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THE INSTRUMENT CONSTANT IN DTA. THEORY OF SENSING UNITS IN DTA INSTRUMENTS

I. State of the art

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The theory of block-type sensing units is reviewed. The two-point method of DTA is described and appropriate computation formulae are derived. The failure of the existing block-type sensing units to conform to the assumptions of the theory is demonstrated.

The instrument constant (calibration constant) is by definition the proportionality coefficient between the experimentally determined heat of reaction and the peak area under the differential curve corresponding to this reaction:

$$\Delta H_t = \Delta H_0 M = -KA_t \tag{1}$$

where ΔH_t is the total heat of reaction, J; ΔH_0 is the specific heat of reaction, J/g; M is the mass of the reactant, g; K is the calibration constant; and A_t is the total peak area under the DTA curve. The minus sign in Eq. (1) indicates that positive heats of reaction correspond to negative peak areas, i.e. in the case of an endothermic reaction the DTA curve bends downwards from the base line (towards negative temperatures). If A_t is expressed in cm^2, the dimension of K is $\mathrm{J/cm}^2$; if it is expressed in deg·*s*, the dimension of K is W/deg.

To find unknown heats of reaction by means of Eq. (1), it is necessary to determine the value of K, i.e. to calibrate the instrument. For this purpose, the following methods exist:

1. A set of standard substances with known heats of transformation are used, yielding the value of K in the studied temperature interval by means of Eq. (1).

2. Instead of a reference material, a calibrated microheater is placed in the corresponding cell of the instrument and a known current is passed through it. K is found by the formulae

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$$K = \frac{Q}{A_t} = \frac{I^2Rt}{A_t} \text{ (a)}; \quad K = \frac{C^1U^2}{2A_t} \text{ (b)} \tag{2}$$

where Q is the joulean heat evolved in the cell, I is the current intensity, R is the resistance of the microheater, and t is the period during which current passes through the heater. Formula (2b) is applied in cases when calibration is carried out by means of an electrolytic condenser with the known capacity C^1, charged from a source with voltage U. The condenser is discharged through the microheater, evolving heat equivalent to the electric energy of the condenser.

3. For instruments in which insulated sample holders are applied [1], the tail-end of the peak to the right of the end-point of the reaction (the inflexion point) is used, and K is found from the formulae

$$K = -\frac{\bar{C}\dfrac{\mathrm{d}\Delta T_n}{\mathrm{d}t}}{\Delta T_n} \text{ (a)}; \quad K = \frac{\bar{C}\Delta T_n}{A_n} \text{ (b)} \tag{3}$$

where C is the total heat capacity of the sample holder and the sample, A_n is the area of the peak confined within the height of the peak ΔT_n, the base line and the tail-end of the DTA curve, and $\frac{\mathrm{d}\Delta T_n}{\mathrm{d}t}$ is the slope of the tangent to the curve at the point with peak height ΔT_n.

4. Constant K is calculated from the known thermophysical and geometric parameters of the sample holder and the sample.

The value of constant K depends (in the general case) on many factors, such as the experimental temperature, the gas medium in the cell, the state of the sample, the geometry of the sample holder, etc. During the change from calibration conditions to experimental conditions, some of these factors may change, resulting in a change of K to an unknown extent; this major deficiency in calibration methods *1* and *2* is eliminated to a certain extent in method *3*, for in this method constant K is determined directly at the moment of the experiment, in the process of recording the thermal curve. With method *4*, the accuracy of calibration depends on the extent to which the mathematical model by which the explicit expression for constant K is derived corresponds to the true DTA instrument. The potential of method *4* has not been studied satisfactorily in the literature. An explicit expression for K has been developed only for block-type instruments [2–4] for the particular case of heat exchange by conduction, without accounting for convection and radiation. In principle, various types of DTA instruments are feasible, to each of which a particular kinetic equation and instrument constant correspond. In this paper an attempt is made to classify DTA instruments on the basis of the physical and geometric characteristics of the heat barrier and of the mathematical assumptions of the theory. The following fundamental types will be discussed below: (a) block type without a special heat barrier; (b) block type with a solid heat barrier; (c) insulated sample holder with a gas-phase heat barrier; the latter includes several sub-types resulting from differences in sample packing in the holder (Fig. 1, types I–V).

