

SOME OBSERVATIONS ON HIGH RESOLUTION THERMOGRAVIMETRY A Warning

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(Received January 10, 1992)

The advantages and disadvantages of ramp-iso-ramp-iso heating rate TG are discussed using water and copper sulphate pentahydrate as examples.

Keywords: copper sulphate pentahydrate, ramp-iso-ramp-iso heating rate TG

Introduction

Although quasi-isothermal TG has been known for many years [1], its value has been limited to certain particular studies [2]. In recent times there appears to have been a resurgence of interest in TG studies of this nature [3]. We would, however, sound a warning that care should be taken on the interpretation and significance of TG curves derived in this manner.

Experimental

The first example reported here is that of water. Two experiments were carried out:

- i) Conventional continuous high heating rate TG
- ii) Ramp-iso-ramp-iso heating rate TG

Figure 1 shows the weight loss curve for water using a heating rate of 200 deg/min with a detectable weight loss commencing, as expected, below

100°C, and, because of the fast heating rate, completed at around 250°C. The comparable DTG curve shows a linear increase in rate with a peak rate of weight loss at 227.44°C.

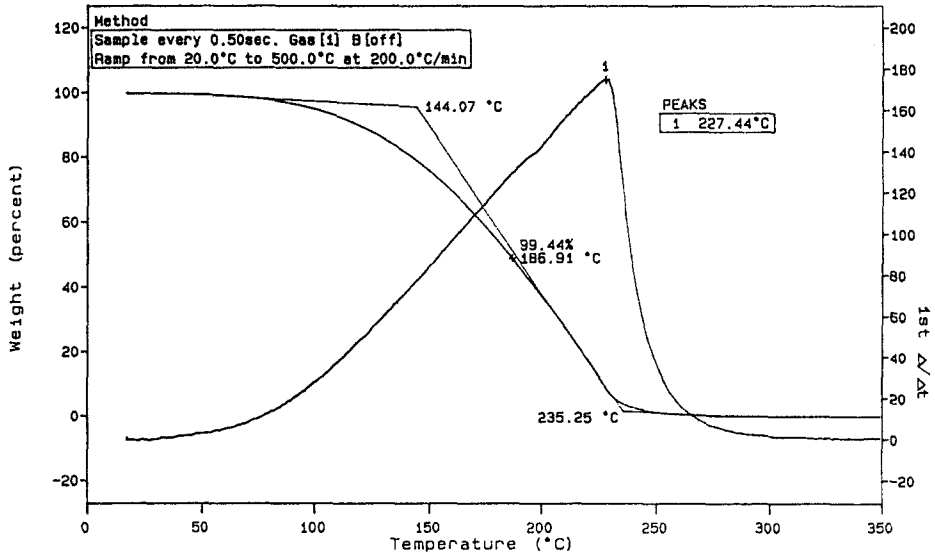


Fig. 1 Weight loss of water at 200 deg/min heating rate; size: 8.901 mg; static air

