THEORY OF DIFFERENTIAL THERMAL ANALYSIS
TAKING INTO ACCOUNT HEAT EXCHANGE BETWEEN
THE SPECIMEN AND REFERENCE CELLS

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A basic formula of differential thermal analysis is evolved for the case when the heat transfer coefficient between the specimen cell and the reference cell is not zero. The more general formula obtained differs from the classical formula by including the parameters of the reference cell and the heat transfer coefficient between the cells. It indicates that utilization of the classical formula is not correct if heat exchange occurs between the cells. To utilize the generalized formula, additional measurements of the temperature changes of the reference material are required. However, if the time constants of the two cells are identical, the formula can be changed to assume the form of the classical formula for DTA if a correction factor is introduced which takes into account the effect of heat exchange between the cells.

The deficiency of the classical formula of DTA first introduced in 1957 by Borchardt and Daniels [1] is that its utilization is restricted insofar as it postulates the non-occurrence of heat exchange between the specimen and the reference sample. However, cases occur in DTA practice in which such heat exchange does take place. In the various instruments for DTA described in the literature [1–4] the absence of heat exchange between the specimen cell and the reference cell is assumed. However, the correctness of this assumption is unfounded. No theoretical investigation of the problem is to be found in the literature.

To increase the stability of the baseline of the instrument, it is favourable to position the holders of the specimen cell and of the reference cell as close as possible to one another within a small volume of the furnace capacity where the probability of a homogeneous temperature distribution is higher. However, as the holders approach, the heat transfer coefficient between them increases to a value at which the temperature change of the specimen by virtue of the thermal reaction induces a corresponding change in the temperature of the reference material. If, for instance, the reaction is endothermic, the temperature of the specimen will lag behind the temperature of the reference material during the reaction, and heat will be transferred from the latter to the specimen. As a result, the reference material will cool down slightly and the specimen will warm up. The negative temperature difference in the specimen (its absolute value) will decrease, and an additional negative temperature will be produced in the reference material, depending on its heat capacity and on the heat transfer
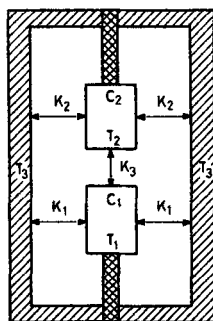
Fig. 1 Diagrammatical representation of the DTA sensor. C_1 — heat capacity of the specimen with holder, C_2 — heat capacity of the reference material with holder, K_1, K_2 — heat transfer coefficients of the specimen cell and the reference cell, resp., K_3 — coefficient of heat transfer between the specimen cell and the reference cell, T_1, T_2, T_3 — temperatures of the specimen, the reference material and the heating block, resp.

coefficient. Analogous considerations hold for exothermic reactions. It is evident that the differential signal recorded when there is a thermal connection between the cells may differ essentially from the differential signal recorded in the absence of such a connection.

It is of interest to examine the above phenomenon quantitatively and to develop a method allowing an experimental check on whether a thermal connection exists between the cells or not. In the following, the generalized formula of DTA will be derived for a weak thermal connection. The symbols are the same as in our previous paper (cf. also caption to Fig. 1).

Let us write the equation of heat balance for the cells with a thermal connection between them. For the specimen cell before the reaction we have:

$$C_1 dT_1 = K_1 (T_3 - T_1)\, dt + K_3 (T_2 - T_1)\, dt \tag{1}$$

For the reference cell before the reaction:

$$C_2 dT_2 = K_2 (T_3 - T_2)\, dt + K_3 (T_1 - T_2)\, dt \tag{2}$$

For the specimen cell during the reaction:

$$C_1 d(T_1 + \Delta T_1) + d\Delta H =$$
$$= K_1 (T_3 - T_1 - \Delta T_1)\, dt + K_3 (T_2 + \Delta T_2 - T_1 - \Delta T_1)\, dt \tag{3}$$

For the reference cell during the reaction:

$$C_2 d(T_2 + \Delta T_2) =$$
$$= K_2 (T_3 - T_2 - \Delta T_2)\, dt + K_3 (T_1 + \Delta T_1 - T_2 - \Delta T_2)\, dt \tag{4}$$

where ΔT_1 is the incremental temperature of the specimen, and ΔT_2 the incremental

temperature of the reference material. For endothermic reactions $\Delta H > 0$, $\Delta T_1 < 0$ and $\Delta T_2 < 0$; for exothermic reactions $\Delta H < 0$, $\Delta T_1 > 0$ and $\Delta T_2 > 0$.

Let us assume that $K_1 = K_2 = K$; this condition is satisfied with cells having identical thermal barrier resistances. Let the heating programme of the block be (Fig. 1):

$$T_3 = T_0 + \phi t \tag{5}$$

When a linear temperature rise is established at $\Delta H = 0$:

$$T_1 = T_0 + \phi t - \phi \tau_1 \tag{6}$$

$$T_2 = T_0 + \phi t - \phi \tau_2 \tag{7}$$

if the small terms $K_3(T_1 - T_2)$ dt in Eqs (1) and (2) are neglected. Hence the theory can be utilized if $K_3 \ll K$ and $C_1 \approx C_2$, since the term $K_3(T_1 - T_2)$ is negligibly small only under these conditions. This case will be attained in practice on the correct choice of the parameters of the reference cell.

