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CALCULATION OF THERMAL EFFECTS IN DTA

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By considering that the temperature of the end of the thermal effect and the return of the thermal curve to the baseline do not coincide new calculation methods for the thermal effect become possible. Both the integral value of the thermal effect and its distribution over temperature may be calculated by processing only that part of the DTA curve which corresponds to the temperature interval of the transformation.

It is demonstrated on the examples of non-variant transformation and transformation with an even distribution of the thermal effect over the temperature interval of the transformation that, under certain assumptions, the values of the thermal effect calculated by the suggested method and by the area of the peak are identical.

In the overwhelming majority of studies involving the application of differential thermal analysis, no sharp difference is made between two values: the temperature at which the transformation ends, and the temperature at which the thermal curve returns to the baseline. As a result, not only is the accuracy of reading the temperature interval of the transformation reduced, but the means of calculating the thermal effects will be limited, and calculations concerning the distribution of the thermal effect within the temperature interval of the transformation will be incorrect or deficient.

Let us use the following symbols:

T_i, T_f = initial and final temperature, respectively, of the deviation of the thermal curve from the baseline;

T_I, T_F = initial and final temperature, respectively of the transformation (for non-variant transformations, $T_I = T_F = T_{non}$);

τ_I, τ_F = moment of the start and the end, respectively, of the transformations;

ΔI = difference in the heat contents of the substance in question at the temperatures T_F and T_I, relative to unit volume;

$Q = \Delta I - \int\limits_{T_I}^{T_F} C_s \mathrm{d}T$ = thermal effect of the transformation, where C_s is the heat capacity of the substance in question, relative to unit volume (for transformations, of the type of second-order phase transitions and λ-type heat capacity functions, the term C_S may be understood as the "background" value of the heat capacity, and Q as the excess part of the enthalpy above the "background");

$q = \mathrm{d}Q/\mathrm{d}T$ = intensity of the thermal effect.

It is obvious that

$$Q = \int_{T_I}^{T_F} q \mathrm{d}T \tag{1}$$

For a non-variant transformation

$$Q = \Delta I = Q_{\mathrm{non}} \tag{2}$$

The traditional way to calculate the thermal effect is to introduce some time function whose integral is proportional to the value of the thermal effect. This approach is justified if one assumes that the function in question describes the temperature difference of the sample under study as compared to the temperature that the sample would have if no thermal effect of the transformation existed. It is important to note that this difference, arising at the moment when the transformation starts (to which the point T_i corresponds in the thermal curve) will not disappear immediately after the end of the transformation. Therefore, a portion termed the after-effect portion will exist in the thermal curve. It begins at T_F and ends in an asymptotical transition into the baseline (to which the observed point T_f corresponds). Consequently, in the traditional calculation of the thermal effect one operates with an area bordered by the thermal curve in the section $T_i - T_f$, which will not coincide with the integral of the transformation $T_I - T_F$. The proportionality factor between the area of the peak and the thermal effect will be discussed in a later part of this paper.

The analytical description of the thermal processes in DTA will be carried out similarly to [1–4] and others, assuming that the temperature and other parameters of the sample under study and of the reference sample are constant over their volume at each moment of time. The experimental approach to this model is an instrument in which the heat exchange between the block and the samples takes place over sufficiently large heat resistances, so that temperature transfers in the interior of the samples are small in comparison to the transfers over the above-mentioned resistances. Reduction in the size of the samples, lower heating rates, and also agitation of liquid or powdered materials will promote the approach to the model of the calculation.

A calculation using a linear approach of the heat exchange between the sample being tested at the temperature $T_s(\tau)$ and the block at the temperature $T_b(\tau)$, of the heat exchange between the sample and a number of heat outlets with the temperatures T_{oj} ($j = 1, 2, \ldots, k$; τ = time), and also of the heat exchange between the samples, leads to the following equation for the capacity absorbed in unit volume of the sample studied:

$$n = A(T_b - T_s) - \sum_{j=1}^{j=k} B_j(T_s - T_{oj}) - D(T_s - T_r) \tag{3}$$

where A, B_j and D are coefficients independent of temperature.

