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EFFECT OF THE INTERNAL THERMAL RESISTANCE OF THE SAMPLE HOLDER ON THE ACCURACY OF DIFFERENTIAL THERMAL ANALYSIS

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With the aims of accounting for the effects of the internal thermal resistance of the sample holder on the parameters of recorded DTA curves, and of estimating the difference between the instrument with a thermally insulated sample holder and the gradientless model, a novel two-point method of differential thermal analysis has been developed. Its essence is that two thermoanalytical curves are recorded simultaneously, with the differential thermocouple at central and side positions relative to the sample. The theory of the method has been elaborated, and formulae are derived which allow quantitative estimation of the thermal resistance of the sample holder, depending on the manner of packing and on the state of the sample in the holder, and which also indicate the optimum manner of packing. If the packing is not dense and not uniform, the thermal resistance of the holder increases and the accuracy of instrument calibration at the tail-end of the differential curve decreases by 10–20%. Through introduction of a correction term into the formula, this effect can be eliminated. A basic formula is given for DTA calculation in the general case of a sample holder with non-zero internal thermal resistance.

In a previous paper [1], a sample holder was described consisting of a thin-walled metal vessel suspended on the sufficiently long and thin wires of a differential thermocouple into the cavity of the heater. Replacing the supports of the sample holder by suspension on wires of low mass and high thermal resistance resulted in the practical elimination of the effect of the support on the sample holder, and sharply increased the isothermalness of its surface, this being the first step towards gradientless solid-state calorimetry. However, this measure did not eliminate the temperature gradients in the interior of the holder containing the sample and in particular the different heating rates in its individual parts, leading to the following consequences: 1. the parameters of the DTA curves depend on the location of the hot junction of the thermocouple in the interior of the holder; 2. the exponential part (the tail-end) of the DTA curve loses its strictly exponential character, thereby lowering the accuracy of calibration by the method described in [1]; 3. calculation of the reaction kinetics via the formula derived in [2] for the gradientless sample holder will be incorrect, as a consequence of non-conformity between the measured values and the mean (effective) values corresponding to the gradientless holder.

In the literature, one of the above aspects of the theory and practice of gradient calorimetry has been studied: the dependence of the peak area and shape on the position of the thermocouple in the crucible [3, 4]. In this paper, an attempt is made to give a generalized concept of the problem of the volume (residual) gradient for an insulated sample holder with an isothermal shell.

This task cannot be solved within the scope of methods in which the temperature of the sample is measured at one point (DTA) or on its surface (DSC). A two-point DTA method has therefore been developed, involving the simultaneous recording of two differential curves, one with the differential thermocouple positioned in the centre of the holder, and the other with the differential thermocouple positioned on its external surface. The thermocouples are connected alternately for short periods (some seconds) to the reference thermocouple positioned on the wall of the heater. The two differential curves recorded will thus be separated by an interval corresponding to the temperature gradient on the internal thermal resistance of the sample holder.

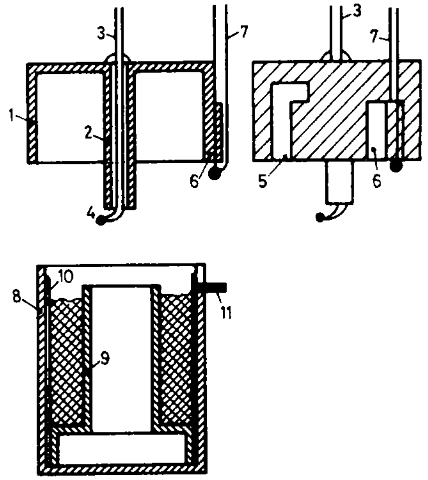

Fig. 1 Diagrammatical representation of the sample holder

The sample holder used in this work is shown diagrammatically in Fig. 1. It consists of the suspension device *1* fitted with a central hollow shaft *2*, into which the end of the thermocouple *3* is cemented so as to allow the hot junction *4* to protrude from the hollow shaft. The device has an inverted L-shaped groove *5* and a groove *6* with a flanged end clamping the end of the thermocouple *7*. Before the sample is introduced, the insert *9* and the shielding aluminium foil *10* are placed in the crucible *8*; this yields a cylindrical clearance for the sample and a channel for the end of the thermocouple *3*. The sample is then introduced and the crucible is attached to the suspension device so that the tongue *11* fits into the groove *5*. By turning, the crucible is secured to the suspension device. The wall thickness of both the silver crucible and the suspension device is 0.2 mm; the crucible is 4.0 mm in diameter, and 8 mm in height.