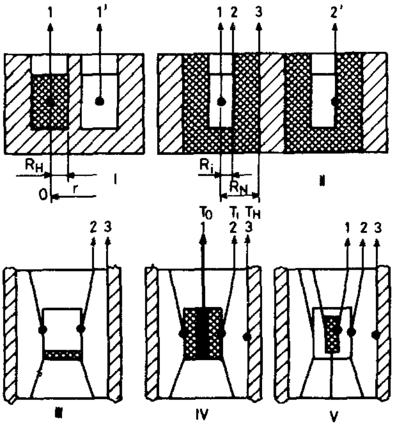

Fig. 1 Schematical representation of DTA instrument types: I – block-type without special heat barrier; II – block-type with special heat barrier; III – insulated sample holder with zero internal resistance; IV and V – insulated sample holder with non-zero internal resistance

1. Block type without special heat barrier

This type is used in traditional (qualitative) DTA. In it, the sample itself plays the part of the heat barrier on which the drop of the incremental temperature of the reaction measured in the experiment takes place. Its mathematical model is an infinite-length cylinder whose surface temperature changes in accordance with the linear heating rate, and the incremental temperature of the reaction on the surface of the cylinder is equal to zero: $(\Delta T_p)_{r=R_H} = 0$. This equality may be considered as the definition of the external limit of the heat barrier of the cell, as a surface on which the ΔT_p of the reaction is equal to zero (within experimental error); this limit may be shifted, depending on various factors, accompanied by a corresponding change in the measured value ΔT_p and a decrease in the accuracy of the method. However, if (as usual) a differential connection scheme is used for the recording of ΔT_p, and no thermal connection exists between the sample cell and the reference cell [5], the uncertainty in the position of the external limit of the heat barrier will be of no importance, since in such connection schemes of recording the total value of ΔT_p will appear.

In the case of cylindric symmetry with an isothermal surface, the heat flow will be directed along the radius vector perpendicular to the surface of the cylinder (cf. Fig. 1), independent of the angular coordinate, and dependent only on the radius r. According to the Fourier law

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = 2\pi r l_s \lambda_s \frac{\mathrm{d}T_s}{\mathrm{d}r} \tag{4}$$

where λ_s is the thermal conductivity of the sample, l_s is the height (length) of the sample, T_s is the temperature of the sample, and r is the distance from the axis of the cylinder to the current point (the surface through which the heat flow $\frac{\mathrm{d}Q}{\mathrm{d}t}$ passes). Differentiation of Eq. (4) with respect to r results in

$$\frac{\mathrm{d}^2Q}{\mathrm{d}t\,\mathrm{d}r} = \frac{2\pi l_s \lambda_s\,\mathrm{d}T_s}{\mathrm{d}r} + \frac{2\pi r l_s \lambda_s\,\mathrm{d}^2T_s}{\mathrm{d}r^2} \tag{5}$$

On the other hand,

$$\mathrm{d}Q = c\varrho\,\mathrm{d}V_s\,\mathrm{d}T_s = c\varrho 2\pi r l_s\,\mathrm{d}r\,\mathrm{d}T_s \tag{6}$$

where $\mathrm{d}V_s$ is an elementary volume with specific heat capacity c and density ϱ. Differentiation of Eq. (6) with respect to t and rearrangement yields

$$\frac{\mathrm{d}^2Q}{\mathrm{d}t\,\mathrm{d}r} = c\varrho 2\pi r l_s \frac{\mathrm{d}T_s}{\mathrm{d}t} \tag{6a}$$

Solving this equation jointly with Eq. (5) yields the differential equation of thermal conductivity for our case:

$$\frac{\mathrm{d}T_s}{\mathrm{d}t} = a\left(\frac{\mathrm{d}^2T_s}{\mathrm{d}r^2} + \frac{\mathrm{d}T_s}{r\,\mathrm{d}r}\right) \tag{7}$$

where $a = \frac{\lambda_s}{c\varrho}$ is the thermal conductivity of the sample.

