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

II. An introduction to time-space calorimetry

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Volume-isothermal and surface-isothermal sensing units with a gas-phase thermal barrier are described. Use of the two-point method of DTA with the surface isothermal sensing unit permits experimental determination of the internal heat resistance of the sample holder (of the reaction zone), thereby allowing elucidation of the mechanism (topochemistry) of the reaction and the finding of more exact kinetic data via a novel method of split heat capacities.

Insulated sample holder with gas-phase thermal barrier (variants).

The variants of such instruments are represented schematically in Figs 1 III, 1 IV and 1 V. Their essential element is a thin-walled cylindrical holder, fixed on thermally insulating wire supports in the cavity of the cylindrical heater so that a uniformly wide gas gap is formed between them, and the wire supports are located in the isothermal heat-transferring surface plane. As two of the four supports, the wires of the differential thermocouple are used; its hot junctions are soldered to the wall of the heater. The optimum dimensions, according to [1], are as follows: heater cavity diameter 10 mm, height 140 mm; sample holder dimensions 4.4 × 8.0 mm, wall thickness 0.15–0.20 mm; support wire diameter 0.2 mm, length from the metal vessel to the supporting point 20–40 mm. The sample holder and the reference material holder are positioned one below the other at a distance of 30 mm, at equal distances from the heater. With these parameters, the heat exchange over the thermocouple wires is negligibly small as compared with the heat exchange over the gas gap [1], and consequently a high degree of isothermalness is observed and the recorded temperature of the surface is not distorted. The major fundamental differences from the usual instruments are as follows:

(i) The perfect thermal insulation of the sample holder from the heater, the gas gap playing the role of a heat barrier with high resistance and very small heat capacity.

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(ii) A low-inertia sample holder with a low heat capacity of its own and a high thermal conductivity of its wall.

(iii) A low-inertia temperature sensor, not participating in heat exchange, with zero contact heat resistance.

(iv) The high symmetry and homogeneity of temperature fields.

These features lead to two important properties: the stability of the isothermalness of the surface of the holder, not affected by the state of the sample and by the thermal transformation proceeding in it, and the fact that the parameters C and R, i.e. the heat capacity and thermal resistance, are separated, C being concentrated in the region of the sample holder, and R in the region of the gas gap. That the surface of the holder is necessarily isothermal is made clear by comparing the values of the thermal resistance of the holder wall and the gas gap; for this comparison, the criterion of Biot from the theory of heat transfer [2] can be used: calculations yield a value of the Biot criterion of the order of $Bi = \frac{K_2}{K_w} \approx 10^{-2}$, indicating that temperature differences on the surface of the holder will be equalized at a much higher rate than temperature perturbances (ΔT_p) on the heat barrier. The concentrated character of the parameters C and R follows from the properties of the gas-phase heat barrier and from the mode of fixing the sample holder on thermally insulating supports with zero additional heat capacity [1].

As demonstrated by theoretical analysis and experimental confirmation, this type of instrument corresponds to the requirements of theory to a much higher degree. For further improvement of the correspondence between the mathematical model and the instrument, the shape and density of the sample in the holder should be defined. For this purpose, depending on the mode of packing, three variants are feasible; these are described in the following.

Sample holder isothermal over its total volume. In this variant the sample has the shape of a thin layer in reliable thermal contact with the bottom and walls of the holder (Fig. 1 III). The mathematical conditions are

$$C_B = 0; \quad T_s = T_i \neq T_H; \quad \frac{dT_H}{dt} = \varphi = \text{const.}$$

$$\Delta T_2 = T_i - T_H - (T_i - T_H)_{st}; \quad \Delta T_1 = 0; \quad \Delta T_p = \Delta T_2 \tag{23a}$$