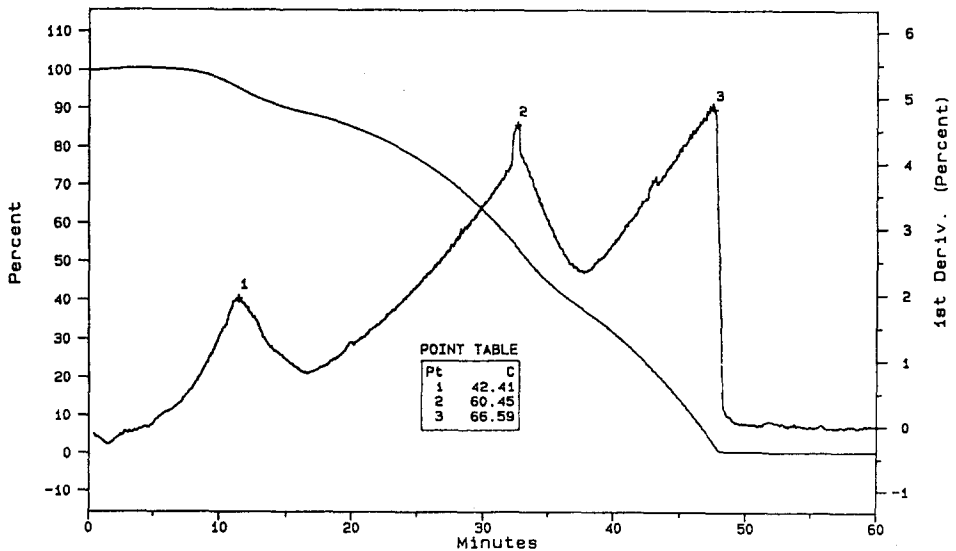


Fig. 2 Iso-ramp-iso method; three distinct peaks for water; size: 8.520 mg; static air

The ramp-iso-ramp-iso technique was carried out using a simultaneous TG-DSC thermal analyser (the PL Thermal Sciences STA 625). A ramp rate of 5 deg/min was used up to 40°C, then an isotherm was held until the weight loss slowed down, the run was resumed up to 60°C with a further isotherm; finally ramping up to 80°C and then isotherming again. The TG results (Fig. 2) show 3

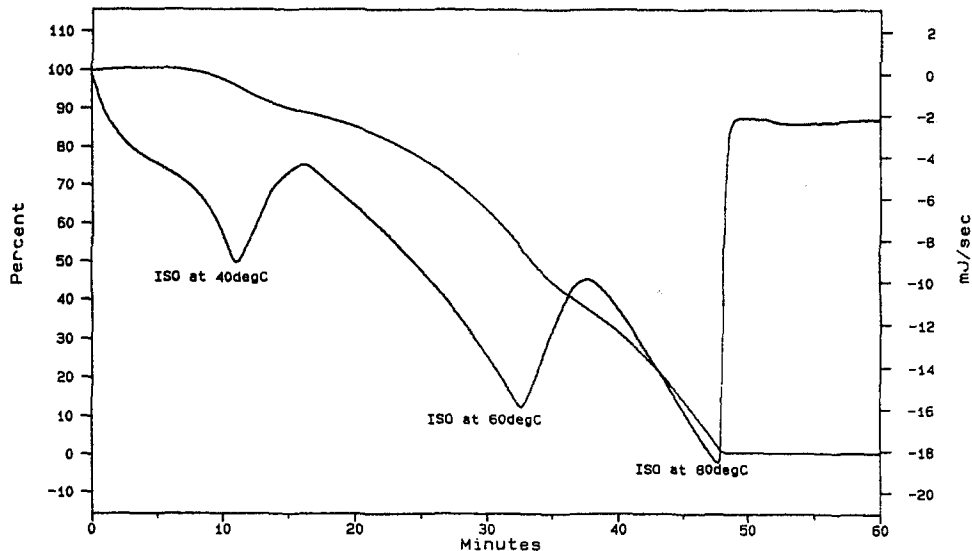


Fig. 3 Iso-ramp-iso method; three distinct peaks for water; size: 8.520 mg; static air