It follows from Eqs (5), (6) and (7) that

$$T_3 - T_1 = \phi \tau_1$$

$$T_2 - T_1 = \phi(\tau_1 - \tau_2)$$

$$T_3 - T_2 = \phi \tau_2$$

Substituting these expressions into Eqs (3) and (4) and carrying out the necessary transformations, we obtain

$$-\frac{d\Delta H}{K dt} = \Delta T_1 + \tau_1 \frac{d\Delta T_1}{dt} + \frac{K_3}{K}(\Delta T_1 - \Delta T_2) - \frac{K_3 \phi}{K}(\tau_1 - \tau_2) \tag{8}$$

$$\Delta T_2 + \tau_2 \frac{d\Delta T_2}{dt} - \frac{K_3}{K}(\Delta T_1 - \Delta T_2) + \frac{K_3 \phi}{K}(\tau_1 - \tau_2) = 0 \tag{9}$$

Subtraction of Eq. (9) from Eq. (8) yields

$$-\frac{d\Delta H}{K dt} =$$

$$= \left(1 + \frac{2K_3}{K}\right)(\Delta T_1 - \Delta T_2) + \tau_1 \frac{d\Delta T_1}{dt} - \tau_2 \frac{d\Delta T_2}{dt} - \frac{2K_3 \phi}{K}(\tau_1 - \tau_2) \tag{10}$$

while adding Eqs (8) and (9) results in

$$-\frac{d\Delta H}{K dt} = \Delta T_1 + \Delta T_2 + \tau_1 \frac{d\Delta T_1}{dt} + \tau_2 \frac{d\Delta T_2}{dt} \tag{11}$$

In the case of identical time constants for the specimen cell and the reference cell, Eqs (10) and (11) become simpler:

$$-\frac{d\Delta H}{Kdt} = \left(1 + \frac{2K_3}{K}\right)(\Delta T_1 - \Delta T_2) + \tau \frac{d(\Delta T_1 - \Delta T_2)}{dt} \tag{10a}$$

$$-\frac{d\Delta H}{Kdt} = \Delta T_1 + \Delta T_2 + \tau \frac{d(\Delta T_1 + \Delta T_2)}{dt} \tag{11a}$$

In the usual position of the differential thermocouple (hot junction of one branch in the specimen, and hot junction of the other branch in the reference material) the signal recorded is equal to the difference of the incremental temperatures of the specimen and the reference material, if counted from the dynamic baseline of the instrument. To measure these temperatures separately, one branch of the differential thermocouple should be located on the external surface of the heat barrier of the corresponding cell (on the wall of the block); then, by locating the other branch in the specimen, we can record ΔT_1, and the locating it in the reference material, we record ΔT_2. Thus, of the above equations, only Eq. (10a) can be utilized, since with the traditional positioning of the differential thermocouple we cannot determine ΔT_1 and ΔT_2 separately, but only their difference.

A comparison of Eq. (11a) with the common equation of DTA

$$-\frac{d\Delta H}{Kdt} = \Delta T_p + \tau \frac{d\Delta T_p}{dt} \tag{12}$$

demonstrates that the sum of the incremental temperatures of the specimen and the reference material, for the case when the time constants of the cells are identical, is equal to the incremental temperature of the specimen in the absence of a thermal connection between the cells; i.e. at $\tau_1 = \tau_2$, the incremental temperature of the reference material is equal in value to the decrease in the incremental temperature of the specimen.

Equations (10) and (10a) demonstrate that if a thermal connection exists between the cells, the signal recorded decreases due to the decrease of the incremental temperature form ΔT_p to ΔT_1, and also due to the incremental temperature of the reference material being subtracted from the incremental temperature of the specimen in the differential thermocouple circuit. Since the term $\dfrac{d\Delta H}{dt}$ is defined by the reaction in question and does not depend on the method of measurement, the decrease in the signal registered must, by some means, be compensated in the calculation. Such a compensation is effected by the factor $\left(1 + \dfrac{2K_3}{K}\right)$ before the term $(\Delta T_1 - \Delta T_2)$. With increasing K_3 values, the difference $(\Delta T_1 - \Delta T_2)$ decreases but the value of the factor $\left(1 + \dfrac{2K_3}{K}\right)$ increases, and thereby compensation is accomplished. The above is valid for not too high values of K_3, this being the condition initially pointed out.

Equations (10), (10a), (11) and (11a) are the general equations of differential thermal analysis. The classical Eq. (12) follows from them as a particular case in which $K_3 = 0$ and $\Delta T_2 = 0$.

