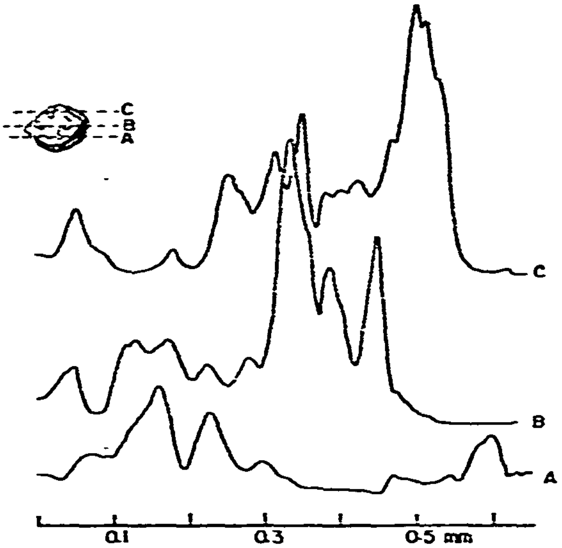

Fig. 4. Scanning microreflectance curves of a single crystal of $CuSO_4 \cdot 5H_2O$; wavelength of incident light 450 nm; crystal scans as illustrated; temperature 30.0 °C; magnification 100×.

The curves represent the reflectance of the surface at scans across the crystal at points A, B, and C. Since a reflectance geometry of 90°/90° was used, the curve maxima represent maximum specular reflection from the crystal surface. Thus, surfaces perpendicular to the incident beam reflect the strongest, giving the curve peak maxima. The curves are not very reproducible from crystal to crystal due to the different surfaces of the individual crystals.

The SMR curves of the same crystal at various temperatures are illustrated in Fig. 5. The SMR curves changed little on increasing the temperature of the crystal from 30–50 °C. However, at 70 °C the specular reflectance maxima all showed a

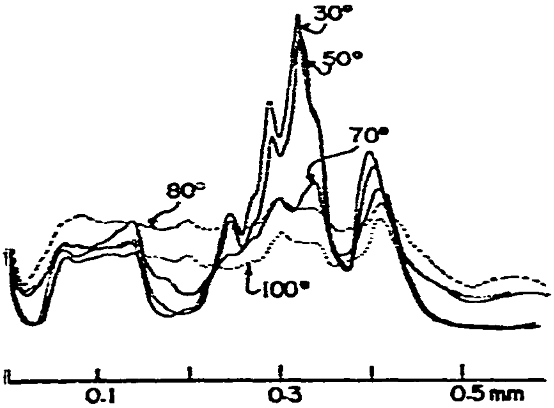

Fig. 5. Scanning microreflectance curves of a single crystal of $CuSO_4 \cdot 5H_2O$ at various temperatures; wavelength of incident light 450 nm; magnification 100×.

general decrease which became more pronounced as the temperature was increased to 80 and 100°C. The decrease in the specular reflectance of the crystals was due to the formation of a surface layer of $CuSO_4 \cdot 3H_2O$ which is more opaque than the original compound. Thus, the formation of the 3-hydrate can easily be followed by the SMR technique. The observed lower temperature for the initial dehydration of the 5-hydrate is to be expected because of the exposure of the entire crystal to the dynamic air atmosphere of the heated hot-stage. This lower decomposition temperature to the 3-hydrate is also illustrated in the single crystal transmittance curve of copper sulfate 5-hydrate, as illustrated in Fig. 6. The transmittance began to decrease at about 55°C and decreased very rapidly between 60 and 65°C.

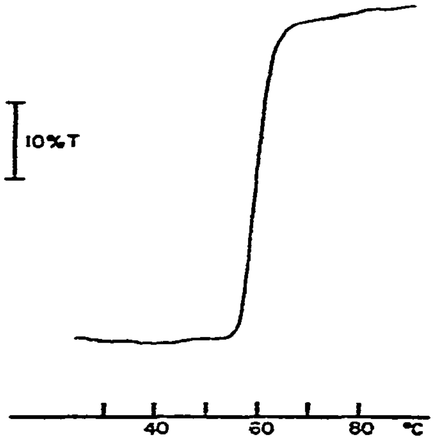

Fig. 6. Single-crystal transmittance curve of $CuSO_4 \cdot 5H_2O$; wavelength of incident light 450 nm; heating rate 10°C/min; magnification 100×.

The liberation of liquid water, as given in reaction (1), is vividly illustrated by the microreflectance of powdered $CuSO_4 \cdot 5H_2O$ in sealed and open capillary tubes, as shown in Fig. 7.

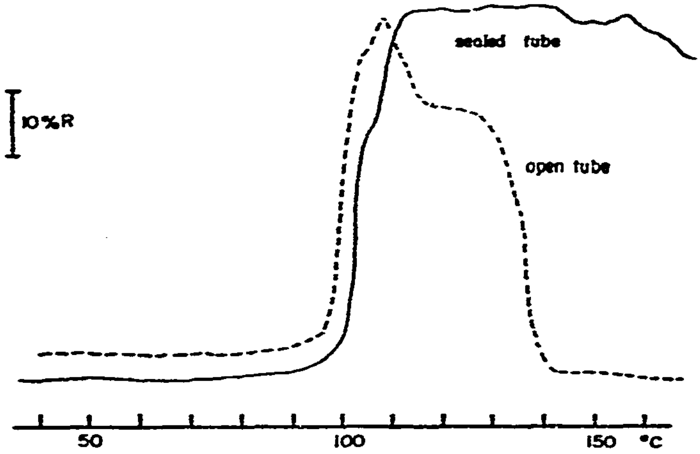

Fig. 7. Microreflectance of sealed and open tube samples of $CuSO_4 \cdot 5H_2O$; heating rate 10°C/min; wavelength of incident light 450 nm; magnification 80×.

In an open capillary tube, the reflectance of the sample decreased as the temperature was increased, due to the liberation of water. On further heating, the reflectance increased due to the vaporization of the liquid water and the formation of $CuSO_4 \cdot H_2O$. The reactions take place in the same temperature range as was observed in the DTA curves. In the sealed-tube, the reflectance of the sample decreased as the temperature increased. However, since the liquid water is confined in the tube, the reflectance did not increase on further heating.

Due to the rather drastic change in the microreflectance or transmittance of single crystals of $CuSO_4 \cdot 5H_2O$ on heating, it may be possible to do single-crystal kinetics studies or at least follow the rate of nucleation of the crystals. Also, the kinetics of powdered $CuSO_4 \cdot 5H_2O$ may be obtained by use of the capillary tube microreflectance method. It would be of interest to compare the kinetics data for the single crystal and the powdered samples.

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