For its mathematical description, this sample holder can be approximated by a model in which an external isothermal shell of heat capacity C_2 is separated from the sample of heat capacity C_1 by a heat barrier of thermal resistance R_1 (thermal conductivity K_1). The isothermal shell is separated from the heater by a heat barrier (the working space of the cell) of thermal resistance R_2 (thermal conductivity K_2).

The area and shape of the peak in the DTA curve are functions of two factors: the heating rate of that part of the sample holder where the hot junction of the differential thermocouple is located, and the period of the reaction. The first factor controls the slopes of the initial and final parts of the curve and consequently acts on the height and shape of the peak, while the second factor controls the height and width of the peak. For any point of the differential curve and for any type of instrument, the most general equations of DTA may be applied:

$$\Delta T = T_1 - T_2 \tag{1}$$

$$\frac{\mathrm{d}\Delta T}{\mathrm{d}t} = \varphi_1 - \varphi_2 \tag{2}$$

where ΔT is the temperature difference, equal in the DTA curve to the distance between the differential curve and the zero line ($\Delta T = 0$); T_1 and T_2 are the temperatures of the hot junctions of the differential thermocouple and the reference thermocouple, respectively; $\mathrm{d}\Delta T/\mathrm{d}t$ is the slope of the tangent to the differential curve at the current point; and φ_1 and φ_2 are the rates of temperature rise in the hot junctions of the differential and the reference thermocouple, respectively.

When linear temperature increase is established, i.e. at $\varphi_0 = \text{const.}$, $\Delta T = -\tau_1\varphi_1$ ($\Delta T = -\tau_1\varphi_0$ if $\tau_1 = \text{const.}$) for DTA without reference material, and $\Delta T = \varphi_2\tau_2 - \varphi_1\tau_1$ ($\Delta T = \varphi_0\tau_2 - \varphi_0\tau_1$ if $\tau_1 = \text{const.}$, $\tau_2 = \text{const.}$) for DTA with reference material [5]. In the present case, at $\tau_1 = \text{const.}$,

$$\Delta T = -\tau_1\varphi_0 + \Delta T_r \tag{1a}$$

$$\frac{\mathrm{d}\Delta T}{\mathrm{d}t} = \varphi_1 - \varphi_0 \tag{2a}$$

where the temperature difference during the reaction is represented by the sum of a constant term $\tau_1\varphi_0$, equal to the initial temperature jump at the thermal barrier of the cell, and a variable term ΔT_r, equal to the incremental temperature caused by the reaction. According to Eq. (2a), the slope of the initial portion of the peak increases with decreasing φ_1 (for endothermic reactions) and becomes equal to the heating rate of the block for isothermal reactions ($\varphi_1 = 0$).

Accepting the above model of the sample holder, let us write the heat balance equation for the sample, assuming the absence of a temperature gradient within the sample itself:

$$C_1\frac{\mathrm{d}T_1}{\mathrm{d}t} + \frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_1(T_2 - T_1) \tag{3}$$

where ΔH is the current heat of reaction; dT_1/dt is the rate of temperature change in the sample during the reaction; and $(T_2 - T_1)$ is the temperature difference between the shell of the crucible and the sample.