From the above analysis it follows that if a thermal connection exists between the specimen cell and the reference cell, calculations using the classical formula of DTA, Eq. (12), will be incorrect. Calculations with the above-derived general equations, however, require additional measurements of the incremental temperature of the reference material, i.e. the process will become more intricate. The general formula includes the parameters of the reference cell, the heating rate and the coefficient of the thermal connection between the cells, all these being absent from Eq. (12). The situation becomes somewhat simpler if the time constants of the specimen cell and the reference cell are equal, since Eq. (10a) can then be used, this being similar in form to the usual equation of DTA. However, an additional constant, the coefficient of heat transfer between the cells is included, and accordingly its use will be cumbersome.

In the general case, it is impossible to establish from the form of the thermoanalytical curve whether or not, in the actual instrument, a thermal connection exists between the specimen and the reference material. To answer this question the thermocouple of the specimen must be placed on the wall of the heating block and the thermoanalytical curve of the reference material recorded. If a peak appears in the curve in the interval of the thermal transformation of the specimen, this finding will indicate the existence of a thermal connection between the cells.

Another technique is also suitable to find out whether such a connection exists. This technique allows determination of the optimum distance between the sample holders and, if necessary, the value of the coefficient of thermal connection K_3. For this purpose, let us transform the general equation of DTA into the integral form. Let us integrate Eq. (10) from the moment when the differential curve deviates from the baseline to the moment when it returns to the baseline:

$$\Delta H = (K + 2K_3) \int_{t_1}^{t_2} (\Delta T_1 - \Delta T_2)\, dt + 2K_3 \phi (\tau_2 - \tau_1)(t_2 - t_1) \tag{13}$$

where ΔH is the total heat of the thermal transformation, and $A = \int_{t_1}^{t_2} (\Delta T_1 - \Delta T_2)\, dt$ is the area under the peak in the DTA curve, reduced in comparison to the area of the peak in the absence of a thermal connection between the cells. Let us move the specimen holder and the reference material holder to a distance at which the thermal connection between them is negligibly small (this will correspond to the maximum area not changing further). Such a shift of the holders can readily be performed in an instrument such as that represented diagrammatically in Fig. 1; the motion of the holders along the axis of the furnace will not change the distance between the crucible walls and the block, and consequently will have little effect on the heat transfer coefficient K. The DTA curve with the maximum area A under the peak is recorded and the value K is found by means of the formula

$$\Delta H = K \cdot A \tag{14}$$

which is the integral form of Eq. (12). The value ΔH in Eq. (14) must, of course, be known, so that only a material whose heat of transformation is known is suitable.

Using Eq. (13), we can then calculate the coefficient of the thermal connection K_3:

$$K_3 = \frac{K(A - A_1)}{A_1 + 2\Delta T_B(t_2 - t_1)} \tag{15}$$

where $\Delta T_B = \phi(\tau_2 - \tau_1)$ is the initial displacement of the baseline from the zero line on recording of the DTA curve with a peak area of value A_1.

The coefficient K_3 can also be found by varying the heat capacity of the specimen of the reference material. This causes the recorded values of ΔT_B and A_1 to change, while the unknowns K and K_3 remain unchanged. The latter can then be found by solving the system of two equations with two unknowns.

References

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Zusammenfassung – Für den Fall, dass der Übertragungskoeffizient zwischen der Proben- und der Referenzzelle nicht Zero ist, wurde eine Grundformel der Differentialthermoanalyse entwickelt. Die entstandene Formel, die vielmehr allgemein ist, weicht von der klassischen dadurch ab, dass sie auch die Parameter der Referenzzelle, und den Wärmeübertragungskoeffizient zwischen den Zellen enthält. Sie deutet darauf hin, dass die Anwendung der klassischen Formel in dem Fall nicht einwandfrei ist, wenn ein Wärmeaustausch zwischen den Zellen zustande kommt. Zur Anwendung der verallgemeinerten Formel sind weitere Messungen des Temperaturaustausches vom Referenzmaterial erforderlich. Sind aber die Zeitkonstanten der zwei Zellen identisch, kann die Formel so geändert werden, dass sie die Gestalt der klassischen DTA-Formel annimt, wenn ein, mit der Wirkung des Wärmeaustausches zwischen den Zellen rechnender Korrektionsfaktor eingeführt wird.

Резюме — Приводится вывод основной формулы дифференциального термического анализа для случая, когда коэффициент теплопередачи между ячейками образца и эталона не равен нулю. Полученная более общая формула отличается от классической тем, что в нее входят параметры эталонной ячейки и коэффициент теплопередачи между ячейками, что указывает на неправомерность использования классической формулы при наличии теплообмена между ячейками. Использование полученной общей формулы требует дополнительных измерений температурных изменений эталона. Однако, при равенстве постоянных времени двух ячеек становится возможным применение общей формулы, принимающей форму классической формулы ДТА, при условии введения в нее поправочного множителя, учитывающего влияние коэффициента теплопередачи между ячейками.