

## The temperature calibration of scanning calorimeters. Part 2. Calibration substances \*

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(Recommendation of the working group “Calibration of Scanning Calorimeters” of the Gesellschaft für Thermische Analyse e.V. (GEFTA), Germany)

### 1. PURPOSE OF THE RECOMMENDATION

The recommendation for temperature calibration consists of two parts. Part 1 (see section 2.3) presented a correct method for the calibration of scanning calorimeters (DSC) and of instruments for differential thermal analysis (DTA), irrespective of the instrument type. The present paper recommends calibration substances for the range 120–1350 K.

Sections 2 and 3 indicate the documents to be taken into account and define the most important terms used. Section 4 consists of general requirements to be met by the calibration substances, a list of the substances and explanations with respect to their use. Basically, such materials have been selected as calibration substances which define fixed points of the International Temperature Scale of 1990 (ITS-90). Added to these are fixed point materials from the previously valid International Practical Temperature Scale of 1968 (IPTS-68, see References in Table 1). Moreover, two substances are recommended for temperature ranges for which no suitable fixed point material exists, and the respective uncertainty of measurement is stated.

### 2. DOCUMENTS TO BE TAKEN INTO ACCOUNT

#### 2.1. *Temperature scale in force*

H. Preston-Thomas, *The International Temperature Scale of 1990 (ITS-90)*, *Metrologia*, 27 (1990) 3–10.

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\* Off-prints are available from the GEFTA office: Prof. Dr. V. Krämer, Kristallographisches Institut der Universität Freiburg, Hebelstraße 25, D-7800 Freiburg, Germany. A German version of this paper was published in *PTB-Mitteilungen*, 102 (1992) 13–18. The present publication contains revised data.

## 2.2. Standard in force

DIN 51005, Thermische Analyse (TA), Begriffe, Edition Nov. 1983.

## 2.3. First part of the recommendation

G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin, and W. Hemminger, The Temperature Calibration of Scanning Calorimeters, *Thermochim. Acta*, 160 (1990) 1–12.

G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin, and W. Hemminger, Die Temperaturkalibrierung dynamischer Kalorimeter, *PTB-Mitteilungen*, 100 (1990) 25–31.

## 3. DEFINITION OF TERMS

*Temperature calibration* means the unequivocal assignment of the temperature indicated by the instrument to the *true temperature*  $T_{tr}$  (see section 2.3). The true temperature is defined in accordance with the ITS-90 temperature scale (see section 2.1) by fixed points (transition temperatures) of suitable substances, suitable measuring instruments and rules for computing.

In this context, the extrapolated peak-onset temperature for zero heating rate  $T_e(\beta \rightarrow 0)$  (see section 2.3) determined from measurement curves (peaks) is used as the *temperature indicated by the measuring instrument*. For temperature calibration, the temperatures indicated by the instrument are assigned to the transition temperatures of *calibration substances*. Calibration substances must comply with specific requirements (see section 4.1).

## 4. SELECTION AND RECOMMENDATION OF CALIBRATION SUBSTANCES

### 4.1. General requirements for calibration substances

Calibration substances should, if possible, represent fixed points of the ITS-90 (or fixed points of the IPTS-68 converted to the ITS-90). When additional substances are required, their relevant transition temperatures must be measured precisely and linked-up with the ITS-90.

The following additional requirements must be fulfilled.

- (i) The transition temperature must be defined unequivocally from the point of view of thermodynamics.
- (ii) Measurable overheating must not occur (rate of transformation not measurably controlled by nucleation).
- (iii) The rate of the transition must be high.

- (iv) The grain sizes of the phases concerned must not influence the transition temperature.
- (v) The substance must be available in sufficiently high purity (no measurable influence of existing impurities on the transition temperature).
- (vi) Reaction with crucible material or purge gas (surrounding atmosphere) and photoreactions must not occur.
- (vii) The substance must be stable over a long period of time, not hygroscopic and not appreciably volatile.
- (viii) The substance should be physiologically harmless.