The heat flow from the wall of the heater is

$$\frac{dQ}{dt} = C_s \varrho_s \pi l_s R_i^2 \varphi + C_h \varphi = C_\Sigma \varphi \tag{23b}$$

where C_Σ is the sum of the heat capacities of the holder and the sample. On the other hand, for $R_i \leqslant r \leqslant R_H$ the equality

$$\frac{dQ}{dt} = 2\pi r l_h \lambda_B \frac{dT_B}{dr} \tag{24}$$

holds. Solving these equations jointly and integrating from R_i to R_H, we obtain

$$(T_H - T_i)_{st} = \frac{C_\Sigma \varphi \ln R_H/R_i}{2\pi l_h \lambda_B} \tag{24a}$$

Let us express the heat flow by means of the temperature drop over the gas gap:

$$\frac{dQ}{dt} = \frac{2\pi l_h \lambda_B}{\ln R_H/R_i}\left(\frac{C_\Sigma \varphi \ln R_H/R_i}{2\pi l_h \lambda_B}\right) = K_2(T_H - T_i)_{st} \tag{24b}$$

where

$$K_2 = \frac{2\pi l_h \lambda_B}{\ln R_H/R_i} \tag{25}$$

and during the reaction

$$\frac{dQ}{dt} = K_2[-\Delta T_2 + (T_H - T_i)_{st}] = -K_2 \Delta T_2 + C_\Sigma \frac{dT_H}{dt} \tag{25a}$$

Let us establish the heat balance, using Eq. (10):

$$-\frac{d\Delta H}{dt} = K_2 \Delta T_p + C_\Sigma \frac{d(T_s - T_H)}{dt} \tag{26}$$

It follows from the above mathematical conditions that

$$T_s - T_H = T_i - T_H = \Delta T_p + \text{const.}$$

and after substitution into Eq. (26) we obtain

$$-\frac{d\Delta H}{dt} = K_2 \Delta T_p + C_\Sigma \frac{d\Delta T_p}{dt} \tag{27}$$

In the constant K_2 defined by Eq. (25), the last parameter involving the sample is eliminated: instead of l_s, i.e. the sample height, we have l_h, i.e. the holder height; this is a consequence of the postulate claiming the isothermal surface of the holder before and during the reaction, on the basis of which Eq. (24) is written. Thus, the insulated sample holder is a logical improvement on block-type instruments, insofar as one of the major deficiencies is eliminated: the dependence of the calibration constant on the properties of the sample in the holder.

The integrated form of Eq. (27)

$$\Delta H_t = \Delta H_0 M = -K_2 A_t \tag{27a1}$$

demonstrates that if $\Delta H_0 = \text{const}$ and $K_2 = \text{const}$, peak area A_t is directly proportional to sample mass M at any value of M. In the block-type instrument, in contrast, A_t is independent of M: A_t does not change with M after a sample with satisfactory height is reached [1].

Insulated sample holder isothermal on its surface, but non-isothermal over its volume. In many cases one cannot use the sample in the form of a thin layer or ensure its close contact with the walls of the holder (e.g. when powders are being investigated). In such cases one must expect that the internal resistance of the holder will increase to a value comparable with that of the gas gap; the isothermalness over the volume of the sample will then disappear, but the isothermalness of the surface will be retained, if the sample packing in the holder is satisfactorily uniform. The mathematical conditions for this variant (Fig. 1 IV) are as follows:

$$C_B = 0;\ T_0 \neq T_i \neq T_H;\ \frac{dT_H}{dt} = \text{const};\ T_s = \frac{T_0+T_i}{2}$$

$$\Delta T_1 = T_0 - T_i - (T_0 - T_i)_{st} \tag{27a}$$

$$\Delta T_2 = T_i - T_H - (T_i - T_H)_{st};\ \Delta T_p = \Delta T_1 + \Delta T_2$$

and hence

$$T_s - T_H = \frac{T_0 - T_H}{2} + \frac{T_i - T_H}{2} = \frac{\Delta T_p}{2} + \frac{\Delta T_2}{2} + \text{const} \tag{27b}$$

and, after substitution into Eq. (26), we obtain

$$-\frac{d\Delta H}{dt} = K_2 \Delta T_2 + \frac{C_\Sigma}{2}\left(\frac{d\Delta T_p}{dt} + \frac{d\Delta T_2}{dt}\right) \tag{28}$$

Equations (27) and (28) are both particular cases of the general equation (22); Eq. (27) follows from Eq. (22) at $C_B = 0$ and $\Delta T_p = \Delta T_2$, while Eq. (28) follows from Eq. (22) at $C_B = 0$.