In a linear heating regime and with non-changing time constants of the sample and the holder, the temperatures of the sample, the shell and the wall of the heater may be written in the following form:

$$T_1 = \varphi t + \Delta T_1 \tag{4}$$

$$T_2 = \varphi t + \tau_1\varphi + \Delta T_2 \tag{5}$$

$$T_3 = \varphi t + \tau_1\varphi + \tau_2\varphi \tag{6}$$

where $\tau_1 = C_1/K_1$ and $\tau_2 = (C_1 + C_2)/K_2$; ΔT_1 is the incremental temperature at the internal thermal barrier of the sample holder, equal to the height of the DTA peak recorded with the centrally positioned thermocouple; and ΔT_2 is the incremental temperature at the external thermal barrier, equal to the height of the peak recorded with the laterally positioned thermocouple.

By substituting Eqs (4)–(6) into Eq. (3), one obtains, after the necessary transformations,

$$-\frac{d\Delta H}{dt} = K_1(\Delta T_1 - \Delta T_2) + C_1\frac{d\Delta T_1}{dt} \tag{7}$$

and in the integral form for infinite integration limits

$$-\Delta H_t = K_1(A_{1t} - A_{2t}) \tag{8}$$

where ΔH_t is the total heat of reaction; and A_{1t} and A_{2t} are the total areas of the DTA peaks recorded with centrally and laterally positioned thermocouples, respectively.

Equations (7) and (8) allow determination of the rate of heat absorption and the heat of reaction, if the internal thermal resistance of the sample holder and the heat capacity of the sample are known. Two peaks, A_{1t} and A_{2t}, however, must necessarily be recorded.

Let us now write the heat balance equation for the isothermal shell of the sample holder:

$$\frac{C_2 dT_2}{dt} = K_2(T_3 - T_2) - K_1(T_2 - T_1) \tag{9}$$

By introducing Eqs (3), (5) and (6) into Eq. (9), one obtains

$$-\frac{d\Delta H}{dt} = K_2\Delta T_2 + C_2\frac{d\Delta T_2}{dt} + C_1\frac{d\Delta T_1}{dt} \tag{10}$$

This formula differs from the common formula for gradientless sample holders

$$-\frac{d\Delta H}{dt} = K\Delta T + C\frac{d\Delta T}{dt} \tag{11}$$

by the presence of the additional term $C_1(\mathrm{d}\Delta T_1/\mathrm{d}t)$. Equation (10) is transformed into Eq. (11) at $K_1 \to \infty$, since then $\Delta T_1 = \Delta T_2$ and $A_{1t} = A_{2t}$, and $C = C_1 + C_2$ (cf. Eqs (7) and (8)). Integration of Eq. (10) yields

$$-\Delta H_t = K_2 A_{2t} \tag{12}$$

Equation (10) demonstrates that kinetic calculations using the common formula (11) may involve substantial errors in cases when the internal thermal resistance of the sample holder differs from zero. On the other hand, the integral forms of Eqs (10) and (11) do not differ; in other words, the internal thermal resistance of the sample holder does not affect the accuracy of the total heat of reaction determination if the DTA peak is recorded with the differential thermocouple located on the external surface of the sample holder. The derivation of Eq. (12) may be considered mathematical proof of the principle of Boersma [6], which is the basis of quantitative DTA. Since Eq. (12) was obtained on the assumption of an isothermal surface of the sample holder, it may be stated that the principle of Boersma (shifting the thermocouple to the surface of the sample holder) follows, in fact, from the more general postulate for isothermalness of the holder surface, which is fundamental in quantitative DTA. If the surface of the holder is non-isothermal, i.e. its various parts are heated at different rates during the reaction, the parameters of the DTA peak will begin to depend on the position of the thermocouple on the surface of the holder, and quantitative DTA will become impossible (the Boersma principle will prove insufficient).

The above model of the sample holder and the theory based on it are approximations only, as in reality no sharp boundary exists between the reacting part of the sample and the crucible with a constant value of K_1; also, C_1 may change in the course of the reaction. This circumstance may be accounted for to a certain extent by replacing the heat capacity values C_1 and C_2 in Eqs (7) and (10) by effective (apparent) values; in the following a method is suggested for how to find them. (It is also a more exact variant of the calibration method of the instrument described in [1].)

