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A SYSTEMATIC THEORY OF ONE-CELL DIFFERENTIAL THERMAL ANALYSIS

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The mathematical theory is developed for heat transfer in the cells of DTA instruments with no temperature gradient. Equations are derived for the various portions of the differential curve. The concepts of real and hypothetical base lines are introduced and rules are formulated for plotting them. Three methods are proposed for processing the curves, with and without the introduction of base lines. The physical meanings of the geometrical elements of the thermal curves and their relationship with the experimentally determined thermal quantities are elucidated. Equations in differential and integral forms are derived for the base line of the cell and the base line of the reaction.

One-cell DTA is performed by placing the working thermocouple into the sample and the reference thermocouple on the wall of the heater turned towards the sample. The advantage of this variation of the method lies in its simplicity: there is no need for a reference cell or for a reference material; also, the mathematical theory of the sensor is well-defined and expressive, since no parameters of the reference material or of the reference cell figure in it. Some attempts to utilize one-cell DTA have previously been described [1, 2]; however, only DTA with a reference cell is in practical use at this stage. Historically, this may be explained by the fact that, when DTA first developed, researches did not dispose of satisfactorily accurate apparatus, and the use of the reference cells allowed an increase in the stability of the base line, without the inclusion of special control devices into the apparatus design. At present, however, with electronic temperature programmers and potentiometers, the application of reference standards has become superfluous in many cases, particularly when reactions are being studied that do not need a high sensitivity of the differential record. For this reason, the development of the theoretical and practical aspects of one-cell DTA has become most timely.

Figure 1 shows thermal curves recorded in one-cell DTA (*a*) and in DTA with a reference cell (*b*), in the coordinates temperature difference *vs.* time. These thermal curves do not differ as concerns the size and shape of the peak, but they do differ as

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concerns the distance of the thermal curve (and the peak) from the zero line. In (*a*), the total temperature jump on the thermal barrier of the cell, responsible for heat transfer to the sample, is visible, while in (*b*), only that part of the jump is shown which corresponds to the difference between the total jump on the thermal barriers of the sample cell and the reference cell. According to [3], the equation of the differential thermal curve in DTA with a reference cell is

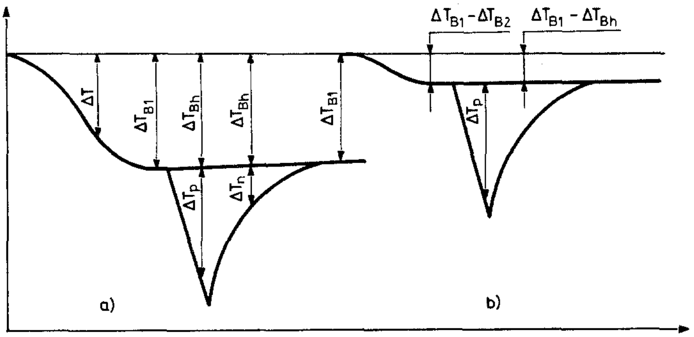

Fig. 1 Temperature diagram of the thermal barrier of the cell for one-cell DTA (a) and DTA with reference cell (b)

$$\Delta T = \Phi_2\tau_2 - \Phi_h\tau_1 + \Delta T_p$$

while the corresponding equation in one-cell DTA is

$$\Delta T = \Phi_h\tau_1 + \Delta T_p$$

Thus, the difference between the two methods is solely the presence of the term $\Phi_2\tau_2$, influencing the position of the base line of the instrument.

Let us consider the relationship between the geometric elements of the thermal curve and the thermal quantities determined experimentally.

The geometric elements can be divided into basic and derived elements. Basic elements are sections of two types: those parallel to the time axis (pull of the record chart), their dimension being time, and those perpendicular to the time axis, their dimension being temperature. Formulae exist for the transition from the linear dimensions of the sections on the thermal curve (in cm) to dimensions in °C and seconds:

$$\Delta T = l_1 a$$

$$\Delta t = l_2 b$$

where l is the length of the section, in cm, a is the sensitivity of the differential record, in degree/cm, and b is the reciprocal pulling velocity, in s/cm.

The derived geometric elements of the thermal curves are areas: $A = \Delta T \cdot \Delta t$, degree·s, and angles, measured by the ratio of sections having different dimensions: $\tan \alpha = \frac{\Delta T}{\Delta t}$, degree/s.