For the sample in a holder with isothermal walls, these walls will play the part of the heater, with the difference that $\frac{dT_i}{dt} \neq \text{const}$; nonetheless, the heat flow from the walls of the holder to the sample (from their external surface) may be expressed by an equation of the form of Eq. (9a) (cf. Fig. 2 in Part I):

$$\frac{dQ}{dt} = K_1[(T_i - T_0)_{st} - \Delta T_1] = C_\Sigma \frac{dT_H}{dt} - K_1 \Delta T_1 \tag{29a}$$

Here

$$K_1 = \frac{1}{K_\omega^{-1} + K_c^{-1} + K_s^{-1}}$$

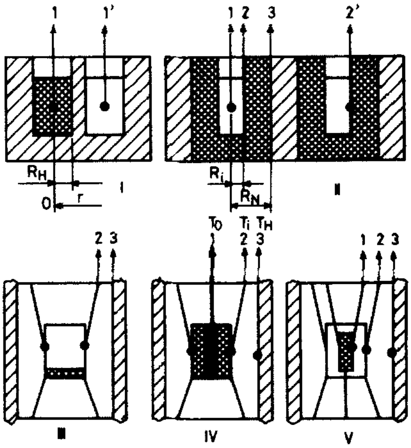

Fig. 1 Schematic representation of DTA instrument types: I – block-type without special heat barrier; II – block type with special heat barrier; III – insulated sample holder with zero internal resistance; IV and V – insulated sample holder with non-zero internal resistance

where K_ω^{-1}, K_c^{-1} and K_s^{-1} are the thermal resistance of the holder wall, the wall-sample contact resistance and the thermal resistance of the sample, respectively, while $\Delta T_1 = \Delta T_\omega + \Delta T_c + \Delta T_s$ is the sum of the drops of the incremental temperature of the reaction on these resistances. By combining Eqs (29) and (10), we obtain we obtain

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_1 \Delta T_1 + \frac{C_\Sigma}{2}\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} + \frac{\mathrm{d}\Delta T_2}{\mathrm{d}t}\right) \tag{29b}$$

From Eq. (28) and the above equation it follows that

$$K_1 \Delta T_1 = K_2 \Delta T_2 \tag{30}$$

The overall heat of reaction may be found by making use of the areas of the peaks A_{1t} and A_{2t} in the integrated forms of Eqs (23) and (28):

$$\Delta H_t = -K_1 A_{1t} \tag{31}$$

$$\Delta H_t = -K_2 A_{2t} \tag{32}$$

Let us find the formula allowing calculation of ΔH_t from the peak area A_t at height ΔT_p. By dividing Eq. (31) by K_1 and Eq. (32) by K_2 and adding the resulting equations, we obtain

$$\begin{aligned} \Delta H_t(R_1' + R_2') &= A_{2t} + A_{1t} = A_t \\ \Delta H_t &= \frac{A_t}{R_1' + R_2'} = K A_t \end{aligned} \tag{33}$$

where $R'_1 = K_1^{-1}$ and $R'_2 = K_2^{-1}$. Consequently

$$K = \frac{1}{\dfrac{1}{4\pi l_s \lambda_s} + \dfrac{\ln R_H/R_i}{2\pi l_h \lambda_B}} \tag{34}$$

Thus, the constant K expressed in terms of the peak area A_t is the reciprocal of the sum of the thermal resistances of the internal and the external heat barrier. As will be demonstrated below, the expression for K depends on the accepted model of the reaction. To consider this relationship, it is necessary to define the term heat barrier as used in this paper in more detail.