For any point on the differential curve situated after the end-point of the reaction, the following equation, obtained from Eq. (10) at $\mathrm{d}\Delta H/\mathrm{d}t = 0$, holds:

$$K_2 = -\frac{C_1 \dfrac{\mathrm{d}\Delta T_1}{\mathrm{d}t} + C_2 \dfrac{\mathrm{d}\Delta T_2}{\mathrm{d}t}}{\Delta T_2} \tag{13}$$

and in its integral form

$$K_2 = \frac{C_1 \Delta T_1 + C_2 \Delta T_2}{A_2} \tag{14}$$

where A_2 is the area delineated by the height ΔT_2, the differential curve and the base line.

Analogously, from Eq. (7):

$$K_1 = \frac{-C_1 \dfrac{\mathrm{d}\Delta T_1}{\mathrm{d}t}}{\Delta T_1 - \Delta T_2} \tag{15}$$

and

$$K_1 = \frac{C_1 \Delta T_1}{A_1 - A_2} \tag{16}$$

The solution of Eqs (8) and (12) together gives

$$K_1 = \frac{K_2 A_{2t}}{A_{1t} - A_{2t}} \tag{17}$$

Substituting Eq. (17) into Eq. (16) leads to

$$C_1 = \frac{K_2 A_{2t}(A_1 - A_2)}{(A_{1t} - A_{2t})\Delta T_1} \tag{18}$$

Introducing C_1 into Eq. (14) and taking into account that $C = C_1 + C_2$, where C is the calculated total heat capacity of the holder and the sample:

$$K_2 = \frac{C\Delta T_2}{A_2 + B\left(\dfrac{\Delta T_2}{\Delta T_1} - 1\right)} \tag{19}$$

where

$$B = \frac{A_{2t}(A_1 - A_2)}{A_{1t} - A_{2t}}$$

For the gradientless holder, $\Delta T_1 = \Delta T_2$, and hence

$$K_2 = \frac{C\Delta T_2}{A_2} \tag{20}$$

The term $B[(\Delta T_2/\Delta T_1) - 1]$ may thus be considered a correctional term, accounting for the effect of the internal thermal resistance of the holder on the shape of the tail-end of the differential curve from which K_2 is being calculated. The sign of the correctional term is opposite to the sign of A_2: it is positive for endothermic reactions (negative A_2 values) and negative for exothermic reactions (positive A_2 values). Calculation with Eq. (19) will therefore, yield higher K_2 values than with Eq. (20).

Eliminating K_2 from Eqs (18) and (19):

$$C_1 = \frac{C\Delta T_2}{\Delta T_2 + \Delta T_1\left[\dfrac{A_2(A_{1t} - A_{2t})}{A_{2t}(A_1 - A_2)} - 1\right]} \tag{21}$$

Formula (21) gives the effective value for the heat capacity of the portion of the crucible in the range of the centrally positioned thermocouple; it may not coincide with the calculated value.

The basic calculation formula for DTA has the final form

$$-\frac{d\Delta H}{dt}=\frac{C\Delta T_2\Delta T_2'}{A_2'+B\left(\frac{\Delta T_2'}{\Delta T_1'}-1\right)}+(C-C_1)\frac{d\Delta T_2}{dt}+C_1\frac{d\Delta T_1}{dt} \tag{22}$$

where the values marked with dashes are values taken on the differential curve after the end-point of the reaction (tail-end of the curve). The C_1 value is taken from Eq. (21). Since the total heat capacity C features in Eq. (22), a separate determination of C_1 and C_2 becomes unnecessary. The absence of the instrument constant K from the equation makes calibration of the instrument by means of a reference material unnecessary, if the total heat capacity C is known.