In calorimetry, twoconversion factors are used to transform the geometric elements of the thermal curve into thermal quantities: the heat transfer coefficient of the working space of the cell, K (J/s degree), and the heat capacity of the sample, C (J/degree). For instruments with insulated sample holders [4] (the theory exposed is best suited for such cases), the thermal capacity C is the total thermal capacity of the sample holder and the sample. The thermal quantities containing various combinations of the geometric elements and the multiplication factors C and K are listed in Table 1.

Table 1 Caloric values (Joule, Watt) expressed through the geometrical elements of the thermal curves determined experimentally

Conversion factors	Fundamental geometrical elements		Derived geometrical elements	
	ΔT, °C	Δt, s	A, °C s	$\mathrm{tg}\,\alpha = \frac{\Delta T}{\Delta t}$ °C/s
K, W/°C	$K\Delta T$, W	—	KA, J	—
C J/°C	$C\Delta T$, J	—	—	$C\frac{\mathrm{d}\Delta T}{\mathrm{d}t}$, W

Combinations having no physical sense are marked in the table by dashes.

The Table evidences that the thermal quantities, heat and heat flow, have two forms of expression: with the heat capacity of the sample figuring in one of them, and the heat transfer coefficient of the cell figuring in the other. The quantities with the coefficient K express heat transferred to the sample, while those with the coefficient C express heat absorbed by the sample, or more accurately, that part of the absorbed heat serving to change the temperature of the sample. The heat quantity absorbed or evolved by the sample without changing its temperature after the end of the reaction is denoted by the special symbol ΔH and is termed the latent heat of reaction. The thermal curves in Fig. 1 allow the determination of all three types of heat: the total heat transferred to the sample (Q), the heat increasing the temperature of the sample ($C\mathrm{d}T$) and the latent heat (ΔH); the latter is found as the difference between the first two types of heat.

Let us find the mathematical expression for the differential curve of one-cell DTA. For convenience of analysis, we shall divide the curve into four portions:

1. the initial transitional portion corresponding to the transition to the steady-state heating regime; 2. the steady-state heating regime portion (we shall call this the base line of the cell before the reaction); 3. the differential curve corresponding to the thermal transformation (reaction) proceeding in the sample; 4. the steady-state heating regime portion after the reaction (the base line of the cell after the reaction).

For a cell without a temperature gradient, the Newton equation is valid:

$$\mathrm{d}Q = \alpha S(T_3 - T_1)\mathrm{d}t = -K\Delta T\,\mathrm{d}t \tag{1}$$

where $\mathrm{d}Q$ is the heat transferred to the sample during time $\mathrm{d}t$; α is the heat loss coefficient; S is the surface area of the sample holder; T_3 is the temperature of the heater wall; T_1 is the temperature of the sample; ΔT is the differential temperature; and K is the heat transfer coefficient.

The heat transferred to the sample is absorbed by it, raising its temperature by $\mathrm{d}T_1$:

$$\mathrm{d}Q = C\mathrm{d}T_1 \tag{2}$$

By combining Eqs (1) and (2), we obtain the differential equation

$$\frac{\mathrm{d}T_1}{\mathrm{d}t} + \frac{T_1}{\tau_1} - \frac{T_3}{\tau_1} = 0 \tag{3}$$

or, written in another form

$$\Delta T = -\tau_1 \Phi_1$$

where Φ_1 is the heating rate of the sample and $\tau_1 = \frac{C}{K}$ is the time constant of the cell.

The value of ΔT is equal to the distance of the differential curve from the zero line; the position of the zero line is determined by recording with a short-circuited amplifier, thereby simulating the equality of temperature of the hot junctions of the differential thermocouple: $\Delta T = T_1 - T_3 = 0$. This is the equation of the zero line, from which the differential temperature is counted.

