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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

THE BASELINE CONSTRUCTION AND ITS INFLUENCE ON THE MEASUREMENT OF HEAT WITH DIFFERENTIAL SCANNING CALORIMETERS

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In DSC's the shape of the interpolated baseline under a peak is determined by a change in the heat capacity of the sample and the heat transfer characteristics between sample and temperature sensor. The interpolated baseline is constructed according to formal criteria, experimentally or analytically on the basis of physico-chemical assumptions on the change of the heat capacity during transition. By the example of the melting of ice this paper shows analytically on the basis of a simple calorimeter model and a synthetic measuring curve, and experimentally, that the uncertainty of the enthalpy determination depends in general on the type of baseline and is in the order of magnitude of the repeatability of the DSC's (±0.5%).

1. Introduction

In Differential Scanning Calorimetry (DSC) the baseline must be known in order that the

- enthalpy (from the peak area between measured curve and baseline),
- heat capacity (from the difference between the baselines recorded with and without sample),
- transition temperature of sharp (first-order) phase transitions (by extrapolation of the ascending or descending slope of the endothermic or exothermic peak, resp., to the extrapolated initial baseline)

can be determined.

Various methods of baseline construction are described and recommended in the literature. In the evaluation software DSC manufacturers also offer various options for the baseline construction, but generally a straight

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line between peak start and peak end is used. The influence of changes in the sample's heat capacity or heat transfer characteristics is not, however, taken into consideration.

In the following it is shown, that when different methods of baseline construction are applied in the enthalpy determination of first-order transitions, a systematic error may occur which is equal to the repeatability of the instruments.

2. Definitions and terms

Fig. 1 shows the terms used for the description of the measured curves and explained below.

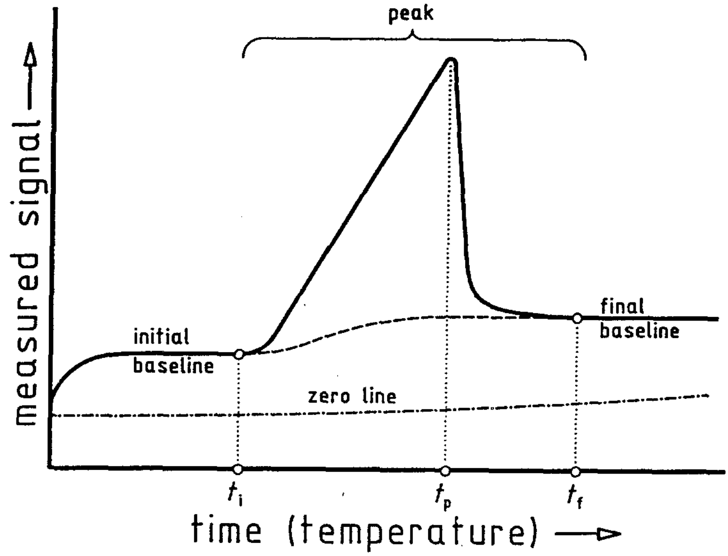


Fig. 1 Explanation of terms (schematic curve for a first-order phase transition). Ordinate: measured signal of the calorimeter (heat flux difference or temperature difference), abscissa: time or temperature. t_i peak start, t_p peak extremum, t_f peak end

Measured curve: Trace of the measured signal as a function of time or temperature (furnace temperature or sample-sensor temperature)

Zero line: Curve measured by the instrument without sample, reference sample.

Baseline: Curve measured by the instrument with sample and reference sample, while no reaction heat flow $\frac{dH}{dt}$ is liberated in the sample and the curve interpolated in the region of the peak which reflects the reaction of the measuring system to all changes of the sample with the exception of the heat produced or consumed due to a transition

Peak: Curve measured during liberation of a heat due to a transition in the sample

Peak start t_i: Initial deviation of the measured signal from the baseline in the region of the peak

Peak extremum t_p: Maximum difference between interpolated baseline and peak

Peak end t_f: Final deviation of the measured signal from the baseline in the region of a peak

The zero line reflects the asymmetry of the instrument with respect to the heat capacities of the supports of sample and reference sample, including the respective temperature sensors, and to the heat transfer from the furnaces to the supports of sample and reference sample.

The baseline corresponds to the signal which sample and reference sample develop only because of the difference between their heat capacities (containers are neglected).

When no reaction heat is released, the baseline is the measured curve. However, when reaction heat is released in the sample, the instrument records a peak. The baseline in this region is first unknown and must be somehow interpolated from the shape of the initial and final baseline or must be determined by other means.

3. Thermodynamic aspects

The first law of thermodynamics describes the enthalpy H of a system as a function of the variables of state: pressure p, temperature T and composition ξ:

$$H = H(p, T, \xi) \tag{1}$$

The total differential is:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_{T,\xi} \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_{p,\xi} \mathrm{d}T + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \mathrm{d}\xi \tag{2}$$

For isobaric processes the following is valid:

$$\mathrm{d}H = \delta q \tag{3}$$

Calorimetrically, the differential heat δq is measured which is:

$$\delta q = \left[\left(\frac{\partial H}{\partial p}\right) - \mathrm{V}\right]_{\mathrm{T},\xi} \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_{\mathrm{p},\xi} \mathrm{d}T + \left(\frac{\partial H}{\partial \xi}\right)_{\mathrm{p,T}} \mathrm{d}\xi \tag{4}$$

For the second term in Eq. (4), with p, ξ = constant,

$$\left(\frac{\partial H}{\partial T}\right)_{\mathrm{p},\xi} = C_{\mathrm{p}}(T) \tag{5}$$

is valid by definition, where C_{p} is the heat capacity of the system at constant pressure.

The third term in Eq. (4),

$$\left(\frac{\partial H}{\partial \xi}\right)_{\mathrm{T,p}} = \Delta H \tag{6}$$

is the isothermal and isobaric enthalpy change, for example due to a phase transition ($\Delta H \equiv \Delta_{\mathrm{trs}} H$), a mixing effect ($\Delta H \equiv \Delta_{\mathrm{mix}} H$) or a reaction ($\Delta H \equiv \Delta_{\mathrm{r}} H$).

