Journal of Thermal Analysis, Vol. 27 (1983) 113–124

THE ROLE OF THE REFERENCE MATERIAL IN DIFFERENTIAL THERMAL ANALYSIS

Yu. L. Shishkin

DEPARTMENT OF PHYSICAL AND ANALYTICAL CHEMISTRY,
V. I. LENIN MOSCOW STATE PEDAGOGICAL INSTITUTE, MOSCOW, USSR

(Received December 20, 1982)

The fundamental computation formula of differential thermal analysis and the equation of the base-line are presented for two cases: *a)* the time constants of the specimen and the reference material cells do not change in the course of the experiment, and *b)* these constants change continuously in the course of the experiment. For the second case—which is the general case—a computation formula is obtained, allowing determination of the rate of the reaction for any shape of the base-line. Rules for the course of the base-line are proposed for various types of reactions, in particular for reactions accompanied by mass loss of the specimen and the formation of volatile products, their base-lines having especially large slopes and curvatures. Formulas are derived to determine the calibration constant in the course of the experiment within the total investigated temperature interval.

From the basic problems to be elucidated within the general theory of differential thermal analysis, two will be dealt with: the elaboration of the fundamental notions of the method and their deeper understanding, and the establishment, in a quantitative form of the relationships between the experimental factors and the geometrical elements of the thermoanalytical curves, i.e. the proposal of computation formulas.

Some basic notions of the theory that need concrete elucidation are, for example the DTA curve, the base-line, the reference material, and the instrument constants. As concerns the experimental factors it is expedient to divide them into two groups: operational parameters, which—in principle—can be varied at will by the experimenter, such as the heating rate, atmosphere in the reaction zone, mass of specimen, geometrical and thermophysical parameters of the cell; and non-operational parameters independent of the experimenter: the heat, rate and mechanism of the reaction, i.e. the thermodynamic and kinetic constants of the reaction in question. The objective of thermoanalytical studies is to find the parameters of this second group. For this purpose it is frequently advantageous to vary the parameters of the first group (heating rate, pressure, etc.). The constants to be found are obtained by means of computation formulas from the geometrical elements of the thermoanalytical curves, such as the actual height and area of the peak corresponding to the transformation, indicated by the temperature of the specimen at the given moment of the reaction; the overall area of the peak; the slope of the tangent to the DTA curve at the actual point. As will be shown in the following, two further geometrical elements must be considered: the distance between the zero-line and the DTA curve, and the slope of the tangent to the base-line in the interval of the thermal transformation.

This paper will deal with the effects of the thermophysical parameters of the cell housing the reference material and the specimen, respectively, on the shape and position of the base-line in cases when these parameters are a) independent of, and b) dependent on the temperature (time) of the experiment. The following are valid for instruments with no temperature gradient, of the isolated container type.

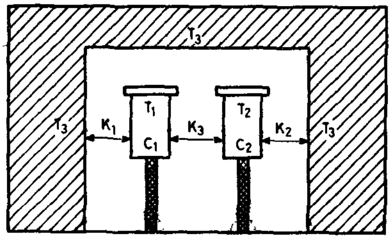

Fig. 1 Diagram of the sensor part of the DTA instrument

The basic equation of DTA is obtained by solving the heat balance equations of the specimen cell and the reference cell [1] (Fig. 1):

$$C_1 \mathrm{d}T_1 + \mathrm{d}\Delta H = K_1(T_3 - T_1)\,\mathrm{d}t + K_3(T_2 - T_1)\,\mathrm{d}t \tag{1}$$

$$C_2 \mathrm{d}T_2 = K_2(T_3 - T_2)\,\mathrm{d}t + K_3(T_1 - T_2)\,\mathrm{d}t \tag{2}$$

where C_1 and C_2 are the heat capacities of the specimen and the reference material, respectively (including the sample holder); T_1, T_2 and T_3 are the temperatures of the specimen, the reference material and the walls of the heating block facing the sample holders, respectively; K_1 and K_2 are the heat transfer coefficients of the specimen cell and the reference cell; K_3 is the heat transfer coefficient between the specimen cell and the reference cell; ΔH is the overall heat of reaction; and t is time.

