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Differential scanning calorimetry. A reliable method of enthalpy calibration

G. Wolf *, H.-G. Schmidt and K. Bohmhammel

Institute of Physical Chemistry, Freiberg University of Mining and Technology,
Leipziger Str. 29, D-09596 Freiberg (Germany)

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Abstract

Thin-layer platinum resistors (Pt 100) are used as temperature sensors in the DSC-L63 apparatus manufactured by Linseis GmbH. In addition to good temperature resolution and precise temperature measurement, these resistors provide a defined Joule's heat allowing simple and reliable enthalpy calibration. Systematic investigations have revealed the potential and advantages of this method.

INTRODUCTION

The temperature and enthalpy calibration of DSC devices is a necessary precondition for the quantitative evaluation of results. Calibrations require great care and considerable effort.

For temperature calibration, a recommended procedure for correct temperature determination that is independent of the type of device and heating rate used, has been proposed [1, 2]. Enthalpy calibration is either by means of known transformation enthalpies of reference samples or by means of the electrical energy emitted in a special crucible [3]. Due to various circumstances, the heat flow (heat resistances and heat capacities) in the measurement system between sample or reference and sensors or environment are, in both cases, in unsatisfactory agreement with the conditions prevailing during the actual measurement. In many cases, the heat conductivity of the reference sample differs considerably from that of the investigated material. Also, the changes in the measurement system necessary for electrical calibration, i.e. the installation of a heating resistor in the measurement crucible and its wires, have a considerable effect on the heat flow. Even the two-conductor technique for the measurement of Joule's heat requires a correction of approx. 5% if copper wires of 40 μm diameter are used [3, 4]. Apart from these general problems, particular difficulties are known for

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* Corresponding author.

both methods. If reference samples are used, calibration is possible only at certain (phase transformation) temperatures. The demands on the substances used with respect to their chemical and physical purity are extremely strict, which makes maintenance and handling rather costly. Even for the small number of recommended reference samples [4], the best values given in data collections include major uncertainties (0.5–1%). On the whole, it can be said that neither method is suited for quantitative applications of DSC in routine operation in terms of effort and reliability. Without doubt, the advantage of calibration with electrical energy is that calibration is possible at any temperature. One aim of this study was to make use of this advantage while eliminating the disadvantage of the temporary installation of a heating resistor with its wires.

Thin-layer platinum resistors (Pt 100) are used as temperature sensors in the Linseis GmbH DSC-L63. This paper demonstrates the possibility of also using these sensors as heating resistors, thus providing electrical calibration. Without changing the heat flow path in the measurement system, a calibration heat which can be preset in terms of power and time can thus be produced immediately before and after the measurement effect. The source producing the measured signal follows the same heat flow path between the sensor and the analyzed sample as is used for the measurement effect itself. It is shown that this provides a simple, reliable method providing reasonably accurate results from DSC devices.

EXPERIMENTAL

The Linseis DSC-L63 uses a disk-type measurement system. Two thin-layer platinum resistors are vapor-deposited as meanders on a sapphire plate. The resistance is measured by direct current using a special bridge circuit. The first advantage is that the reliability of the temperature indication is considerably higher than with thermocouples or thermopiles, because the use of standardized thin-layer Pt resistors provides an accuracy in the temperature measurements that fall within the limits prescribed by the standards. In addition, the difference signal is obtained immediately as a real temperature difference. By superimposing a rectangular alternating current of defined power and duration on the direct current sensor, the platinum resistors can be used to produce defined heating pulses in addition to their function as temperature sensors. The software used (under Windows) allows the power and the time applied to be selected; the power can be varied in discrete steps from 0.1 to 20 mW. The time or temperature of the pulse can be programmed so that it is automatically triggered at the corresponding point of the measurement cycle. Thus, calibration and measurement can be realized within one single cycle without modifying the heat flow path of the system. By producing a heating peak as close as possible before and after the effect caused by the sample, even the temperature

