Thermochimica Acta, 187 (1991) 323–334
Elsevier Science Publishers B.V., Amsterdam

Determination of Characteristic Temperatures with the Scanning Calorimeter

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Abstract

The uncertainty of the temperature determination by means of scanning calorimeters can be considerably reduced if the heat flow rate to be assigned to the event under discussion is extrapolated up to the abscissa, not up to the interpolated baseline, and the temperature of the intersection point is taken. This reduces, for example, the standard deviation of the measurement of the melting temperature of indium samples of different mass from 109 mK to 18 mK.

1. DETERMINATION OF CHARACTERISTIC TEMPERATURES

According to a recommendation of the Gesellschaft für Thermische Analyse in Germany (GEFTA) and of several manufacturers of scanning calorimeters, the temperature of any event is determined by means of these instruments in that the heat flow rate to be assigned to this event is extrapolated to the interpolated baseline at an angle α and the temperature of the intersection point is taken. The angle α results from the ascending slope of the melting peak of a pure substance (Figure 1).

In analogy, the extrapolated peak-onset temperature is assigned to the melting temperature of a pure substance, the former being defined by the intersection point of the inflexional tangent, or of an auxiliary line drawn through the linear section of the ascending peak slope, and the extrapolated initial baseline (GEFTA method [1]).

In an alternative method, the characteristic temperature is defined as the temperature of the intersection point of the auxiliary line (inflexional tangent) with the interpolated isothermal baseline which is obtained by drawing a line connecting the isothermal initial baseline with the isothermal final baseline (BARRALL method [2,3]).

It will be demonstrated in the following on the basis of experiments that these methods furnish extrapolated peak-onset temperatures of melting peaks which are not independent of sample properties, i.e. heat capacity of the sample, heat resistance between sample and sample temperature probe, properties of the sample pan.

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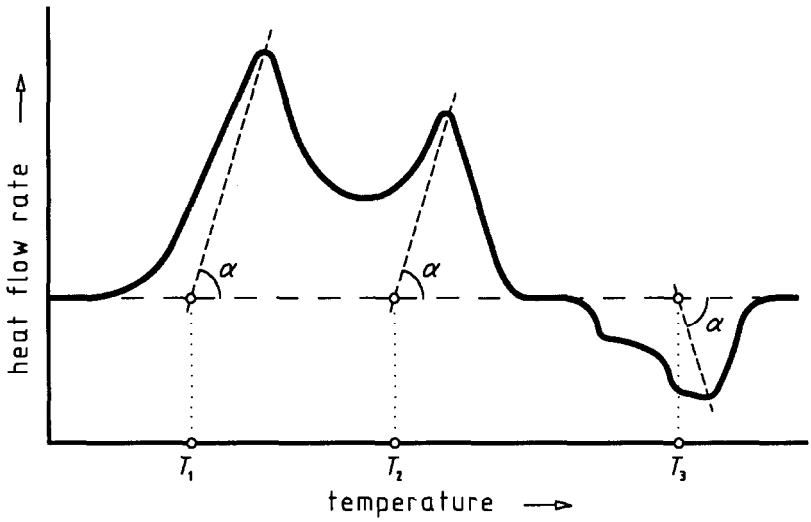

Figure 1. Determination of characteristic temperatures of a complex event according to [1].

In the case of the extrapolated peak-onset temperature determined by the GEFTA method, the measured heat flow rate, i.e. the level of the initial baseline, corresponds to a temperature difference between the temperature probes of sample and reference sample. This temperature difference must be added to the temperature of the reference sample temperature probe to obtain the temperature of the sample temperature probe. The temperature of the reference sample temperature probe is only slightly influenced by the sample properties. In steady-state conditions at a given heating rate it therefore differs by a constant amount from the measured furnace temperature, or it is equal to the furnace temperature when extrapolation to zero heating rate is carried out; by temperature calibration of the instrument it is assigned to the true temperature.

