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PERFORMANCES OF A HEAT FLUX DSC CELL

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ABSTRACT

Five different metals have been used to determine the calibration constant of a heat flux DSC cell and measurements have been performed under a variety of experimental conditions. Different results have been obtained by different standard meaning that some physical property of the sample may affect the instrument response. An analysis of the details of the instrument response showed that sample density and latent heat of fusion per unit mass can both affect the final result. In addition the heating rate too has been shown to exert an influence on the calibration constant value.

INTRODUCTION

The ability to correctly and rapidly determine reaction enthalpies is probably the most appreciated feature of a heat flux DSC cell and quantitative determinations are usually carried out on the assumption that the cell calibration constant is independent both on the type of sample and experimental conditions.

The determination of the calibration constant of a heat flux DSC cell was the object of a previous paper by our group (ref.1).

In that paper statistical analysis was applied to a great number of experimental data and the conclusion was reached that sensibly different calibration constant values are obtained depending on indium and tin or zinc are used as standards.

Further measurements, whose results are reported here, demonstrate that different calibration constant values are obtained also when gallium and lead are used as standards and that these values are practically identical to those obtained by indium-tin and zinc respectively. This indicates that the nature of the sample must be regarded as an experimental parameter and that a complex relationship exists between such a parameter and the calibration constant. In our opinion an accurate analysis of this relationship can be made by studying the details of the instrument response and their variations with the experimental conditions. This study has been undertaken and its final aim is to propose a model for the instrument response by which experimental results can be explained and previsions can be made.

As a part of this work, whose conclusions will be published elsewhere (ref.2), here a discussion is reported on the influence of the heating rate, sample density and heat of fusion per unit mass on the instrument response.

EXPERIMENTAL

All the measurements have been performed with the Du Pont 1090 Thermal Analysis System equipped with the Du Pont 910 Differential Scanning Calorimeter under a nitrogen flux of 2 l/h. Heating rates of 0.1 - 1 - 10 and 100 °C/min and sample masses ranging between 13 and 78 mg have been used. Gallium and lead Fluka puriss were utilized. Information on the origin of the indium, tin and zinc samples as well as literature data on their latent heats of fusion can be found in (ref.1). For the latent heats of fusion of gallium and lead the values of 80.12 (ref.3) and 24.64 J/g (ref.4) have been used respectively.

The peak slopes $\Delta W/\Delta t$ have been graphically determined and each value is the mean of at least two independent measurements on the same sample. They represent the slope of that part of the peak in which the recorded signal has a linear dependence on time and are expressed in mW/min. Sample mass and heating rate are expressed in mg and °C/min respectively.

RESULTS AND DISCUSSION

Fig.1 reports the calibration constants (E) obtained by the five different metals used as standards. Details on the statistical analysis of the data can be found in (ref.1). Here it is to be remembered that the results of six independent measurements were at least utilized for each standard, the measurements being different from each other for sample mass or heating rate.

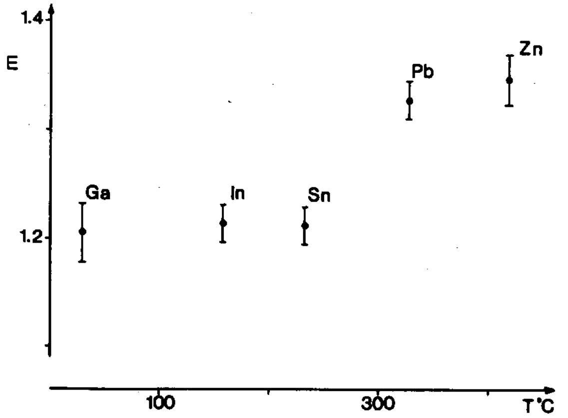

Fig.1. Calibration constant by different standards. Each value has been obtained as a result of measurements performed at different heating rate and with different sample mass. Each metal was submitted to the same set of measurements.

The measurements performed at 100 °C/min gave the smallest calibration constant and were not included in the statistical analysis.

It can be seen that the results can be divided in two groups respectively constituted by Pb-Zn and Ga-In-Sn : while the difference in the calibration constant values is very small inside each group, it is unaceptably high between the two groups. Trying to explain this surprising result an analysis was undertaken of the effect of the experimental parameters on the calibration constant value. So it has been noted there is a trend to lower calibration constant values with increasing heating rate and to better data reproducibility with increasing sample mass. Both these effects were however showed of doubtful statistical significance by variance analysis (mass range : 13-78 mg; heating rate range : 0.1-10 °C/min). Moreover sensibly lower calibration constants have always been obtained for Ga,In,Sn than for Pb,Zn irrespective of sample mass or heating rate . So, while sample mass and heating rate can affect in some way the instrument response they cannot explain the origin of the difference between the calibration constant values by different standards.

