

A CALIBRATION STUDY OF THE DUPONT DSC 910 MODULE

J. VAN HUMBEECK * and M. BIJVOET

Department of Metallurgy and Materials Engineering, De Croylaan 2, 3030 Heverlee (Belgium)

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ABSTRACT

In this paper a calibration study of the Dupont 910 DSC module is presented. According to our view of the cell construction, this type of calorimeter combines the advantages and disadvantages of a DTA and DSC cell. It was found that the calibration constant E is independent of temperature (as it should be for any DSC cell) but is dependent on the heating rate and the mass or the total absolute heat exchange by the sample.

INTRODUCTION

When using a new type of equipment to measure properties of systems or materials which are difficult to distinguish, the researcher should first reflect on the working principles of his new instrument. Especially nowadays, when the signals coming from any instrument are sent directly to a computer to carry out the essential calculations and to present a good lay-out of the results, many users rely too soon on what the computer shows and what the manual briefly describes.

In the case of thermal analysis, many incorrect conclusions are drawn from miscalibration although the description in the manual was correct as was the computer program. The cause of these errors is often found in the fact that the researcher did not pay enough attention to the principles of signal generation and detection of the new instrument and thus he was not aware of the possible influencing parameters.

In differential thermal analysis (DTA) or differential scanning calorimetry (DSC) a "classic" error is that the thermal inertia of the sample and the system is not taken into account when using high heating rates, although these effects are very well described in textbooks [1]. Since, for these techniques, the determination of the calibration constant E linking the observed peak area to the exchanged amount of heat is the most important item, the stability of this factor E should be controlled very accurately and

* Research Associate of the N.F.W.O. (National Foundation for Scientific Research).

even under the most extreme conditions. Such a study is presented in this paper for the Dupont DSC 910 module coupled to the thermal analyser 990.

THE DETERMINATION OF TRANSFORMATION ENTHALPY AND SPECIFIC HEAT

The basic formulae to calculate the transformation enthalpy and heat capacity are respectively:

$$H = \frac{A}{m} (60BEq_s) \quad (1)$$

and

$$C_p = 60 \left(\frac{Eq_s}{H_r} \right) \frac{Y}{m} \quad (2)$$

where H (J g^{-1}) is the heat exchange, C_p ($\text{Jg}^{-1}\text{K}^{-1}$) the specific heat, A (cm^2) the peak area, m (mg) the mass of the sample, B (min cm^{-1}) the time-base setting, q_s (mV cm^{-1}) the Y axis range setting, H_r ($^{\circ}\text{C min}^{-1}$) the heating rate, Y (cm) the difference in Y axis deflection between the sample and blank curves of the temperature of interest and E (mW mV^{-1}) the cell calibration coefficient at the temperature of the experiment. Thus, E is the linking factor between the chemico-physical properties and the measured signals.

MAIN DIFFERENCES BETWEEN DTA, DSC AND DUPONT DSC CELLS

The main difference between a DTA and DSC cell is the fact that in a DTA cell a temperature difference between the sample and reference is measured and given as the output signal, while in DSC, the sample and reference are held essentially at the same temperature by correcting the heat input of the sample and reference separately. The principles have significant consequences for the calibration coefficient E as detailed in Table 1.

To complete the description of Table 1, it should be noted that in a classic DTA the thermocouples are generally positioned in the centre of the sample and reference, while in DSC they are placed in the path of the heat stream from the source to the sample and reference. Hence, E in DSC is less dependent on the sample characteristics which is advantageous for quantitative measurements.

The Dupont DSC 910 module is similar to a Boersma-type cell and should thus be considered to be of a type intermediate between the DTA and the DSC cells. Indeed, this module works as a DTA cell: a temperature difference is measured. However, an essential part in the instrument is the E -curve linearizator following the temperature amplifier so that the mea-

TABLE 1

The calibration coefficient E in DTA and DSC

Influencing parameter	$E(\text{DTA})$	$E(\text{DSC})$
Temperature	E is a function of T	Independent
Heating rate	E is a function of H_r	Independent
Atmosphere	No influence at low pressures	No influence at low pressures
Thermal resistance R of the system	E is a function of R	Independent
Mass m	E is a function of m	Almost independent except for large quantities
Sample characteristics, i.e. thermal conductivity ρ , thermal capacity C	Clear influence	Almost independent

sured signal becomes independent of the temperature, which is an essential characteristic of DSC. Moreover, the thermocouples are not placed in the centre of the sample and reference but under their platforms, and thus the influence of the sample parameters (ρ , C) on the calorimetric sensitivity is decreased. Also, a block-type sample holder is not used but separate sample and reference pans. This increases the sensitivity of the system but decreases the resolution (the peaks may become broader). However, the pans are not completely isolated as in an actual DSC cell.