The heat resistance between sample and temperature probe comprises a sample-dependent component, which influences the ascending slope of the melting peak and depends on the sample surface in contact with the bottom of the sample pan and on the thermal conductivity of this surface. The other component is instrument-specific and independent of the sample; it influences the level of the baseline and depends in first approximation only on instrument properties, i.e. the thermal resistance between temperature probe and bottom of the sample pan.

The temperature difference due to the heat flow rate can be eliminated by extrapolating the heat flow rate of the extrapolated peak-onset temperature determined by the GEFTA method to the abscissa, at an angle corresponding to the sample-independent component of the thermal resistance. Only in this way it is ensured that

various measurements, or temperature calibration and determination of unknown temperatures, are related to the same origin of the temperature displayed.

Figure 2 gives a survey of the three methods of temperature determination.

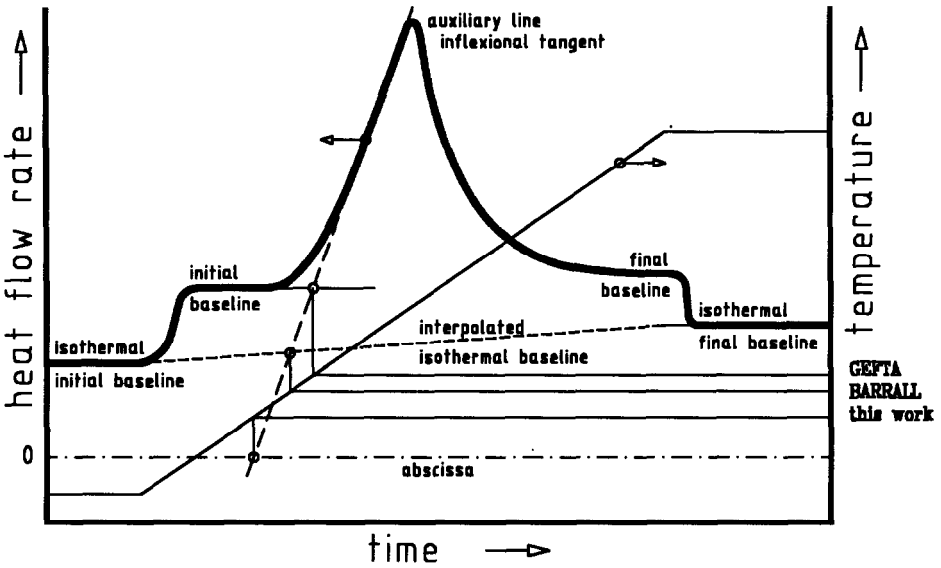

Figure 2. Definition of the extrapolated peak-onset temperature according to GEFTA [1], BARRALL [2,3], this paper.

The thermal resistance to be used for extrapolation to the abscissa can be determined from the melting peaks of high-purity materials by two methods:

- When optimum coupling of the sample to the sample pan is ensured and the sample's thermal conductivity is high, the searched thermal resistance can be determined from the slope of the ascending peak area.
- Alternatively, the extrapolated peak-onset temperatures determined by the GEFTA method can be plotted as a function of the measured heat flow rate at this temperature. The slope of the resulting straight line then corresponds to the searched thermal resistance.[1]

[1] In modern differential scanning calorimeters (e.g. DSC-7, Messrs. Perkin-Elmer, Norwalk, CT, USA), the position of the abscissa is arbitrarily and variably chosen so that, in the graph, the measured curve is above the abscissa. No information about the absolute peak position is given to the user which is why the procedure described here is not applicable to such instruments of this type. This qualification does not apply to the DSC-2 used in our experiments, since the data were acquired with a digital voltmeter at the recorder output, with a computer connected to the equipment.

2. EXPERIMENTS

The experiments to study the dependence of the extrapolated peak-onset temperature on the sample's heat capacity were performed using three scanning calorimeters (Table 1). The variation of the sample's heat capacity was ensured by different sample masses, indium being the sample material.

