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METROLOGICALLY BASED PROCEDURES FOR THE TEMPERATURE, HEAT AND HEAT FLOW RATE CALIBRATION OF DSC*

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Abstract

Metrologically based measuring procedures and evaluation methods are recommended as guidance for practical temperature, heat and heat flow rate calibration of DSC instruments which are largely independent of instrumental, test and sample parameters. The relevant terms are defined, the measuring procedures and evaluation methods described, calibration materials and their characteristic data stated and guidance for the sample handling provided. Reference is made to three extended papers on calibration. The recommendations were developed by the working group 'Calibration of Scanning Calorimeters' of the German Society of Thermal Analysis (GEFTA).

Keywords: calibration material, calibration procedure, DSC, heat calibration, heat flow rate calibration, standards, temperature calibration

Introduction

This recommendation describes procedures for temperature, heat and heat flow rate calibration of differential scanning calorimeters (DSC), which are largely independent of the instrument type and allow for the influence of significant test parameters (temperature, heating rate, sample mass) and sample parameters (thermal effect, thermal diffusivity).

It summarizes three previous publications and is intended to serve as guidance for practical calibrations. (In German: G. W. H. Höhne *et al.*, PTB-Mitt., 100 (1990) 25–31; H. K. Cammenga *et al.*, PTB-Mitt., 102 (1992) 13–18; S. M. Sarge *et al.*, PTB-Mitt., 103 (1993) 491–512; in English: G. W. H. Höhne *et al.*, Thermochim. Acta, 160 (1990) 1–12; H. K. Cammenga *et al.*, Thermochim. Acta, 219 (1993) 333–342; S. M. Sarge *et al.*, Thermochim. Acta, 247 (1994) 129–168).

The following sections will define the terms used, describe the procedures and evaluation methods, state calibration materials and their characteristic data and pro-

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* Recommendation of the working group 'Calibration of scanning calorimeters' of the Gesellschaft für Thermische Analyse e.V. (GEFTA)

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vide guidance for how to handle the samples. The procedures recommended start from the central idea that the calibration measurement and the sample measurement should be as similar as possible. To detect and eliminate dependences of sample and instrument parameters, the sample measurement is 'bracketed' by carrying out calibration measurements with the respective parameter being varied. If significantly nonlinear dependences are expected, additional calibration measurements will be necessary.

The procedures recommended relate to standard applications in scanning calorimetry. If there are differences from the customary temperature, heating rate and sample mass ranges, the calibration is to be modified by analogy. Detailed descriptions are contained in the three publications mentioned above.

A calibration by the procedures recommended is necessary whenever a new instrument is taken into operation or essential components of the instrument (for example, sensors) are replaced or modified (for example, by cleaning the measuring system by heating). These procedures offer the best accuracy possible. If such a best accuracy possible need not be achieved, the procedures recommended can be simplified, however, additional uncertainties will than have to be reckoned with. In routine operation, it will be sufficient to carry out a simplified procedure for checking and updating the calibration.

Definitions

The following terms are used (cf. also Fig. 1):

– temperature calibration: establishment of the relationship between the temperature T_m indicated by the instrument and the true temperature T_{tr}. The relation $T_{tr}=T_m+\Delta T_{corr}(T)$ is valid

– heat calibration: establishment of the relationship between the heat Q_m (peak area A) measured by the instrument and the true heat Q_{tr} absorbed or released by the sample as a result of a transition or reaction at the transition temperature T_{trs}. The relation $Q_{tr}=K_Q(T)Q_m$ is valid

– heat flow rate calibration: establishment of the relationship between the heat flow rate Φ_m indicated by the instrument and the heat flow rate Φ_{tr} absorbed or released by the sample due to its heat capacity C_p. The relation $\Phi_{tr}=K_\Phi(T)\Phi_m$ is valid, Φ_{tr} being equal to $C_p\beta$

– interpolated baseline Φ_{bl}: here defined as a straight line between initial peak temperature and final peak temperature

– start temperature T_{st}: temperature at the moment t_{st} at which the temperature program starts

– end temperature T_{end}: temperature at the moment t_{end} at which the temperature program ends

– initial peak temperature T_i: here the temperature of the first deviation of the curve of measured values from the interpolated baseline (at time t_i)

– final peak temperature T_f: temperature at which the curve of measured values reaches the final baseline (at time t_f)

– extrapolated peak onset temperature T_e: here the temperature of the point of intersection of the inflectional tangent through the ascending peak slope with the interpolated baseline

