

EFFECTS OF HEATING RATE ($1\text{--}300^\circ \text{h}^{-1}$) ON THE NON-ISOTHERMAL THERMOGRAVIMETRY OF $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$

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ABSTRACT

The course of the reaction $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O} - \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4 \text{H}_2\text{O}$ was studied by non-isothermal thermogravimetry with various heating rates ranging from 1 to 300°h^{-1} . The measurements were made either in static air, in a dry nitrogen stream, or in water vapor at a reduced pressure (9 mm Hg). In static air, the shape of the TG curve changed drastically at a heating rate of 13 to 15°h^{-1} , and this change was explained by considering the nature of the plateaus and inflections present. In a dry nitrogen stream, the dehydration is made much easier at slow heating rates and occurs almost in one step at 2°h^{-1} ; in water vapor at 9 mm Hg, on the other hand, a very distinct two-step curve is obtained at 1°h^{-1} . This can reasonably be compared with the phase diagram of copper sulfate.

INTRODUCTION

The results of dynamic non-isothermal thermogravimetry (TG) are influenced by many factors [1], such as the heating rate, the size (or volume) of the sample and its particles, the mode of packing and the nature of the atmosphere. Moreover, these factors are interdependent.

The effects of the heating rate on the shape of the thermogram and the kinetic parameters have been extensively examined by many workers [1–6]. However, the heating rate ranges studied are limited, and nearly always lie above 30°h^{-1} .

Recently, Paulik and Paulik [7] introduced the so-called quasi-isothermal technique into thermal dehydration of inorganic salts. Here the sample temperature is elevated continuously as long as there is no weight change, but as soon as such a change begins to occur, the temperature is automatically kept constant, and the dehydration continues quasi-isothermally until completion. This technique implemented under quasi-isobaric conditions proved to

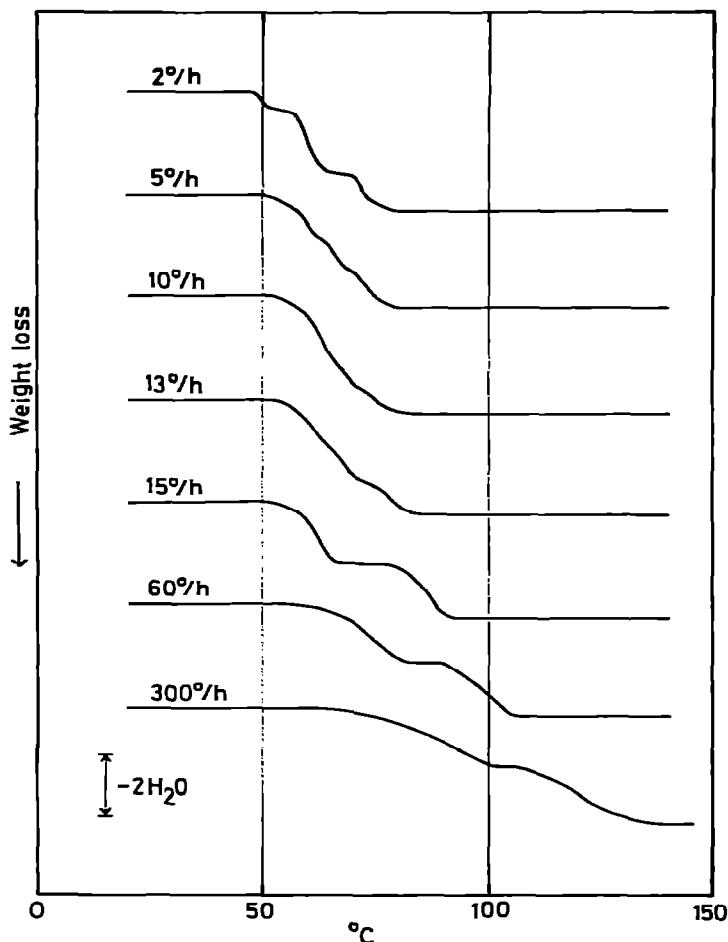
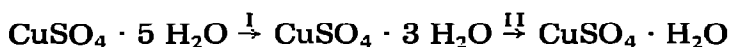


Fig. 1. TG curves for $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O} - \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4 \text{H}_2\text{O}$ in static air, with heating rates of 2–300° h^{-1} .

be very effective in the detection of intermediate products whose existence could not be verified by conventional non-isothermal methods [8].