(Superimposed effects, e.g. melting of a substance of eutectic impurity, with its heat of mixing superimposed on its heat of fusion will not be discussed here.)

In the following considerations it will be assumed that a calorimeter measures the enthalpy difference as heat (p = constant). All other energy forms (surface energy etc.) are not taken into consideration.

As an example, the enthalpy and heat capacity of a substance are shown in Fig. 2.

Higher-order phase transitions are not connected with an enthalpy of transition; in this case the measured curve is the baseline. First-order phase transitions take place isothermally, the heat capacity is discontinuous and shows a step. In thermally activated chemical reactions the heat capacity changes continuously as a function of the fraction transformed during the reaction.

The problem is to assign changes in the sample's heat capacity in the region of the peak to the correct shape of the baseline.

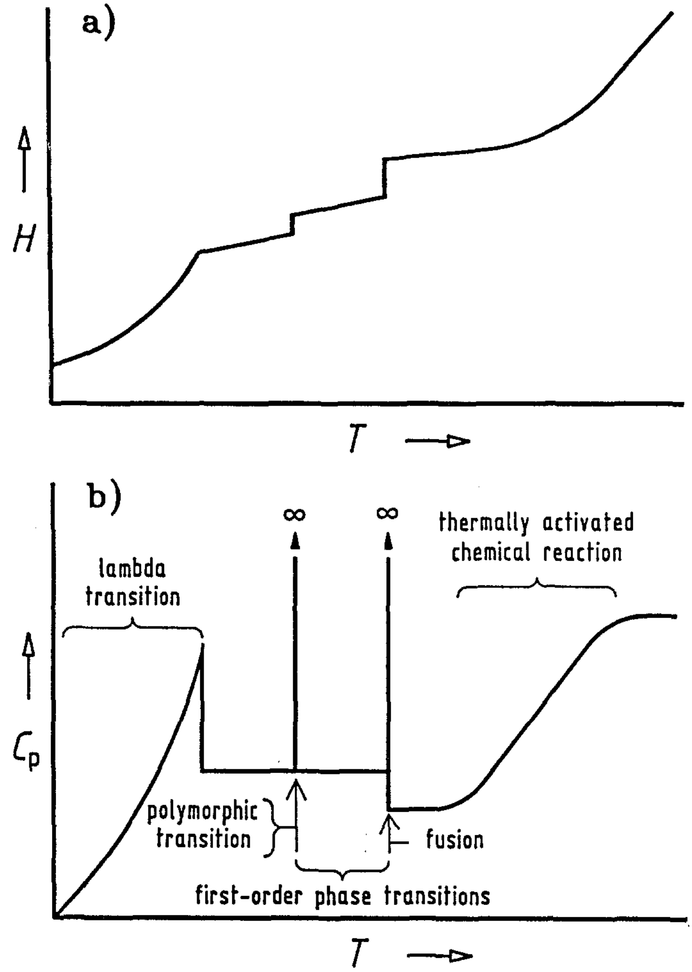


Fig. 2 Enthalpy (a)) and heat capacity (b)) of a substance as a function of temperature
H enthalpy, C_p heat capacity at constant pressure

4. Theoretical, ideal baselines

According to the change of the heat capacity during phase transitions/reactions, a distinction can be made between 4 cases as far as the shape of the baseline under a peak is concerned:

1. The enthalpy production of the sample, $\left(\frac{dH}{dt}\right)$, is zero (Fig. 3). This case applies e. g. to lambda transitions or pure heat capacity measurements; then the 'baseline' is the measured curve.

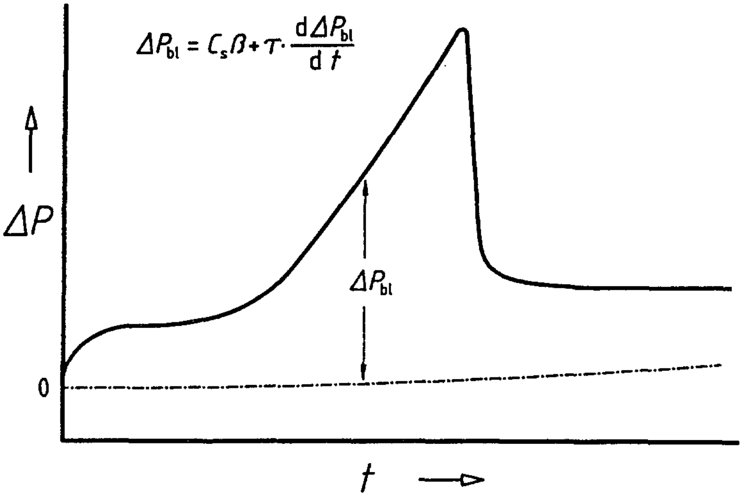


Fig. 3 Shape of the baseline for transitions without enthalpy production. The equation of the baseline, $\Delta P_{bl}(t)$, describes the relation between the measured signal of a power compensation DSC and the change of the sample's heat capacity as a function of time (cf. 5.2). ΔP_{bl} equation of the baseline related to the zero line (measured curve minus zero line), ΔP measured signal, t time, C_s heat capacity of the sample, β heating rate, τ time constant of the measuring system

2. The heat capacity of the sample, C_S, remains constant (Fig. 4):

$$C_S'' = C_S' ; \qquad \Delta C_S = 0 \tag{7}$$

C_S'' : heat capacity of the high-temperature phase
C_S' : heat capacity of the low-temperature phase
$\Delta C_S = C_S'' - C_S'$: heat capacity difference

This case is trivial. The interpolated baseline under the peak is simply the extrapolated initial baseline which merges into the final baseline.