– heating rate β: change of the temperature with time (generally linear)

– peak area A: area between peak and interpolated baseline Φ_{bl} from t_i to t_f

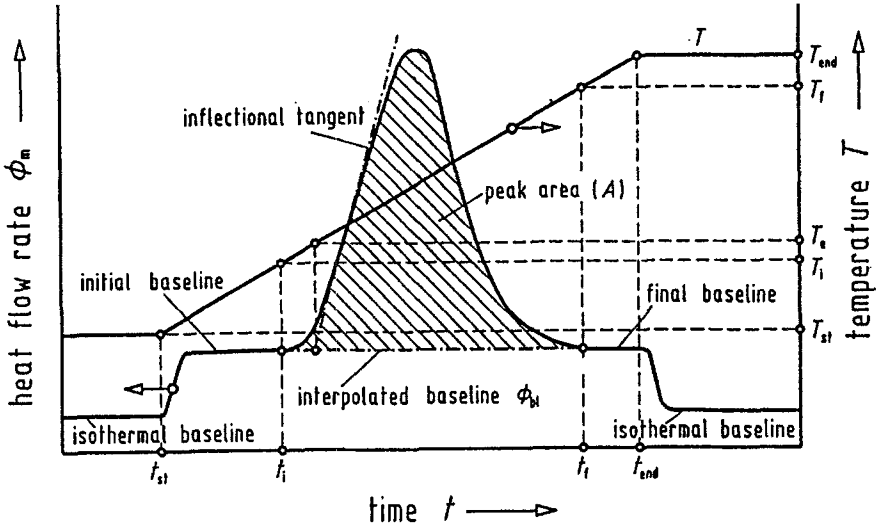

Fig. 1 Definition and terms for describing curves of measured values (with peak) representing a transition or reaction in the sample

Procedures

Temperature and heat calibration

The transition temperature and heat of transition of the calibration substances recommended are generally well defined. Therefore it is possible without additional experimental effort to simultaneously carry out the temperature calibration and the heat calibration.

– From the list of recommended calibration substances (cf. Table 2) three substances are selected which cover the temperature range of interest.

– Two samples of each substance with the approximate masses 3 and 10 mg are weighed into aluminium crucibles with an oxidized surface. (If necessary, use other suitable crucible materials. Concerning the reaction of the calibration substances recommended with the customary crucible materials, cf. Cammenga *et al.*)

– Each sample is subjected to two measurements at each of the three heating rates of 1, 5 and 10 K min^{-1}. The first measurements of each sample are neglected in the further evaluations.

– For each peak the extrapolated peak onset temperature T_e (for the temperature calibration) and the peak area A (for the heat calibration) are to be determined (cf. Fig. 1).

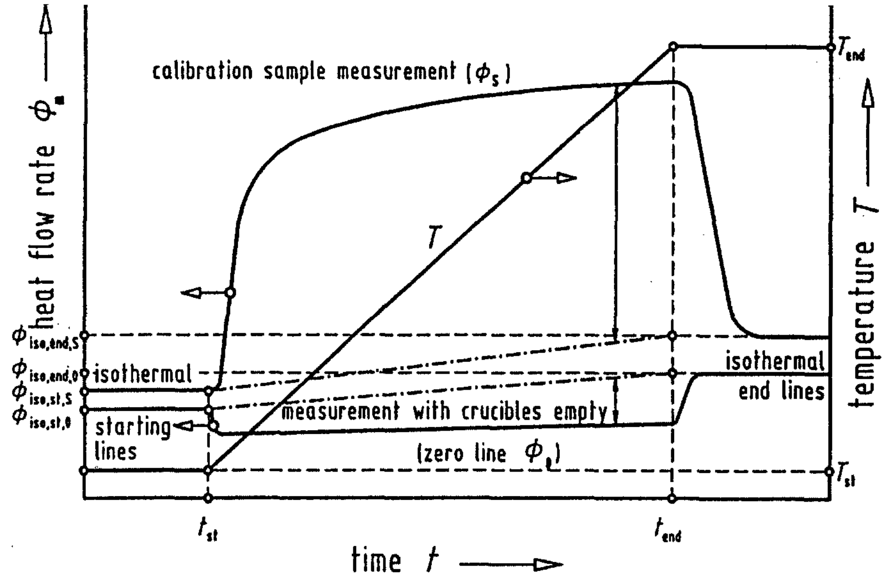

Fig. 2 Definition and terms for describing curves of measured values for determining the heat capacity of the sample

– The extrapolated peak onset temperatures are to be represented for each calibration substance as a function of the heating rate and to be linearly extrapolated to the heating rate $\beta=0$ (cf. Fig. 3).