As demonstrated in [3], in a steady-state heating regime, at $\varphi = \text{const}$ and $a = \text{const}$, and with the condition that $t > \frac{R_H^2}{a}$, the solution of Eq. (7) may be written in the form

$$T_s = T_H + \varphi\left(t - \frac{R_H^2 - r^2}{4a}\right) \tag{8}$$

where T_H is the temperature on the sample surface (on the heater wall), and R_H is the radius of the sample. It follows from Eq. (8) that the steady-state temperature drop over the sample is

$$(T_H - T_0)_{st} = \frac{\varphi R_H^2}{4a}$$

Differentiation of Eq. (8) with respect to r yields

$$\frac{\mathrm{d}T_s}{\mathrm{d}r} = \frac{\varphi r}{2a}; \quad \left(\frac{\mathrm{d}T_s}{\mathrm{d}r}\right)_{r=R_H} = \frac{\varphi R_H}{2a} \tag{8a}$$

The heat flow entering the sample from the wall of the block, expressed through the temperature drop in the sample, is

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = 2\pi R_H l_s \lambda_s \left(\frac{\mathrm{d}T_s}{\mathrm{d}r}\right)_{R_H} = \frac{2\pi R_H l_s \lambda_s \varphi R_H}{2a} = 4\pi l_s \lambda_s (T_H - T_0)_{st} \tag{8b}$$

This same heat flow gives rise to the temperature increase of the sample at the rate φ, and hence we may write

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \int_0^{R_H} c\varrho 2\pi r l_s \varphi \, \mathrm{d}r = c\varrho \pi l_s R_H^2 \varphi = \bar{C}_s \frac{\mathrm{d}T_H}{\mathrm{d}t} \tag{9}$$

where C_s is the heat capacity of the sample with volume $\pi R_H^2 l_s$. When the reaction starts, the temperature drop in the cylinder will decrease by the incremental temperature ΔT_p in the case of exothermic reactions, for which $\Delta H < 0$, $\Delta T_p > 0$, and increase by ΔT_p in the case of endothermic reactions, for which $\Delta H > 0$, $\Delta T_p < 0$, and the expression for heat flow will assume the form

$$\begin{aligned} \frac{\mathrm{d}Q}{\mathrm{d}t} &= 4\pi l_s \lambda_s [(T_H - T_0)_{st} - \Delta T_p] = \\ &= \bar{C}_s \frac{\mathrm{d}T_H}{\mathrm{d}t} - 4\pi l_s \lambda_s \Delta T_p \end{aligned} \tag{9a}$$

The heat flow absorbed during the time of the reaction is equal to

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}\Delta H}{\mathrm{d}t} + \bar{C}_s \frac{\mathrm{d}T_s}{\mathrm{d}t} \tag{10}$$

From Eqs (9a) and (10), the heat balance of the cell during the reaction is

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = 4\pi l_s \lambda_s \Delta T_p + \bar{C}_s \frac{\mathrm{d}(T_s - T_H)}{\mathrm{d}t} \tag{11}$$

The incremental temperature measured during the experiment is the difference between the actual temperature drop and the steady-state drop:

$$\Delta T_p = T_0 - T_H - (T_0 - T_H)_{st} \tag{12}$$

If the hot junction of the thermocouple is located at the centre of the sample, T_p will have the maximum possible value and will be defined by Eq. (12). The temperature T_s is between T_0 and T_H and is equal in the first approach to

$$T_s = \frac{T_0 + T_H}{2},$$

and consequently

$$T_s - T_H = \frac{T_0 - T_H}{2}$$

Combining this with Eq. (12), we have

$$T_s - T_H = \frac{\Delta T_p + (T_0 - T_H)_{st}}{2}$$

Introducing this expression into Eq. (11), we obtain the kinetic equation for the instrument of considered type:

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = 4\pi l_s \lambda_s \Delta T_p + \frac{\bar{C}_s}{2} \frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} \tag{12a}$$

Integration from the start of the reaction to the return of the curve to the base line yields

$$\Delta H_t = -4\pi l_s \lambda_s \int \Delta T_p \, \mathrm{d}t = -K_1 A_t \tag{13}$$

The constant K_1 in Eq. (13) is not in fact an instrument constant, but a characteristic of the sample, acting as a heat barrier with the parameters l_s and λ_s, and will therefore necessarily change when the reference material is exchanged for the sample. This means that calibration with reference materials is impossible. In addition, λ_s changes to an unknown extent during the reaction, causing further difficulties in using Eq. (13) for quantitative computations.