Eliminating A_{2t} from Eqs (8) and (12):

$$A_{1t}=\Delta H_t\left(\frac{1}{K_1}+\frac{1}{K_2}\right)=\Delta H_t(R_1+R_2) \tag{23}$$

demonstrating that the area A_{1t} is larger than the area A_{2t} by ΔH_tR_1. Solving with respect to ΔH_t:

$$\Delta H_t=\frac{K_1K_2}{(K_1+K_2)}A_{1t}=\frac{A_{1t}}{R_1+R_2} \tag{24}$$

Equation (24) indicates that to determine the heat of reaction by means of the peak area A_{1t} it is necessary to determine not one, but two instrument constants. The factor $K_1/(K_1+K_2)$ is a correctional factor whereby the effect of the internal thermal resistance of the sample holder on the peak area A_{1t} is taken into account; it decreases this value to the "correct" value, A_{2t}, since (from Eq. (17)) $A_{2t}=A_{1t}K_1/(K_1+K_2)$.

Experimental

The theoretical conclusions and the applicability of the formulae were checked by varying the internal thermal resistance of the sample holder: we varied the packing density of the sample in the holder.

Figure 2 presents thermoanalytical curves for the melting of 21.4 mg indium. The case when the sample fastened to the end of the thermocouple is in contact with the bottom of the crucible is represented by curves *1'* and *2'* and the case when the sample is not in contact with the wall of the crucible by curves *1* and *2*. A third method of packing is shown in Fig. 3: this depicts the melting and solidification of a tin sample (mass 105.4 mg) in the shape of a curved strip wrapped in the foil, symmetrically arranged around the insert and loosely touching the wall of the crucible. All experiments were carried out in nitrogen, at a heating rate of 7 deg min^{-1}. The

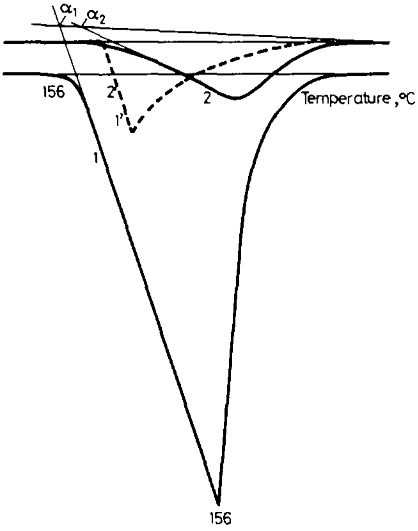

Fig. 2 DTA curves of the melting process of indium. 1 – curves recorded with the differential thermocouple positioned centrally, the sample not being in contact with the wall of the crucible, 2 – curve recorded with the differential thermocouple positioned laterally, the sample not being in contact with the wall of the crucible, 1 ', 2' – curves recorded with the differential thermocouple positioned centrally and laterally, respectively, the sample being in contact with the wall of the crucible

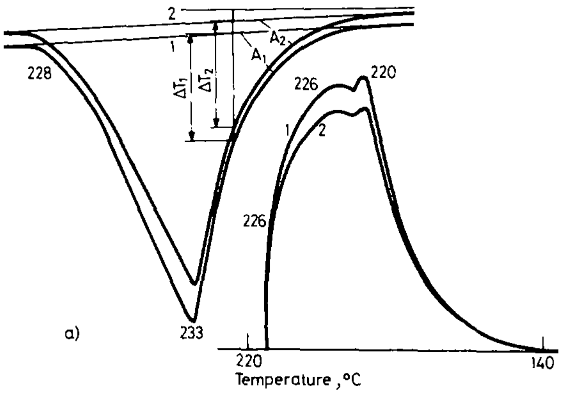

Fig. 3 DTA curves of the melting process (a) and the solidification process (b) of tin

curves denoted by *1* correspond to the central position, and those by *2* to the lateral position of the thermocouple.

Figure 2 demonstrates that when the small metallic sample is in contact with the wall of the crucible, peaks *1'* and *2'* practically coincide, indicating a very low thermal resistance between the hot junctions of the central and lateral thermocouples. This resistance is sharply increased when direct contact between the sample and the crucible wall ceases; the rate of heat transfer to the sample decreases, and the melting process takes more time. Peak *2'* is transformed into peak *2*, equal in area but differing in shape. Peak *1'* is transformed into peak *1*, very much larger in area and with the slope of the descending branch equal to the heating rate φ_0 of the block; this follows from Eq. (2a) with $\varphi_1 = 0$. From the slope of peak *1* a value $\varphi_0 = 7.0$ deg min^{-1} is found; the slope of peak *2* is 1.2 deg min^{-1}, and from Eq. (2a) the heating rate of the crucible wall during melting is 5.8 deg min^{-1}. The difference in the areas of peaks *1* and *2* (at identical widths of the peaks at their bases) is explained by the different heating rates of the hot junctions of the central and lateral thermocouples.