From among the 21 measurements carried out with the Mettler FP84 calorimeter, Figure 3 shows one for each of the seven different masses used in the experiments. All samples have been melted at least once. The detail from Figure 3 gives an enlarged representation of the initial baselines. Their levels not only depend on the sample's heat capacity but also on random influences, such as position of the sample pan in relation to the temperature probe, radiation properties of the sample pan, position of the sample in the sample pan etc. The curves obtained with the other two calorimeters were of the same quality.

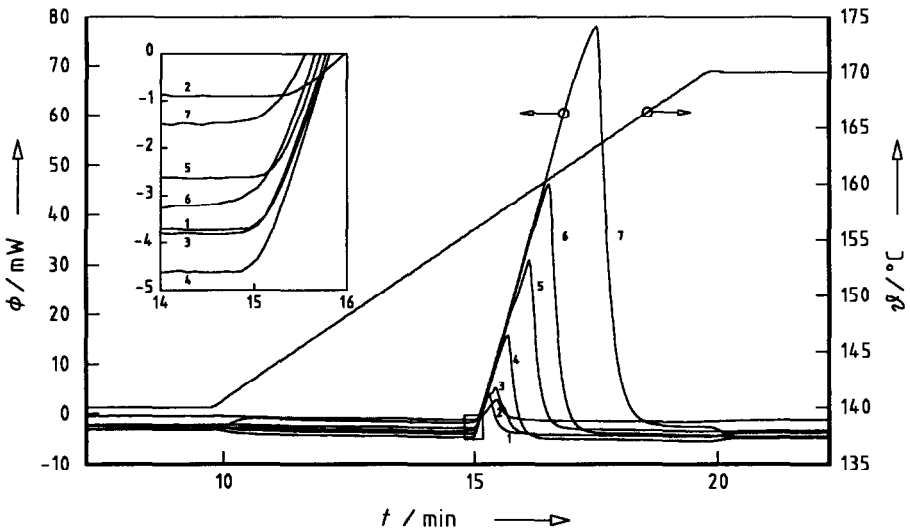

Figure 3. Melting peaks of indium samples of different mass, recorded with the Mettler FP84 calorimeter. Sample masses: 1 2.989 mg, 2 5.110 mg, 3 9.670 mg, 4 24.122 mg, 5 54.236 mg, 6 106.696 mg, 7 286.648 mg.
Φ heat flow rate, t time, ϑ temperature

The experiments with the Perkin-Elmer DSC-2 and Heraeus TA 500 calorimeter were recorded and evaluated according to the GEFTA method and the method described in this paper. Only in the case of the the Mettler FP84 calorimeter the initial and final baselines were recorded which enabled the additional evaluation according to the BARRALL method.

Table 1
Description of instruments, samples and experiments

Instrument	FP84 TOA/DSC Messrs. Mettler, Greifensee, Switzerland	DSC-2 Messrs. Perkin-Elmer, Norwalk, CT, USA	TA 500 Messr. Heraeus, Hanau, Germany
Characterization	Simultaneous thermo-optical analyzer / Heat flow differential scanning calorimeter	Power compensation differential scanning calorimeter	Heat flow differential scanning calorimeter
Temperature determination	Furnace temperature (Pt-100 resistor)	Actual value of the control timer, rated value determined by averaging sample and reference sample temperature (Pt-10 resistors)	Sample temperature (Pt-100 resistor)
Differential temperature probe	Quinteeple Au/Ni thermopile	Pt-10 resistors	Pt-100 resistors
Sample pan	hermetically sealed Al pan, $m \approx 40$ mg, $V \approx 40\,\mu$l	hermetically sealed Al pan, $m \approx 30$ mg, $V \approx 25\,\mu$l	hermetically sealed Al pan, $m \approx 50$ mg, $V \approx 50\mu$l
Sample material	In, Messrs. Balzers, 99.9995% by weight	In, Messr. Preussag, 99.99999% by weight	In, Messr. Balzers, 99.9995% by weight
Sample mass	$2.9 < m < 290$ mg	$0.9 < m < 72$ mg	$1.5 < m < 57$ mg
Sample's heat capacity at melting point [4]	$0.69 < C_p < 67.33$ mJK^{-1}	$0.22 < C_p < 16.62$ mJK^{-1}	$0.36 < C_p < 13.02$ mJK^{-1}
Initial temperature	140 °C	405 K	130 °C
Initial isothermal	10 min	-	-
Heating rate	3 K min^{-1}	5 K min^{-1}	5 K min^{-1}
End temperature	170 °C	455 K	180 °C
Final isothermal	10 min	-	-