A consequence of this concept is that the Dupont DSC 910 module is a highly sensitive instrument which combines the advantages of DTA and DSC. Referring to its operating principles, the name DSC does not properly specify the actual system. The naming of this system as a "calorimetric DTA" would be more suitable.

Since the basic principle of a DTA cell is retained anyway, the two main factors which should be checked are: (1) the influence of the experimental parameters on the E value; (2) the independence of E of the temperature when using the linearizator.

EVALUATION OF E BY CALIBRATION

The calibration study was carried out using three pure metallic elements, indium, tin and gallium, as given in Table 2. With these elements, the calibration results are certainly valid in the temperature range 273–523 K and probably a significant extrapolation of this range might be acceptable.

As reference material an empty aluminium pan was used.

Influence of the cell

Figure 1 represents the standard deviation in E for a certain number of experiments on two cells. The calibration was made using indium and each

TABLE 2

Standards for calibration

Standard	Melting temperature (K)	Latent heat (J g^{-1})
In	429.5	28.4
Sn	504.9	59.6
Ga	302.75	80.4

point represents the average of three to five measurements with the same sample.

As can be seen, one cell is very unstable and the other cell is very reliable. The origin of this difference is probably that cell no. 1 was at the end of its lifetime. Indeed, soon after these measurements the heating coil was found to be broken. The good results (cell no. 2) were obtained with a new cell. At present, about 1500 measurements later, the error in E has not changed.

These results prove that with a limited number of measurements, the quality of the cell can be evaluated.

Influence of the experimental parameters

The influence on E of all the experimental parameters that are directly related to the thermal resistance and thermal inertia of the system, including the sample, was checked. These experiments were carried out on cell no. 2. The results are summarized in Table 3.

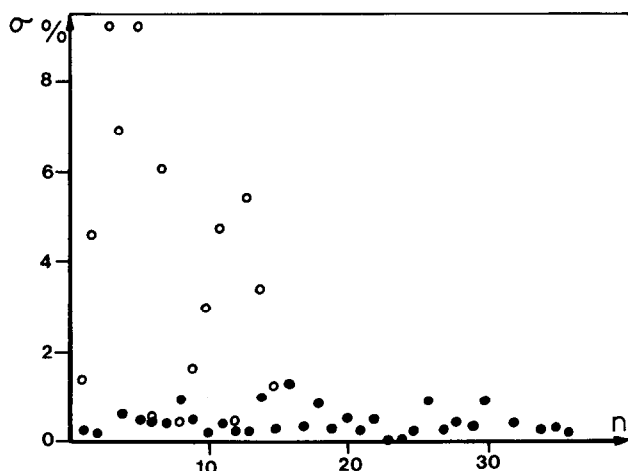


Fig. 1. Standard deviation in E for various identical calibration tests measuring the melting point of indium: ○, cell no. 1; ●, cell no. 2.

TABLE 3

Influence of the experimental parameters on the calibration constant E

Parameter	Standard deviation in E (%)	Relation	Reference elements used	Remarks
Position of the pan (using the same pan)	0.90	—	In	
Using different pans (in the same position)	1.5	—	In	
Shape of the sample	1.2	—	In	
Heating rate	—	$E = 202 + 1.1 H_r$ ^a	In	For $H_r < 20^\circ \text{ min}^{-1}$, the peak-shift $T < 1^\circ$ (see Fig. 3)
Mass of the sample	—	$E = 198 + 0.62 m$ ^a	In	See Fig. 4
Heat exchange (at constant mass)	—	$E = 196 + 18 Q$ ^a	In, Sn, Ga	See Fig. 5 ^b
Temperature	—	E is independent of T	In, Sn, Ga	See Fig. 6

^a Units for variables are given in parentheses: E ($\mu\text{W mV}^{-1}$), H_r (K min^{-1}), m (mg), Q (J).

^b Figure 5 is derived from Fig. 6.