When the sample comes into contact with the wall of the crucible, peaks *1* and *2* fuse and form the peak *1'* (*2'*); the total surface of the sample holder now assumes the temperature of the sample, and each portion of the surface is heated at the same rate as the sample itself. Direct measurements revealed a very high degree of isothermalness: the temperature differences between the upper edge of the sample holder and its lower part where the sample was located did not exceed 0.1–0.2° in the course of the melting process. As in the previous case, heat was transferred to the sample from the whole surface of the sample holder, but at a much higher rate: melting was completed in 14.7 s, whereas when the sample was not in contact with the crucible wall, melting took 94 s.

These observations can be explained by the above theory and the formulae derived from it. The unchanged areas of peaks *2'* and *2*, i.e. the non-dependence of A_{2t} on the state of the sample in the crucible, follows from Eq. (12), and the fusion of peaks *1* and *2* into peak *1'* (*2'*) follows from Eqs (8) and (23) with $R_1 \to 0$ ($K_1 \to \infty$). The difference between peaks *1* and *2* is proportional to the internal thermal resistance R_1. Figure 3 presents the case when R_1 is small, but not zero; the peaks differ only slightly in area and shape.

Quantitative estimation of K_1 and K_2 and comparison of the different methods of calculation of the thermal effects from the equations of the theory are also of interest. The required data for the calculations are obtained in the manner shown in Fig. 3a. A line perpendicular to the zero line is constructed from any point of the tail-end of the curves, and the geometrical elements A_1, A_2, ΔT_1 and ΔT_2 are measured. To increase the accuracy of the calculations, several points may be used and the mean values taken. Results of such calculations are listed in Tables 1 and 2.

Table 1 presents the constants K'_{2C}, K_{2C}, K_{2H}, K_{1C} and K_{1H} calculated via Eqs (20), (19), (12), (16) and (8) with data from the literature [7] for heat capacities (constants with subscript C) and heats of melting (constants with subscript H). Percentage standard deviations for three measurements (three points at the tail-end of the curve) are also listed.

The calculation of the constants K_{2H} from thermoanalytical curves recorded with varying masses of standard materials corresponds to the normal calibration procedure of the instrument. Its accuracy is shown by the scattering of the peak area values A_{2t} due to the inconstant thermal resistance between the hot junction of the lateral thermocouple and the wall of the sample holder. When the contact resistance increases, the peak area decreases. A constant value of this resistance is related with a systematic

Table 1 Instrument constants calculated from data of two-point DTA

Sample material and mass, mg	K'_{2C}, mW K^{-1}	σ, %	K_{2C}, mW K^{-1}	σ, %	K_{2H}, mW K^{-1}	K_{1C}, mW K^{-1}	σ, %	K_{1H}, mW K^{-1}
Phenanthrene								
6.2	5.15	5.8	5.90	2.5	6.2	9.91	2.8	10.4
39.4	5.10	5.6	5.76	7.4	5.80	35.1	3.0	35.0
Indium								
21.4	5.12	16.0	5.90	7.3	6.0	1.4	7.1	1.4
21.5	5.70	9.6	6.72	5.8	7.0	32.0	5.3	34.0
21.5	4.15	0.6	5.16	4.5	5.36	20.0	5.3	20.9
(solidification)								
92	7.0	1.6	7.90	1.3	8.0	73.6	1.2	75.0
Lead								
136.0	10.4	–	10.8	–	10.73	86.0	–	85.0
179.0	7.13	9.1	8.01	8.9	8.06	72.0	8.6	72.6
Tin								
105.4	7.74	2.8	8.38	6.5	8.17	114.0	6.1	111.0
160.0	8.26	2.4	8.60	3.5	8.02	113.0	2.6	105.0
Zinc								
56.0	11.86	5.1	14.0	3.3	13.2	32.7	3.6	30.6
74.4	12.6	–	14.3	–	14.26	104.9	–	104.7
92.0	11.6	4.3	14.0	11.4	14.10	39.0	10.2	39.4
110.4	12.9	–	14.8	–	14.43	71.8	–	70.3
110.4	15.2	–	15.8	–	15.14	142.7	–	136.2