3. The heat capacity of the sample, C_S, changes continuously and proportional to the degree of conversion, α, (Fig. 5):

$$C_S = (1-\alpha)C_S' + \alpha C_S'' \tag{8}$$

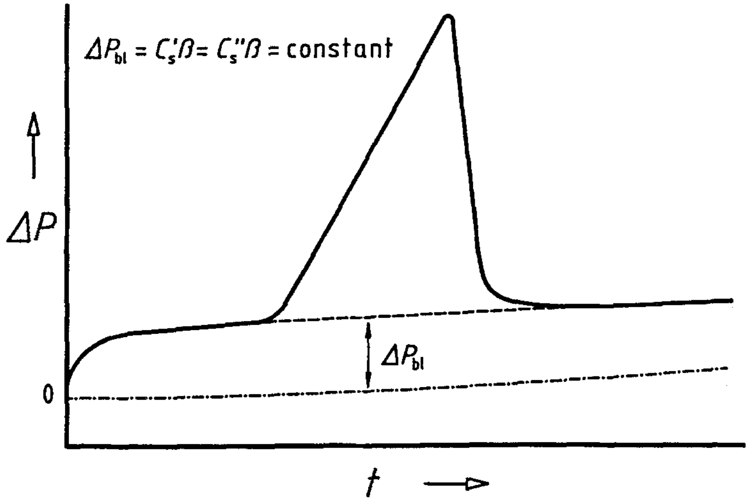


Fig. 4 Shape of the baseline for transitions without heat capacity change. ΔP_{bl} equation of the initial, interpolated and final baseline related to the zero line, ΔP measured signal, t time, C_s', C_s'' heat capacity of the low and high temperature phase, resp., β heating rate

This assumptions valid e. g. for chemical reactions or, according to Van't Hoff's law, for the melting of eutectic systems above the eutectic temperature.

4. The heat capacity of the sample changes suddenly upon transition (transition temperature T_{trs}), e. g. in first-order phase transitions:

$$C_s = \begin{cases} C_s' & \text{for } T < T_{trs} \ (t < t_i) \\ \infty & \text{for } T = T_{trs} \ (t = t_i) \\ C_s'' & \text{for } T > T_{trs} \ (t > t_i) \end{cases} \tag{9}$$

The sample temperature is constant during first-order phase transitions. Below the transition temperature the heat capacity of the sample is given by the low temperature phase, above the transition temperature by the high temperature phase. This heat capacity change, $\Delta C_s(T) = C_s''(T) - C_s'(T)$, is described as a function of temperature by a step function at $T = T_{trs}$. By the 'RC elements' (cf. Fig. 7) of the calorimeter (measuring system) this step function is transformed into an exponential function (function of time). This exponential function starts at t_i and reaches the final baseline at t_f, it represents the interpolated baseline. The peak area – and thus the transition enthalpy – are given by the area between the measured curve and the calculated baseline in the region of the peak (Fig. 6) [2–4].

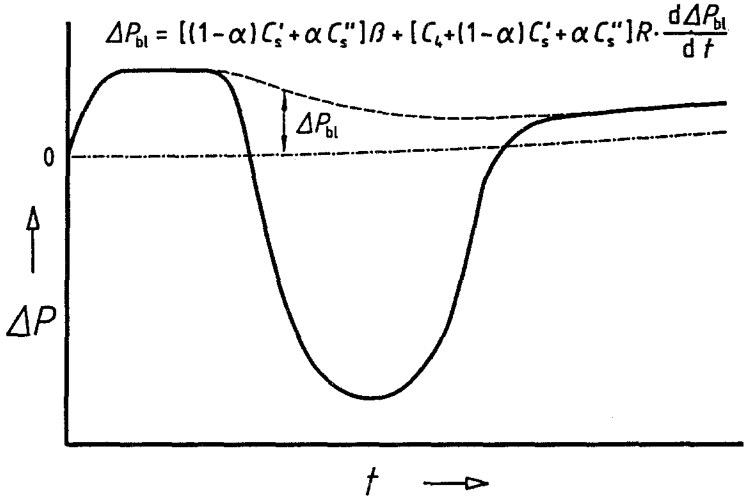


Fig. 5 Shape of the baseline for transitions with the heat capacity change proportional to the degree of conversion. ΔP_{bl} equation of the initial, interpolated and final baseline related to the zero line, ΔP measured signal, t time, α degree of conversion, C_s', C_s'' heat capacity of the low and high temperature phase, resp., β heating rate, C_4 heat capacity of sample container, R heat resistance between sample and sample-temperature sensor

5. Baseline construction, calorimeter model and peak analysis

The methods for the construction of the baseline, which are used in practice, can be divided into 3 groups:

1) Formal methods without physico-chemical justification

2) Methods where physico-chemical assumptions on the change of the heat capacity during transition are made (cf. 4)

3) Experimental methods

In the following it will be shown analytically and experimentally what systematic errors may occur in the peak integration (enthalpy determination) with differently constructed baselines.

The melting of ice is used as an experimental example. A theoretical DSC curve is constructed as the 'true' measured curve using a model DSC (cf. 5.1). The various methods of baseline construction taken from the literature are analytically and numerically applied to this curve to determine the resulting systematic measurement error. For this purpose a simple model of the calorimeter used must be developed.

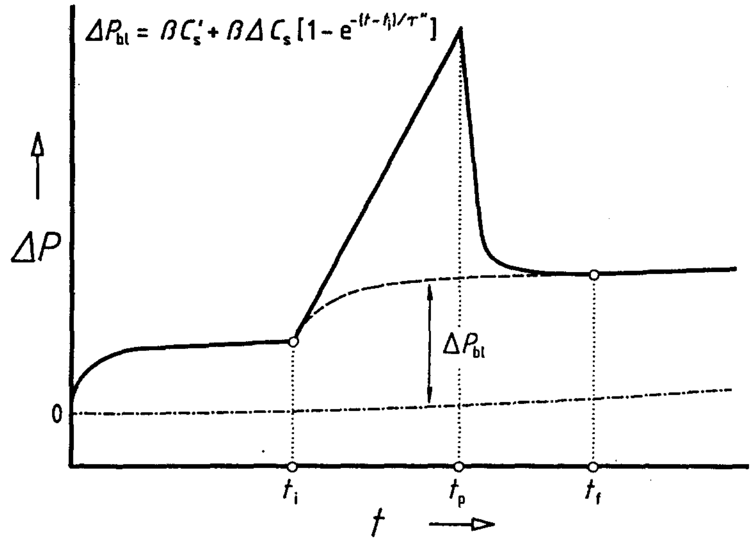


Fig. 6 Shape of the baseline for first-order phase transition.s ΔP_{bl} equation for the interpolated baseline related to the zero line, ΔP measured signal, t time, t_i peak start, t_p peak extremum, t_f peak end, C_s', C_s'' heat capacity of the low and high temperature phase of the sample, resp., β heating rate, $\Delta C_s = C_s'' - C'_{s'}$, τ'' time constant of the measuring system for $C_s = C_s''$