The specific heat of reaction ΔH_0, from Eq. (13), is

$$\Delta H_0 = -\frac{4\pi l_s \lambda_s A_t}{M} = -\frac{4\lambda_s A_t}{\varrho R^2} \tag{13a}$$

In Eq. (13a), $\Delta H_0 = \text{const}$ and $R = \text{const}$, and consequently the peak area A_t recorded is inversely proportional to the ratio $\frac{\lambda_s}{\varrho}$; from this respect, λ_s and ϱ are effective values depending on the packing density of the sample (they become true parameters of the sample at maximum packing density). The formula (13a) is correct if λ_s and ϱ do not depend on temperature and do not change during the reaction, while l_s is large enough to allow neglect of marginal effects (heat exchange across the bottom of the cylinder). Physically, this corresponds to the condition

$l_s \geqslant 4R_H$ [6]. If this condition is not observed, the following consequences will arise. When the sample holder contains a small amount of sample which will then not assume a cylindrical shape, but rather a spherical shape, the Fourier equation of the following form will hold:

$$\frac{dQ}{dt} = \frac{4\pi r^2 \lambda_s \, dT}{dr} \tag{13b}$$

After transformation similar to that for the cylindrical sample, we obtain

$$\frac{dT}{dt} = a\left(\frac{d^2T}{dr^2} + \frac{2\,dT}{r\,dr}\right) \tag{13c}$$

The solution of this equation at $\frac{dT}{dt} = \text{const}$ is the function

$$T = T_0 + \frac{\varphi r^2}{6a} \tag{13d}$$

where T_0 is the temperature at the centre of the spherical sample. The heat flow entering the spherical sample is

$$\frac{dQ}{dt} = \frac{4\pi R^2 \lambda_s R\varphi}{3a} = 8\pi\lambda_s R(T_H - T_0) \tag{13e}$$

Continuing analogously as above from Eq. (8) to Eq. (11a), the kinetic equation for the spherical sample is found:

$$-\frac{d\Delta H}{dt} = 8\pi R\lambda_s \Delta T_p + \frac{\bar{C}_s}{2}\frac{d\Delta T_p}{dt} \tag{14}$$

Integration of Eq. (14) will then yield the formula for the specific heat of reaction:

$$-\Delta H_0 = \frac{KA_t}{M} = \frac{8\pi\lambda_s RA_t}{4/3\pi R^3 \varrho} = \frac{6\lambda_s A_t}{\varrho R^2} \tag{15}$$

Equation (15) is analogous to Eq. (13a); however, it demonstrates the dependence of the peak area A_t on sample mass by reason of a mass increase of a spherical sample involving an increase of its radius, whereas a mass increase of the cylindrical sample in Eq. (13a) takes place as a result of increasing length, at an unchanged value of the radius. By expressing R in terms of M in Eq. (15), we have

$$A_t = \frac{\Delta H_0 \sqrt{\varrho/6}}{\lambda_s}\left(\frac{M}{8\pi}\right)^{2/3} \tag{16}$$

It is evident from what has been said that when small sample amounts are used with the cylindrical sample holder, i.e. when the shape of the sample is close to spherical, the dependence A_t *vs.* M expressed by Eq. (16) is to be expected; as the increasing sample mass leads to the cylindrical shape, A_t will become less and less dependent on M and will become practically independent of it when the condition $l_s \geqslant 4r$ is satisfied. This conclusion has been confirmed experimentally [1].