#### 4.2. *Recommended calibration substances*

The calibration substances shown in Table 1 have been selected in consideration of the criteria indicated in section 4.1. Many other substances recommended in the literature were tested; they did not, however, comply with the requirements.

#### 4.3. *Experimental prerequisites to be taken into account*

The experimental requirements defined in section 4.1 must be observed. In addition, the following must be taken into consideration.

- (i) The calibration sample must be weighed anew for each calibration (i.e. for the procedure described in Part 1 (see section 2.3) and not the individual measurement). In the case of metals, a possibly existing oxide layer must be removed.
- (ii) If possible, only one grain (crystal, particle) should be used for calibration in order to avoid multiple peaks.
- (iii) The particle size must not be too small to guarantee the approximation “infinitely extended phase”.
- (iv) The location of the calibration sample in the crucible must correspond to the location of the sample to be investigated during the measurements (temperature gradient in the crucible).
- (v) The furnace atmosphere, gas pressure and gas flow rate, as well as the crucible, (in consideration of section 4.1) must be the same for calibration and measurement.
- (vi) The calibration samples should not be heated more than absolutely necessary to temperatures above the transition temperature ( $\leq 10$  K) in order to minimize reactions between crucible material and sample. After heating, the samples must immediately be cooled at high cooling rate, until transition to the initial phase has been observed.

TABLE 1

## Recommended calibration substances

Substance	Transition temperature		Uncertainty $\Delta T$ in mK	Phase transition
	$T$ in K	$t$ in °C		
Cyclopentane <sup>a</sup>	122.38	-150.77	50	Solid–solid
Cyclopentane <sup>a</sup>	138.06	-135.09	50	Solid–solid
Cyclopentane <sup>a</sup>	179.72	-93.43	50	Solid–liquid
Water <sup>a</sup>	273.15	0.00	10	Solid–liquid
Gallium	302.9146	29.7646		Solid–liquid
Indium	429.7485	156.5985		Solid–liquid
Tin	505.078	231.928		Solid–liquid
Lead <sup>a</sup>	600.61	327.46	10	Solid–liquid
Zinc	692.677	419.527		Solid–liquid
Lithium sulphate	851.43	578.28	250	Solid–solid
Aluminium	933.473	660.323		Solid–liquid
Silver	1234.93	961.78		Solid–liquid
Gold	1337.33	1064.18		Solid–liquid

<sup>a</sup> Temperatures converted to ITS-90.

## REMARKS

- (i) Calibration substances of the highest purity available should be used (normally at least 99.999%).
- (ii) Gold reacts with all metallic calibration substances and is not suitable as a crucible material.

## ANNEX I

## COMPATIBILITY OF THE CALIBRATION SUBSTANCES WITH DIFFERENT CRUCIBLE MATERIALS

The calibration substances recommended in Table 1 form mixed phases with some of the crucible materials normally used in scanning calorimetry. In these cases there is the risk of the melted sample dissolving part of the crucible material which may result in a change of the melting temperature. Table 2 shows the “incompatibilities” which can be inferred from the respective phase diagrams.\*

\* Special thanks are due to Dr. H.-L. Lukas, Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium (PML), Stuttgart, Germany, for his substantial contributions to this table.

Ref.	Remark
1	Only in hermetically sealed crucible
1	Only in hermetically closed crucible; only applicable when transition at 122.38 K has taken place previously
1	Only in hermetically closed crucible
2	Air-saturated, bidistilled water in hermetically closed crucible
3	Melt reacts with aluminium; attention must be paid to strong supercooling
3	
3	Melt reacts with aluminium and platinum
2	Reacts with platinum; quick oxidation
3	Melt and vapour react with aluminium and platinum; high vapour pressure at the melting point (about 20 Pa)
4	Anhydrate is hygroscopic; weigh-in as $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ; dehydration takes place from 110°C; violent movement of particles in the crucible; high water-vapour pressure (do not use hermetically closed crucible); discard first run
3	Melt reacts violently with platinum
3	Melt dissolves oxygen, reacts with platinum
3	Melt dissolves oxygen, reacts with platinum