5.1 Calorimeter model

The model is to describe in simple terms the essential properties of the calorimeter used, a power compensation DSC.

The surroundings of the calorimeter (Fig. 7) is at constant temperature T_0 and contains sample and reference sample measuring system. These systems (1 and 2) comprise the heat capacity C, the temperature sensor to measure the temperature T, the heating element with the electrical power P and the sample support. The containers for sample and reference sample with heat capacities C_3 and C_4 ($C_3 = C_4 \equiv C$) and at temperatures T_3 and T_4 are connected to these supports via the heat resistances R_1 and R_2 ($R_1 = R_2 \equiv R$). The sample container accommodates the sample with heat capacity C_s, enthalpy production $\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)$ and temperature T_s. There should be no heat resistance between sample and container, therefore the container is always at sample temperature. The heating powers P are controlled in such a way that the temperature sensors undergo a linear temperature change.

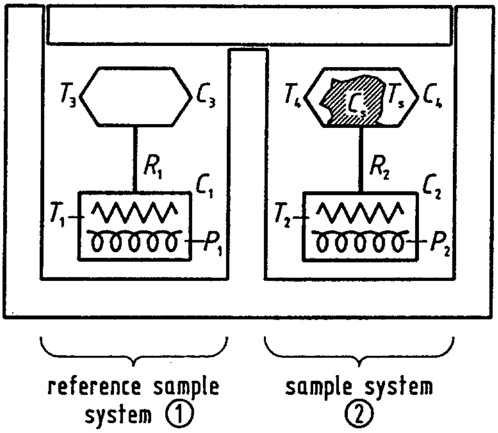


Fig. 7 Model of a power compensation differential scanning calorimeter (for explanations cf. text)

The measured signal of the calorimeter is the temperature difference T_2–T_1 which corresponds to a difference in heating power P_2–$P_1 = \Delta P$. With the reference sample container empty, this difference is [1]:

$$\Delta P = \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) + C_s\beta - (C_4 + C_s)R\,\frac{\mathrm{d}\,\Delta P}{\mathrm{d}t} \tag{10}$$

the product $(C_4 + C_s)R$ being interpreted as the time constant τ of the measuring system with sample.

Thus the measuring system is described by a simple differential equation. It depends on the enthalpy production of the sample, its heat capacity, the heating rate and the change of the measured signal multiplied by the time constant of the system. The time constant consists of the product of the heat capacities of sample and container and the heat resistance between heating element and container.

(Under steady-state conditions, ΔP = constant, the influences of the two containers compensate each other ($C_3 = C_4$); therefore only $C_s\beta$ appears in Eq. (10). The non-steady-state conditions during a transition in the sample affect only the sample and its container (C_s and C_4); therefore the sum ($C_4 + C_s$) appears in the term of Eq. (10) which describes the influence of the non-steady-state.)