An analogous equation for the reference sample with the temperature $T_r(\tau)$ can be established, including on the left-hand side the heat capacity of the reference sample C_r:

$$C_r \frac{dT_r}{d\tau} = A_4(T_b - T_r) - \sum_{j=1}^{j=k} B_j(T_r - T_{oj}) + D(T_s - T_r) \tag{4}$$

Assuming that the temperature change rate of the reference sample is constant, $\frac{dT_r}{d\tau} = \beta$, and introducing the terms $\delta = T_s - T_r$ and $B = \sum_{j=1}^{j=k} B_j$, we obtain from Eqs (3) and (4)

$$n = C_r\beta - \delta(A + B + 2D) = C_r\beta \left(1 - \frac{\delta}{\beta\Theta}\right) \tag{5}$$

The parameter Θ is introduced into Eq. (5):

$$\Theta = C_r(A + B + 2D) \tag{6}$$

A similar parameter figures in [2–4] as a time constant. Its value can be obtained from a calibration experiment using a sample with a known heat capacity value, differing from that of the reference sample. For such an experiment, the left-hand side of Eq. (5) is equal to $C_r\beta$, and hence

$$\Theta = \delta/\beta(1 - C_s/C_r) \tag{7}$$

Since the point in question is heat capacity relative to unit volume, the calibration sample may be made of the material of the reference sample, differing from the latter in its mass, due to internal cavities. In this case, the ratio of the masses should figure in Eq. (7), instead of the ratio of the heat capacities. The changes of Θ observed in the temperature interval of the study allow one to take into account the temperature course of the coefficients A, B and D, and consider them as constants (as in the above deduction) only within limited temperature intervals.

The integral of Eq. (5) from τ_I to τ_F is equal to ΔI, and hence

$$Q = \int_{\tau_I}^{\tau_F} C_r\beta(1 - \delta/\beta\Theta)d\tau - \int_{\tau_I}^{\tau_F} C_s dT \tag{8}$$

The time boundaries of the transformation interval indispensable for calculations with Eq. (8) are obtained in the most simple manner by means of the DTA curve for a non-variant transformation. This curve, in the coordinates δ and τ, has a linear section, whose beginning and end will correspond to τ_I and τ_F. Analytically, it is expressed by the equation

$$\delta(\tau) = \delta_I - \beta\tau \tag{9}$$

Using Eq. (7), δ_I can be expressed as

$$\delta_I = \Theta\beta(1 - C_s/C_r) \tag{10}$$

The relationship (8) may be put into a concrete form for non-variant transformations. Let us introduce the symbols

$$\tau_{F-I} = \tau_F - \tau_I, \; \delta_{F-I} = \delta_F - \delta_I$$

It should be noted that for the non-variant transformation (with heat absorption at $\beta > 0$)

$$\delta_{F-I} = -\beta\tau_{F-I} \tag{11}$$

is true.

Finally, we obtain from Eq. (8)

$$Q_{\mathrm{non}} = \frac{C_r}{\Theta}\left(\frac{\beta\tau_{F-I}}{2} + \Theta\beta - \delta_I\right) \tag{12}$$

and

$$Q_{\mathrm{non}} = \frac{C_r}{\Theta}\left(-\frac{\delta_{F-I}\tau_{F-I}}{2} - \Theta\delta_{F-I} - \delta_I\tau_{F-I}\right) \tag{13}$$

Equation (13) may be interpreted by elements of the area bordered by the thermal curve and the baseline (Fig. 1). The first term within the brackets is equal to the area S_1 bordered by the baseline, the part of the DTA curve in the portion between τ_I and τ_F, and the ordinate at the point τ_F. The third term is equal to the area S_3 between the baseline and the zero line in the portion from τ_I to τ_F. To interpret the second term, one must demonstrate its correspondence to the area S_2, bordered by the baseline, the ordinate at point τ_F and the after-effect portion of the curve.