3. RESULTS

Table 2 lists the measurements and the results. m ist the mass of indium, R the thermal resistance between sample and temperature probe determined from the ascending slope of the melting peak. $\Phi(\vartheta_{e,GEFTA})$ indicates the heat flow rate at the peak-onset temperature extrapolated according to the GEFTA method. The following three (a) and two columns (b and c) state the extrapolated peak-onset temperatures ϑ_e determined by the above-decribed methods.

It is conspicuous that the thermal resistance calculated for samples of small mass is very high. Obviously, after inital melting, these samples form droplets with very small contact areas and, thus, high thermal resistance to the bottom of the sample pan. The low thermal resistance of larger samples is due to the fact that there has been contact between the lid of the sample pan and the sample material which resulted in the contact

area being enlarged. The thermal resistance determined for these samples thus approximates the minimum thermal resistance due to the instrument's design.

The lines at the bottom of the table indicate the average value and the standard deviation of the extrapolated peak-onset temperatures determined by the methods described above.

Table 2
Extrapolated peak-onset temperatures, average values and standard deviations calculated by the methods described

a) Mettler FP 84 calorimeter

No.	m / mg	R / KW^{-1}	$\Phi(\vartheta_{e,GEFTA})$ / mW	ϑ_e / °C (GEFTA)	ϑ_e / °C (BARRALL)	ϑ_e / °C this paper
1	2.989	255	-1.146	156.225	156.299	156.314
2	2.989	259	-0.872	156.211	156.187	156.279
3	2.989	247	-0.810	156.253	156.249	156.316
4	5.110	101	-4.088	155.970	156.067	156.289
5	5.110	104	-4.038	155.969	156.093	156.284
6	5.110	196	-4.100	155.981	156.076	156.301
7	9.670	91	-4.182	155.985	156.070	156.311
8	9.670	100	-4.009	155.981	156.048	156.294
9	9.670	95	-4.058	155.998	156.036	156.315
10	24.122	86	-5.006	155.924	155.987	156.314
11	24.122	86	-5.019	155.919	155.997	156.310
12	24.122	85	-5.123	155.949	156.016	156.349
13	54.236	85	-2.893	156.102	156.126	156.328
14	54.236	86	-2.922	156.064	156.092	156.292
15	54.236	86	-2.948	156.059	156.079	156.289
16	106.696	82	-3.601	156.010	156.079	156.291
17	106.696	82	-3.623	156.007	155.960	156.290
18	106.696	81	-3.617	156.026	156.031	156.308
19	286.648	75	-1.971	156.173	156.084	156.327
20	286.648	75	-1.607	156.198	156.012	156.323
21	286.648	75	-1.555	156.207	156.041	156.328
		average value		156.058	156.078	156.307
		standard deviation		0.109	0.082	0.018

b) Perkin-Elmer DSC 2

No.	m / mg	R / KW^{-1}	$\Phi(\vartheta_{e,GEFTA})$ / mW	ϑ_e / °C GEFTA	ϑ_e / °C this work
1	0.952	130	8.402	155.255	154.936
(2	0.952	157	7.916	155.972	155.671)
3	5.098	95	8.557	155.277	154.952
4	5.098	99	8.562	155.235	154.910
5	18.788	46	14.844	155.584	155.020
6	18.788	50	14.799	155.393	154.831
7	25.418	81	8.988	155.257	154.915
8	25.418	82	9.001	155.260	154.918
9	71.493	81	10.054	155.327	154.945
10	71.493	81	10.242	155.312	154.923
		average value		155.322	154.928
		standard deviation		0.110	0.049