## REFERENCES

- 1 J.G. Aston, H.L. Fink and S.C. Schumann, The Heat Capacity and Entropy, Heats of Transition, Fusion and Vaporization and the Vapor Pressures of Cyclopentane. Evidence for a Non-Planar Structure. *J. Am. Chem. Soc.* 65 (1943) 341–346.
- 2 H. Preston-Thomas, The International Practical Temperature Scale of 1968. Amended Edition of 1975, *Metrologia*, 12 (1976) 7–17.
- 3 ITS-90, see section 2.1.
- 4 Private communication (1992) from Dr. M. Tischler, Instituto Nacional de Tecnología Industrial, Argentina. We are indebted to Dr. M. Tischler for determining this transition temperature.

It is recommended that those combinations in Table 2 marked with – should not be used, because dissolution of the crucible can not only invalidate the calibration but also destroy the measuring head. The combinations marked with + should preferably be used for calibration. A · (point) marks systems where no significant falsification of the temperature is to be expected, although, in these cases, certain caution is advisable with respect to the consequences of a partial solution of the crucible material.

As can be seen in Table 2, there is at least one crucible material suitable for each of the recommended calibration substances. If necessary,

TABLE 2

Compatibilities of calibration substances with crucible materials

Crucible material	Calibration substance										
	Cyclopentane	Water	Gallium	Indium	Tin	Lead	Zinc	Lithium sulphate	Aluminium	Silver	Gold
Corundum, Al <sub>2</sub> O <sub>3</sub>	○	○	+	+	+	+	+	+	+	+	+
Boron nitride, BN	○	○	+	+	+	+	+	+	+	?	?
Graphite, C	○	○	+	+	+	+	+	+	+	+	-
Silicate glass	+	+	+	+	+	+	?	+	-	×	×
Quartz glass, SiO <sub>2</sub>	+	+	+	+	+	+	+	+	-	+	+
Aluminium, Al	+	·	-	+	-	+	-	+	×	×	×
Aluminium oxidized	+	+	+	+	+	+	+	+	×	×	×
Silver, Ag	+	+	-	-	-	-	-	?	-	×	×
Gold, Au	+	+	·	·	-	-	-	+	-	-	×
Nickel, Ni	+	+	·	·	·	·	·	?	-	+	-
Iron, Fe	+	·	·	+	·	+	-	?	-	+	-
Stainless steel	+	+	·	+	·	+	-	?	-	+	-
Platinum, Pt	+	+	·	·	-	-	-	+	-	-	-
Molybdenum, Mo	+	+	·	?	·	?	·	?	?	?	-
Tantalum, Ta	+	+	?	+	?	?	?	+	-	+	-
Tungsten, W	○	○	·	?	?	·	+	?	·	+	+

Key: +, no solubility and no influence on the melting temperature to be expected; -, melt dissolves crucible material, greater change in the melting temperature; ·, partial solution processes are possible with negligible change in the melting temperature; ×, crucible melts; ?, compatibility unknown; ○, hermetic sealing of crucible not easily possible.

the crucible used must be coated with a protective layer for calibration purposes. Aluminium oxide is ideally suited for this purpose; in the case of the aluminium crucibles normally used, this protective layer can be produced in sufficient thickness by heating to 570°C (allowing access of air).

## ANNEX II

### EXAMPLES OF TEMPERATURE CALIBRATIONS

Calibration is described by the example of a power-compensated DSC for two different measuring ranges, from 140 K to 430 K and from 150°C to 660°C. It is explained below how the calibration substances should be handled in order to make reliable calibration possible, and the calibration results are discussed. It is assumed that the calibration procedure is known (see section 2.3).