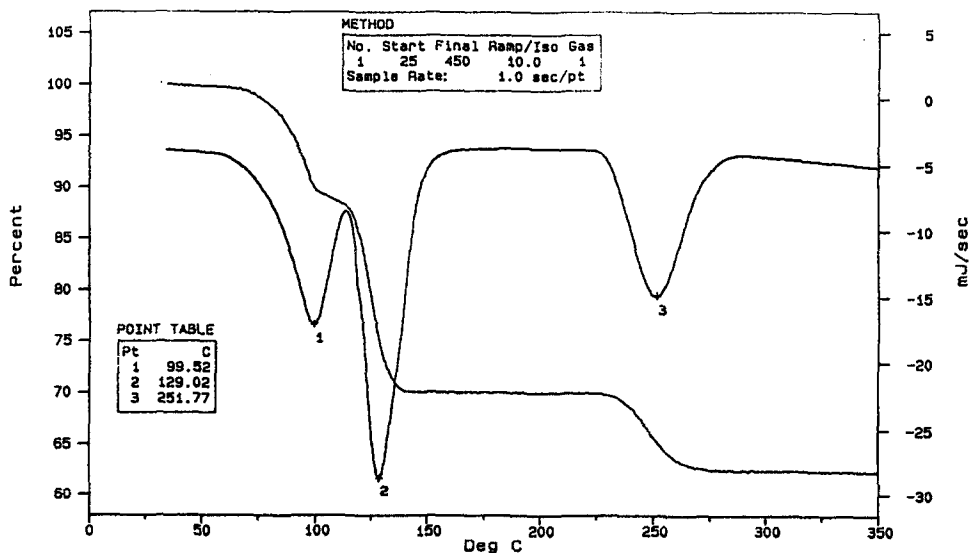


Fig. 4 Copper sulphate pentahydrate - open pans; water loss; size: 6.580 mg; static air

clear, identifiable weight loss regions with DTG peaks at 42.4°, 60.5° and 66.6°C respectively. Similarly the DSC curve (Fig. 3) shows three distinct endotherms.

A further series of experiments was carried out on copper sulphate pentahydrate. A somewhat similar series was carried by Paulik *et al.* [4] using much larger samples. However, some of the conclusions agree partly with our studies reported here. This present series of experiments clearly illustrate a number of features of the dehydration pattern of this compound, whose crystal structure embodies four molecules of water arranged in a plane around the central copper and the sulphate anion bonded through oxygen to the copper above and below the plane of the water molecules. The fifth water molecule is triply hydrogen bonded within the structure.

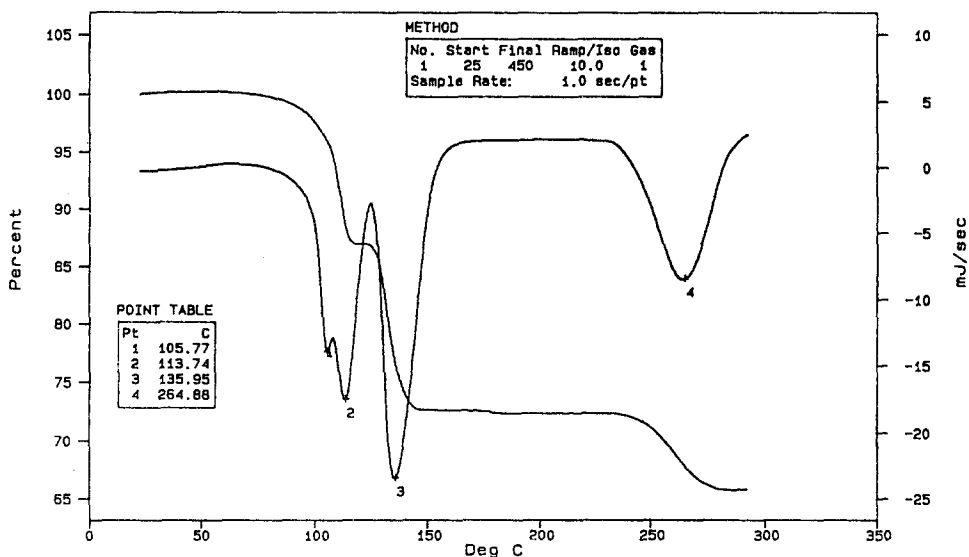


Fig. 5 Copper sulphate pentahydrate - encapsulated with pin hole; water loss; size: 7.080 mg; static air

The first experiment (Fig. 4) shows a conventional continuous heating rate TG-DSC run using open pans. The second experiment (Fig. 5) again using a continuous heating rate, but using a sealed crucible with a pin hole in the lid, shows on the TG curve a clearer separation of the initial two-stage water loss while the DSC curve shows a doublet endotherm (peaks 1 and 2) followed by a further endotherm (peak 3). In the next experiment the sample of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was sealed in a closed gold-plated copper pan (Fig. 6) we find that the loss of water as shown by the TG curve is restricted until the encapsulation begins to rupture. A clear endotherm on the DSC curve (peak 1) is now visible and does not correspond to any substantial weight loss in that temperature region, which suggests a single event

now occurring in this region. Peaks 2 and 3 correspond to the total loss of the five waters apart, that is, from a very small residual loss above 200°C (peak 4). Furthermore if an encapsulated sample is cycled between 25° and 115°C the DSC pattern is most interesting (Fig. 7). An endotherm (peak 1) occurs at 100°C, upon