Fig.2 reports the peak slopes for unit mass as a function of the heating rate.

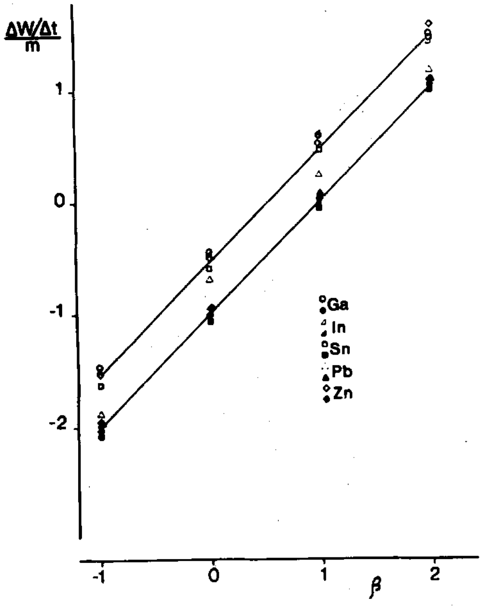

Fig.2. Peak slope per unit mass ($\Delta W/\Delta t\cdot m$) as a function of the heating rate (β).Empty symbols : sample mass 13-15 mg.Full symbols: sample mass 65-78 mg.

It can be noted that two parallel straight lines have been obtained, the first one for small mass samples (13-15 mg) and the second one for large mass samples (65-78 mg).

Moreover it can be seen that the proportionality between the instrument response and the heating rate extends over a range of three orders of magnitude of the heating rate so showing that no instrumental failure arises as a consequence of very high or very slow heating rates. This make it difficult to understand why smaller calibration constant values are obtained at very high heating rates. Last it is to note the behaviour of lead: while points obtained by small mass samples do not lie on the straight line, those obtained by large mass samples are on the straight line.

Why sample mass exerts a different effect on lead than on other standards, as well as two straight lines have been obtained, will be more clear with the aid of Fig.3. Here the peak slopes are divided by the sample mass and heating rate (so that measurements performed with different sample mass and heating rate can be put together) and plotted as a function of 1/m.

It can be seen that for each standard there is a mass range in which the plotted quantity is mass independent and that the value of $\Delta W/\Delta t\cdot m\cdot\beta$ in this range is different for each standard. Moreover, once a critical mass value has been reached, points by each metal lie on the same straight line. The critical mass value depends on the sample density and increases as it increases .

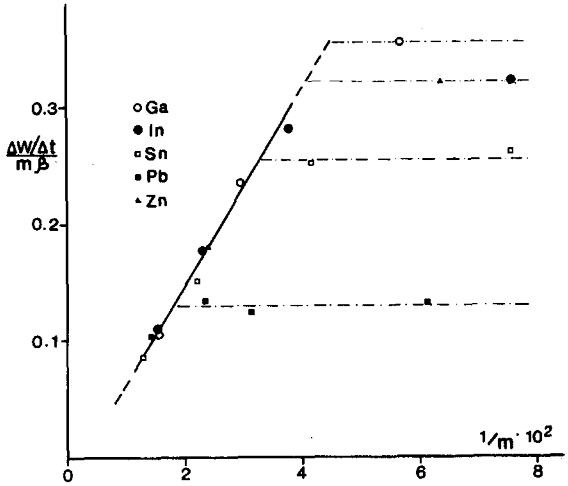

Fig.3. Peak slopes per unit mass and unit heating rate as a function of 1/m. Points are representative of measurements performed at different heating rate and with different sample mass.

While the lead density is nearly two times that of gallium, indium - tin and zinc have very similar densities, about 25% higher than the gallium density. The fact that measurements performed at the same heating rate and with the same sample mass give systematically higher values of the calibration constant for zinc than for indium or tin means that one more parameter over sample mass/density and heating rate can affect the instrument response.

This parameter is the heat of fusion per unit mass : when any other experimental condition is kept constant larger calibration constant values are obtained with increasing heat of fusion per unit mass.

Why and in which way the parameters we discussed till now can affect the calibration constant value will be explained in a next work in which an analytical model of the instrument response will be proposed (ref.2).

It is however to be noted that the relevant parameters don't act separately and what affects the final results is their combination, not their individual values. Moreover, while sample density and latent heat of fusion cannot be changed, samples mass and heating rate can be varied in a quite large range. As a consequence reliable quantitative results can again be obtained provided that the combination of the relevant parameters of the measurement run is as similar as possible to that of the calibration run.

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