By combining equations of type (4) for the sample under study and the reference sample at periods $0 \leq \tau_1 \leq \infty$, where $\tau_1 = \tau - \tau_F$, one obtains

$$\frac{C_s}{C_r} = \frac{1 - \delta/\Theta\beta}{1 + \mathrm{d}\delta/\beta\mathrm{d}\tau_1} \tag{14}$$

Integration of Eq. (14) for the boundary conditions $\delta_{(0)} = \delta_F$, $\delta \rightarrow \delta_I$ yields, at $\tau_1 \rightarrow \infty$

$$\delta - \delta_I = \delta_{F-I} \exp\left(-\tau_1 C_r/C_s\Theta\right) \tag{15}$$

Relationship (15) describes the after-effect portion of the thermal curves. The area enclosed by this portion and the baseline is equal to the integral of Eq. (15) within the limits $\tau_1 = 0$ to $\tau_1 \rightarrow \infty$, yielding

$$\delta_{F-I}\Theta C_s/C_r$$

If $C_s = C_r$, the second term in the brackets in Eq. (13) will be equal to S_2, under the condition that $S_3 = 0$. Finally, the rule of proportionality between the thermal effect and the area of the peak will be confirmed. The proportionality factor is equal to C_r/Θ.

For a transformation taking place within a temperature interval, the determination of the integration boundaries for Eq. (8) is not quite so obvious as for the non-variant transformation. Namely, while T_I coincides with T_i, T_F will not in the general case coincide with the peak height, and the situation shown in Fig. 2 will occur. The distribution of the thermal effect will be given by the function φ:

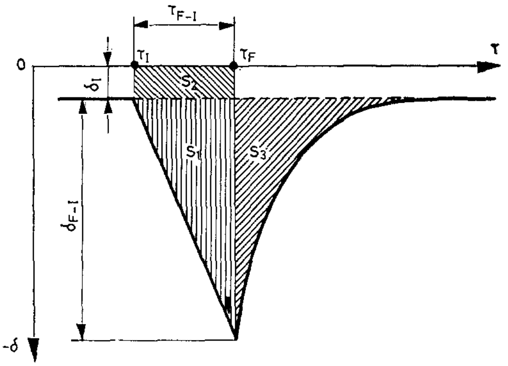

Fig. 1. Thermal curve of non-variant transformation obtained on heating of the samples

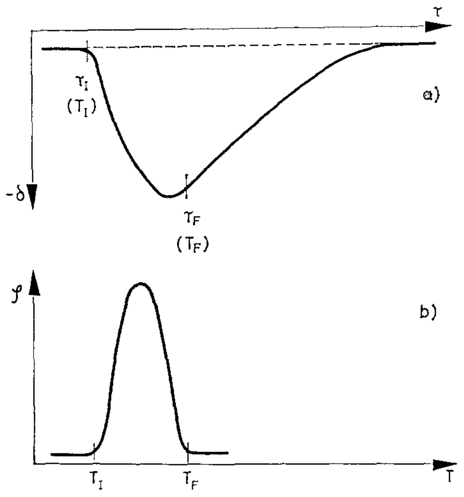

Fig. 2. Typical thermal curve (a) and the corresponding distribution of the thermal effect (b)

$$\varphi = (C_s + q)/C_r$$

The connection of ϕ with the thermal curve is determined from a relationship similar to Eq. (14), which, within the temperature interval of the transformation, includes, in place of C_s, the complex $C_s + q$:

$$\varphi = \frac{1 - \delta/\Theta\beta}{1 + \mathrm{d}\delta/\beta\mathrm{d}\tau} \tag{16}$$

Equation (16) should be considered the basic equation of the DTA curve, and Eq. (14) as its special case for the after-portion of the curve. The moment τ_F (and consequently the temperature T_F also) can be identified as that point in the thermal curve after which this curve is described by the exponential relationship Eq. (13). For this purpose it is expedient to straighten the corresponding portion of the curve by plotting it in semi-logarithmic coordinates [1].

Another approach to determine T_F utilizes Eq. (16). By calculating from the thermal curve (Fig. 2a) the parameter φ corresponding to Eq. (16), one can obtain its dependence on temperature (Fig. 2b), on which T_F appears as the point of transition of the curve $\varphi(T)$ into the "baseline".

A curve of the type of Fig. 2b additionally contains sufficient information for calculation of Q and the distribution of the intensity of the thermal effect in the temperature interval of the transformation. The reverse process is also feasible: from a given function $\varphi(T)$, the corresponding thermal curve can be calculated [5].