## Preparation of the samples

### *Cyclopentane*

Cyclopentane (No. 9662, for gas chromatography, Merck, 99.9%) was placed in an aluminium crucible using a micropipette. The crucible was weighed and immediately closed hermetically (cold-welded with the aid of a press) in order to prevent evaporation. Afterwards, the weighed-in quantity was determined and the tightness checked by reweighing. The uncertainty of the melting temperature given in Table 1 refers to the value of Aston [1]. A deviation of  $-0.3$  K was measured for the less pure material used here.

### *Water*

Water (bidistilled, air-saturated) was enclosed in a crucible as described for cyclopentane. Prior to this, the crucible has been heated to  $570^{\circ}\text{C}$  in the presence of oxygen to produce a water-resistant, solid oxide layer.

### *Gallium*

Gallium (m6N, Alfa Products) was cut as a single particle from a pellet using a scalpel. Care was taken to expose a fresh surface on all sides. For weighing-in, the same kind of crucible was used as for the other calibration substances. Premature melting of the gallium in the aluminium crucible, e.g. by warming up on the hand, must be avoided, because the melt destroys the oxide layer after some time.

### *Indium, tin and lead*

Indium, tin and lead (m6N, Alfa Products) were handled in the same way as gallium using aluminium crucibles for the lower measuring range, and graphite or aluminium crucibles for the upper measuring range. Lead oxidizes quickly. Liquid lead dissolves its oxide. This is recognizable in that the extrapolated peak-onset temperature of the lead sample increases from one test to the other.

### *Lithium sulphate*

Lithium sulphate (ultrapure, Alfa Products) was weighed-in as monohydrate powder (anhydrous  $\text{Li}_2\text{SO}_4$  is hygroscopic). In this case it is vital not to use a hermetically closed crucible, because the pressure produced during dehydration would be too high and might cause damage.

### *Zinc*

Zinc (m5N, Alfa Products) should only be weighed-in in a graphite crucible, because melt and vapour react with aluminium. If it is guaranteed that the oxide layer of the crucible is sufficiently stable, a few measurements can be risked in aluminium crucibles. The measurements

should, however, be discontinued at the slightest sign of a widening of the peak or even a lowering of the melting temperature.

### Aluminium

Aluminium (m6N, Alfa Products) as a calibration substance may only be melted in a graphite crucible; aluminium crucibles are, of course, excluded. Other metals are also unsuitable as crucible materials.

### Execution of the calibration measurements

Calibration was carried out according to the procedure described in the first part of the recommendation (see section 2.3). For all samples, the

TABLE 3

Results of the calibration in the lower temperature range (Fig. 1): purge gas, He; temperature of the cooling block, 80 K; crucible, Al, hermetically closed

Substance	$T_{tr}$ in K	$T_e(\beta \rightarrow 0)$ in K	$\Delta T_{corr}(\beta = 0)$ in K	Repeatability in K
Cyclopentane	138.06	138.87	-0.81	0.2
Cyclopentane	179.4 <sup>a</sup>	179.94	-0.54	0.2
Water	273.15	273.13	+0.02	0.1
Gallium	302.9146	302.95	-0.03	0.1
Indium	429.7485	432.73	-2.98	0.2

<sup>a</sup> Measured value of this material (99.9%).

TABLE 4

Results of the calibration in the upper temperature range: purge gas, N<sub>2</sub>; temperature of the cooling block, 10°C

Substance	$t_{tr}$ in °C	$t_e(\beta \rightarrow 0)$ in °C	$\Delta T_{corr}(\beta = 0)$ in K	Repeatability in K
Covered graphite crucibles (Fig. 2, ○)				
Indium	156.5985	156.86	-0.26	0.1
Tin	231.928	232.26	-0.33	0.2
Lead	327.46	327.73	-0.27	0.2
Zinc	419.527	420.92	-1.39	0.3
Li <sub>2</sub> SO <sub>4</sub>	578.28	583.80	-5.52	0.4
Aluminium	660.323	667.35	-7.03	0.4
Covered aluminium crucibles (crimped) (Fig. 2, ×)				
Indium	156.5985	156.52	+0.08	0.1
Tin	231.928	231.79	+0.14	0.1
Lead	327.46	327.50	-0.04	0.2
Zinc	419.527	420.14	-0.61	0.2
Li <sub>2</sub> SO <sub>4</sub>	578.28	583.00	-4.72	0.2