Equation (3) can be solved if it is assumed that $\tau_1 = \text{const}$. For this case, the solution is the following function:

$$T_1 = T_3 + (T_{01} - T_{03})e^{-\frac{t-t_0}{\tau_1}} - e^{-\frac{t_0}{\tau_1}} \int\limits_{t0}^{t} e^{\frac{t}{\tau_1}} \frac{\mathrm{d}T}{\mathrm{d}t}\mathrm{d}t \tag{4}$$

For a linear temperature increase of the heater wall:

$$T_3 = T_{03} + \Phi_0(t - t_0)$$

where Φ_0 is the actual constant heating rate; assuming that, at the moment when heating is started ($t = t_0$), $T_{01} = T_{03}$, Eq. (4) yields

$$\Delta T = -\tau_0\Phi_0(1-e^{-\frac{t-t_0}{\tau_0}}) \tag{5}$$

Equation (5) is the integral form of Eq. (3); it describes the initial transitional section of the differential curve and the steady-state section in the interval $t \geqslant (4\ldots5)\tau_0$, $t = t_S$, in which it may be represented in its limiting form

$$\Delta T = -\tau_0\Phi_0 \tag{5a}$$

Although Eqs (3a) and (5a) are identical in form, Eq. (5a) is integral and correct only for the steady-state section of the curve and only for $\tau_0 =$ const.; in contrast, Eq. (3a) is differential and correct for any section of the differential curve and for any value of τ_1. The heating rate Φ involved in the equation is the heating rate of the sample and not the block; also, $\Phi_1 \neq \Phi_0$, if $\tau \neq$ const.

From the most general integral equations of the differential curves for one-cell DTA and DTA with a reference cell

$$\Delta T = T_1 - T_3 = \int \Phi_1\,\mathrm{d}t - \int \Phi_0\,\mathrm{d}t \tag{6}$$

$$\Delta T = T_1 - T_2 = \int \Phi_1\,\mathrm{d}t - \int \Phi_2\,\mathrm{d}t \tag{7}$$

we can obtain the expression for the slope of the differential curve to the zero line:

$$\begin{aligned}\frac{\mathrm{d}\Delta T}{\mathrm{d}t} &= \Phi_1 - \Phi_0 \\ \frac{\mathrm{d}\Delta T}{\mathrm{d}t} &= \Phi_1 - \Phi_2\end{aligned} \tag{8}$$

indicating that the slope of the tangent to the DTA curve at any point is equal to the difference of the heating rates of the hot junctions of the differential thermocouple at that point of the curve.

Let us now consider the portion of the curve in the range of the thermal transformation. Let us first investigate an endothermic reaction (Fig. 2).

As the reaction proceeds, the heating rate of the sample decelerates, and becomes equal to zero or even assumes a negative value, due to the reaction consuming the heat transferred—partially, completely or in excess of this. According to the definition of the latent heat of reaction as the difference between the total heat transferred and the heat consumed for raising the temperature of the sample, for the rate of heat absorption by the sample we can write

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K(T_3 - T_1) - C\frac{\mathrm{d}T_1}{\mathrm{d}t} = -K\Delta T - C\Phi_1 \tag{9}$$

Replacing the heating rate of the sample in Eq. (9) by the experimentally determined values by means of Eq. (8), we obtain the fundamental equation of one-cell DTA:

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K\Delta T + C\left(\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + \Phi_0\right) \tag{10}$$

In the integral form, for the current heat of reaction, the equation assumes the form

$$-\Delta H = \bar{K}\int_{ts}^{t} \Delta T\,\mathrm{d}t + \bar{C}(\Delta T - \Delta T_s) + \bar{C}\Phi_0(t - t_s) \tag{11}$$

and for the total heat of reaction

$$-\Delta H_t = \bar{K}\int_{ts}^{t_e} \Delta T\,\mathrm{d}t + \bar{C}(\Delta T_e - \Delta T_s) + \bar{C}\Phi_0(t_e - t_s) \tag{11a}$$

where $\bar{K}$ and $\bar{C}$ are the mean values of K and C in the temperature interval studied; ΔT_s is the value of ΔT at the start of the reaction ($t = t_s$); ΔT_e is the value of ΔT at the end of the reaction.