We will now demonstrate the application of these methods to calculate Q for the case of the simplest distribution of the thermal effect: at φ = const., and $C_s = C_r$.

For the temperature difference *vs.* time relationship (in the period of the transformation) we have, from Eq. (16):

$$\delta = \beta\Theta(1 - \varphi)[1 - \exp(-\tau/\varphi\Theta)] \tag{17}$$

for the after-effect portion, an expression of the type of Eq. (13) will be true:

$$\delta = \delta_F \exp(-\tau_1/\Theta) \tag{18}$$

The values δ_F, T_I and T_F are related by the equation

$$T_F = T_I + \beta\tau_{F-I} + \delta_F \tag{19}$$

The first method to calculate Q consists in the use of the experimental thermal curve within the interval τ_I to τ_F, and the calculation formula Eq. (8). By substituting Eq. (17) into Eq. (18), and taking into account Eq. (19), we obtain

$$Q = C_r(T_F - T_I)(\varphi - 1) \tag{20}$$

The second method consists in calculating the function $\varphi(T)$ from the same portion of the experimental curve (and together with this, the function $q(T)$ too, and subsequently utilizing Eq. (1). For the case in question, the result will be identical with Eq. (20).

The third possibility consists in calculating the area of the peak and multiplying it by C_r/Θ. This area is equal to the sum of the following integrals: Eq. (17) from

$\tau = 0$ to τ_{F-I}, and Eq. (18) from zero to $\tau_I \to \infty$. One may ascertain that the result is again identical with Eq. (20).

However, the dependence of the intensity of the thermal effect on temperature and time can only be determined by the first two methods.

Depending on the task to be solved and on the experimental conditions, one or the other method of calculation, or their combination may prove expedient. An example of such a combination important in practice is the case when neighbouring peaks partially overlap. Usually, the temperature intervals of the transformations do not in fact overlap, but the after-effect portion of the first peak will overlap with the following peak. In such cases, the thermal effect of the first transformation may be determined by calculation using the first or second method, and the total thermal effect by measuring the total area of the peaks.

References

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Résumé — En considérant le fait que la température de la fin de l'effet thermique et le retour à la ligne de base de la courbe ATD ne coïncident pas, on a développé de nouvelles méthodes du calcul de l'effet thermique. La valeur intégrale de l'effet thermique ainsi que sa distribution dans l'intervalle de températures peuvent être calculées en ne considérant que la partie de la courbe ATD qui correspond à l'intervalle de température de la transformation.

A l'aide d'exemples de transformations invariantes et de transformations à distribution uniforme de l'effet thermique dans l'intervalle de températures de la transformation, on a montré qu'avec certaines hypothèses, les valeurs de l'effet thermique calculées par la méthode proposée et à partir des surfaces des pics, sont identiques.

Zusammenfassung — Bei Berücksichtigung, daß die Temperatur des Endes des thermischen Effekts und die Rückkehr der thermischen Kurve zur Grundlinie nicht zusammenfallen, werden neue Methoden zur Berechnung des thermischen erschlossen. Sowohl der Integralwert des thermischen Effekts, als auch seine Verteilung in dem Temperaturbereich können durch Behandlung ausschließlich desjenigen Teils der DTA-Kurve berechnet werden, welcher dem Temperaturbereich der Umwandlung entspricht.

Anhand von Beispielen der nicht-varianten Transformation und der Transformation mit gleichmäßiger Verteilung des thermischen Effekts im Temperaturbereich der Umwandlung wurde gezeigt, daß — unter gewissen Voraussetzungen — die Werte des durch die vorgeschlagene Methode und des aus der Peakfläche berechneten thermischen Effekts identisch sind.

Резюме — Новые возможности расчета тепловых эффектов открываются при учете несовпадения температур конца теплового эффекта и возврата термической кривой к базовой линии. Как интегральное значение теплового эффекта, так и его распределение по температуре могут быть рассчитаны при обработке только той части ДТА-кривой, которая соответствует температурному интервалу превращения.

На примерах нонвариантного превращения и превращения с равномерным распределением теплового эффекта в температурном интервале превращения показано, что при некоторых допущениях, значения теплового эффекта рассчитанные по предлагаемой методике и по площади пика совпадают.