calorimeter was first set to an initial temperature far below the transition temperature so that the substance was definitely present in the desired phase. Because the melts of pure metals show strong supercooling, this initial temperature was in some cases far below the melting temperature (in the case of gallium and tin, 20–50 K). Generally, a sufficiently low initial temperature was selected for the measurement so that the period between the start of the measurement and melting was sufficient to reach steady-state conditions (here about two minutes). For a heating rate of  $10 \text{ K min}^{-1}$ , the initial temperature was therefore set to a value 20 K below the transition temperature (and to a value 2 K below this temperature for a heating rate of  $1 \text{ K min}^{-1}$ ).

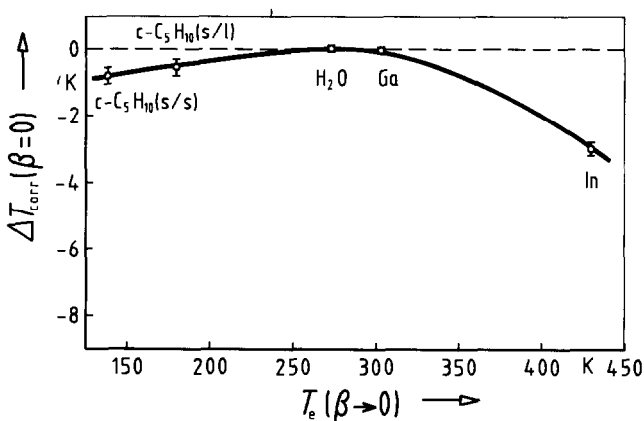


Fig. 1. Dependence of the temperature correction  $\Delta T_{\text{corr}}(\beta=0)$  on the temperature  $T_e(\beta \rightarrow 0)$  for the lower temperature range as the result of the calibration.

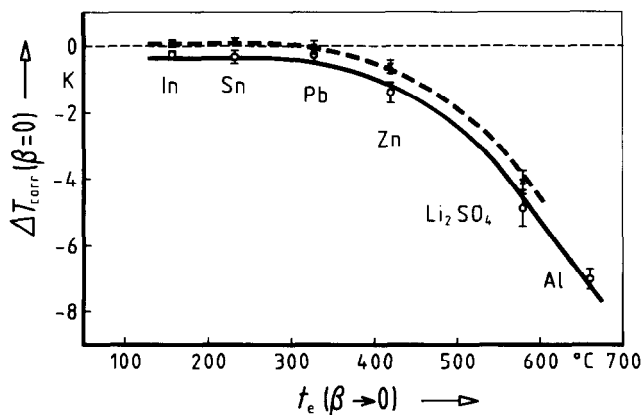


Fig. 2. Dependence of the temperature correction  $\Delta T_{\text{corr}}(\beta=0)$  on the temperature  $t_e(\beta \rightarrow 0)$  for the upper temperature range as the result of the calibration in graphite crucibles (O) and aluminium crucibles (X).

The measurements were observed on the screen and immediately discontinued after the peak end. Immediately afterwards, cooling was carried out at the highest possible cooling rate, until reconversion had taken place; this process was also checked.

### *Results*

For the two temperature ranges in question, the extrapolated peak-onset temperatures (extrapolated to zero heating rate) shown in Tables 3 and 4 were found, resulting in the calibration curves shown in Figs. 1 and 2. The results of both calibrations differ, owing to the different isoperibol operating temperatures (cooling block) and the use of different purge gases. Moreover, Table 4 and Fig. 2 indicate a slight but significant difference in the calibrations when crucibles made of aluminium or graphite are used.