Hence, to find the heat of reaction from the thermal curve of one-cell DTA, it is necessary to find the area enclosed between the zero line and the differential curve,

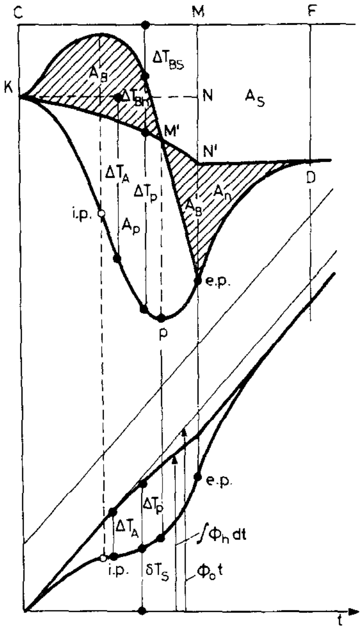

Fig. 2 Temperature diagram of the cell of one-cell DTA with the hypothetic and the real base line (explanation in the text)

and add to it the increase of the differential temperature $\Delta T - \Delta T_s = \Delta T_A$ multiplied by $\bar{C}$, and the term $\bar{C}\Phi_0(t-t_s)$. The first two terms are negative; the last is positive. The sum of the last two terms in Eq. (11) is equal to the temperature rise of the sample during the reaction, multiplied by $\bar{C}$, since, according to the definition of ΔT_A:

$$\Delta T_A = \int_{t_s}^{t} \Phi_1 \, \mathrm{d}t - \Phi_0(t-t_s)$$

Calculations utilizing Eq. (11) require the measurement of one area and two distances (ΔT_A and Δt). It is also necessary to know the value of Φ_0, which is not always possible. Further, accurate determination of the end-point of the reaction in the curve is needed to find ΔH_t. Hence, Eq. (11) is inconvenient for calculations. In principle, two other methods exist for processing the thermal curves of one-cell DTA; in these methods, base lines are introduced and the heat of reaction is calculated from the area enclosed between the differential curve and the base lines. As will be demonstrated later, various base lines are possible; one will be termed the real base line, the other the hypothetical base line of the reaction.

When the transformation in the sample starts, the base line of the cell disappears; it is replaced by the differential curve of the reaction, reflecting both the thermal properties of the reaction and the thermophysical parameters of the cell. However, it can be reproduced by calculation; for this purpose we have to introduce into Eq. (3a) the real heating rate of the sample during the reaction and the theoretical (calculated) value of the time constant of the cell. The value Φ_1 may be found by means of Eq. (8), and the value τ_1 from the assumed $\bar{C}$ and $\bar{K}$ values of the cell during the reaction. The area enclosed between the zero line and the base line constructed in this manner will be proportional—as before the reaction—to the heat consumed for heating the sample:

$$\bar{K}A_s = \int K \Delta T_{Bs} \, \mathrm{d}t = -\int K \tau_1 \Phi_1 \, \mathrm{d}t = -\bar{C}\delta T_s \qquad (12)$$

where δT_s is the temperature rise of the sample during the reaction. In Fig. 2 the real base line is represented by the curve *K M′ e.p.*

The equation for the second method is obtained by integrating Eq. (9) and utilizing Eq. (12):

$$-\Delta H = \bar{K}\int_{t_s}^{t} \Delta T \, \mathrm{d}t + \bar{C}\int_{t_s}^{t} \Phi_1 \, \mathrm{d}t = \bar{K}A - \bar{K}A_s \qquad (13)$$

and in the differential form:

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = \bar{K}\Delta T - \bar{K}\Delta T_{Bs}$$

The third calculation method coincides with the method used in DTA with a reference cell [3].

The differential temperature in the reaction range is represented as the sum of two terms:

$$\Delta T = \Delta T_{Bh} + \Delta T_p = -\Phi_h \tau_1 + \Delta T_p \tag{14}$$

where Φ_h is the hypothetical heating rate of the sample, equal by definition to the rate at which the sample would be heated in the absence of heat absorption (heat evolution), but maintaining the value τ_1 corresponding to the real conditions of the proceeding reaction. If $\tau_1 = \tau_0 = \text{const.}$ during the reaction, the sample would heat up at the same rate as before the reaction, i.e. $\Phi_1 = \Phi_0 = \text{const.}$, and the hypothetical base line of the reaction is then the continuation of the base line of the cell:

$$\Delta T_{Bh} = -\Phi_0 \tau_0$$

If τ_1 changes during the reaction, then $\Phi_h \Phi_0 \neq \text{const.}$ and, as will be demonstrated later, these base line ΔT_{Bh} is curved: with increasing τ_1, the base line moves away from the zero line; with decreasing τ_1 it comes closer to the zero line. Introducing Eq. (14) into Eq. (13), we obtain

$$\begin{aligned} -\Delta H &= \int_{t_s}^{t} K\Delta T_{Bh}\,\mathrm{d}t + \int_{t_s}^{t} K\Delta T_p\,\mathrm{d}t - \int_{t_s}^{t} K\Delta T_{Bs}\,\mathrm{d}t = \\ &= \bar{K}A_H + \bar{K}A_p - \bar{K}A_s \end{aligned} \tag{15}$$

where A_H is the area enclosed between the zero line and the hypothetical base line; A_p is the area enclosed between the differential curve and the hypothetical base line; and A_S is the area enclosed between the zero line and the real base line (cf. Fig. 2).

We shall demonstrate that the area between the two base lines (shaded in the Figure) may be expressed by the height of the peak, i.e. the additional temperature ΔT_p. This follows from the equation

$$\begin{aligned} A_H - A_S = A_B &= \int \Delta T_{Bh}\,\mathrm{d}t - \int \Delta T_{Bs}\,\mathrm{d}t = \int \tau_1 \Phi_h\,\mathrm{d}t - \int \tau_1 \Phi_1\,\mathrm{d}t = \\ &= \tau_1(\delta T_H - \delta T_S) = \bar{\tau}_1 \Delta T_p \end{aligned} \tag{16}$$

(cf. also the diagram below in Fig. 2).

By substituting Eq. (16) into Eq. (15), we obtain

$$-\Delta H = \bar{K}\cdot A_p + C\Delta T_p \tag{16a}$$

and in the differential form

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = \bar{K}\Delta T_p + \bar{C}\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} \tag{17}$$

Since $\Delta T_p = \Delta T - \Delta T_{Bh}$, we have

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = \bar{K}\Delta T_p + \bar{C}\left(\frac{\mathrm{d}\Delta T}{\mathrm{d}t} - \frac{\mathrm{d}\Delta T_{Bh}}{\mathrm{d}t}\right) = \bar{K}\Delta T_p + \bar{C}(\operatorname{tg}\alpha - \operatorname{tg}\beta) \tag{17a}$$

where α is the angle between the zero line and the tangent to the differential line at the current point, and β is the angle between the zero line and the tangent to the base line at the point above the current point in the differential curve.

From Eq. (16) and Fig. 2 it is seen that an express correspondence exists between the area enclosed between the two base lines and the additional temperature. With increasing ΔT_p, the area $A_H - A_S = A_B$ increases proportionally; at the point where ΔT_p is maximum (at the top of the peak) the difference $A_H - A_S$ is also maximum, while to the right of this point the difference begins to decrease, since the increase in the area A'_B changes sign after this point.

Let us now consider in more detail how the real and the hypothetical base lines are drawn. We shall start from the assumption that the function $\tau_1 = F(t)$ is known.

To draw $\Delta T_{BS} = -\Phi_1 \tau_1$, we can find a number of points in the interval of the reaction in process, and then connect them by a continuous curve. As base points we may choose the starting point of the reaction, the top or the base line above the inflexion of the differential curve where $\Phi_1 = \min$, $\dfrac{d\Delta T}{dt} = \Phi_1 - \Phi_0 = \max$ and $\Delta T_{BS} = \max$, the point of intersection of the base lines, which as pointed out above, lies above the top of the peak, and the end-point of the reaction, defined as the point where the exponential portion of the differential curve begins (visually observed as an inflexion point). At this point, the real base line ends and the base line of the cell recorded by the instrument starts.

Let us now demonstrate that the area enclosed between the differential curve and the real base line is equal to the area enclosed between the differential curve and the hypothetical base line. For this purpose the correctness of the equality

$$A_B = A'_B + A_n \tag{18}$$

must be demonstrated, i.e. the equality of the areas to the right and to the left of the point of intersection of the base lines (Fig. 2).

