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Short Communication

GAS EVOLUTION AS AN ARTEFACT IN DIFFERENTIAL SCANNING CALORIMETRY

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With $CuSO_4 \cdot 5H_2O$ as test system, it is demonstrated that the evolution of a gaseous product with thermal conductivity much lower than that of the purge gas in differential scanning calorimetry, leads to artefacts in the form of intense exotherms. This is due to a reduction of the heat flow from the sample to the environment.

Differential scanning calorimeters (DSCs) require a well-defined heat flow from the sample or the reference to their environments for operation [1]. Heat flow is achieved largely via convection by a purge gas. In the DSC instruments made by Pekin–Elmer, N_2 is recommended for this purpose at elevated temperatures, whereas He is used at subambient temperatures. The evolution of a gaseous product with a significantly different thermal conductivity from that of the purge gas can therefore lead to artefacts, because the temperature difference developing between the sample and the reference is compensated by the power input. In Perkin–Elmer's manual [2] for the DSC 4 instrument, it is recommended either to increase the purge gas flow rate, or to change to a different purge gas, the thermal conductivity of which more closely matches that of the evolved gas. Artefacts due to a mismatch in thermal conductivities were also reported by Vannice et al. [3, 4], who used a modified DSC instrument for isothermal measurements of heats of adsorption on metal catalysts, and who observed the artefacts to be most pronounced when H_2 was used as adsorbate and Ar as purge gas.

We accidentally encountered this artefact in a DSC investigation of the thermal behaviour of vapour-deposited amorphous solid water (ASW) which had been exposed to N_2, during heating from 103 K to 300 K, with He as purge gas. ASW is known to give off N_2 in distinct steps during heating [5–7]; the evolution of N_2 from

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the sample was apparent as intense exotherms in the DSC scans, because the thermal conductivity of the purge gas He is much higher than that of N_2, and the heat flow from the sample to the environment is therefore reduced in comparison with that of the reference system. Although this artefact had been anticipated, as pointed out above, its extent was unexpected and to our knowledge such a large artefact has not been reported so far. ASW is an unusual material, its gas uptake depending on its thermal history. The dehydration of $CuSO_4 \cdot 5H_2O$ was therefore chosen to demonstrate the artefact in this Note.

Experimental

A Perkin–Elmer DSC 4 differential scanning calorimeter with a computerized data acquisition system (TADS) was used. The baseline obtained with empty sample pans was subtracted during each scan made with a 17.4 mg sample. $CuSO_4 \cdot 5H_2O$ (Merck) with crystal sizes up to ~1 mm³ was used without further grinding. 17.4 mg of sample was heated in the high-pressure cell offered for the DSC 4 instrument, with the lid closed only loosely to allow the escape of gaseous H_2O, from 330 K to 560 K, at a rate of 10 deg min^{-1}, with He as purge gas in one scan and N_2 in the other. We used a He pressure of 3.5 bar or a N_2 pressure of 1.5 bar to flush the instrument head. For He, this gave a flow rate of ~50 cm^3 min^{-1}. For a 17.4 mg sample of this hydrate, the total amount of evolved gaseous H_2O corresponds to 7.8 cm^3 (STP).

Results

Figure 1 shows DSC scans obtained on heating $CuSO_4 \cdot 5H_2O$ either with N_2 as purge gas (curve 1, solid line) or with He as purge gas (curve 2, broken line), from 330 K to 560 K, at a rate of 10 deg min^{-1}. Sample weights were identical and both curves are drawn on the same scale. Curve 1, with N_2 as purge gas, is the curve that has been reported many times in the literature, the three distinct endotherms corresponding to the removal of two, two and one molecule of gaseous H_2O, respectively, from $CuSO_4 \cdot 5H_2O$ [8]. The literature values for these three process, 358 K, 388 K and 503 K, correspond fairly well with those shown in curve 1. Splitting of the endotherm at low temperature was observed for "open tube" conditions [9]. Curve 2, with He as purge gas, demonstrates the combined effects of the change in thermal conductivity of He due to the evolved gaseous H_2O, and the endothermic effects shown in curve 1. It is dominated by two intense exotherms, with onset temperatures of ~387 K and ~466 K, superposed on the

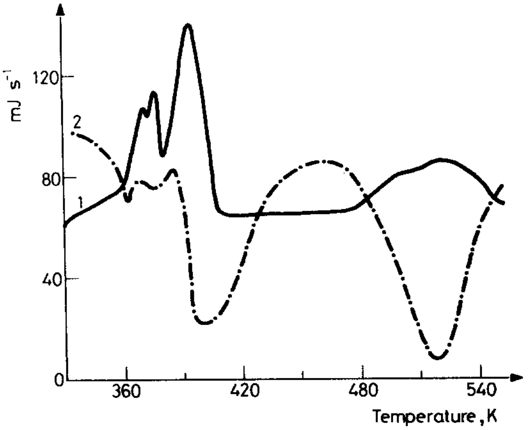

Fig. 1 DSC heating curves of two samples of $CuSO_4 \cdot 5H_2O$, demonstrating the artefact due to the evolution of a gaseous products for "open tube" conditions with He as purge gas. Curve 1 was obtained with N_2 as purge gas, curve 2 with He. Two samples of the hydrate, each of 17.4 mg, were heated at a rate of 10 deg min^{-1} in high-pressure cells, with the lid closed only loosely to allow gaseous H_2O to escape

endotherms of curve 1. Contributions from the endotherms are weakly observable only at ~360 K and ~380 K.

The relative areas of the two exotherms in curve 2 are not simply related to the number of water molecules given off at the corresponding temperatures. This might be due to various factors, e.g. the kinetics of decomposition, the purge gas flow rate, the "leakage" of the sample pan, the grain size of the hydrate, the scan rate and the dependence of the thermal conductivities on temperature. For example, for a heating rate of 30 deg min^{-1} with He as purge gas, we also obtained intense exotherms, but with different relative areas. It is conceivable that better control of the various parameters can even lead to a semiquantitative determination of the amount of evolved gas as a function of temperature. At present, this can be accomplished only by combining DSC with a second technique, e.g. by using thermogravimetric analysis or effluent gas analysis [8, 10] to determine the amount of evolved gas.

It is remarkable that such a drastic artefact should not have been reported before. We believe that it has escaped attention so far because, for common gaseous products, a purge gas of high thermal conductivity such as He or H_2 is necessary in addition to the "open tube" conditions to make it observable. He is used as purge gas mainly in studies at subambient temperatures, which constitute only a small fraction of DSC investigations. However, the recent report by Jang et al. [11] of peak resolution enhancement by using He as purge gas might lead to an increasing use of He at elevated temperatures, and therefore to observation of the artefact for samples which give off gaseous products.

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