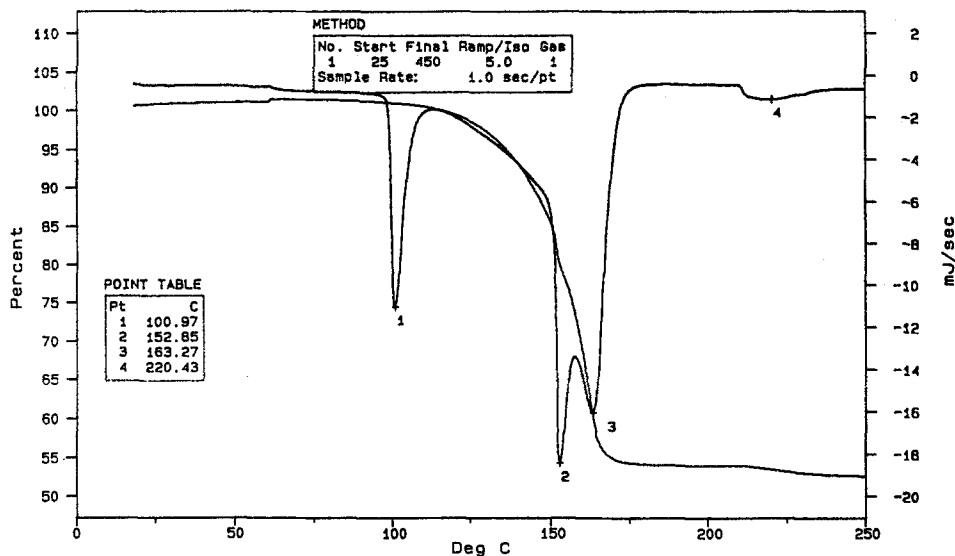


Fig. 6 Copper sulphate pentahydrate - encapsulated; water loss; size: 4.560 mg; static air

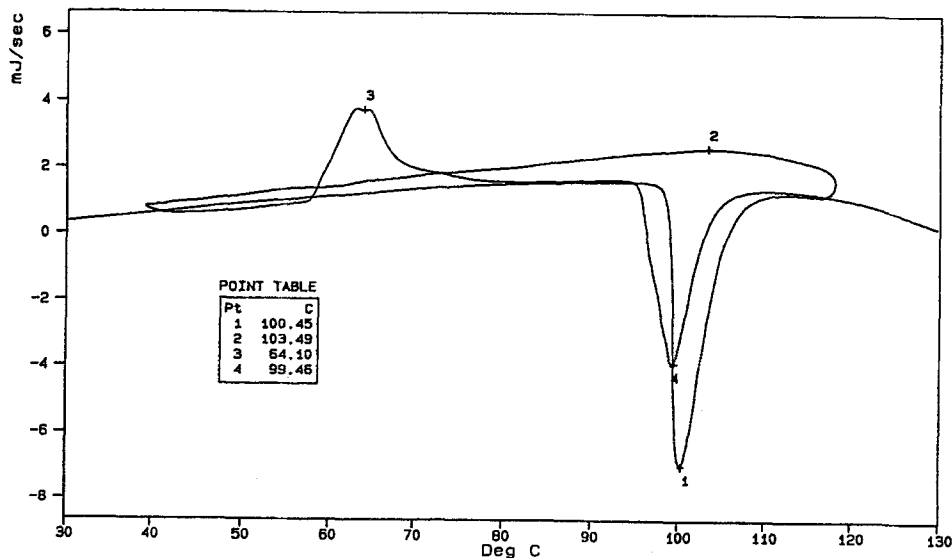


Fig. 7 Copper sulphate pentahydrate - encapsulated (no pin hole); water loss; size: 5.560 mg;