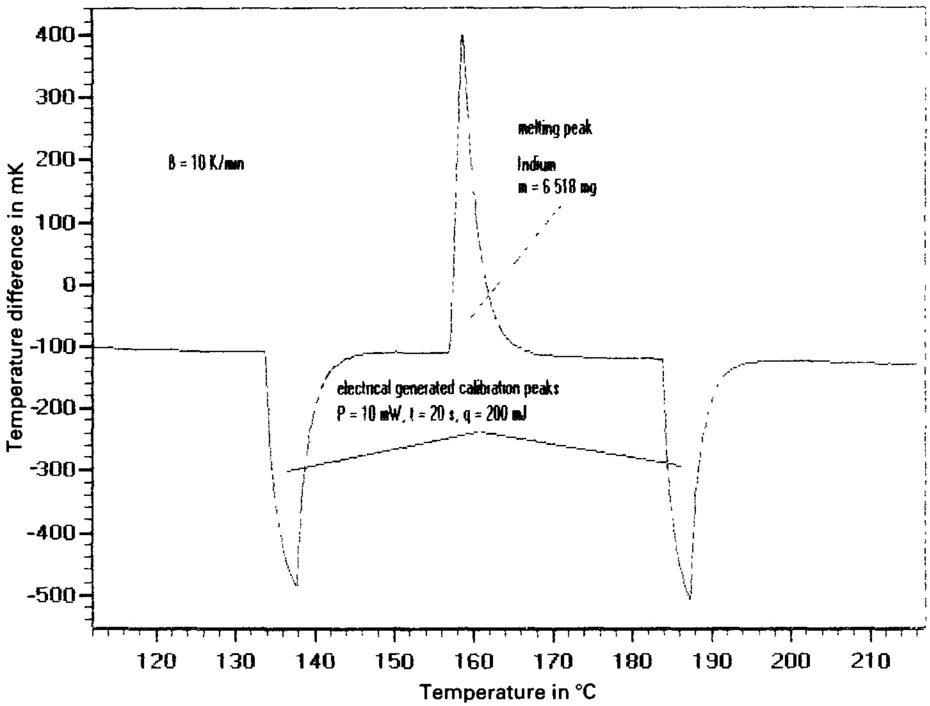

Fig. 1. Determination of melting enthalpy by simultaneous electrical calibration.

dependence of the calibration factor can be taken into account. Figure 1 illustrates this approach for indium; a similar technique has been described by Hemminger and Raetz [5, 6]. By systematic analysis of the following problems that are closely connected with the electrical calibration, the reliability of the new method has been demonstrated: the standard deviation of area integration; the repeatability of the heating peak with respect to the heating power and duration; the determination of transformation enthalpies and comparison with table data; and the repeatability of the transformation enthalpies determined.

The heating rate was 10 K min^{-1} for all the investigations.

RESULTS AND DISCUSSION

The calibration factor is calculated from the electric heat produced q and the peak area integral

$$K = 1/E = q \Bigg/ \int_{t_A}^{t_E} \Delta T(t)\, \mathrm{d}t$$

where E is the sensitivity of the measurement system. In the case of electrical calibration, the factor or the sensitivity can also be obtained from the maximum temperature difference which is established as a steady state in isothermal operation after a sufficiently long period after switching on an additional constant electrical power in the calorimeter sensor. The calibration factor is obtained from the maximum temperature difference $\Delta T_{\max}$ and the related heating power P in accordance with

$$K = P/\Delta T_{\max}$$

Parallel measurements show that the two methods produce identical results with respect to $K(T)$ and $E(T)$. No deviation from proportionality was observed between heat flow and measurement signal $\Delta T_{\max}$ within accuracy limits.

The observed temperature dependence of the calibration factor has parabolic character as is known for different DSC devices [3, 4]. The temperature function can be described very well by a fifth-order polynomial. In order to analyze the repeatability of the determination of transformation enthalpies by the proposed method, the individual steps were investigated.

The integration of the peak area has a standard deviation σ of 0.5%. This value is the result of the statistical average of 5 integrations of each individual peak and the subsequent averaging of the results of 150 peak-area measurements. The five integrations of the individual peaks were performed systematically, shifting the integration time limits t_A and t_E; depending on the effect, the interpolation of the baseline was performed by the usual methods [7].

The repeatability of the electrical calibration peak which was determined from 10 individual measurements at a given temperature and constant heating power and time was calculated as $\pm 0.55\%$. This value is essentially controlled by the repeatability of the integration and not by the uncertainty of the heating power and time.

Subsequently, the heating power (3.75-20 mW) and time (40-7.5 s) were varied at eight different temperatures so that the heating energy remained constant. Taking into account the above standard deviation, no systematic influence of the heating power or time on the calibration factor was observed, i.e. the calibration factor is obviously independent of the selected heat flow under the selected conditions. This is the first indication that the described method is suitable for absolute enthalpy calibration.

To determine the uncertainty of enthalpy determinations, the melting enthalpy of tin was selected. Ten individual measurements were made in the above way, i.e. producing two calibration peaks, one before and one after the melting peak. The ten measurements used ten different input quantities (7-8 mg) with two heating periods each. The averaged result was $\Delta_f H(\mathrm{Sn}) = 60.33 \pm 0.40\ \mathrm{J\ g^{-1}}$, which is in very good agreement with the recommended best value of $\Delta_f H(\mathrm{Sn}) = 60.37 \pm 0.22\ \mathrm{J\ g^{-1}}$ [6].

To further investigate the reliability of the proposed method, 23 phase transformation enthalpies of 18 pure substances were measured and com-

TABLE 1

Results of the determination of phase transformation enthalpies on the basis of simultaneous electrical calibration (instrument 1)