According to Eq. (16), the area A_B to the left of the point M' is equal to $\tau_1 \Delta T_M$. We shall demonstrate that it is also equal to the sum of the areas A'_B and A_n, lying to the right of the point M'. In fact, after the end of the reaction (denoted *e.p.*), all heat transferred to the sample, expressed by the sum $\bar{K}A_S + \bar{K}A_n$, will be used to heat the sample; its temperature increase is

$$\Delta T_S = \int_{t_e}^{t} \Phi_h \, dt + \int_{t_e}^{t} d\Delta T_p$$

and consequently

$$\bar{K}A_S + KA_n = \bar{C} \int_{t_e}^{t\alpha} \Phi_h \, dt + \bar{C} T_{e.p}$$

Hence

$$A_n = \bar{\tau}_1 \Delta T_{e.p.}$$

According to Eq. (16), the area A'_B is equal to the increase in ΔT_p on passing from the point p to the point *e.p.*, multiplied by τ_1:

$$A'_B = \bar{\tau}_1 \Delta T_p |_{p.}^{e.p.}$$

$$A_n + A'_B = \bar{\tau}_1 (\Delta T_{e.p.} + \Delta T_p |_{p}^{e.p.}) = \bar{\tau}_1 \Delta T_M$$

From the above proof of the equivalent of the areas enclosed by the two base line types, it follows that to determine the total heat of reaction by the third method it is not necessary to know the position of the end-point of the reaction in the differential curve. This is the essential advantage of this mode of calculation as compared to the first and second modes, there a knowledge of the *e.p.* position is required.

To draw the hypothetic base line correctly, it is preferable to have the equation of this line in the integral form yielding ΔT_{Bh} *vs.* time. To derive this equation, let us differentiate the equation of the hypothetical base line ΔT_{Bh} (cf. Eq. (14)):

$$\Delta T'_{Bh} = -\Phi'_h \tau_1 - \Phi_h \tau'_1 \tag{19}$$

On the other hand, according to Eq. (8):

$$T'_{Bh} = \Phi_h - \Phi_0 \tag{20}$$

Combining Eqs (19) and (20), we have

$$\frac{1}{\tau_1} - \frac{\Phi_0}{\Phi_h \tau_1} = -\frac{\Phi'_h}{\Phi_h} - \frac{\tau'_1}{\tau_1}$$

or

$$\frac{\mathrm{d}t}{\tau_1} + \frac{\Phi_0 \, \mathrm{d}t}{\Delta T_{Bh}} = -\mathrm{d}\ ln \Phi_h \tau_1 \tag{21}$$

Let us integrate Eq. (21) from t_S to t:

$$\Phi_0 \int_{t_s}^{t} \frac{\mathrm{d}t}{\Delta T_{Bh}} = \ln \frac{(\Delta T_{Bh})_{t_s}}{(\Delta T_{Bh})_t} - \int_{t_s}^{t} \frac{\mathrm{d}t}{\tau_1(t)} \tag{22}$$

where $(\Delta T_{Bh})_{t_s}$ and $(\Delta T_{Bh})_t$ are the values of the base line at the lower and upper limits.

It follows from Eq. (22) that the form of the function ΔT_{Bh} is unequivocally defined by the form of the function $\tau_1(t)$. Therefore, for ΔT_{Bh} we may accept the same form of functional dependence as for $\tau_1(t)$ and, by varying the coefficients in this relationship, we can arrive at the coincidence of the left and right sides of Eq. (22). This relationship is then introduced into the diagram. It is serviceable to construct the base line by means of Eq. (22) in the interval from the start of the reaction to the end-point of the reaction, since, from the end-point on, T_{Bh} no longer depends on the reaction, but only on temperature. The portion from t_e to t can be obtained by extrapolation of the base line of the cell after the experiment to its intersection with the perpendicular line to the zero line, drawn from the end-point of the reaction in the differential curve. The distance MN' in Fig. 2 is equal to the value of ΔT_{Bh} at the upper limit of integration, and the distance CK to its value at the lower limit of integration. In the example illustrated by Fig. 2, it was assumed that τ_1 increases in the course of the reaction, for instance by virtue of the increase in C,the heat capacity of the reaction products being higher than that of the initial substances. As a result, the base line descends till the end-point of the reaction, and subsequently continues at lower level at the level of the base line of the cell after the reaction. This level gradually increases with increasing temperature, owing to a more rapid increase in $\bar{K}$ as compared to $\bar{C}$.