c) Heraeus TA 500 calorimeter

No.	m / mg	R / KW^{-1}	$\Phi(\vartheta_{e,GEFTA})$ / mW	ϑ_e / °C GEFTA	ϑ_e / °C this work
1	1.548	163	0.665	155.757	155.667
2	1.548	175	0.980	155.767	155.635
3	3.623	138	0.742	156.005	155.905
4	3.623	153	0.811	155.813	155.703
5	9.838	85	0.811	155.794	155.684
6	9.838	89	0.833	155.691	155.578
7	24.397	92	1.458	155.870	155.673
8	24.397	91	1.474	155.763	155.564
9	56.011	96	1.944	156.135	155.873
10	56.011	105	2.151	155.917	155.627
		average value		155.851	155.691
		standard deviation		0.135	0.113

Figures 4a, 4b and 4c show the dependence of the extrapolated peak-onset temperatures determined by the GEFTA method, BARRALL method and the method described in this paper on the heat flow rate for the extrapolated peak-onset temperature determined by the GEFTA method.

From the measurements by the GEFTA method using the Perkin-Elmer DSC-2, an average value for ϑ_e of 155.322 °C results, with a standard deviation of 110 mK; the method presented here furnishes an average value for ϑ_e of 154.928 °C, with a standard deviation of 49 mK (Figure 4b). In this case the measurement values No. 2 (bracketed in Table 2b and Figure 4b) were not taken into consideration in the evaluation. Prior to this measurement, the sample pan had been removed from the instrument and then put back into it: obviously, this resulted in the sample being shifted from the center to the edge of the pan where the temperature gradient of the measuring system was steep [5].

Evaluation of the measurements performed by means of the Heraeus TA 500 calorimeter applying the GEFTA method furnishes an average value for ϑ_e of 155.851 °C, with a standard deviation of 135 mK (Figure 4c). With the method described here to determine the extrapolated peak-onset temperature, an average value for ϑ_e of 155.691 °C is obtained, with a standard deviation of 113 mK. This only slight reduction of the uncertainty is due to the calorimeter design, where the temperature is measured with the sample temperature probe. As a result, the instrument-specific component of the thermal resistance between temperature probe and sample is small compared with the sample-dependent component; in addition, the baseline shift due to the samples' differing heat capacities is directly included in the temperature measurement. With this calorimeter, there is moreover a strong coupling between sample and reference sample (thermal resistance: 80 to 100 KW^{-1} [6]) so that the requirements for the method presented here to determine the extrapolated peak-onset temperatures are no longer met.

With the GEFTA method, the Mettler FP84 calorimeter furnishes an average value for ϑ_e of 156.058 °C, with a standard deviation of 109 mK; the average value is 156.078 °C with a standard deviation of 82 mK when the BARRALL method is applied. The method described in this paper furnishes an average value of 156.307 °C and reduces the standard deviation to 18 mK (Figure 4a).

The thermal resistance has determined from the slope of the line $\vartheta_{e,GEFTA}=f(\Phi(\vartheta_{e,GEFTA}))$ and found to be 78 KW^{-1} (Figure 4a). This value is in good agreement with the average value of 87 KW^{-1} calculated from the ascending slopes of the melting peaks using medium and large samples masses.