It seems that, in general, a break (a plateau or an inflection) on a non-isothermal TG curve arises from the differences in the rates of the decompositions involved; for example, in the dehydration sequence of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$



step I is easier (and thus faster at the same temperature) than step II, so that by heating $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ it decomposes in a stepwise manner (the curve of 15° h^{-1} in Fig. 1 corresponds to this situation). However, when the heating rate becomes very high, the temperature of the sample rises so quickly that there is insufficient time for decompositions I and II to occur at the appropriate temperatures, so that the steps on the TG curve will be shifted to the high-temperature side. On the other hand, if the heating rate is very low, there will be sufficient time at every temperature for every possible reaction to occur as far as it can, so that at the limit of ideally isothermal

(heating rate $\rightarrow 0$) and isobaric conditions, the TG curve will become identical to the phase diagram of the system. In other words we can say that, when the heating rate is high, the shape of the TG curve is governed by the rates of the changes involved, but when the heating rate is low it is governed more by the free energies of the substances in the system. It can therefore be expected that, when the heating rate is changed over a very wide range, the TG curves obtained at the highest and lowest limits may be quite different. In such a case, there will be a transitional heating rate, above and below which the shape of the TG curve begins to change in different ways.

It therefore seems worthwhile to study how these effects actually appear, by extending the heating rate range to a very low value. The dehydration of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ was studied from this point of view in the present work. This reaction is probably the most convenient model for a study of this nature, owing to the large number of experimental data available and also to the ease with which the chemical changes in progress may be identified [2,9].

EXPERIMENTAL

Reagent grade $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ was used throughout the study. A Shinku Riko TGD-3000 thermal microbalance equipped with a Shinku Riko HPC-5000 module-unit thermal program controller, which can change the heating rate in the range 1°h^{-1} to $999^\circ \text{sec}^{-1}$, was used for TG measurements. The temperature readings of the instrument were calibrated using the NH_4NO_3 phase transitions which occur at 50 [10], 84.2, 125.2 and 165°C , respectively, and room temperature. 30 mg of powdered $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, packed lightly in a cylindrical Pt crucible, was heated at rates ranging from 1 to 300°h^{-1} in static air, in dry nitrogen streaming at a rate of 60 ml min^{-1} , and in water vapor at a constant reduced pressure. In the latter case, the crucible was covered with a thin Pt lid, so that water vapor leaving the sample could only escape through a small opening beneath it. The vapor was evacuated continuously using a strong motor-driven aspirator containing refluxing cold water regulated at 8°C . With the use of these devices, the atmosphere around the sample (almost completely water vapor) was maintained at a pressure of 9 mm Hg, slightly above the equilibrium pressure of water at 8°C (8.04 mm Hg).

Intermediate substances produced at every characteristic step observed on the TG curves were identified by X-ray powder diffraction.

RESULTS AND DISCUSSION

The TG curves obtained for the dehydration of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ at various heating rates in static air are shown in Fig. 1. At a heating rate of 15°h^{-1} , the reaction clearly occurs in two steps, with a plateau corresponding to the formation of $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$. When the heating rate is increased, both the steps are shifted to the high temperature region, apparently owing to the effect described in the Introduction; at 300°h^{-1} the first step is shifted so

much that the second step begins just after (or even somewhat before) the completion of the first, so that the plateau almost disappears. Since the width of the plateau thus tends to diminish with increasing heating rate, the separation of $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ is favored by lowering the heating rate to 15°h^{-1} .

On the other hand, when the heating rate is decreased to 13°h^{-1} or below, a different kind of change occurs. The initial dehydration temperature does not alter appreciably with a decrease in the heating rate, while the second step is absorbed into the first, leaving a few poorly-characterized inflections instead of the plateau. The inflections are somewhat better defined when the heating rate is as low as 2°h^{-1} . It seems likely that these inflections correspond to some new intermediates like $\text{CuSO}_4 \cdot 4 \text{H}_2\text{O}$ or $\text{CuSO}_4 \cdot 2 \text{H}_2\text{O}$, but X-ray diffraction data show that $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ is the only intermediate present, even in this case. The origin of the inflections is therefore not clear as yet.

It should be noted that, according to the phase diagram of copper sulfate [11], the hydrates of this salt can exist in equilibrium when the atmospheric water vapor pressure is not very different from that found in ordinary air ($\sim 10 \text{ mm Hg}$). Thus the existence and pressure of water vapor in the air may play an important role in determining the shape of the TG curve, especially when the heating rate is very low. To investigate this point further, TG measurements were carried out in a stream of dry nitrogen. The data obtained are given in Fig. 2 together with those measured in static air for the sake of easy comparison. At a heating rate of 300°h^{-1} , the TG curves obtained in nitrogen and in air overlap during the first half of the dehydration reaction, but as the dehydration proceeds they gradually separate; here the dehydration is suppressed by the presence of moisture. The reverse reaction (recombination with water vapor) becomes more effective at a slower heating rate, 60°h^{-1} , but here again the initial dehydration temperature is not affected because only a very small amount of $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ is produced during the initial stage.