The dependence of constant K is Eqs (13a) and (15) on the properties of the sample, and the dependence of A_t on the extent to which the sample holder is filled at small sample amounts, mean that instruments of the considered type are practically useless for quantitative determinations. For this reason, instruments with special heat barriers came into use in calorimetry. The heat barrier consists of a solid shell enclosing the sample, the temperature sensor, a differential thermocouple or a battery of such thermocouples being fixed on the shell [2, 7]. This construction has the advantage that constant K does not depend on the thermal conductivity or density of the sample.

2. Block-type instrument with a solid heat barrier

To describe this type satisfactorily, and in particular to derive the kinetic equation describing its operation, it is necessary to introduce an additional thermocouple at the centre of the sample, to increase the number of signal amount of information obtainable. The construction shown in Fig. 1 has a central thermocouple *1*, located at the centre of the sample, and a lateral thermocouple *2*, located on the interface between the sample and the solid shell. These thermocouples are connected alternately with thermocouple *3* (the reference thermocouple), located on the interface between the shell and the heater. The input of the amplifier of the differential recorder is alternately the output of thermocouples *1–3* and *2–3*, and two curves with peaks A and A_2 are recorded on the diagram paper, corresponding to the incremental temperatures ΔT_p and ΔT_2 (the pen of the recorder periodically passes from one curve to the other). Peak A_1 is found as the difference between peaks A and A_2; it can also be recorded directly by connecting the terminals of the thermocouples *1* and *2* to the recorder.

As shown in Fig. 2, during the heating regime the differential curve with peak A proceeds below the curve with peak A_2 by a distance $\Delta T_{B1} = -\varphi_1\tau_1 = -\varphi_1\frac{C_1}{K_1}$, where φ_1 is the heating rate of the sample, C_1 is the thermal capacity of the sample, and K_1 is the thermal conductivity of the sample over the section *1–2*. On the other hand, the curve with peak A_2 proceeds below the zero line by a value equal to the temperature jump on the heat barrier of the cell, $\Delta T_{B2} = -\varphi_2\tau_2 = \frac{-\varphi_2(C_1+C_2)}{K_2}$, where φ_2 is the heating rate of the heat barrier, C_2 is its thermal capacity, and K_2 is

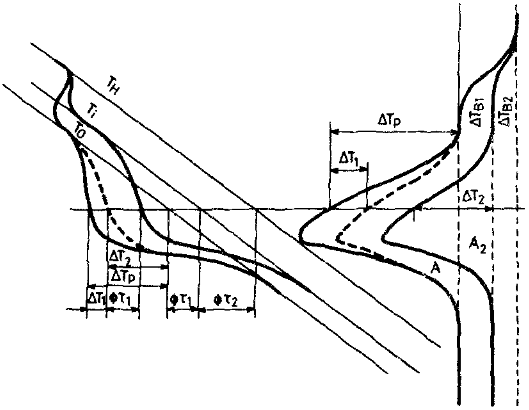

Fig. 2 Temperature diagram illustrating the theory of two-point DTA

the thermal conductivity (heat transfer coefficient) of the heat barrier over the section *23*. On passing from the regime without reference material to the DTA regime with reference material, thermocouple *3* is exchanged for thermocouple *2'*, located in the reference cell on the interface of the reference material and the shell (heat barrier); as a result, the value of the recorded temperature jump, ΔT_{B2}, will decrease (to zero, if the constant times τ_2 and τ'_2 are equal and $\Phi = \Phi'$).

Use of a reference cell in this instrument type has the following advantages: (i) the recorded value ΔT_p is the maximum possible value, independently of whether or not the limiting condition $\Delta T_p = 0$ is satisfied at $r = R_H$; (ii) the decrease of the value ΔT_{B2} will save space on the diagram paper and will allow operation with a high amplifying coefficient of the differential record; (iii) the stability of the base line will increase, and its slope and bend will decrease [8]; (iv) it becomes possible to measure the thermal capacity of the sample via the difference signal, proportional to the difference between the thermal capacities of the sample cell and the reference cell, respectively, other experimental variables being kept equal.