Definition of the term heat barrier

The heat barrier is the material medium between the isothermal surface of the heat exchanger (first boundary of the heat barrier) and the heat-receiving isothermal surface of the sample (reactant) (second boundary of the heat barrier), having the property of decelerating heat exchange between the sample and the heat exchanger. In studies of thermal transformations, the quantity to be measured is the incremental heat of reaction, and the heat barrier can therefore be defined in the following particular manner: it is that part of the material medium between the heat exchanger and the reactant, over which the total drop of the incremental temperature of reaction proceeds. For its measurement, the measuring thermocouples must be located on the boundaries of the heat barrier, the position of the first boundary being defined by the condition $\Delta T_p = 0$, while that of the second boundary coincides with the heat-receiving surface of the reactant. The reference thermocouple located on the first boundary may also be located in the reference cell, with the condition that for this cell $\Delta T_p = 0$ (no thermal connection for the incremental temperature exists between the working cell and the reference cell [3]).

In the case of homogeneous reactions, the incremental temperature drops within the total volume of the reacting sample, and therefore the working thermocouple must be located at the centre of the sample. In the case of heterogeneous reactions proceeding on the surface of the reactant, the working thermocouple should be located on the moving reaction front separating the reactant from the reaction product; since this is impossible, it is located at the centre of the sample. If the working thermocouple is in the zone of the reaction products, the incremental temperature measured will be lower than the total value. This is made clear by Fig. 2. If the dashed line in the Figure represents the boundary between the reactant (zone 1) and the reaction product (zone 2), then in the case of heterogeneous reactions no reaction takes place in zone 1 and hence no incremental temperature is

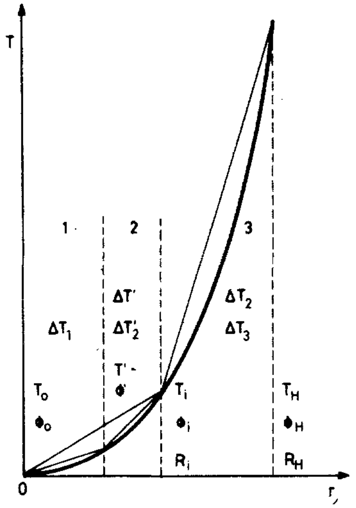

Fig. 2 Temperature distribution *versus* radius

present ($\Delta T_1 = 0$), while in the case of homogeneous reactions taking place in the bulk of the reactant, $\Delta T_1 \neq 0$.

A knowledge of the total value of ΔT_p and of the total thermal resistance of the heat barrier is necessary for kinetic calculations, since the measured rate of heat absorption depends not only on the external resistance (that of the gas gap), but also on the internal resistance (that of the holder with the sample). For thermodynamic studies it is sufficient to know only a part of the total resistance of the heat barrier, namely the external resistance and the share of the incremental temperature ΔT_2 assigned to it (cf. Eq. (32)).

The position of the second boundary of the heat barrier depends on the topochemistry of the reaction. Let us consider the following topochemical models:

(a) A homogeneous reaction, with a motionless second boundary of the heat barrier coinciding with the axis line of the sample. This case has been considered in the derivation of Eq. (34).

(b) A homogeneous reaction in which the area of the reaction decreases and a boundary exists between this area and the reaction product. For this case

$$K = \frac{1}{\dfrac{1}{4\pi l_s \lambda_s} + \dfrac{\ln R_2/R_1}{2\pi l_s \lambda_p} + \dfrac{\ln R_H/R_i}{2\pi l_h \lambda_B}} \tag{35}$$

where R_2 and R_1 are the external and internal radius, respectively, of the cylindrical layer formed by the reaction product. Since R_1 decreases when the boundary is shifted ($R_1 \to 0$), the resistance of the reaction product increases and K decreases during the reaction.