– The temperature correction terms ΔT_{corr} are obtained by subtraction of the temperature $T_e(\beta=0)$ thus determined from the true transition temperature T_{tr} with $T_{trs}=T_{tr}$. The relation $\Delta T_{corr}=T_{tr}-T_e(\beta=0)$ is valid.

– The temperature correction terms calculated are to be represented as a function of $T_e(\beta=0)$ and thus yield the temperature calibration curve $\Delta T_{corr}(T)$ (cf. Fig. 4).

– The division of the true transition heats Q_{trs} with $Q_{trs}=Q_{tr}$ by the measured peak areas A yields the heat calibration factors $K_Q(T_{trs})=Q_{trs}/A$.

– The six heat calibration factors K_Q obtained for each calibration substance are to be represented as a function of the transition temperature T_{trs} (cf. Fig. 5). If the dependences on heating rate and sample mass are negligible, the heat calibration factors $K_Q(T_{trs}, m, \beta)$ serve to determine the heat calibration function $K_Q(T)$. If the dependences are not negligible, the calibration functions $K_Q(T, m)$ and/or $K_Q(T, \beta)$ are to be determined separately.

Heat flow rate calibration

– The calibration substance is to be selected according to the temperature range of interest (cf. Table 1).

– Two samples are to be weighed in; their masses are to be selected such that the heat capacity of the measurement sample lies between the heat capacities of the

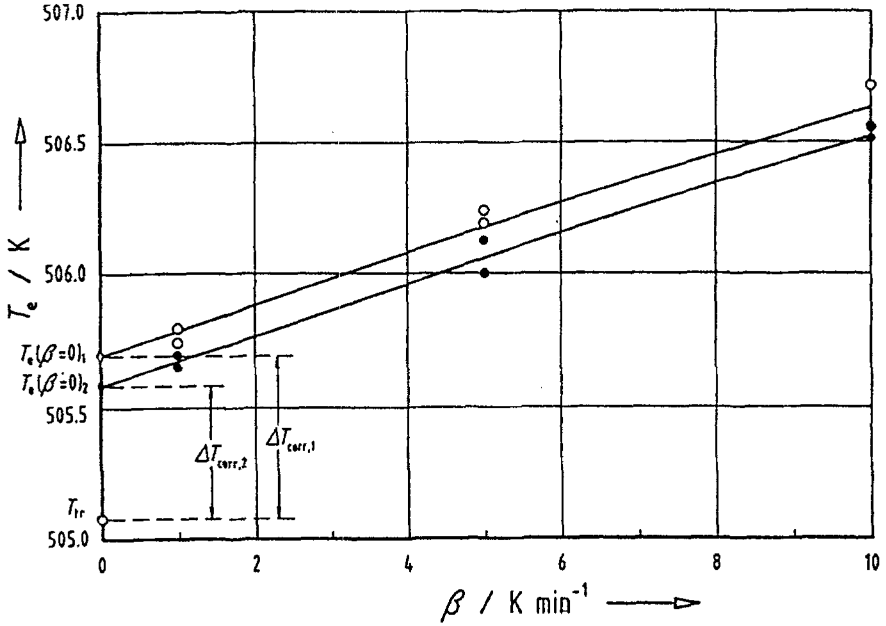

Fig. 3 Extrapolation of the extrapolated peak onset temperatures to zero heating rate for determining the temperature correction term for tin. o sample mass 3.234 mg (1); • sample mass 9.800 mg (2)