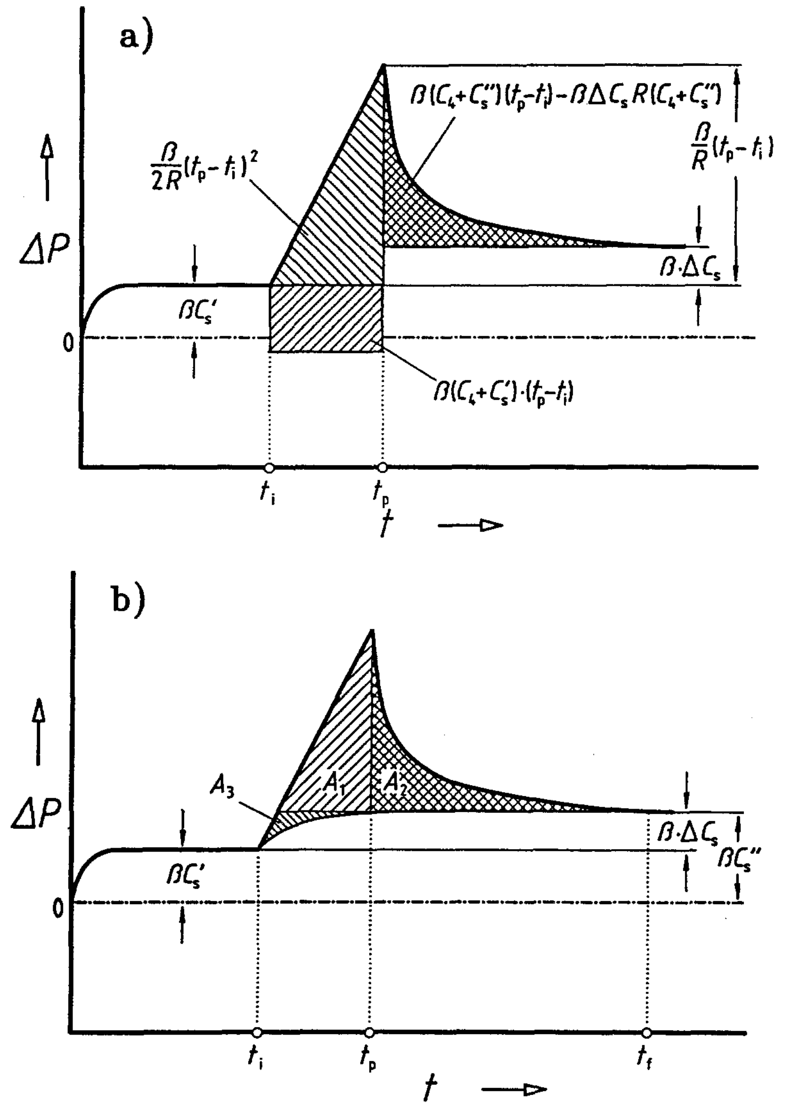


Fig. 8 Analysis of a peak of a first-order phase transition, a) partial areas b) partial areas obtained by using an exponential function as interpolated baseline
ΔP measured signal, t time, t_i peak start, t_p peak extremum, A partial areas, β heating rate, C_s', C_s'' heat capacity of the low- and high temperature phase of the sample, resp., $\Delta C_s = C_s'' - C_s'$, C_4 heat capacity of the sample container, R heat resistance between sample and sample-temperature sensor

The dependence described in Eq. (10) is analogously valid for heat flux-DSC's where the difference between the heating powers, ΔP, is to be replaced by the quotient of temperature difference and heat resistance, $\Delta T/R$ [2].

5.2 Peak analysis

Using Eq. (10) which is valid for the model described above, the following equations are formally obtained for the shape of the $\Delta P(t)$ curve for first-order phase transitions including a change in the heat capacity (cf. Fig. 8).

Integration of the differential equation (10) yields the shape of the measured curve for $t < t_i$, $T_s < T_{trs}$, $\left(\frac{dH}{dt}\right) = 0$ (cf. [5], Eq. (5)):

$$\Delta P = C_s'\beta\,(1 - e^{-t/\tau'}) \tag{11}$$

(τ' time constant for $C_s = C_s'$)

The exponential part disappears with increasing time. The shape of the initial baseline is then given by:

$$\Delta P = C_s'\beta \tag{12}$$

During transition, the temperature of the sample remains constant. Now, an expression for ΔP is needed. According to ref. [4], Eq. (8) it is for the shape of the peak for $t_i \le t \le t_p$, $T_s = T_{trs} = \text{constant}$, $\left(\frac{dH}{dt}\right) \neq 0$:

$$\Delta P = C_s'\beta + \frac{\beta}{R}(t - t_i) \tag{13}$$

From this it follows for the ascending slope of the endothermic peak:

$$\frac{d\Delta P}{dt} = \frac{\beta}{R} \tag{14}$$

After the end of the transition the peak merges exponentially into the final baseline (Eq. (10)). Again according to [4] Eq. (9) it is for $t > t_p$, $T_s > T_{trs}$, $\left(\frac{dH}{dt}\right) = 0$:

$$\Delta P = C_s''\beta + \left(\frac{\beta}{R}(t_p - t_i) - \Delta C_s\beta\right)\cdot e^{-(t - t_p)/\tau''} \qquad (15)$$

(τ'' time constant for $C_s = C_s''$)

Insertion of (13) and (14) in (10) and integration from t_i to t_p give the transition enthalpy ΔH:

$$\Delta H = \int_{t_i}^{t_p} \frac{dH}{dt}\,dt = \frac{\beta}{2R}(t_p - t_i)^2 + (C_4 + C_s')\beta(t_p - t_i) \qquad (16)$$

The time necessary for the transition, $t_p - t_i$, is calculated from (16) (cf. [5], Eq. (11)):

$$(t_p - t_i) = -R(C_4 - C_s') + \sqrt{\left[R(C_4 + C_s')\right]^2 + \frac{2R}{\beta}\Delta H} \qquad (17)$$

Eq. (16) describes a triangle and a rectangle between t_i and t_p (Fig. 8a). Since it is characteristic of the exponential function that the integral from 0 to ∞ is equal to the ordinate section, y_0, multiplied by the time constant $\left(\int_0^{\infty} y_0 e^{-t/\tau}dt = y_0\tau\right)$, the area of the rectangle $(C_4 + C_s')\beta(t_p - t_i)$ $= (C_4 + C_s'')\beta(t_p - t_i) - \Delta C_s\beta(t_p - t_i)$ (Eq. (16)) with $C_s' = C_s'' - \Delta C_s$ can be partially replaced by using the area of the exponential function (A_2) between t_p and ∞ above the extrapolated final baseline.

Figure 8b shows the peak and the equations for the partial areas considered here. The area under the exponential function (A_2) between t_p and ∞ is given by (with $y_0 = \frac{\beta}{R}(t_p - t_i) - \beta\Delta C_s$ and $\tau = R(C_4 + C_s'')$):

$$A_2 = (C_4 + C_s'')\beta(t_p - t_i) - \beta\Delta C_s R(C_4 + C_s'') \qquad (18)$$

The second term of this equation is contained in A_3, the area between the baseline (an exponential function, cf. 4.4 and Fig. 6), the extrapolated final baseline and the ascending slope of the peak:

$$A_3 = \beta\Delta C_s R(C_4 + C_s'') - \frac{1}{2}\beta R\Delta C_s^2 \qquad (19)$$

The area A_1 is:

$$A_1 = \frac{\beta}{2R}(t_p - t_i)^2 - \beta\Delta C_s(t_p - t_i) + \frac{1}{2}\beta R\Delta C_s^2 \tag{20}$$

which contains the second term of the rectangle area $\Delta C_s\,\beta(t_p - t_i)$.

The transition enthalpy according to Eq. (16) is now given by the sum of the partial areas,

$$\Delta H = A_1 + A_2 + A_3 = \frac{\beta}{2R}(t_p - t_i)^2 - \beta\Delta C_s(t_p - t_i) + \beta(C_4 + C_s'')(t_p - t_i) \tag{21}$$

as the sum of the area between measured curve (peak) and extrapolated final baseline plus the area between ascending slope of the peak, extrapolated final baseline and an exponential function which would describe the curve if no heat of transition had been released, i.e. the interpolated baseline.