lowering of A_{2t} and a corresponding rise in K_{2H}; this systematic error, however, does not affect the accuracy of the determinations, since it is accounted for in the calibration of the instrument.

The values of K_{2C} will also be increased for non-zero contact resistance of the lateral thermocouple (as shown by experiment, to the same degree as K_{2H}); the reason is that lower areas A_{2t} mean a more rapid approach to the base line, i.e. a shorter relaxation time of the incremental temperature, and consequently a higher value of $K_{2C} = C/\tau$ will be determined from the curve.

In the calculation method for K_{2H} the mean value of the constant (which, for the temperature in question, does not vary) is used; it is multiplied by the peak area A_{2t}, which is affected by scattering. The accuracy of the method therefore depends on the extent of scattering. In contrast, in the method utilizing the constant K_{2C}, the formula $\Delta H = K_{2C}A_{2t}$ does not involve the mean value of K_{2C}, but the value characteristic for the thermoanalytical curve in question. As mentioned earlier, the more A_{2t} is lowered,, the more K_{2C} increases, i.e. a mutual compensation of the factors in the above formula will occur, and the method appears independent of the scattering in the peak area A_{2t}. Unfortunately, this advantage is lost because of the dependence of the constant K_{2C} on the internal thermal resistance of the sample holder. With increasing R_1, the exponential form of the tail-end of the peak becomes distorted, the value τ to be determined increases, and consequently K_{2C} decreases. A comparison of K_{2C} and K_{2H} in Table 1 demonstrates that the difference between these constants at low K_1 may reach 20%. With increasing K_1 and decreasing differences between A_1 and A_2, the difference between K_{2C} and K_{2H} also decreases. For instance, for K_1 values of 86 mW K^{-1} (lead), 111 and 113 mW K^{-1} (tin) and 142.7 mW K^{-1} (zinc), the constants K_{2C} and K_{2H} coincide within experimental error (5–6%).

If the isothermalness of the sample holder is high, A_{1t} and A_{2t} differ by less than 10%; in such cases there is no reason to use Eq. (19) to calculate K_{2C}, since the accuracy of the calculations with this formula decreases considerably, owing to the closeness of the values involved. This may be seen in the examples for zinc at K_1 = = 142.7 mW K^{-1} and for tin.

Table 2 Heats of melting of reference materials, calculated from data obtained with the two-point DTA method

Material and mass, mg	$\frac{A_{2t}}{A_{1t}}$, %	$\Delta H_0 m$, J	$K'_{2C}A_{2t}$, J		$K_{2C}A_{2t}$, J		$K_{1C}(A_{1t}-A_{2t})$, J	$\frac{A_{1t}}{R_1+R_2}$
Phenanthrene								
6.2	63.0	0.63	0.53	(83.4)	0.60	(95.4)	0.60	0.60
39.4	86.0	4.00	3.52	(88.0)	3.98	(99.4)	3.97	3.97
Indium								
21.4	19.0	0.60	0.52	(85.3)	0.60	(100)	0.60	0.60
21.5	82.6	0.61	0.48	(80.0)	0.57	(95.0)	0.57	0.57
21.5	79.6	0.61	0.46	(77.4)	0.57	(95.0)	0.60	0.57
(solidification)								
92.0	90.7	2.62	2.28	(86.7)	2.60	(98.5)	2.60	2.60
Lead								
136.0	89.0	3.13	3.03	(97.0)	3.15	(100.6)	3.16	3.15
179.0	90.0	4.11	3.71	(90.5)	4.08	(99.3)	4.36	4.10
Tin								
105.4	93.2	6.27	5.96	(95.1)	6.45	(103)	6.45	6.45
160.0	93.0	9.54	9.80	(103.0)	10.20	(107)	10.2	10.2
Zinc								
56.0	70.0	6.28	5.70	(90.7)	6.66	(106)	6.66	6.66
74.4	88.0	8.34	7.33	(88.0)	8.31	(99.5)	8.31	8.31
92.0	73.5	10.32	8.40	(81.4)	10.14	(97.0)	10.15	10.14
110.4	83.0	12.34	11.0	(89.2)	12.6	(102)	12.6	12.6
110.4	90.0	12.34	12.37	(100.2)	12.9	(104.5)	12.9	12.9