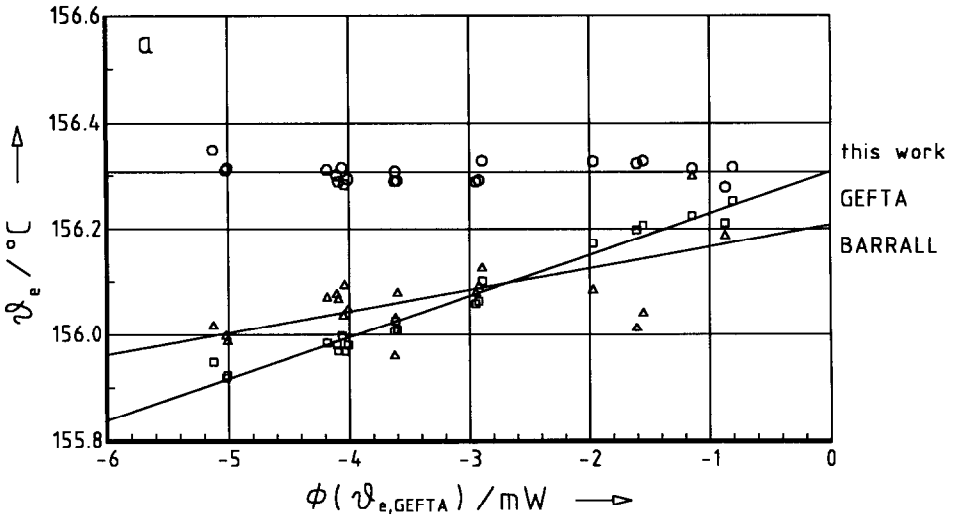

Figure 4a. Dependence of the extrapolated peak-onset temperatures, ϑ_e, on the heat flow rate for the extrapolated peak-onset temperature, $\Phi(\vartheta_{e,GEFTA})$, determined by the GEFTA method (Mettler FP 84 calorimeter).

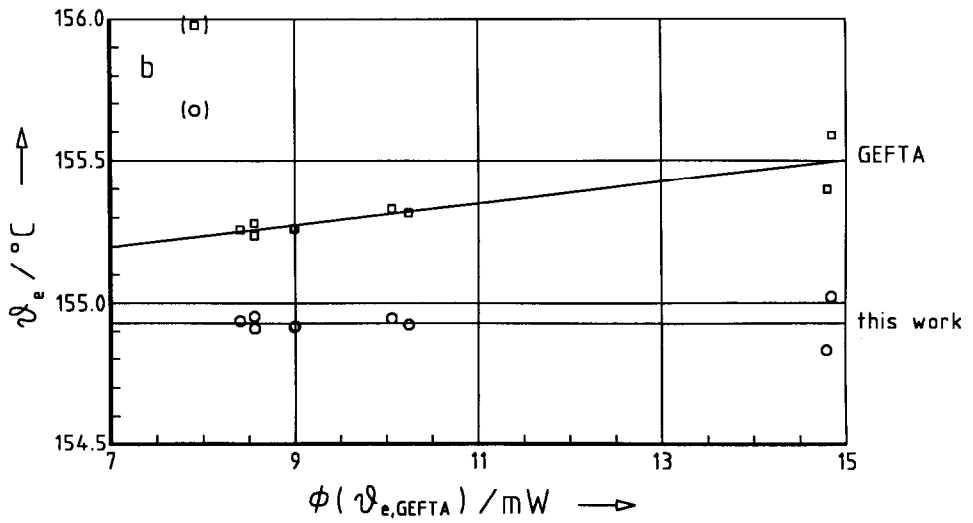

Figure 4b. Dependence of the extrapolated peak-onset temperatures, ϑ_e, on the heat flow rate for the extrapolated peak-onset temperature, $\Phi(\vartheta_{e,GEFTA})$, determined by the GEFTA method (Perkin-Elmer DSC-2).