So, finally the peak analysis showed that ΔH is indeed represented by the 'peak area'.

Analysis of the melting peak of ice

The melting of ice was measured by means of a power compensation DSC (DSC-2C, Perkin-Elmer Corp., Norwalk, CT, USA). The experimental parameters and results are listed in Table 1.

Figure 9 shows the experimental melting peak together with the curve calculated on the basis of the parameters of Table 1 and Eq. (11) (first part of measured curve and initial baseline, $t < t_i$), Eq. (13) (ascending slope of the peak, $t_i < t < t_p$), Eq. (15) (descending slope of the peak and final baseline, $t > t_p$) and Eq. (17) (duration of the ascending slope of the peak). The deviations between experimental and theoretical curve show that the model describes the reality only approximately. However, this model is a sufficient good compromise for the intended purpose, i. e. the analytical description of a measured curve. (The analysis of more complex calorimeter models requires mathematical approximations [13] or numerical procedures [20]).

This calculated, analytically representable (curve 'synthetic measured curve') is used in 6.1 to determine the relative errors of the peak areas due to the use of different baselines which avoids the difficulties that would arise by using an actually measured curve with no simple mathematical description. An exponential function with $\tau = 5.4$ s (cf. Table 1) is used as the'true' baseline (cf. 5.2).

Table 1 Melting of ice (experimental parameters and results)

Sample mass	m	= 4.650	mg	
Heating rate	β	= 5	$K\cdot min^{-1}$	
Enthalpy of fusion [15]	$\Delta fusH$	= 6.007	$kJ\cdot mol^{-1}$	($\Delta fusH = 1.55$ J)
Heat capacity of ice (0°C) [16]	C_p'	= 37.9	$J\cdot K^{-1}\cdot mol^{-1}$($C_s$'= $9.8\cdot10^{-3}$ $J\cdot K^{-1}$)	
Heat capacity of water (0°C) [17]	C_p''	= 76.0	$J\cdot K^{-1}\cdot mol^{-1}$($C_s$''= $19.6\cdot10^{-3}$ $J\cdot K^{-1}$)	
Heat capacity change	ΔC_p	= 38.1	$J\cdot K^{-1}\cdot mol^{-1}$($\Delta C_s = 9.8\cdot10^{-3}$ $J\cdot K^{-1}$)	
Heat resistance	R	= 100	$K\cdot W^{-1}$	(meas. acc. to Eq. (14))
Tine constant	τ	= 5.4	s	(meas. acc. to Eq. (15))
Duration of the peak	$t_f - t_i$	= 106	s	
Heat capacity of the container	C_4	= $34.4\cdot10^{-3}$	$J\cdot K^{-1}$	(calc.)
Duration of melting	$t_p - t_i$	= 56.8	s	(calc.)
Partial areas:	$\frac{\beta}{2R}(t_p - t_i)^2$	= 1.34	J	
	$\beta(C_4 + C_s'')(t_p - t_i)$	0.26	J	
	$\beta\,\Delta C_s R(C_4 + C_s'')$	$4.4\cdot10^{-3}$	J	
	$\beta\Delta C_s(t_p - t_i)$	= $4.6\cdot10^{-2}$	J	
	$\frac{1}{2}\beta R\Delta C_s^2$	= $4.0\cdot10^{-4}$	J	

6. Determination of the relative errors

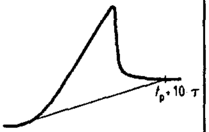
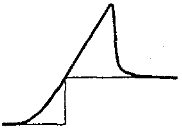
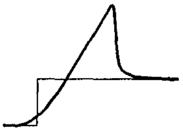
Relative errors can in principle be determined only for the formal methods (6.1). For the other methods, only estimates or influencing factors can be given.

6.1 Formal methods

The table below (Table 2) shows the relative errors which result when various formal methods of baseline construction are applied analytically to the calculated curve (rel. error (analyt.)) and numerically to the experimental curve (rel. error (num.)).

It is assumed that the true baseline can be represented by an exponential function (cf. 4.4 and Fig. 6) which is the correct baseline for the melting of ice. For comparison, the error is also given which is due to the use of a

Table 2 Relative error of the enthalpy of the melting of ice due to different baseline constructions (relative to an exponential function taken as the 'true' baseline)

Method	Representation	rel. error (analyt.)	rel. error (num.)
a) e-function ('true' baseline) [2,3]		$= \dfrac{\Delta H_{exp} - \Delta H_{true}}{\Delta H_{true}} = 0$	0
b) straight line [10]		$\approx \dfrac{\beta \Delta C_s}{\Delta H}\left[\sqrt{\dfrac{R \Delta H}{2\beta}} + 4\tau\right] = 0.027$	0.008
c) step [8]		$\approx \Delta C_s \sqrt{\dfrac{2\beta R}{\Delta H}} = 0.032$	0.020
d) polygon [9]		$\approx \Delta C_s \sqrt{\dfrac{\beta R}{2\Delta H}} = 0.016$	0.016
e) intersection		$\approx -\Delta C_s \beta \dfrac{\tau}{\Delta H} = -0.003$	−0.012
f) intersection + triangle [8]		$\approx -\Delta C_s \beta \dfrac{\tau}{\Delta H} = -0.003$	−0.007
g) parabola [1]		$\approx \Delta C_s \sqrt{\dfrac{8\beta R}{9\Delta H}} = 0.021$	0.003
h) 'thermodynamic' [6]		$\approx -\Delta C_s \beta \dfrac{\tau}{\Delta H} = -0.003$	−0.002
i) proportional to degree of conversion [7]			0.016

baseline proportional to the degree of conversion (method i) (in Table 2, cf. 4.3 and Fig. 5).