Substance	Type[a]	θ_t in °C	$\Delta_t H$ in kJ mol^{-1} (lit.)	Ref.	θ_{ons} in °C	$\Delta_t H_{exp}$ in kJ mol^{-1}	δ in %	Origin of materials
H_2O	S	0.0	6.012	8	−0.4	6.07	0.83	Bidistilled
Diphenyl-ether	S	26.9	17.22	9	26.1	16.81	−2.40	Twice recrystallized Kap.-GC tested
Gallium	S	29.8	5.59	3	29.6	5.55	−0.70	99.999; Spume Freiberg
Benzophenone	S	48.0	19.30	10	47.7	19.00	−1.55	p.A. Laborchemie Apolda
Naphthalene	S	80.3	19.06	9	80.6	18.90	−0.84	p.A. Laborchemie Apolda
Benzil	S	94.7	23.55	9	94.8	23.42	−0.56	Test substance for micro-heating table
Benzoic acid	S	122.3	18.063	9	122.3	18.12	0.29	Calorim. test sample of ASMW of Germany
KNO_3	P	128.7	5.05	11	128.7	5.27	4.36	NBS-ICTA standard
Indium	S	156.6	3.28	11	156.6	3.33	1.34	99.9995; Fluka
$RbNO_3$	P	166.0	3.87	11	165.2	3.81	−1.55	99.99; Aldrich
$AgNO_3$	P	168.0	2.27	10	162.3	2.33	2.07	99.998; Aldrich
$AgNO_3$	S	211.0	12.13	10	209.4	11.90	−1.90	
$RbNO_3$	P	222.7	3.19	11	223.6	3.14	−1.60	
Tin	S	231.9	7.19	11	232.2	7.19	0.11	99.999; Fluka
Bismuth	S	271.4	11.09	11	272.1	11.36	2.40	99.9995; Fluka
$RbNO_3$	P	285.0	1.301	12	283.9	1.30	−0.77	
$KClO_4$	P	299.4	14.53	11	300.3	14.40	−0.90	NBS-ICTA standard
$RbNO_3$	S	313.0	5.61[b]	8	312.8	4.93	−12.1	
Lead	S	327.4	4.79	11	328.4	4.77	−0.36	99.9995; Carl Roth
KNO_3	S	334.0	9.94	11	334.2	10.07	1.30	
Zinc	S	419.5	7.10	11	419.3	6.86	−3.40	99.999; Carl Roth
Ag_2SO_4	P	426.4	15.90	11	426.7	16.10	1.26	NBS-ICTA standard
CsCl	P	476.0	2.90	10	475.9	2.91	0.30	p.A. Merck

[a] S, melting; P, polymorphic transition. [b] Value probably less accurate.

TABLE 2

Results of the determination of phase transformation enthalpies on the basis of simultaneous electrical calibration (instrument 2)

Substance	$\Delta_t H$ in kJ mol^{-1} (lit.)	$\Delta_t H_{exp}$ in kJ mol^{-1}	δ/ %	δ (instrument 1)/ %
Benzophenone	19.30	19.51	1.09	−1.55
Benzil	23.545	23.14	−1.73	−0.56
Benzoic acid	18.063	18.39	1.83	0.29
Indium	3.283	3.324	1.35	1.34
Tin	7.19	7.17	−0.29	0.11
Bismuth	11.09	11.26	1.52	2.40
Ag_2SO_4	15.90	15.30	−3.77	1.26

pared with literature data. The experimental values were obtained by two heating processes with a constant crucible position. The comparison in Table 1 shows that the measured values do not show any systematic deviations over the whole temperature range. The mean error of all the values determined in this series is less than ±2%. For accurate error analysis, each sample would have to be measured repeatedly, and a definite sample characterization would be required.

Finally, to eliminate the random characteristics of the apparatus used, several measurements were repeated with a second instrument. The results in Table 2 show that deviations from literature data do not exceed the values previously obtained.

These results show that the proposed method of electrical calibration is well suited for the quantitative measurement of enthalpy changes taking place during transformations. Thus, a much simpler calibration method which is widely independent of the specific properties (heat conductivity and heat transition) of the investigated substances, is possible.

REFERENCES

1 G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, Thermochim. Acta, 160 (1990) 1–12.

2 H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G.W.H. Höhne and S.M. Sarge, Thermochim. Acta, 219 (1993) 333–342.

3 S.M. Sarge, Dissertation, Techn. Univ. Braunschweig, 1988.

4 S.M. Sarge and H.-W. Krupke, Poster, Jahresversammlung GEFTA, Braunschweig, 1992.

5 W. Hemminger and K. Raetz, PTB-Mitt., 99 (1989) 83–88.

6 K. Raetz, Thermochim. Acta, 151 (1989) 323–31.

7 W.F. Hemminger and S.M. Sarge, J. Therm. Anal., 37 (1991) 1455–77.

8 J. D'Ans and E. Lax, Taschenbuch für Chemiker und Physiker, 3. Auflg., Springer-Verlag, Berlin, 1970.

9 W.F. Hemminger and H.K. Cammenga, Methoden der thermischen Analyse, Springer-Verlag, Berlin, 1989.

10 K.-H. Breuer and W. Eysel, Thermochim. Acta, 57 (1982) 317–29.

11 W. Eysel and K.-H. Breuer, Differential scanning calorimetry: simultaneous temperature and calorimetric calibration, in J.F. Johnson and P.S. Gill (Eds.), Analytical Calorimetry, Vol. 5, Plenum Press, New York, 1984, p. 67–80.

12 G.W.H. Höhne, W. Eysel and K.-H. Breuer, Thermochim. Acta, 94 (1985) 199–204.