The mathematical conditions for this type are as follows:

$$\begin{gathered} \bar{C}_B = \text{const} \neq 0; \quad T_0 \neq T_i \neq T_H \\ T_s = \frac{T_0 + T_i}{2}; \quad T_B = \frac{T_i + T_H}{2}; \quad \frac{\mathrm{d}T_H}{\mathrm{d}t} = \varphi = \text{const} \end{gathered} \tag{16a}$$

The heat flow from the heater through the cylindrical surface with radius r and height l_s must be sufficient to heat the shell, $r - R_i$ thick, and the sample with radius R_i at the rate φ:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = c_B \varrho_B \pi l_s (r^2 - R_i^2)\varphi + c_s \varrho_s \pi l_s R_i^2 \varphi \tag{17}$$

If $r = R_H$, then

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \pi l_s R_i^2 \cdot (c_s \varrho_s - c_B \varrho_B)\varphi + c_B \varrho_B \pi l_s R_H^2 \varphi \tag{17a}$$

On the other hand, according to the Fourier law, for $R_i \leqslant r \leqslant R_H$

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = 2\pi r l_s \lambda_B \frac{\mathrm{d}T_B}{\mathrm{d}r} \tag{17b}$$

Solving the above equations jointly and integrating with respect to r from R_i to R_H, we find the law of temperature distribution on the heat barrier for steady-state heating regimes:

$$\begin{aligned}(T_H - T_i)_{st} = {} & \frac{(R_i^2 \ln R_H/R_i)(C_s \varrho_s - C_B \varrho_B)\varphi}{2\lambda_B} + \\ & + \frac{C_B \varrho_B (R_H^2 - R_i^2)\varphi}{4\lambda_B}\end{aligned} \tag{18}$$

Let us express the heat flow emerging from the wall of the heater over the total temperature jump on the heat barrier. For this purpose we transform Eq. (17a) by means of Eq. (18):

$$\begin{aligned}\frac{\mathrm{d}Q}{\mathrm{d}t} = {} & \frac{2\pi l_s \lambda_B}{\ln R_H/R_i}\left[\frac{R_i^2 \ln R_H/R_i (c_s \varrho_s - c_B \varrho_B)\varphi}{2\lambda_B} + \frac{c_B \varrho_B (R_H^2 - R_i^2)\varphi}{4\lambda_B}\right] + A' = \\ & = K_2 (T_H - T_i)_{st} + A'\end{aligned} \tag{18a}$$

where A' is a constant.

During the reaction an incremental temperature jump ΔT_2 will appear on the heat barrier, the heat flow then being equal to

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = K_2[(T_H - T_i)_{st} - \Delta T_2] + A' = -K_2 \Delta T_2 + \bar{C}_B \varphi + \bar{C}_s \varphi \tag{18b}$$

This heat flow is used up for the reaction, to heat the shell at a rate $\varphi_B = \frac{\mathrm{d}T_B}{\mathrm{d}t}$ and to heat the sample at a rate $\varphi_s = \frac{\mathrm{d}T_s}{\mathrm{d}t}$:

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}t} + \bar{C}_B \frac{\mathrm{d}T_B}{\mathrm{d}t} + \bar{C}_s \frac{\mathrm{d}Ts}{\mathrm{d}t} = -K_2 \Delta T_2 + \bar{C}_B \frac{\mathrm{d}T_H}{\mathrm{d}t} + \bar{C}_s \frac{\mathrm{d}T_H}{\mathrm{d}t} \tag{18c}$$

and hence

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_2\Delta T_2 + \bar{C}_B\frac{\mathrm{d}(T_B - T_H)}{\mathrm{d}t} + \bar{C}_s\frac{\mathrm{d}(T_s - T_H)}{\mathrm{d}t} \tag{19}$$

Since

$$\Delta T_2 = T_i - T_H - (T_i - T_H)_{st} \tag{19a}$$

and utilizing the conditions for T_B and T_s, we have

$$T_B - T_H = \frac{T_i + T_H}{2} - T_H = \frac{T_i - T_H}{2} = \frac{\Delta T_2 + \mathrm{const}}{2} \tag{19b}$$

$$T_s - T_H = \frac{T_0 + T_i}{2} - T_H = \frac{T_i - T_H}{2} + \frac{T_0 - T_H}{2} \tag{19c}$$