Exothermic reactions

Latent heat evolved during exothermic reactions causes additional heating of the sample, and the amount of transferred heat decreases if $\Phi_0 \geq 0$ (heating regime), or the amount of eliminated heat increases if $\Phi_0 \leq 0$ (cooling regime). Hence, the heat

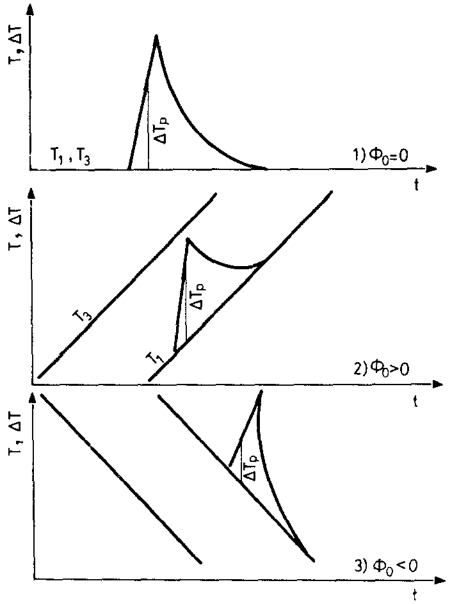

Fig. 3 Temperature diagram of the cell for exothermic reactions and different heating (cooling) regimes of the sample

of exothermic reactions can be defined as follows for its detection by DTA: the heat of an exothermic reaction is the heat causing the sample temperature to increase above the temperature set by the heating (cooling) program, plus the amount of heat to be transferred to the sample to decrease (the amount to be eliminated to increase) as a result of additional heating-up of the sample. In mathematical form:

$$\begin{aligned} -\Delta H &= \bar{C}\int_{t_s}^{t} \Phi_1\,\mathrm{d}t - \int_{t_s}^{t} \Phi_h\,\mathrm{d}t + \bar{K}A - \left(\bar{K}A - \bar{K}\int \Delta T_p\,\mathrm{d}t\right) = \\ &= \bar{C}\Delta T_p + \bar{K}\int_{t_s}^{t} \Delta T_p\,\mathrm{d}t \end{aligned} \tag{23}$$

Figure 3 presents various heating programs of the sample, with superimposed exothermic effects: 1. $\Phi_0 = 0$; 2. $\Phi_0 > 0$; 3. $\Phi_0 < 0$; in all cases $\Phi_1 > \Phi_0 \approx \Phi_h$, $\Delta T_p > 0$.

Equation (23) demonstrates that exothermic reactions are described by the same formula as endothermic reactions, independently of the heating regime; the only difference is in the sign of the values involved, these being the opposite of those for endothermic reactions. The two terms on the right side of Eq. (23) are positive ($\Delta T_p > 0$), and hence, when numerical values are applied, the heat of the exothermic reaction will be negative.

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Zusammenfassung — Eine mathematische Theorie für den Wärmeübergang in Zellen von DTA-Geräten ohne Temperaturgradient wird entwickelt. Für die einzelnen Abschnitte der differentiellen Kurve werden Gleichungen abgeleitet. Das Konzept der reellen und hypothetischen Grundlinien wird eingeführt und Regeln für deren Konstruktion werden aufgestellt. Drei Methoden zur Darstellung der Kurven mit und ohne Einführung der Grundlinien werden vorgeschlagen. Die physikalische Bedeutung der geometrischen Elemente der thermischen Kurven und deren Beziehung zu den experimentell bestimmten thermischen Größen werden klargestellt. Für die Grundlinie der Zelle und für die der Reaktion werden Gleichungen in differentieller und integraler Form abgeleitet.

Резюме — Излагается математическая теория теплопередачи в ячейке прибора ДТА, в которой отсутствуют температурные градиенты. Приводятся уравнения для различных участков дифференциальной кривой. В водятся понятия реальной и гипотетической базовых линий и формулируются правила их нанесения. Предлагаются три способа обсчета кривых — с нанесением базовых линий и без нанесения базовых линий. Выясняется физический смысл геометрических элементов термограммы и связь последних с измеряемыми в опыте калорическими величинами. Выводятся уравнения базовой линии ячейки и базовой линии реакции в дифференциальной и интегральной формах.