(c) A heterogeneous reaction proceeding on the surface of the reactant; the second boundary of the heat barrier coincides with the reaction front moving towards the centre of the sample; the thermal resistance of the reaction zone may be neglected by reason of its narrowness. Then

$$K = \frac{1}{\dfrac{\ln R_2/R_1}{2\pi l_s \lambda_p} + \dfrac{\ln R_H/R_i}{2\pi l_h \lambda_B}} \tag{36}$$

Effect of internal resistance on rate of heat absorption of the reaction and accuracy of rate determination

On the change-over from the gradientless holder to the holder with volume gradient, K_1 decreases from an infinitely high value to its final value; simultaneously, as shown by experiment [10], the values $|\Delta T_2|$ and $\left|\frac{\mathrm{d}\Delta T_2}{\mathrm{d}t}\right|$ decrease, i.e. the peak A_2 becomes lower and more elongated in time (though its total area A_{2t} does not change); this is caused by the more rapid heating-up of the periphery of the sample (and of the thermocouple *2*) by reason of the decreased heat flow to the reaction zone; in contrast, the value ΔT_1 increases in parallel with the area of the peak A_{1t} (only the product $K_1 A_{1t}$ remains constant, cf. Eq. (31)); this is explained by the tendency of the reaction to pass to the isothermal regime: all heat input will be absorbed by the reaction, no heat is left to heat up the sample, $\Phi_s \to 0$ and $\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} = \Phi_s - \Phi \to -\Phi$. As a final result, $\frac{\mathrm{d}\Delta H}{\mathrm{d}t}$, the recorded rate of heat absorption, will decrease. For significant decreases of K_1 (or K_2), the reaction passes to the isothermal regime, in which kinetic analysis by means of the formulas of our theory loses its meaning.

Let us now consider the effect of the internal resistance on the term $C\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$, i.e. on the accuracy of the calculations with formulas (23), (27) and (28). At non-zero resistance of the holder with the sample, the term $C\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$ loses its physical definiteness. To explain this, let us express it in the form

$$C\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} = C(\Phi_s - \Phi) = q_s - q$$

where Φ_s is the heating rate of the sample, C is its heat capacity, and Φ is the heating rate of the block. From the above expression it is clear that the term $C\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$ is the difference between two heat flows: the heat flowing to the sample by reason of the existence of a constant temperature jump over the air gap (q), and the heat flow serving to raise the temperature of the sample at a rate Φ_s (q_s). This difference is the heat flow absorbed by the reaction. The rest of the flow absorbed by the reaction is expressed by the term $K_2\Delta T_2$. In the case of the isothermal holder, only one value exists for Φ_s, this being one and the same for any point in the volume of the sample, and the term $C\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$ has the definite physical meaning explained above. In the case of the non-isothermal holder, however, the values of Φ_s are continuously distributed over the volume of the sample, from the maximum value at its periphery to the minimum value at its centre, and the measured value $C\left|\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right|$ depends on the position of the thermocouple, changing from the maximum at the central position (thermocouple *1*) to the minimum at the lateral position (thermocouple *2*). Among all these values of $C\frac{\mathrm{d}\Delta T_i}{\mathrm{d}t}$, only one is the true value, corresponding to the mean heating rate $\bar{\Phi}_s$, equal, by definition, to the rate valid for sample heating when there is no thermal resistance of the sample and the holder. However, to find this rate and the position of the measuring thermocouple in the holder corresponding to it is impossible. Only the calculation path remains. If Eq. (27) and the curve with the peak A_2 are used for the calculation, the result will be too low, owing to the reduced value of the term $C\left|\frac{\mathrm{d}\Delta T_2}{\mathrm{d}t}\right|$; if, with the same equation, the curve with the peak A is utilized in the calculation, the result will be too high, owing to the increased value of $C\left|\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right|$. On turning to formulas (23) and (28), we observe that the second term on the right-hand side of these equations means a certain approach to the mean value of $C\frac{\mathrm{d}\Delta T_i}{\mathrm{d}t}$; the total heat capacity of the sample is divided by two, one half is multiplied by the term with the minimum value $\Phi_s\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}\right)$, the other half by the term with the maximum value $\Phi_s\left(\frac{\mathrm{d}\Delta T_2}{\mathrm{d}t}\right)$, and the products are added. A further improvement of the approach to the mean (true) value $C\frac{\mathrm{d}\Delta T_i}{\mathrm{d}t}$ can be obtained in the following manner.