After the necessary operations one obtains, for $K_3 = 0$:

$$-\frac{\mathrm{d}\Delta H}{K_1 \mathrm{d}t} = T_1 - T_2 + \tau_1 \frac{\mathrm{d}(T_1 - T_2)}{\mathrm{d}t} - (\tau_2 - \tau_1)\frac{\mathrm{d}T_2}{\mathrm{d}t} \tag{3}$$

where $\tau_1 = \frac{C_1}{K_1}$ and $\tau_2 = \frac{C_2}{K_2}$ are the time constants of the specimen cell and the reference cell, respectively.

At a given constant rate of raising the temperature of the heating block, $\phi = \text{const.}$, and at τ_1 and $\tau_2 = \text{const.}$, $\Delta H = 0$, with $K_3 = 0$, the solutions of Eqs (1) and (2) for T_1 and T_2 are

$$T_1 = T_3 - \phi\tau_1 + (T_{01} - T_{03} + \phi\tau_1)e^{-\frac{t-t_0}{\tau_1}} \tag{4}$$

$$T_2 = T_3 - \phi\tau_2 + (T_{02} - T_{03} + \phi\tau_2)e^{-\frac{t-t_0}{\tau_1}} \tag{5}$$

and for the linear temperature increase regime establishing itself when $t - t_0 \gg \tau$ [2]:

$$T_1 = T_3 - \phi\tau_1 \tag{4a}$$

$$T_2 = T_3 - \phi\tau_2 \tag{5a}$$

When the reaction starts, the temperature of the specimen stops changing linearly; to simplify computations, however, it can be represented by the sum of linear and non-linear terms:

$$T_1 = T_3 - \phi\tau_1 + \Delta T_p \tag{6}$$

where ΔT_p is the additional (complementary) temperature change produced by the reaction. According to Eqs. (5) and (6), the temperature difference during the reaction is

$$T_1 - T_2 = \phi(\tau_2 - \tau_1) + \Delta T_p = \Delta T_B + \Delta T_p \tag{7}$$

where ΔT_B is the initial shift of the DTA curve from the zero-line. The value ΔT_B defines the position of the base-line during the reaction as the line from which the additional temperature ΔT_p is counted (Fig. 2).

Substituting Eq. (7) into Eq. (3) and assuming that $\frac{dT_2}{dt} = \phi_2 = \phi$, one obtains an equation in which only the temperature ΔT_p figures among the recorded values:

$$-\frac{d\Delta H}{K_1 dt} = \Delta T_p + \tau_1 \frac{d\Delta T_p}{dt} \tag{8}$$

From what has been said, it is obvious that Eq. (8) is applicable within certain limits only; it is correct only for a regular regime, i.e. for portions of the DTA curve that are fairly far removed from the start of the experiment, and for reactions whose occurrence does not change the time constants of the cells, i.e. for reactions whose base-line is straight and parallel to the zero-line.

It follows from Eq. (8) that the shape of the thermoanalytical curves (the value ΔT_p) is independent of the parameters of the reference cell, since they do not figure in this equation. Consequently, the peak of the thermal transformation counted from the base-line, ΔT_p, is independent of the position of the hot junction of the reference thermocouple, which may be located, for instance, on the wall of the heating block. Another consequence is that, to obtain Eq. (8), Eq. (2) is not necessarily involved, i.e. the reference cell may be left out of the picture. Actually, only Eqs. (1), (4) and (6) are required.