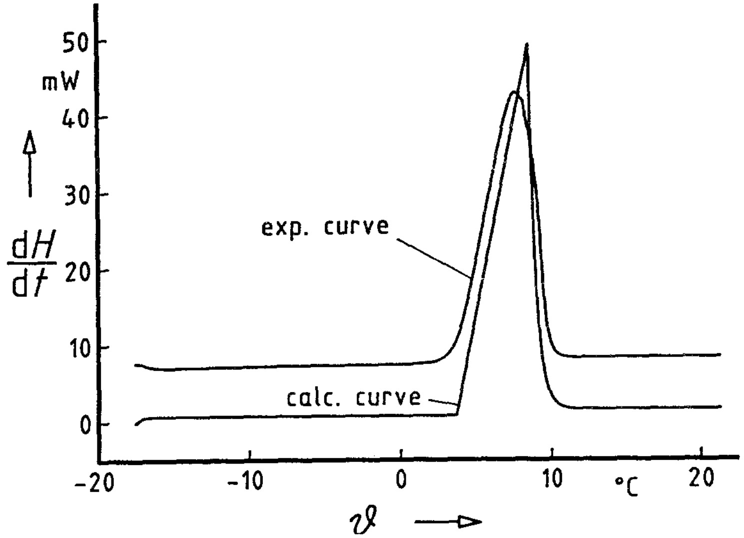


Fig. 9 Experimental and calculated melting curves of ice

The numerical values refer to the experiment on ice described in 5.3.

The identical results for the analytically determined relative errors of method e), f), and h) show that the influence of the small triangle ($\frac{1}{2}\beta R\Delta C_s^2$, cf. Table 1) on the area determination is negligible.

Table 3 shows the errors determined analytically (calculation of the peak area between 'synthetic measured curve' and baseline) and experimentally (integration of the peak area between measured curve and baseline) which result when a straight line is used as baseline instead of an exponential function (for some calibration materials).

Under the experimental conditions chosen (heating rate, sample mass), the relative error can be as high as 0.2% for these metals and is therefore within the repeatability range of the instrument used.

The discrepancies between the analytically and numerically determined relative errors can be attributed to the difficulties in the definition of the peak start and peak end as the initial and final deviation of the measured (noisy) curve from the baseline. The deviations of the experimental curve from the calculated curve, especially for the smooth transition from the initial baseline to the ascending slope of the peak instead of the assumed discontinuity, contribute to these discrepancies, too.

Table 3 Relative errors due to the use of a straight line instead of an exponential function for a few calibration materials (β =5 deg·min^{-1})

Material	ΔfusH,	ΔC_p	Ref.	*m*,	*R*,	τ,	Rel. error, %	
	kJ·mol^{-1}	J·mol-1·K^{-1}		mg	K·W^{-1}	s	analyt.	num.
Ga	5.586	2.05	[11]	5.412	101	3.07	0.087	–0.22
In	3.283	–0.33	[12]	18.788	84	3.21	–0.025	–0.02
Sn	7.195	-2.29	[13]	8.270	84	2.71	–0.071	–0.12
Bi	11.131	0.57	[14]	7.902	109	2.59	0.009	–0.13
Pb	4.772	1.21	[15]	22.402	109	2.73	0.062	–0.21
Zn	7.28	2.04	[18]	4.332	157	3.00	0.078	0.25

6.2 Experimental methods

The experimental methods for baseline interpolation are based either on repeat measurements with inert or reacted samples or on independent simultaneous measurements.

6.2.1 Measurement with inert sample

A repeated measurement with an inert sample whose $C_p(T)$ curve is as similar as possible to that of the sample can provide information on the (approximate) shape of the interpolated baseline. Influences due to the temperature dependence of the instrument's heat resistances and heat capacities are corrected by subtracting this measured reference curve from the measured curve.

As a result, the definition of peak start and peak end becomes easier, too.

In some cases it is more favourable to use the irreversibly reacted measurement sample as inert sample, e. g. for the measurement of the 'stored energy', i. e. the annealing of lattice defects of plastically deformed metals by means of DSC.

Samples with supercoolable transition offer another possibility. For example, after melting, high-purity materials can be supercooled as melts below the melting temperature so that they can serve as an 'inert sample' in the repeat measurement (with a small difference in C_p compared with the solid material, cf. Table 3).

The uncertainty due to the repeatability of the initial and final baselines contributes to the total uncertainty of the baseline construction. This uncertainty amounts to approximately ±20 μW for the instrument used [10]. In the experiment under consideration, this may in the worst case result in a relative error of $\pm 1 \cdot 10^{-3}$.

6.2.2 Measurement with reacted sample

When the C_p change of irreversible or supercoolable transitions is not due to the transition but to other effects (e. g. lambda transition, glass transition), the baseline may be constructed with the reacted sample. The uncertainty of this method depends on the factors mentioned in 6.2.1.

6.2.3 Use of the results of simultaneous measurements

The interpolated baseline may be constructed on the basis of the initial and final baselines when the function of the degree of conversion in reactions with continuous change of the heat capacity is known from other measurements (e. g. for reactions with a change in mass when a simultaneous TG/DSC is used, by optical (simultaneous TOA/DSC) or other (e. g. spectroscopic) experiments). In this case the interpolated baseline is a representation of the function of the degree of conversion $\alpha(t)$ between the initial baseline ($\alpha(t_i) = 0$) and the final baseline ($\alpha(t_f) = 1$).

The uncertainty of this method is determined by the uncertainty of the techniques simultaneously used. It should be borne in mind that optical or spectroscopic methods furnish information only about a selected region of the sample whereas the DSC signal is a volume-integrated signal.

6.3 Numerical methods

The numerical methods are based on strict assumptions on the change of the heat capacity during transition. In general, these assumptions are only insufficiently met during experiments, which is the reason why the uncertainty is essentially given by the deviation from the assumed ideal behaviour.