In the above approach, the total heat barrier has been divided into two parts, for which a linear temperature distribution $T_B = \frac{T_i + T_H}{2}$ and $T_s = \frac{T_0 + T_i}{2}$ is assumed.

If the number of such sections, and correspondingly the number of recorded values of $\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}$, $\frac{\mathrm{d}(\Delta T_p - \Delta T_i)}{\mathrm{d}t}$ is increased (Fig. 3), we obtain a general formula

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_2\Delta T_2 + \frac{C_\Sigma}{n}\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} + \frac{\mathrm{d}(\Delta T_p - \Delta T_1)}{\mathrm{d}t} + \ldots + \frac{\mathrm{d}\Delta T_n}{\mathrm{d}t}\right) \tag{37}$$

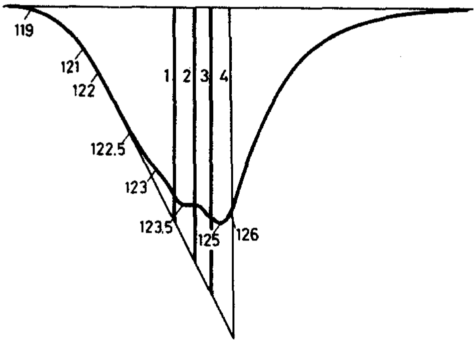

Fig. 3 DTA curve of the melting process of benzoic acid

Let us demonstrate the correctness of Eq. (37) for $n = 3$. For this purpose let us divide the internal heat barrier into two parts by means of the plane with the temperature T' (Fig. 2) and let us locate the thermocouple for recording the incremental temperature $(\Delta T_p - \Delta T_1)$ in this plane. For the incremental temperatures ΔT_1, ΔT_2 and ΔT_3, the following equations can be written:

$$\left.\begin{aligned} \Delta T_1 &= T_0 - T' - (T_0 - T')_{st} \\ \Delta T_2 &= T' - T_i - (T' - T_i)_{st} \\ \Delta T_3 &= T_i - T_H - (T_i - T_H)_{st} \\ \Delta T_p &= \Delta T_1 + \Delta T_2 + \Delta T_3 \end{aligned}\right\} \tag{37a}$$

The mean temperature of the sample is then

$$T_s = \frac{T_0 + T' + T_i}{3} \tag{37b}$$

Following the same train of thought as in the derivation of Eq. (26), we obtain

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_2\Delta T_3 + C_\Sigma\frac{\mathrm{d}(T_s - T_H)}{\mathrm{d}t} \tag{37c}$$

$T_s - T_H$ is found from the equations for T_s and ΔT_i:

$$\begin{aligned} T_s - T_H &= \frac{T_0 - T_H}{3} + \frac{T' - T_H}{3} + \frac{T_i - T_H}{3} = \\ &= \frac{\Delta T_p}{3} + \frac{\Delta T_p - \Delta T_1}{3} + \frac{\Delta T_p - \Delta T_1 - \Delta T_2}{3} + \text{const} \end{aligned} \tag{37d}$$

and after substitution

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_2 \Delta T_3 + \frac{C_\Sigma}{3}\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} + \frac{\mathrm{d}(\Delta T_p - \Delta T_1)}{\mathrm{d}t} + \frac{\mathrm{d}\Delta T_3}{\mathrm{d}t}\right) \tag{37e}$$

On change-over to the gradientless holder, $\Delta T_1 = 0$; $\Delta T_2 = 0$; $\Delta T_3 = \Delta T_p$ (all recorded peaks, approaching one another, merge into one peak with the height ΔT_p), and we arrive at Eq. (27). To the extent that the number of divisions n increases, the accuracy of calculations with Eq. (37) increases; however, this is attained at the price that recording becomes more complicated.