cooling to around 40°C and then reheating an exotherm (peak 3) appears at 64.1°C presumably due to the reverse process to that relating to the endotherm. On further heating in the same cycle a broader endotherm appears at 99.45°C. The encapsulated crucible has a very small internal volume and the pressure build up is substantial ensuring that only a very small proportion of the water released in the first water loss vaporises. The remainder stays as liquid within the crucible, probably with some dissolved trihydrate. If the runs are carried out in a high pressure DSC with open pans (Fig. 8) at 1.5 MPa and 3.0 MPa the results are shown in the lower two curves (Curves 1 and 2). As the pressure increases the peaks move progressively to a higher temperature. Water is lost from the initial breakdown of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ but sufficient remains for the crystal structure change endotherm at 100°C to show as a weak shoulder at 1.5 MPa (endotherm 2) and a more pronounced peak (endotherm 6) at 3.0 MPa. The final experiment involved using an encapsulated sample run with a pin hole under a pressure of 6.8 MPa. This resembles the curve in Fig. 6 up to around 150°C.

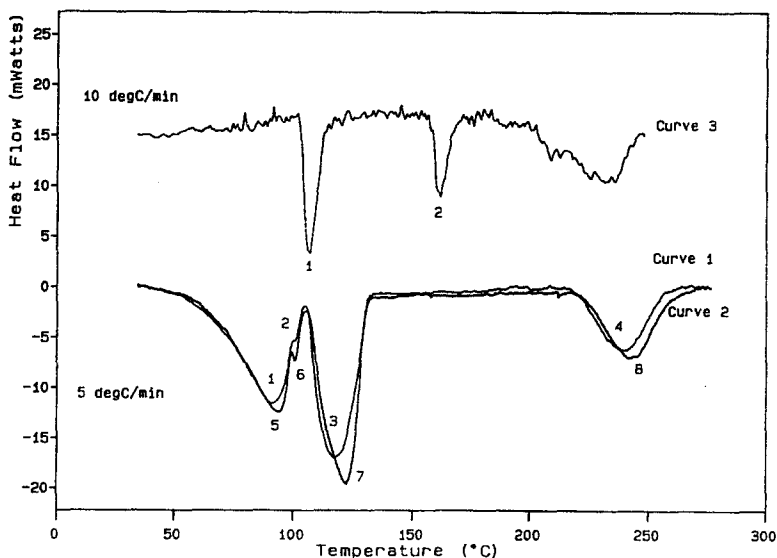
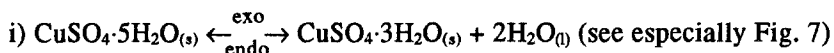


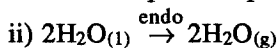
Fig. 8 High pressure DSC analysis; $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$; curve 1: 1.5 MPa; curve 2: 3.0 MPa; curve 3: 6.8 MPa

Results and discussion

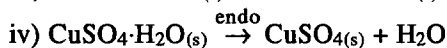
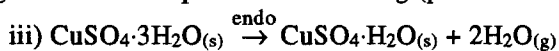
It appears from this set of results that the sequence of water losses are thus:



It is also probable that some of the trihydrate is dissolving in the water evolved from the decomposition process.



i) and ii) are usually observed as a single process in open pans. However Fig. 8 shows both processes occurring (peaks 1 and 2 and peaks 5 and 6).



It is also interesting to note that the work of Paulik *et al.* [4] failed to detect any other hydrates other than the penta-, tri-, and mono-hydrates as is the case in the present studies.

Both of these examples suggest that simplistic explanations of certain reactions should be avoided and wherever possible additional evidence from a range of techniques, in this case simultaneous TG-DSC (whose advantages have been previously documented, [5]), pressure DSC and the use of encapsulation, with and without pinhole, should be evinced to gain a fuller understanding of the thermal processes taking place. Ramp-iso-ramp-iso techniques can form part of the investigation but the results must be validated by supporting experiments. It does not provide a comprehensive answer in its own right.

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The authors would like to thank Mike Nye for technical assistance.

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Zusammenfassung — Anhand der Untersuchung der Dehydratation von Kupfersulfatpentahydrat werden die Vorteile von Sägezahn-iso-Sägezahn Aufheizgeschwindigkeiten bei TG beschrieben.