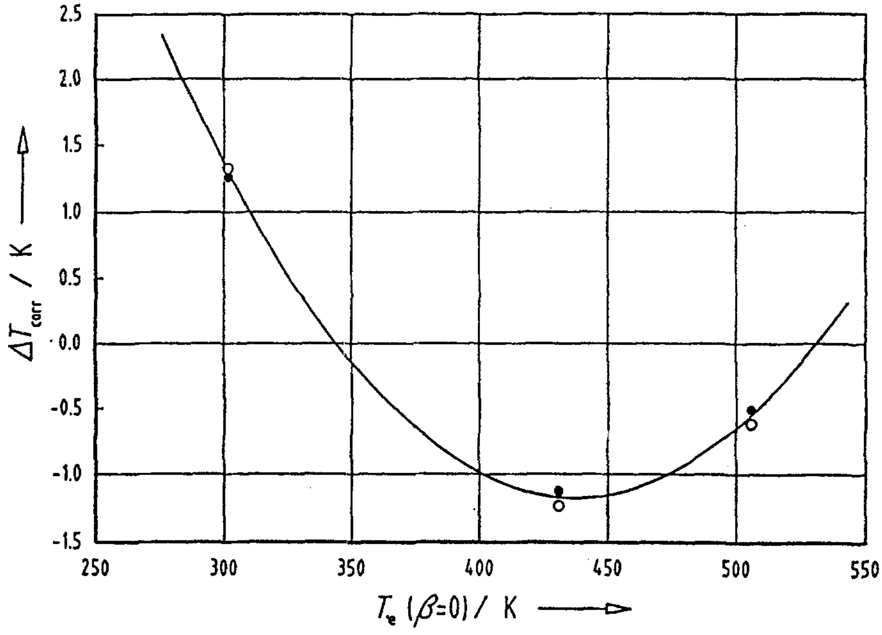

Fig. 4 Temperature calibration function, determined with gallium, indium and tin. o sample mass approx. 3 mg; • sample mass approx. 10 mg

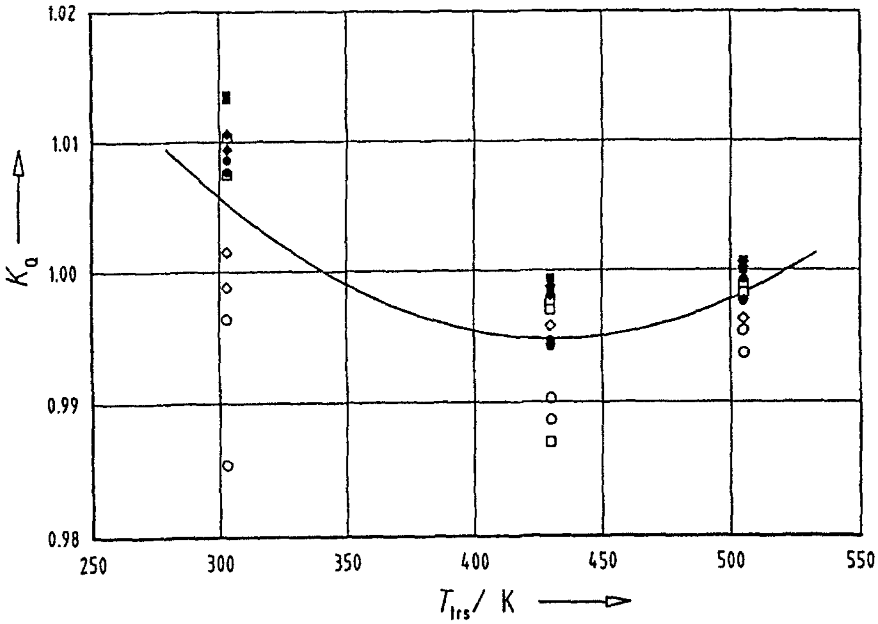

Fig. 5 Heat calibration function, determined with gallium, indium and tin. Empty symbols: sample mass approx. 3 mg; solid symbols: sample mass approx. 10 mg; circles: heating rate 1 K min^{-1}; diamonds: heating rate 5 K min^{-1}; squares: heating rate 10 K min^{-1}

calibration samples. Crucibles are to be selected which in terms of material, shape, type of sealing, emissivity and mass are as similar as possible or identical to the crucibles for the empty measurements and for the measurements of the measurement samples.

– The temperature program is subdivided into three segments (cf. Fig. 2): isothermal segment to determine the isothermal initial lines ($\Phi_{\text{iso,st,S}}$ and $\Phi_{\text{iso,st,0}}$), dynamic segment (heating rate generally 10 K min^{-1}, duration generally 10 to 30 min) (Φ_S and Φ_0), isothermal segment to determine the isothermal final lines ($\Phi_{\text{iso,end,S}}$ and $\Phi_{\text{iso,end,0}}$). Each segment must at least be so long that quasi-stationary conditions can be created (generally after 2 to 10 min).

– Each calibration sample measurement with its following empty measurement is to be carried out three times; the calibration sample measurement and the associated empty measurement are to be performed the same day using the same temperature program.