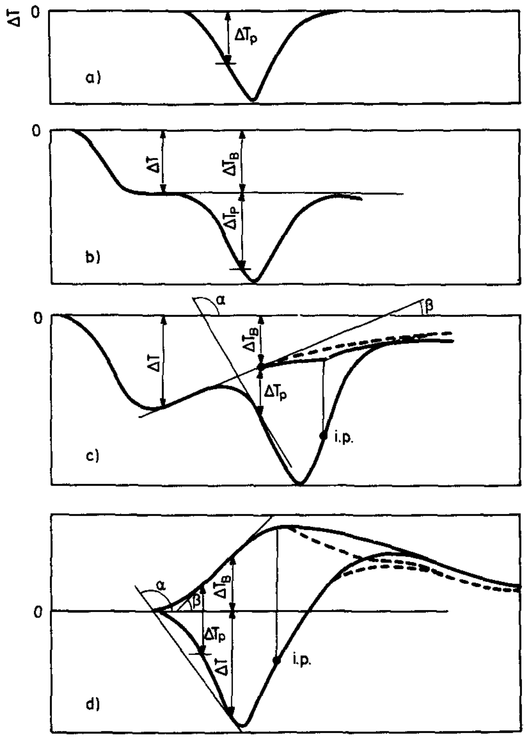

Fig. 2 General shapes of the thermoanalytical curves for different values of the time constants of the specimen cell and the reference cell (a) $\tau_1 = \tau_2$ (b) $\tau_1 > \tau_2$; $\tau_1 =$ const., $\tau_2 =$ const. (c) $\tau_1 > \tau_2$; $\tau_1 \neq$ const., $\tau_2 \neq$ const. (d) $\tau_1 = \tau_2$ before the reaction; $\tau_1 < \tau_2$, $\tau_1 \neq$ const. during the reaction

Let us now investigate the consequences to which abandoning the simplifying conditions $\tau_1 =$ const. and $\tau_2 =$ const. will lead. In this case one must obviously turn to the fundamental equation (3), which was established without any simplifying assumptions regarding the values of τ_1 and τ_2 and the regime of the heating block temperature T_3.

The use of Eq. (8) instead of Eq. (3) in DTA practice led to the result that a deeper analysis of notions such as temperature difference, zero-line and base-line, which do not figure in Eq. (8), became unnecessary. For this reason, it does not appear needless to present stricter definitions of these notions here, since they will be used in the following considerations.

The differential temperature is the difference between the temperatures of the hot junctions of the thermocouples; for an instrument with no temperature gradient, this value will be identical to the temperature difference between the specimen and the reference material.

The differential curve is the record of the differential temperature registered by the instrument in the coordinates temperature difference *vs.* time. The differential temperature is counted from the zero-line of the instrument. The equation of the differential curve is

$$\Delta T = T_1 - T_2 \tag{9}$$

In the diagram, ΔT corresponds to the distance between the zero-line and the differential curve.

The zero-line is the line recorded by the instrument during the time when the input signal to the amplifier of the differential recorder is zero (corresponding to equal temperatures of the hot junctions of the differential thermocouples). The equation of the zero-line is

$$\Delta T = 0$$

which is a particular case of the general equation of the differential curve.

The base-line is the line from which the additional temperature ΔT_p is counted. The base-line is constructed by the experimenter according to defined rules. Most frequently it is obtained by extrapolation of the portion of the differential curve before the peak of the thermal transformation in the reaction range, or by connecting the beginning and end of the peak with a straight line.

Equations (1) and (2) at $\Delta H = 0$ and $K_3 = 0$ may be written as

$$T_3 - T_1 = \phi_1 \tau_1 \tag{1a}$$

$$T_3 - T_2 = \phi_2 \tau_2 \tag{2a}$$

and hence

$$T_1 - T_2 = \phi_2 \tau_2 - \phi_1 \tau_1 \tag{10}$$

Equation (10) demonstrates that the differential temperature is a function of the time constants of the cells and of the heating rates of the specimen and the reference material. This equation may also be obtained from Eq. (3), substituting $\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = 0$.

An interesting note: it follows from the condition $\tau_1 = \text{const.}$ that $\phi_1 = \text{const.}$ too (in regular heating regimes). In contrast, if $\tau_1 \neq \text{const.}$, then $\phi_1 \neq \text{const.}$ and $\phi_1 \neq \phi$. The differential curve will then not be parallel to the zero-line; its slope will be equal to the difference between the heating rates of the specimen and the reference material:

$$\frac{\mathrm{d}\Delta T}{\mathrm{d}t} = \frac{\mathrm{d}\phi_2 \tau_2}{\mathrm{d}t} - \frac{\mathrm{d}\phi_1 \tau_1}{\mathrm{d}t} = \phi_1 - \phi_2 \tag{11}$$

since

$$\phi_1 \tau_1 = \phi t - \int_0^t \phi_1 \,\mathrm{d}t; \quad \frac{\mathrm{d}\phi_1 \tau_1}{\mathrm{d}t} = \phi - \phi_1; \quad \frac{\mathrm{d}\phi_2 \tau_2}{\mathrm{d}t} = \phi - \phi_2$$