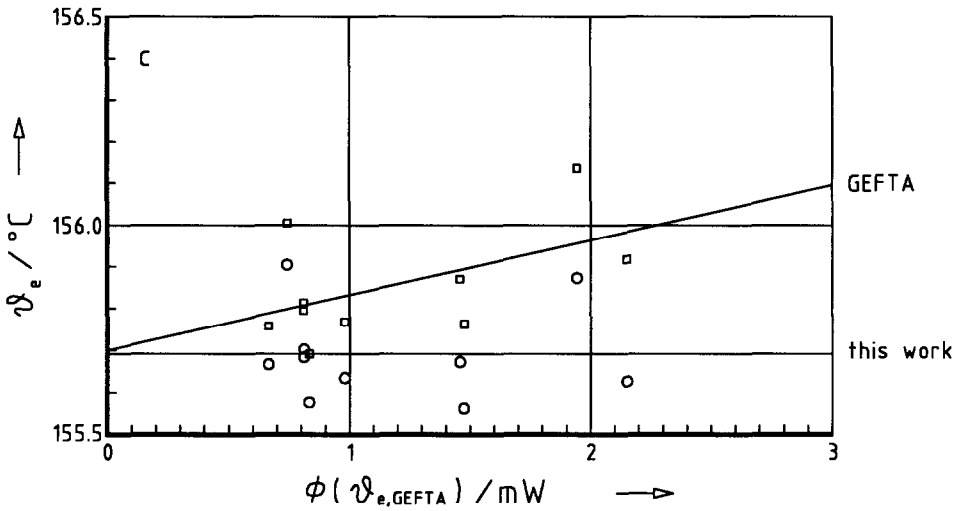

Figure 4c. Dependence of the extrapolated peak-onset temperatures, ϑ_e, on the heat flow rate for the extrapolated peak-onset temperature, $\Phi(\vartheta_{e,GEFTA})$, determined by the GEFTA method (Heraeus TA 500 calorimeter).

4. CONCLUSIONS

The logical conclusion to be drawn from the above is a modification of the GEFTA method applied to determine characteristic temperatures of a complex event with endothermic and exothermic transitions (Figure 5, cf. Figure 1). The heat flow rate of the characteristic event is extrapolated to the abscissa at the angle α and the temperature of the intersection point is taken, a prerequisite being that the heat transfer from the bottom of the pan to the interior of the sample itself is no limiting factor to the heat flow rate into the sample. In such cases, the extrapolation, for example from the peak tip to the interpolated baseline, must be made at an angle which is specific to the sample's thermal resistance and smaller than α. Extrapolation is then performed from the interpolated baseline at the angle α to the abscissa.

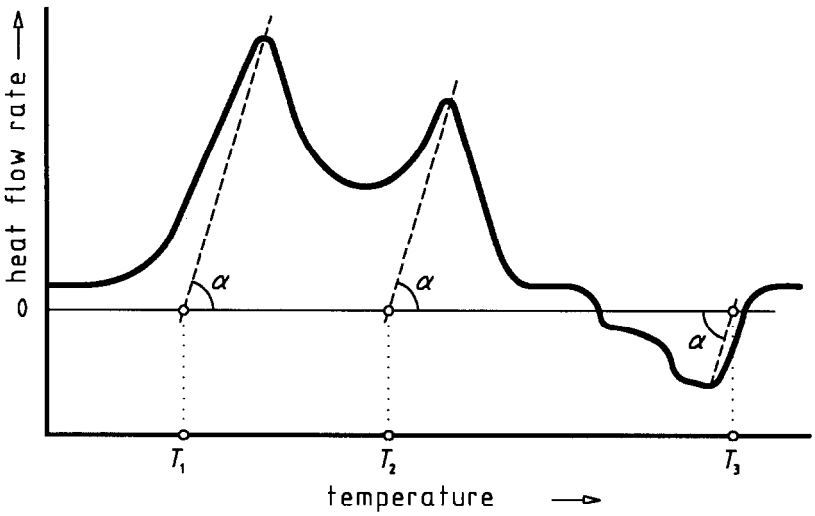

Figure 5. Determination of characteristic temperatures of a complex event according to the method described in this paper.

5. SUMMARY

The method presented in this paper to determine characteristic temperatures using scanning calorimeters allows the uncertainty of temperature measurement to be considerably reduced. The method consists in that the temperature difference between the temperature probes of sample and reference sample, which is due to the heat flow rate (level of the initial baseline) is taken into account by extrapolating the heat flow rate of the characteristic event to the abscissa at an angle resulting from the instrument-specific, sample-independent thermal resistance and taking the temperature of the intersection point. As a result, the standard deviation of the determination of the melting temperature of indium using a heat flow differential scanning calorimeter can, for example, be reduced from 109 mK to 18 mK.

6. ACKNOWLEDGEMENT

The author wishes to express his gratitude to Prof. Dr. H.K. Cammenga, Institut für Physikalische und Theoretische Chemie der Technischen Universität Braunschweig, for giving him the opportunity to carry out in his institute part of the experimental investigations.

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