– In the quasi-stationary range of the dynamic segment, the values obtained by associated pairs of empty measurements and calibration sample measurements (cf. double arrows in Fig. 2) are to be evaluated in accordance with the following equation. For each sample, mean values of $K_\Phi(T)$ are to be calculated and represented as a function of the temperature T_{tr} (cf. Fig. 6).

$$K_{\Phi}(T) = \frac{C_p(T)\beta}{\Phi_{SS} - \Phi_{S0}}$$

where

$$\Phi_{SS} = \Phi_S - \left[\Phi_{iso,st,S} + \frac{\Phi_{iso,end,S} - \Phi_{iso,st,S}}{t_{end} - t_{st}}(t - t_{st})\right]$$

$$\Phi_{S0} = \Phi_0 - \left[\Phi_{iso,st,0} + \frac{\Phi_{iso,end,0} - \Phi_{iso,st,0}}{t_{end} - t_{st}}(t - t_{st})\right]$$

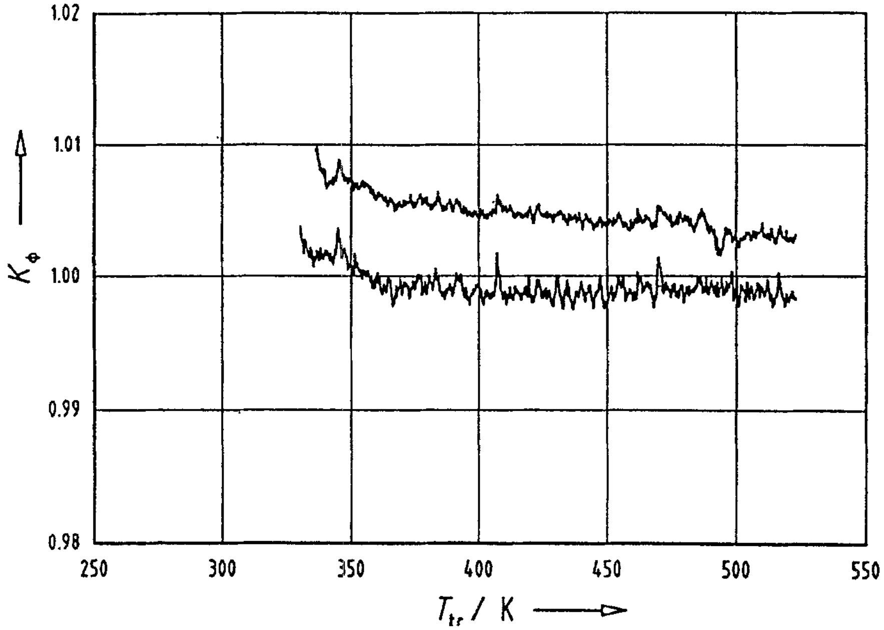

Fig. 6 Heat flow rate calibration function, determined with sapphire. Lower curve: sample mass 80.92 mg; upper curve: sample mass 120.38 mg

Experimental conditions to be observed

– For each calibration (not the individual measurement), a new calibration sample is to be weighed in. If possible, only a single small sample piece should be used, and the position in the crucible should always be the same. In the case of metals, an oxide layer should be removed.

– Crucible, furnace atmosphere, gas pressure and gas flow velocity must be kept constant and comply with the conditions for the sample measurements.

– The surrounding temperature (with power compensated isoperibolic calorimeters that of the cooling device) must be kept constant.

– The samples for heat and temperature calibration are to be heated beyond their melting temperatures only to such an extent that the interpolated baseline can be reliably constructed. Immediately after the measurement, the samples are to be rapidly cooled until retransition to the initial phase has been observed.

Calibration substances

Table 1a Substances for heat flow rate calibration

Substance	T_{range}/ K	Heat capacity, $c_p(T)$/ J g^{-1} K^{-1}	Uncertainty	Remarks
Corundum (α-Al_2O_3)	70–300	$\sum_{i=0}^{7} a_i T^i$	0.4–0.1%	(Corundum, here: synthetic sapphire.) No limitation on crucible material below its melting temperature.
	290–2250	$\sum_{i=0}^{7} b_i T^i$	0.1–0.2%	
Copper (Cu)	20–97.5	$\sum_{i=0}^{6} c_i T^i$	0.1%	OFHC quality. No limitation on crucible material below its melting temperature.
	97.5–320	$\sum_{i=0}^{4} d_i T^i$	0.1%	