The closer the values of τ_1 and τ_2, the closer the value of ϕ_1 to ϕ_2, and the absolute value of ΔT will decrease, approaching the zero-line (Eq. 10); simultaneously, the slope of the differential curve will also decrease (Eq. 11). Hence, the role of the reference material consists in causing the differential curve to approach the zero-line; this is achieved in practice by choosing parameters for the reference cell for which $\tau_1 = \tau_2$. Further, even if $\tau_1 \neq$ const. and $\tau_2 \neq$ const. in the course of the experiment, but $\tau_1 = \tau_2$, the differential curve will coincide with the zero-line. In DTA with no reference material, for which the position of the differential curve is given by the equation

$$\Delta T = T_1 - T_3 = -\phi_1\tau_1$$

and the slope of the differential curve to the zero-line by the equation

$$\frac{\mathrm{d}\Delta T}{\mathrm{d}t} = \phi_1 - \phi$$

the differential curve can never be parallel to the zero-line, unless the condition $\tau_1 =$ const. is satisfied.

The temperature of the specimen during the reaction can be represented by two non-linear terms:

$$T_1 = (T_3 - \phi_1'\tau_1) + \Delta T_p \tag{12}$$

From Eq. (12), Eq. (10) will then assume the form

$$T_1 - T_2 = \phi_2\tau_2 - \phi_1'\tau_1 + \Delta T_p \tag{13}$$

Hence, the base-line from which the additional temperature ΔT_p must be counted is given by the expression

$$\Delta T_B = \phi_2\tau_2 - \phi_1'\tau_1 \tag{14}$$

where τ_1 and τ_2 are the time constants of the specimen cell and the reference cell, respectively, during the reaction, ϕ_2 is the heating rate of the reference material, and ϕ_1' is the hypothetical heating rate of the specimen; it may be defined as the heating rate of the specimen in the absence of the reaction, but under otherwise identical conditions: the heat capacity of the specimen, the heat transfer coefficient and the heating rate of the heating block all corresponding to the conditions of the process of the reaction. All values involved in Eq. (14) change continuously both before and during the reaction and, further, τ_1 is a function not only of temperature, but also of the characteristics of the reaction in question. Particularly important changes of τ_1 are to be expected for reactions accompanied by mass changes and the evolution of volatile products. In principle, Eq. (14) allows a consideration of all essential factors of the experiment and the correct construction of the base-line, the characteristics of the process investigated being taken into account, in contrast to the expression

$$\Delta T_B = \phi(\tau_2 - \tau_1)$$

which was derived from the assumption that τ_1 and τ_2 are constant, and allows only one position for the base-line, parallel to the zero-line, independently of the true conditions of the experiment.

Actually, the true base-line is not only not parallel to the base-line, but cannot be a straight line at all. Parallelism of the base-line and the zero-line is possible only at $\tau_1 = \tau_2$, which will hardly occur in practice, and a straight line must have constant slope, this being in contradiction to the condition

$$\frac{\mathrm{d}\Delta T_B}{dt} = \phi_1 - \phi_2 \neq \text{const.}$$

at varying heating rates ϕ_1 and ϕ_2.

Substituting Eq. (13) into Eq. (3) yields

$$-\frac{\mathrm{d}\Delta H}{K_1 \mathrm{d}t} = \Delta T_p + \tau_1 \frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} \tag{15}$$

which formally coincides with Eq. (8). The difference between the two equations consists in the manner of finding the values ΔT_p and $\frac{\mathrm{d}\Delta T_p}{dt}$. With regard to how Eq. (8) was derived, ΔT_p is counted from a straight base-line parallel to the zero-line, whereas in the case of Eq. (15) ΔT_p is counted from a curved base-line. To find $\frac{\mathrm{d}\Delta T_p}{dt}$ in the first case, it is sufficient to determine the slope at the actual point on the differential curve, i.e. the tangent of the angle between the tangent and the zero-line. In the case of the curved base-line

$$\frac{\mathrm{d}\Delta T}{dt} = \frac{\mathrm{d}(\Delta T_B + \Delta T_p)}{dt}$$

and hence

$$\frac{\mathrm{d}\Delta T_p}{dt} = \frac{\mathrm{d}\Delta T}{dt} - \frac{\mathrm{d}\Delta T_B}{dt} \tag{16}$$

Thus, in order to find $\frac{\mathrm{d}\Delta T_p}{dt}$, in the general case, the tangent of the angle between the tangent and the base-line at a point above the corresponding point of the differential curve must be subtracted from the slope of the tangent to the differential curve (Fig. 2).