At heating rates of 10 and 2°h^{-1} , the situation is somewhat changed; the initial dehydration temperatures clearly shift to lower temperatures due to the absence of moisture and, moreover, nearly all four water molecules are lost in a single step at a heating rate of 2°h^{-1} . According to the T - P phase diagram, the difference in the temperatures at which $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ give the same equilibrium pressure decreases and approaches zero with the decrease of the desired equilibrium pressure. Thus, the TG results strongly suggest that the shape of the TG curve produced at a heating rate of 2°h^{-1} is governed not by the dehydration rates but by the free energies of the compounds in the system, as described in the Introduction.

In order to confirm the importance of the free energy, TG measurements were carried out at a constant water vapor pressure, 9 mm Hg . A well-developed plateau between two steep steps is observed and shown in Fig. 3; when the heating rate is reduced from 2 to 1°h^{-1} , the initial dehydration temperatures (36 and 62°C) of the two steps remain unchanged, but the steps become still steeper.

Under these conditions the TG curve looks very much like the phase dia-

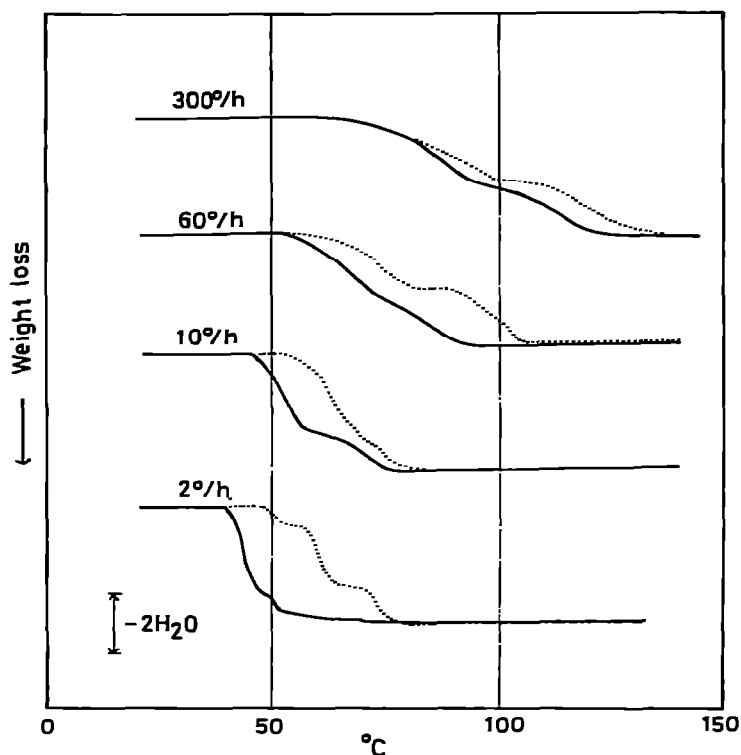


Fig. 2. Comparison of the TG curves of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ obtained in a stream of dry nitrogen with those obtained in static air, at several heating rates: (—) in N_2 ; (· · · · ·) in air.

gram of copper sulfate, although the dehydration temperatures of the two steps are much higher than those (27 and 31°C) expected from the phase diagram [12]. Even with this low heating rate, the temperature at which a measurable weight change begins to occur must be considerably higher than

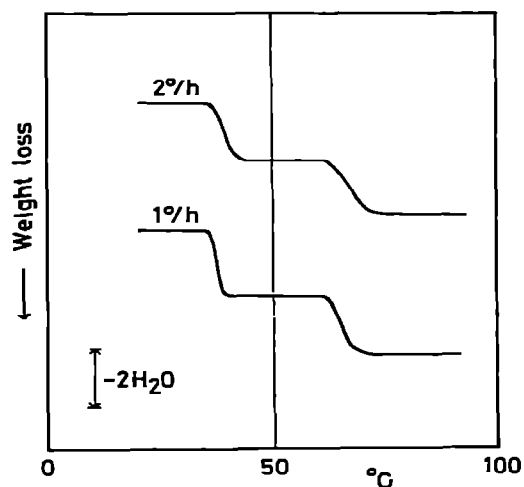


Fig. 3. TG curves of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ at a constant water vapor pressure of 9 mm Hg.

the true transition temperature (the kinetic component does not disappear completely).

All these results can be summarized as follows. (1) In static air, a heating rate of $15^{\circ} \text{ h}^{-1}$ is the lower limit at which a fairly distinct two-step curve can be obtained. (2) Although the TG curves are influenced, to a greater or lesser degree, by the presence of water vapor both in the air and derived from the sample, the shapes of the TG curves produced at higher heating rates are essentially governed by the dehydration rates involved. However, at much slower heating rates, the kinetic component decreases and the equilibrium component increases so that the shape of the TG curve becomes complicated. (3) In Fig. 3 the dehydration proceeds nearly under equilibrium conditions, so that the appearance of the TG curves becomes much more distinct and to some extent comparable with the phase diagram of the system in question.

It is expected that the technique used in this study will be widely applicable to studies on other salt hydrates and may be employed to improve the quality of the TG curves obtained.

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