Introducing this expression into Eq. (19), we obtain

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_2\Delta T_2 + \frac{(\bar{C}_B + \bar{C}_s)}{2}\frac{\mathrm{d}\Delta T_2}{\mathrm{d}t} + \frac{\bar{C}_s}{2}\frac{\mathrm{d}(T_0 - T_H)}{\mathrm{d}t} \tag{20}$$

and in the integrated from

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

$$K_2 = \frac{2\pi l_2 \lambda_B}{\ln R_H/R_i} \tag{21}$$

where $K_2 = \frac{2\pi l_s \lambda_B}{\ln R_H R_i}$.

It may be seen from Fig. 2 that $T_0 - T_H = \Delta T_1 + \Delta T_2 + \mathrm{const} = \Delta T_p + \mathrm{const}$ and consequently

$$\frac{\mathrm{d}(T_0 - T_H)}{\mathrm{d}t} = \frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$$

and Eq. (20) can be rewritten in the form

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_2\Delta T_2 + \frac{\bar{C}_s}{2}\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} + \frac{\mathrm{d}\Delta T_2}{\mathrm{d}t}\right) + \frac{\bar{C}_B}{2}\frac{\mathrm{d}\Delta T_2}{\mathrm{d}t} \tag{22}$$

Equation (22) is the fundamental equation for computations for the block-type instrument with a solid heat barrier, which together with Eq. (21) permits kinetic and thermodynamic calculations by means of the thermal curves recorded.

Let us now turn to the equation in which the incremental temperature ΔT_1 appears.

According to Eq. (9a), the heat flow entering the sample during the reaction is

$$\frac{dQ}{dt} = c_s\varrho_s\pi l_s R_i^2\varphi - 4\pi l_s\lambda_s\Delta T_1 = \bar{C}_s\varphi + K_1\Delta T_1 \tag{22a}$$

solving the heat balance equation for the sample, we obtain an equation analogous to Eq. (11):

$$-\frac{d\Delta H}{dt} = K_1\Delta T_1 + \bar{C}_s\frac{d(T_s - T_H)}{dt} \tag{22b}$$

with the difference that $T_s - T_H$ in this equation has another value, namely

$$T_s - T_H = \frac{2T_0 + (T_i - T_0)}{2} - T_H = -\frac{\Delta T_1 + \mathrm{const}}{2} + T_0 - T_H \tag{22c}$$

Since (cf. Fig. 2)

$$\Delta T_1 = T_0 - T_i - (T_0 - T_i)_{st};\ T_0 - T_H = \Delta T_p + \mathrm{const},\ \Delta T_1 = \Delta T_p - \Delta T_2 \tag{22d}$$

we finally obtain

$$-\frac{d\Delta H}{dt} = K_1(\Delta T_p - \Delta T_2) + \frac{\bar{C}_s}{2}\left(\frac{d\Delta T_p}{dt} + \frac{d\Delta T_2}{dt}\right) \tag{23}$$

The kinetics of the reaction may be calculated from either Eq. (22) or Eq. (23). They may also be utilized for joint correction of the constants K_1 and K_2.

Discussion of the assumptions applied in the theory of block-type instruments

In the theory expounded above, the following major assumptions have been used:

(i) The reaction studied is homogeneous, i.e. it proceeds over the volume of the sample, and $\frac{d\Delta H}{dt}$ does not depend on a spatial coordinate (the term $\frac{d\Delta H}{dt}$ in Eq. (10) refers to the whole sample and not to an elementary volume).

(ii) The volumetric specific heat capacity $c\varrho$ and the heating rate φ are independent of the spatial coordinate; thus, integration by volume can be replaced by multiplication by the volume (Eq. (9)).

(iii) To simplify the computations, the parabolic temperature distribution is replaced by a linear distribution to determine the values of T_s and T_0.

(iv) The values l_s, λ_s and $c\varrho$ are independent of the time of the experiment (the transformation temperature and its extent), allowing the integration of Eq. (11a) in the simplest manner.