Equation (16) is universally suited to find $\frac{\mathrm{d}\Delta T_p}{dt}$, whatever the shape of the base-line. Its use allows determination of the rate of reaction from the thermoanalytical curves even in those cases when the base-line is not a straight line parallel to the zero-line.

Let us consider, from the above-discussed view, the most typical cases encountered in practice.

(i) The reaction is not accompanied by mass loss of the specimen and the formation of volatile products; $\tau_1 = \tau_2$ both before and during the reaction, τ_1 being constant before and not constant during the reaction. The base-line coincides with the zero-line before and during the reaction (Fig. 2a).

(ii) The time constants of the cells do not change during the experiment, but one is larger than the other. The base-line is shifted by a constant value $\Delta T_B = \phi(\tau_2 - \tau_1)$ from the zero-line (Fig. 2b).

(iii) The time constants of the cells change during the experiment, one to a greater extent than the other, e.g. $\tau_1 > \tau_2$. The base-line is shifted towards negative ΔT values, and both the base-line and the differential curve approach the zero-line with rising temperature. This is explained by the decrease in τ_1 due to the more rapid increase in K_1 as compared to the increase in C_1. The differential curve approaches the zero-line with a time lag, and hence a convexity towards the zero-line appears. If τ_1 during the reaction remains a function of temperature only (as before the reaction), the base-line is obtained by extrapolation of the differential curve onto the interval of the reaction (dashed line in Fig. 2c). If τ_1 increases somewhat during the reaction (due to the increase in C_1), the base-line will be shifted slightly downwards, and subsequently the differential curve proceeds lower than in the first case (continuous line in Fig. 2c).

(iv) The reaction is accompanied by mass loss of the specimen, with the formation of volatile products; $\tau_1 = \tau_2$ before the reaction, but when the reaction starts, τ_1 continuously decreases until the completion of the reaction, due to the mass loss of the specimen and the increase in K_1 caused by the evolved volatile products with higher thermal conductivity. Under these conditions the differential curve coincides with the zero-line before the reaction, but as the reaction starts the base-line will be sharply shifted above the zero-line (since $\tau_1 < \tau_2$). From the completion of the reaction on, τ_1 and τ_2 will decrease only as a result of increasing temperature and, since $\tau_1 < \tau_2$, τ_1 will decrease more slowly than τ_2, and the difference $\phi_2\tau_2 - \phi_1\tau_1$ will decrease, i.e. the differential curve will approach the zero-line after the reaction. Since the completion of the reaction corresponds, on the differential curve, to a point to the right of the peak maximum and coinciding in practice with the inflexion point, the following procedure of constructing the base-line is proposed for case (iv). A straight line perpendicular to the zero-line is drawn from the inflexion point to the right of the peak maximum (Fig. 2d). The differential curve recorded after the completion of the peak is then extrapolated backwards until it intersects the perpendicular line, and the point of intersection is connected with the start of the peak by means of a continuous curved line. If the volatile products are eliminated from the sphere of the reaction after its completion, τ_1 will slightly increase, this being equivalent to a more rapid approach of the base-line to the zero-line, and therefore in this case the extrapolated base-line section after the completion of the reaction will have an inflexion point and will proceed lower than in the case when the volatile products remain in the cell (Fig. 2d, dashed line).

