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DIFFERENTIAL SCANNING CALORIMETRY: COMPARISON OF POWER COMPENSATED AND HEAT FLUX INSTRUMENTS

G.W.H. Höhne, K.-H. Breuer and W. Eysel
Sektion für Kalorimetrie, Universität Ulm, 7900 Ulm (F.R.G.)
and
Mineralogisch-Petrographisches Institut der Universität
D 6900 Heidelberg (F.R.G.)

Abstract

Two differential scanning calorimeters, based on different measuring principles, are compared experimentally with respect to their capabilities, bulk errors and calibration. Measurements were carried out using seven selected metals and inorganic salts and by keeping as many experimental conditions as identical as possible for both instruments: Same balance, sample specimens, heating rates and calibration standard. As a result for the power compensated and heat flux instruments the enthalpy differences amount on an average to about + 1,2 %. Some aspects of the calibration of heat flux calorimeters are discussed.

Introduction

Differential scanning calorimetry (DSC) is increasingly used for calorimetric measurements because results are obtained easily in a comparatively short time. Two fundamentally different types of DSC instruments are available: Power compensated and heat flux calorimeters. During a transition the first type keeps sample and

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reference sample at the same temperature by additional electrical resistance heating; the difference of the corresponding electrical energy represents the enthalpy difference ΔH. With the heat flux calorimeter Δ H is determined from the temperature difference between sample and reference sample, which is proportional to the heat flux difference.

Because of the different construction both types exhibit individual instrumental errors. In this paper a power compensated instrument (Perkin-Elmer, DSC-2) and a heat flux DSC (Du Pont T 1090/910) are compared using identical samples as test material Because the calibration factor of most calorimeters is depende on temperature, transitions covering a wide temperature range were chosen.

Experimental and results

The Du Pont instrument was calibrated with standards proposed recently (Breuer and Eysel, 1982, 1983). This calibration resul in 3.28 kJ/mole for the fusion of In. To enable an easy comparison the value of 3.28 kJ/mole was also used to calibrate the Perkin-Elmer DSC-2. Normally this instrument is calibrated with aid of the specific heat capacity of a saphire standard leading to a higher value for the heat of fusion of In. For the comparison of both instruments seven test materials with transitions between 400 K and 900 K were selected. The sample quality and the balance precision are presented in a previous paper (Breuer and Eysel, 1982). Five samples of each material were weighed individually on the same balance and measured with both calorimeters. Possible systematic weighing errors and influences of grain sizes and eventual small impurities were neglected.

Sample sizes ranged from 10 to 12 mg and heating rates from 1.25 to 5 K/min. For both instruments the heats of transition were calculated from the measured data by means of on-line microcomputers.

The results are listed in Table 1. The given uncertainties are standard deviations of the mean for five individually prepared samples.

Discussion

A comparison of the enthalpies (Table 1) as obtained with both methods shows an unexpectedly good agreement. Somewhat larger deviations occur only for the three transitions of $RbNO_3$.

For the transition of $RbNO_3$ at 556 K an unusually large stepchange of the baseline is observed, indicating a remarkable change of the specific heat capacity. Due to specific properties of the instruments (Höhne, 1983) the stepchange appears much larger in the Du Pont plot (Fig. 1a) than in the Perkin-Elmer plot (Fig. 1b). Since, with the computer programs available, only a straight line background correction A-B is possible, a larger error in the area determination occurs for the Du Pont result. For this transition therefore, the Perkin-Elmer value is considered much more reliable, but still slightly too small.

If the area in Fig. 1a is corrected by hand using the dotted background line, the enthalpy increases from 1.29 kJ/mole to 1.37 mole, which compares exactly with the Perkin-Elmer result.

Neglecting the transition of $RbNO_3$ at 556 K, the other enthalpies in Table 1 are, on an average, slightly larger (+ 1.2 %) for the Du Pont instrument than for Perkin-Elmer. The number of substan-

Table 1. Transition enthalpies measured with Perkin-Elmer DSC-2 and Du Pont TA 1090/910. p.t. = polymorphic transition