6.3.1 Method applied when the function of the degree of conversion is known

When the function of the degree of conversion is known from theoretical considerations (e. g. chemical reactions, eutectic melting, first-order phase transition of a pure substance etc.) the baseline under the peak can be calculated from the heat capacities of the low and high temperature phases of the sample, which are known from the shape of the initial ($\Delta P_{bl} = C_s' \beta$) and final baseline ($\Delta P_{\mathrm{bl}} = C_{\mathrm{s}}''\beta$). According to 4.3, Eq. (8) the baseline (related to the zero line) is:

$$\Delta P_{\mathrm{bl}}(t) = C_{\mathrm{s}}(t)\beta = (1-\alpha)\,C_{\mathrm{s}}'\beta + \alpha\cdot C_{\mathrm{s}}''\beta \tag{22}$$

6.3.2 Iterative method applied when the function of the degree of conversion is unknown

The baseline must be calculated iteratively when the function of the degree of conversion is neither known from theoretical considerations (6.3.1) nor from experiments (6.2.3). For this purpose, first a straight line is assumed as baseline and with it a function for the degree of conversion is calculated which enters into the iteration as a second approximation. This procedure is repeated until the baseline no longer changes; experience has shown that this is the case after 3 to 5 iterations [21].

However, this method is suitable only if the change of the heat capacity is really a function of the degree of conversion; for example, it is not applicable to the melting of a pure substance.

7. Uncertainty of the baseline construction

Even if the baseline can be constructed on the basis of a known function of the degree of conversion, its shape is still affected by uncertainties. It follows from the analysis of the calorimeter model that apart from changes in the sample's heat capacity a change of the thermal coupling of the sample to the temperature sensor due to altered heat transfer characteristics influences the shape of the baseline. In particular during the solid/liquid transition, the heat resistance between sample and container changes drastically which is the reason why the determination of the baseline is affected by a corresponding uncertainty. A change in the radiation characteristics (emissivity) of the sample influences the baseline in principle in the same way. For the overall uncertainty of the baseline in the region of the peak the experimentally determined repeatability of the initial and final baselines must also be taken into account.

In thermally activated chemical reactions, even at low temperature, the reaction rate and therefore the enthalpy production are in principle not equal to zero. The initial baseline therefore merges slowly into the peak, which results in the determination of the initial baseline as well as t_{i} being affected by an uncertainty. In practice, there is an additional problem that in the final region of the measured curve a decomposition reaction may be superimposed on the baseline.

Another problem not dealt with here is bent initial and final baselines, which reflect the temperature dependence of the heat capacities and heat transfer characteristics of measuring system and sample. In these cases linear extrapolation of the initial and final baselines is not applicable, but an extrapolation commensurate with their respective shape must be made (polynomial representation for initial and final baselines (cf. 4.2 and 6.3.1)).

8. Instrument and experimental parameters and their effects

The preceeding chapters show clearly that during a transition the baseline shift ($\beta\Delta C_S$, cf. Fig. 8) depends on instrument and experimental parameters and may thus be influenced, i. e. minimized, by the operator.

From Eqs (12) and (15) it follows for the ΔC_S – signal $\Delta P_{\Delta C_s}$:

$$\Delta P_{\Delta C_s} = \beta\Delta C_S, \tag{23}$$

i. e.

$$\Delta P_{\Delta C_s} \propto \begin{cases}\beta\\ m\end{cases}$$

The peak height ΔP_{t_p} (height of the triangle A_1 in Fig. 8b) is given by Eq. (13) with (17):

$$\Delta P_{t_p} = C_S'\beta + \frac{\beta}{R}(t_p - t_i) \simeq \sqrt{\frac{2\beta\Delta H}{R}} \tag{24}$$

i. e.

$$\Delta P_{t_p} \propto \begin{cases}\sqrt{\beta}\\ \sqrt{1/R}\\ \sqrt{m}\end{cases}$$

For the relation of peak height, Eq. (24), to baseline shift, Eq. (23), it follows:

$$\frac{\Delta P_{t_p}}{\Delta P_{\Delta C_s}} \propto \begin{cases} \sqrt{1/\beta} \\ \sqrt{1/R} \\ \sqrt{1/m} \end{cases}$$

To maximize the relation between peak height and baseline shift it is favourable to choose a low heating rate β and a small sample mass m. The heat resistance R should be as small as possible. To keep the time constant of the instrument small, the heat capacity of the container and its support should be small.

These conditions also lead to a better repeatability of the initial and final baselines.

9. Conclusions

The construction of a straight line between peak start, t_i, and peak end, t_f, as the baseline is the simplest method and recommended in all that cases where no additional information about the transition is known. For the examples presented here the deviation relative to the correct baseline lies within the repeatability range of the DSC's (± 0.5%). Therefore this method is to recommend in general even for enthalpy determinations of first-order transitions because the total uncertainty of the enthalpy determination amounts generally to two to four times the repeatability. Although a straight line as the baseline is sufficient for the determination of transition enthalpies, for other purposes (e. g. determination of the degree of conversion by means of partial peak integration) it is recommendable to use the correct baseline (exponential function as the baseline for first-order transitions) because otherwise especially at the beginning of the peak uncorrect values for the enthalpy production of the sample may result.

Should a desmearing (deconvolution) procedure be necessary for the reaction under consideration (cf. [10]) the measured curve is to desmear before the construction of the desmeared baseline is performed.

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Zusammenfassung — In Differential-Scanning Kalorimetern wird die Gestalt der interpolierten Basislinie unter dem Peak durch eine Änderung der Wärmekapazität der Probe und die Wärmetransportcharakteristik zwischen Probe und Temperaturfühler bestimmt. Die interpolierte Basislinie wird nach formellen Kriterien konstruiert, experimentell oder analytisch auf der Grundlage von physikalisch-chemischen Annahmen für die Änderung der Wärmekapazität während des Überganges. Anhand des Beispieles schmelzendes Eis zeigt vorliegende Arbeit auf der Grundlage eines einfachen Kalorimetermodelles und einer synthetischen Meßkurve analytisch sowie experimentell, daß die Ungenauigkeit der Enthalpiebestimmung unter anderem von der Art der Basislinie abhängt und daß ihr Wert in die Größenordnung der Reproduzierbarkeit von Differential-Scanning Kalorimetern liegt (0.5%).