The procedure proposed is an approximation, since the extent of the inflexion of the constructed base-line is unknown. Therefore, the error in determining the rate of reaction from the thermoanalytical curves may be significant, due to the error in the term $\frac{d\Delta T_B}{dt}$ in Eq. (16). By varying the inflexion of the constructed base-line, for one and the same point of the differential curve one may obtain various rates of reaction, of which only one will be the true value. To find the correct position of the base-line, one can utilize the condition that the constants of the reaction in question (order of reaction, frequency factor, activation energy) must be independent of the temperature (time of the experiment), i.e. they should not vary for the different points of the differential curve. Using the method of trial and error, one can find the position of the base-line for which the constancy of the reaction constants is best satisfied; the base-line found in this manner will then be accepted as the true one.

Another feasible method consists in determining the heat of reaction by an independent method (or from data in the literature). If the value of the constant K_1 is known, one may calculate the area of the peak for the given amount of substance, and subsequently construct the base-line in the manner to obtain the calculated peak area.

To find the value of the term $\frac{d\Delta T_p}{dt}$ in Eq. (15) directly, particular geometrical constructions are required if the base-line is curved. To avoid confusion with Eq. (8) and erroneous determination of $\frac{d\Delta T_p}{dt}$, it is expedient to transform Eq. (15) into the following form:

$$-\frac{d\Delta H}{K_1 dt} = \Delta T_p + \tau_1 \left(\frac{d\Delta T}{dt} - \frac{d\Delta T_B}{dt}\right) \tag{17}$$

or into the form

$$-\frac{d\Delta H}{K_1 dt} = \Delta T_p + \tau_1 \, (\mathrm{tgn}\,\alpha - \tan\beta) \tag{17a}$$

where α and β are the angles formed by the tangents with the differential curve and with the base-line, respectively (Fig. 2c, 2d). From this representation it becomes obvious that Eq. (8) is a particular case of Eq. (17) for $\frac{d\Delta T_B}{dt} = 0$.

It is of interest to note that for kinetic computations Eq. (3) can be utilized directly, without constructing the base-line and without determining ΔT_p and $\frac{d\Delta T_B}{dt}$, by substituting the values of the differential temperature directly into Eq. (3). However, in this case it is indispensable to know the value of the term $\phi_2(\tau_2 - \tau_1)$, i.e. the values τ_1, τ_2 and ϕ_2 at any individual moment of the reaction. The complementary construction of the base-line, and the introduction of ΔT_p and $\frac{d\Delta T_B}{dt}$, was made with the objective of overcoming this difficulty and of presenting an alternative solution of the problem.

In usual DTA practice only the differential curve is recorded, without recording the zero-line, and the temperature is counted from a base-line obtained by extrapolating the differential curve before and after the peak corresponding to the reaction, i.e. only the additional temperature, independent of the reference cell parameters, is taken into account. Such practice substantially lowers the information value of the DTA method and impedes the development of its quantitative aspects. When the zero-line also figures in the thermoanalytical curves, the differential curve and the base-line will involve numerical expressions reflecting, in a quantitative manner, the thermophysical parameters of the specimen and reference cells. This can be utilized to calibrate the instrument, i.e. to determine the value of the instrument constant K1 during the experiment within ist total temperature interval, icluding that of the reaction.

In Eq. (10), $(T_1 - T_2)$ is the measured differential temperature. The heating rates ϕ_1 and ϕ_2 are also experimental values. To find the unknowns τ_1 and τ_2, one of them must be known. For identical constructions of the specimen cell and the reference cell, and identical dimensions of the holders, one may assume that $K_1 = K_2 = K$. Then, the number of unknowns in Eq. (10) will be reduced to three: C_1, C_2 and K. If a specimen substance and a reference material are chosen whose heat capacities are known, K can be determined from Eq. (10) for any portion of the differential curve. Equation (10) may obviously be utilized to find the value of any one of the three unknowns, provided that the two other values are known.

Recording of the differential curve as a function of time, with simultaneous recording of the temperature, allows determination of the rate of temperature rise of the specimen ϕ_1. The rate of temperature rise of the reference material is found from Eq. (11). Substituting the value of ϕ_2 from Eq. (11) into Eq. (10), one obtains for the value of K:

$$K = \frac{\phi_1 (C_2 - C_1) - C_2 \frac{\mathrm{d}\Delta T}{\mathrm{d}t}}{\Delta T} \tag{18}$$

Computations with Eq. (18) may be simplified by recording the thermoanalytical curves with an empty reference material holder and using a specimen holder and a reference material holder with identical heat capacities. In this case

$$K = -\frac{\phi_1 C_S + C_0 \frac{\mathrm{d}\Delta T}{\mathrm{d}T}}{\Delta T} \tag{18a}$$

where C_0 is the heat capacity of the empty holders, and C_S is the heat capacity of the holder with the specimen contained.