(v) The surface of the sample (the shell) at the height l_s is isothermal during the time of the experiment, i.e. $\frac{dQ}{dt}$ is independent of the surface coordinate ($T_H - T_i$ is independent of l_s).

(vi) The thermal resistance is zero at the interfaces between sample and shell, shell and heater, heating surfaces and hot junctions of thermocouples.

(vii) The heat exchange along the thermocouple wires is zero.

By condition (i), the applicability of the theory is confined to reactions proceeding homogeneously, i.e. in the volume of the sample and not on its surface; condition (ii) assumes the homogeneous packing density of the sample in the holder, remaining unchanged during the reaction; condition (iii) places some constraint (from above) on the heating rate and on the values and rates of the thermal effects, since a linear approach to parabolic temperature distribution may only be applied at low values of these parameters; condition (v) indicates the necessity that a sufficiently large sample is needed to reduce marginal effects and to sustain the isothermalness of the surface; conditions (vi) and (vii) are particular requirements relating to the construction and to the positioning of the sample.

In effective DTA instruments, practically all of the above conditions are violated to a greater or lesser extent. This is particularly the case for conditions (vi) and (vii). In existing constructions the sample shape is arbitrary and so is the packing density; the sample is positioned in a sample holder carrying a battery of thermocouples, whose hot junctions bear loosely against the surfaces of the heater and the sample holder. The non-tight fit of the different heat-transporting surfaces, the air gaps, the oxide films, and the various impurities give rise to thermal resistances not included in the theory, varying from experiment to experiment and during the experiment itself. In addition, the overall thermal resistance of the heat barrier is substantially reduced by heat exchange over the thermocouple wires located along the propagation of the heat flow and hence short-circuiting it, resulting in decreases in the measured signal and in the sensitivity of the instrument.

The introduction of the solid shell as special heat barrier therefore only partly solves the problem that the instrument constant depends on the properties of the sample. Although the sample parameters λ_s and ϱ have been eliminated from the equation for K by this means, the parameter l_s remains, involving the necessity of working with samples of definite shape and height. Simultaneously, specific difficulties arise owing to the non-homogeneous character of the heat barrier, composed of the material of the shell, the thermocouple wires, the air gaps, etc., participating with different shares in the overall thermal conductivity of the barrier, and depending differently on temperature, so that it is impossible to calculate the instrument constant K_2 theoretically as a function of instrument parameters and experimental conditions. Obviously, the block-type instrument is too complex to be described by the simple theory expounded above, even if the number of signals (thermoanalytical curves) recorded is increased. The gulf between the theory and practice of calorimetry may be eliminated either by making the theory more complex (going into deeper detail), or by attempting to simplify the construction of the calorimeter to the maximum extent. From what has been said above, it follows that such a simplification must be carried out as follows: (i) The homogeneity of the heat barrier must be increased to an extent at which its thermal conductivity may be characterized by a single parameter, λ_B, whose dependence on temperature is known. This can be achieved by reducing the quantity of heat-transferring surfaces and simultaneously eliminating uncontrolled thermal resistances in the path of the heat flow from the heater to the sample. (ii) The symmetry of the temperature fields (in other words the degree of isothermalness of the heat-transferring surfaces) must be increased. (iii) Heat exchange over the thermocouple wires must be eliminated. (iv) The definiteness of the shape and density of the sample in the holder must be increased. Sensing units based on these principles will be described in the second part of this paper.

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Zusammenfassung — Es wird eine Übersicht über die Theorie der Sensor-Baueinheiten des Blocktyps gegeben. Die Zweipunktmethode der DTA wird beschrieben und geeignete Berechnungsformeln werden abgeleitet. Es wird demonstriert, daß existierende Sensor-Baueinheiten des Blocktyps sich nicht den Annahmen der Theorie anpassen.

Резюме — Рассмотрены основные положения теории датчиков блочного типа. Описан метод 2-х точечного ДТА и приведен вывод основных расчетных формул этого метода. Показано, что датчики блочного типа не удовлетворяют большинству требований (допущений) теории, принятой для описания работы этих датчиков.