Table 2 presents the results of heat of melting calculations with the formulae indicated and the constants from Table 1. The extent of isothermalness of the sample holder is estimated as the ratio $(A_{2t}/A_{1t}) \cdot 100$ (column 2); the values calculated with the formula $\Delta H_t = \Delta H_0 \cdot m$ are accepted as true values (ΔH_0 is the value from the literature, and m is the mass of the sample). The figures in parentheses (columns 4 and 5) are the ratios of the found values to the true values, in percent. It should be observed that when the isothermalness of the sample holder is below 80–90%, the application of Eq. (19) instead of Eq. (20) gives an improved accuracy, of on average 2–3%. It is of interest to note that the different methods of calculation presented in columns 5, 6 and 7 lead to identical heat of melting values, i.e. the methods are fully equivalent.

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Zusammenfassung — Zur Erklärung des Effektes des inneren thermischen Widerstandes des Probenhalters auf die Parameter der registrierten DTA-Kurven und zur Schätzung der Abweichung zwischen einem Gerät mit isoliertem Probenhalter und dem gradientenfreien Modell wurde eine neue Zweipunkt-Methode der Differentialthermoanalyse entwickelt, die im wesentlichen darauf beruht, daß zwei thermoanalytische Kurven bei in Bezug auf die Probe zentraler bzw. seitlicher Anordnung des Thermoelements gleichzeitig registriert werden. Die Theorie der Methode wurde ausgearbeitet und Gleichungen wurden abgeleitet, mit deren Hilfe der thermische Widerstand des Probenhalters in Abhängigkeit von der Art der Packung und des Zustandes der Probe im Halter quantitativ bestimmt werden kann und die ermöglichen, die optimale Packungsart zu ermitteln. Bei nicht genügend dichter und gleichmäßiger Packung steigt der thermische Widerstand des Probenhalters an und die Genauigkeit der Gerätekalibration nimmt am Schweifende der differentiellen Kurve um 10–20% ab. Durch Einführung eines Korrektionsgliedes in die Gleichung konnte dieser Effekt eliminiert werden. Eine grundlegende Gleichung für DTA-Berechnungen wurde für den allgemeinen Fall eines Probenhalters mit einem von Null abweichenden inneren thermischen Widerstands abgeleitet.

Резюме — С целью учета влияния внутреннего термического сопротивления держателя образца на параметры регистрируемых кривых ДТА и оценки степени отклонения датчика с изолированным держателем от его безградиентной модели, разработан новый двухточечный метод дифференциального термического анализа, заключающийся в одновременной записи двух термограмм, отвечающих центральному и боковому (относительно образца) размещению измерительных термопар в держателе. Развита теория метода. Полученные расчетные формулы позволяют количественно оценить термическое сопротивление держателя как функцию способа упаковки и состояния образца в держателе и найти оптимальный способ его упаковки. При неплотной и неравномерной упаковке образца возрастает термическое сопротивление держателя и падает точность калибровки прибора по хвостовой ветви дифференциальной кривой (10–20%). Введение поправочного члена в расчетную формулу позволяет устранить этот эффект. Приводится основная расчетная формула ДТА для общего случая держателя с ненулевым внутренним термическим сопротивлением.