The value C_0 can readily be calculated from data in the literature. The heat capacity of the material being tested should be determined previously in the temperature interval studied.

The heating rate ϕ_1 figuring in Eq. (18) is the actual heating rate of the specimen before the reaction, and the hypothetical heating rate during the reaction. The first is obtained directly from experimental data; the second, however, not being directly measurable, is obtained only by making certain assumptions.

The hypothetical heating rate ϕ_1' depends on the shape of the base-line, and differs the more from ϕ_1 before the reaction, the more the base-line differs from the differential curve before the reaction start. In contrast to ϕ_1, the change in ϕ_2 during the reaction is insignificant. As a first approach, one may assume that $\phi_2 = \text{const.}$ during the reaction. This value of ϕ_2 can be found from Eq. (11):

$$\phi_2 = \phi_{1S} - \frac{\mathrm{d}\Delta T_S}{dt} = \text{const.} \tag{19}$$

where ϕ_{1S} is the heating rate of the specimen immediately before the start of the thermal transformation (before the peak), and $\frac{\mathrm{d}\Delta T_S}{dt}$ is the corresponding slope of the differential curve to the zero-line. Utilizing Eq. (11) again, one obtains the hypothetical heating rate ϕ_1':

$$\phi_1' = \frac{\mathrm{d}\Delta T_B}{dt} + \phi_{1S} - \frac{\mathrm{d}\Delta T_S}{dt} \tag{20}$$

Substituting ϕ_1' into Eq. (18a) will then yield

$$K = -\frac{(C_0 + C_S)\frac{\mathrm{d}\Delta T_B}{dt} + C_S\left(\phi_{1S} - \frac{\mathrm{d}\Delta T_S}{dt}\right)}{\Delta T_B} \tag{21}$$

Equation (21) allows one to follow the change in the constant K during the reaction, and thereby to raise the accuracy of kinetic and thermodynamic computations on the basis of DTA data.

References

1 A. P. Gray, Analytical Calorimetry (Eds. R. S. Porter and J. F. Johnson), Plenum Press, New York, 1968, p. 209.

2 G. M. Kondratev, Regular thermal regime (in Russian), Gostekhizdat, 1954.

Zusammenfassung — Die grundlegende thermodifferentialanalytische Berechnungsformel und die die Grundlinie beschreibende Gleichung werden für die zwei Fälle dargelegt, dass sich die Zeitkonstanten der Proben- und Vergleichszelle entweder nicht oder aber kontinuierlich im Laufe des Experiments verändern. Für den zweiten, den allgemeinen Fall wird eine Berechnungsformel erhalten, die die Bestimmung der Reaktionsgeschwindigkeit bei jeder beliebigen Gestalt der Grundlinie ermöglicht. Es werden Regeln für den Verlauf der Grundlinien bei verschiedenen Reaktionstypen vorgeschlagen, insbesondere bei unter Massenverlusten der Probe und Bildung flüchtiger Produkte einhergehenden Reaktionen, bei denen die Grundlinie eine besonders grosse Steigung und Krümmung aufweist. Formeln zur Bestimmung der Kalibrationskonstanten im gesamten untersuchten Temperaturbereich werden abgeleitet.

Резюме — Приводится вывод основной расчетной формулы дифференциального термического анализа, а также уравнение базовой линии для двух случаев: а) постоянные времени ячеек образца и эталона неизменны в продолжении опыта; б) указанные постоянные непрерывно меняются в ходе опыта. Для второго случая, являющегося общим, получена расчетная формула, позволяющая определять скорость реакции по термограмме при любой форме базовой линии. Предлагаются правила проведения базовых линий для реакций различного типа, в частности для таких, которые сопровождаются потерей массы образца и образованием летучих продуктов, базовая линия для которых имеет особенно большой наклон и изгиб. Приводятся формулы для определения калибровочной постоянной в ходе опыта во всем исследуемом диапазоне температур.