From Table 3, some important conclusions can be drawn. E is indeed independent of the temperature (under the stated experimental conditions) so that for this parameter a single calibration is sufficient. However, just as important is the fact that E is found to be linearly dependent on the heating rate, the mass of the sample and the total heat exchange and to such an extent that these factors cannot be omitted. Indeed, if two experiments are performed, one at $10^\circ \text{C min}^{-1}$ and the other, for example, at $20^\circ \text{C min}^{-1}$, the change in E is of the order of 10%. It is also important to note that, when several peaks appear during a single heating run but with a signifi-

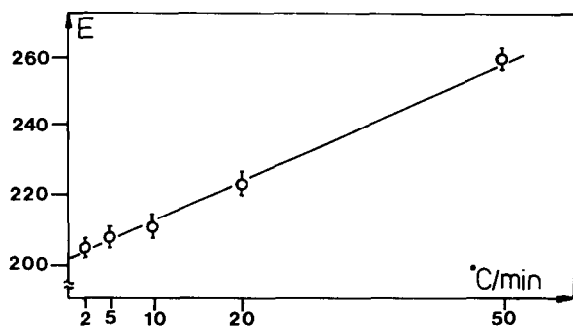


Fig. 2. E as a function of the heating rate ($^\circ\text{C min}^{-1}$) (indium test sample).

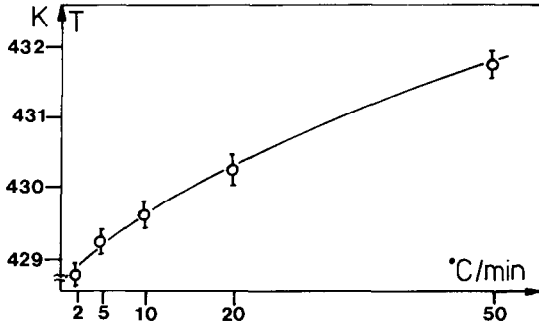


Fig. 3. The peak position of the melting point of indium as a function of the heating rate ($^{\circ}\text{C}/\text{min}^{-1}$).

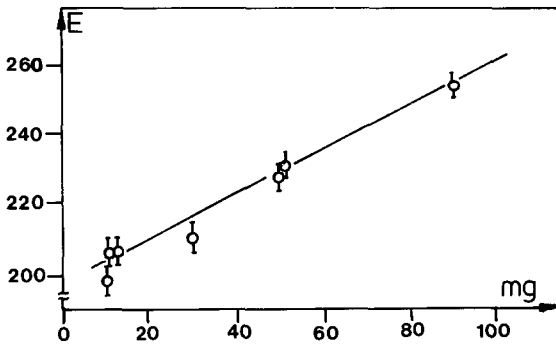


Fig. 4. E as a function of the sample mass (mg) of indium samples.

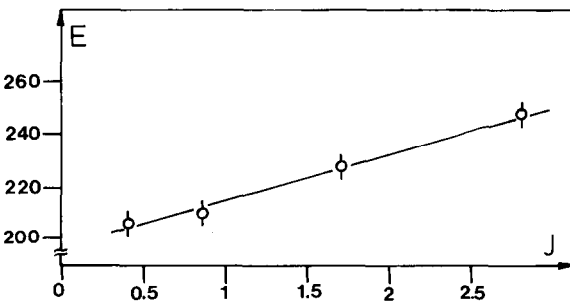


Fig. 5. E as a function of the heat exchange during the endothermic process of indium melting (derived from Fig. 6).

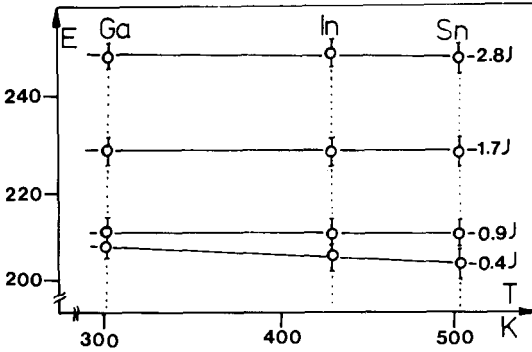


Fig. 6. E as a function of the temperature, determined by measuring the latent heat of melting of gallium, indium and tin and measured for different absolute values of the latent heat: 0.4, 0.85, 1.7 and 2.8 J.

cantly different heat exchange, E is different for the different peaks. It should be mentioned here that for the results in Fig. 6 the masses of the samples indium, tin and gallium were chosen in such a way that the heat exchange was the same.

CONCLUSIONS

The present results show that the cell calibration coefficient E is a function of some important experimental parameters: the heating rate, mass and heat exchange. In order to keep the error in E below 2% the relation between E and these parameters should be used. In this case E can be determined by choosing a good starting value and refining the value in an iterative way. Our experience has shown that two to three steps are sufficient.

It should be mentioned that these relationships might be cell and instrument dependent. Each new cell should thus be checked and the determined relationships can be eventually introduced into the computer program.

REFERENCE

- 1 W.W. Wendlandt, Thermal Methods of Analysis, Vol. 19, Wiley, New York, 1974.