Material	Transition	Perkin-Elmer		Du Pont	Difference	
		T [K]	ΔH [kJ/mole]	ΔH [kJ/mole]	[kJ/mole]	%
In	fusion	429.8	3.28±0.015	3.28±0.02	0 *)	0
$RbNO_3$	p.t.	437.7	3.76±0.03	3.87±0.01	0.11	2.9
$RbNO_3$	p.t.	499.6	3.09±0.03	3.19±0.01	0.10	3.2
Sn	fusion	504.9	7.14±0.04	7.19 ±0.03	0.05	0.7
Bi	fusion	544.8	11.01±0.13	11.09±0.12	0.08	0.7
$RbNO_3$	p.t.	556.3	1.37±0.015	(1.29±0.01)	(-0.08)	(-5.8)
CsCl	p.t.	750.3	2.91±0.03	2.90±0.03	-0.01	-0.3
Li_2SO_4	p.t.	852.5	25.08±0.13	25.02±0.16	-0.06	-0.2
						$\langle +1.2 \rangle$

*) used as calibration standard

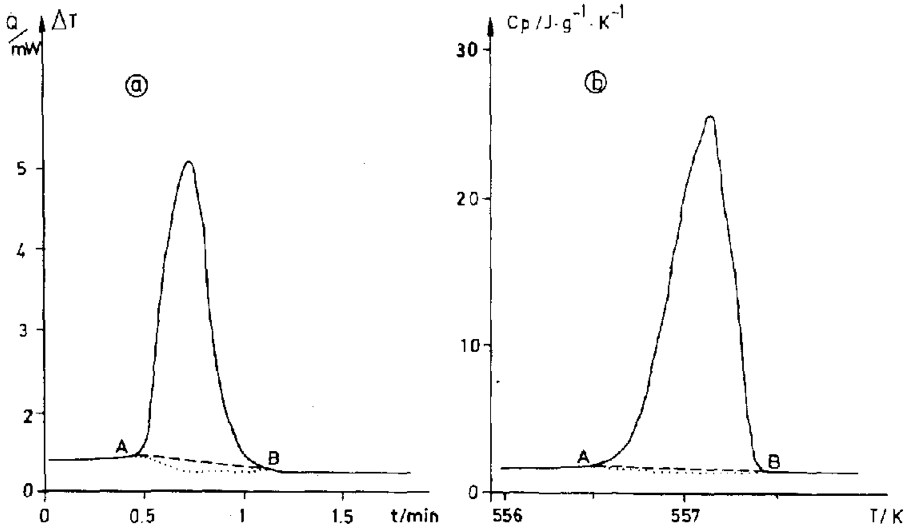

Fig. 1: Plots of $RbNO_3$ transition at 557 K, measured
a) with the heat-flux-calorimeter (Du-Pont) and
b) with the power-compensated calorimeter (Perkin-Elmer).
– – – – Baseline calculated by the computer,
······· "true" baseline.

ces compared is too small and the standard deviations are too large to conclude a systematic error in the calibration of one or both calorimeters from the present results. Likewise the systematic deviations depending on sample parameters, predicted to be in the same order of magnitude (Höhne, 1983), don't show up. Further more detailed investigations, concerning this point, are scheduled. One of the major purposes of this paper was, to check the enthalpy standards proposed by Breuer & Eysel (1982, 1983). The investigation and establishment of these standards were carried out with the Du Pont instrument and are based on a statistical evaluation of 24 compounds with 30 transition-enthalpies fr literature. Seventeen of the transitions were considered reliable enough to derive a calibration curve.

The check (Table 1) with the completely different Perkin-Elmer method allows the following conclusions:

1) The measurements on both instruments are based on the fusior enthalpy ΔH = 3.28 kJ/mole of In which seems the best investigated and most suitable material in the temperature rar of interest. Nevertheless even those ΔH-values, which may b considered as reliable, scatter from 3.28 to 3.32 kJ/mole (Marti et al., 1982), the chosen value of 3.28 kJ/mole is very close to an adiabatically determined value.

   As a consequence the present paper does not establish a new absolute calibration scale and the comparison is made on a relative scale.

2) The good agreement of most enthalpies of both methods (Table indicates that the instruments employed are comparable with respect to their capabilities and bulk errors within an uncertainty of 1 percent.

3) In the course of the investigations the enthalpy of the Li_2S transition as determined with the Du Pont instrument was improved from 24.46 kJ/mole (Breuer & Eysel, 1982) to 25.02 kJ mole.

4) As long as no better background correction programs for transitions with strong baseline steps are available, too small enthalpies are to be expected on heat flux instruments in such cases. The transition of $RbNO_3$ at 556 K, therefore,

should be removed from the list of potential standards in the previous publication. The same applies for AgJ, because it turned out very sensitive towards decomposition.

Acknowledgements

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