Table 1b Coefficients of the fitting polynomials of the heat flow rate calibration materials

i	a	b	c	d
0	$3.63245 \cdot 10^{-02}$	$-5.81126 \cdot 10^{-01}$	$1.43745 \cdot 10^{-02}$	$-1.63570 \cdot 10^{-01}$
1	$-1.11472 \cdot 10^{-03}$	$8.25981 \cdot 10^{-03}$	$-1.21086 \cdot 10^{-03}$	$7.07745 \cdot 10^{-03}$
2	$-5.38683 \cdot 10^{-06}$	$-1.76767 \cdot 10^{-05}$	$-1.23305 \cdot 10^{-05}$	$-3.78932 \cdot 10^{-05}$
3	$5.96137 \cdot 10^{-07}$	$2.17663 \cdot 10^{-08}$	$4.20514 \cdot 10^{-06}$	$9.60753 \cdot 10^{-08}$
4	$-4.92923 \cdot 10^{-09}$	$-1.60541 \cdot 10^{-11}$	$-8.49738 \cdot 10^{-08}$	$-9.36151 \cdot 10^{-11}$
5	$1.83001 \cdot 10^{-11}$	$7.01732 \cdot 10^{-15}$	$6.71459 \cdot 10^{-10}$	
6	$-3.36754 \cdot 10^{-14}$	$-1.67621 \cdot 10^{-18}$	$-1.94071 \cdot 10^{-12}$	
7	$2.50251 \cdot 10^{-17}$	$1.68486 \cdot 10^{-22}$		

Table 2 Substances for temperature and heat calibration

Substance	Transition temperature T_{trs} (true temperature_T_{tr})/		Uncer-tainty/	Transition heat Q_{trs} (true heat Q_{tr})/		Uncertainty (2σ)	Type of transition	Remark
	K	°C	mK	J g^{-1}	kJ mol^{-1}			
Cyclopentane	122.38	−150.77	50	69.60	4.881	0.5%	solid-solid	Measure in a hermetically sealed crucible only. Weigh in as a liquid, backweigh to determine the mass.
Cyclopentane	138.06	−135.09	50	4.91	0.345	1.1%	solid-solid	
Cyclopentane	179.72	−93.43	50	8.63	0.605	1.1%	solid-liquid	
Water	273.15	0.00	10				solid-liquid	Not suitable for heat calibration.
Gallium	302.9146	29.7646	0	79.88	5.569	0.9%	solid-liquid	Melt reacts with Al. Allow for strong supercooling.
Indium	429.7485	156.5985	0	28.62	3.286	0.4%	solid-liquid	
Tin	505.078	231.928	0	60.40	7.170	0.6%	solid-liquid	Melt reacts with Al and Pt.
Bismuth	(544.55)	(271.40)	–	53.84	11.25	3.9%	solid-liquid	Melt reacts with Al. Not suitable for temperature calibration.
Lead	600.61	327.46	10				solid-liquid	Not suitable for heat calibration.
Zinc	692.677	419.527	0				solid-liquid	Not suitable for heat calibration.

Table 2 Continued

Substance	Transition temperature T_{trs} (true temperature T_{tr})/		Uncer-tainty/	Transition heat Q_{trs} (true heat Q_{tr})/		Uncertainty (2σ)	Type of transition	Remark
	K	°C	mK	J g^{-1}	kJ mol^{-1}			
Lithium sulphate	851.43	578.28	250	228.1	25.07	4.6%	solid-solid	Anhydrate hygroscopic; weigh in as $Li_2SO_4 \cdot H_2O$. Dehydration from 110°C, with brisk movement of the particles in the crucible; high water vapour pressure (do not use hermetically sealed crucibles). Backweigh after measurement for mass determination.
Aluminium	933.473	660.323	0	398.1	10.74	2.3%	solid-liquid	Melt reacts strongly with Pt.
Silver	1234.93	961.78	0				solid-liquid	Melt dissolves oxygen, reacts with Pt.
Gold	1337.33	1064.18	0				solid-liquid	Melt dissolves oxygen reacts with Pt.

The transition heats stated are best-value estimates on the basis of evaluations of the relevant literature. The uncertainty stated describes the statistical uncertainty.

The values have been updated compared with those published in H. K. Cammenga *et al.*, PTB-Mitt. and Thermochim. Acta, and S. M. Sarge *et al.*, PTB-Mitt.