In the literature [4] an approach has been reported in which a truncated form of the kinetic equation of DTA is used:

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

Such an approach is acceptable to a certain extent for studying the kinetics of the initial stages of the process, at low relative values of the term $C\frac{\mathrm{d}\Delta T}{\mathrm{d}t}$; however, it is unsatisfactory for a deep study of the whole reaction, and of its different stages and mechanism. It follows from what has been said that the specific feature and particularity of the DTA method are represented exactly by the term $C\frac{\mathrm{d}\Delta T}{\mathrm{d}t}$, serving to fulfil the following important functions: (a) the calibration of the instrument: determination of K if C is known, through the formulas (3a) and (3b); (b) determination of C if K is known, through the same formulas; (c) accounting for the non-isothermalness of the sample holder and raising the accuracy of the calculations. This last function is a particular application of the novel principle of thermoanalytical recording described in the foregoing, including in the record, in addition to the time coordinate, the space coordinate of the development of the reaction. In fact, when the set of terms $\frac{\mathrm{d}\Delta T_i}{\mathrm{d}t}$ are available, it becomes possible to study the distribution of the temperature and heating rate of the sample at various points of the reaction volume at various moments, which opens up the way to the direct determination of the topochemical characteristics of the studied reaction. Let us consider what conclusions may be made regarding the topochemistry of the reaction by analyzing the equations obtained in the theory based on the assumption of the two-point recording of DTA curves (cf. Fig. 2 in Part I).

For homogeneous reactions with the type *(a)* mechanism discussed earlier, Eqs (23), (30) and (34) hold; from the constancy of the constants K_1 and K_2 and from Eq. (30), it follows that

$$\frac{\Delta T_1}{\Delta T_2} = \frac{K_2}{K_1} = \text{const}; \quad \frac{\Delta T_p}{\Delta T_2} = 1 + \frac{K_2}{K_1} = \text{const} \tag{37f}$$

Consequently, mechanism *(a)* may be considered confirmed if the ratio of the peak heights ΔT_p and ΔT_2 remains constant during the reaction. For reactions proceeding by mechanism *(b)*, the heat flow from the boundary to the zone of the reactant is

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = K_1[(T' - T_0)_{st} - \Delta T_1] = C_1 \Phi - K_1 \Delta T_1 \tag{37g}$$

where C_1 is the heat capacity of the reactant, ΔT_1 is the incremental temperature in the region of the reactant, and $K_1 \mp 4\pi l_s \lambda_s$. Continuing the train of thought by the accepted scheme, we arrive at the equation

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_1 \Delta T_1 + \frac{C_1}{2}\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} + \frac{\mathrm{d}(\Delta T_p - \Delta T_1)}{\mathrm{d}t}\right) \tag{38}$$

Equation (38) cannot be utilized, since for measurement of the second term within the parentheses and the value of ΔT_1it would be necessary to position thermocouple *2* on the moving boundary with the temperature T'. In addition, C_1 will decrease in parallel with the consumption of the reactant. It is obvious that the second terms in Eqs (38) and (28) are not equal, and consequently $K_1 T_1 \neq K_2 T_2$. The value of ΔT_p recorded experimentally is the sum of the incremental temperatures in the zone of the reactant, in the zone of the reaction products and in the external heat barrier; the values of the first two, which are indispensable for analysis, remain undefined.

Case *(c)* appears more favourable for analysis, since here the incremental temperature in the zone of the reactant is zero, while the incremental temperature in the zone of the reaction product can be measured. Following the same train of thought as in the derivation of Eq. (23), we obtain the equation

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K'_1 \Delta T'_1 + \frac{C_\Sigma}{2}\left(\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} + \frac{\mathrm{d}(\Delta T_p - \Delta T'_1)}{\mathrm{d}t}\right) \tag{39}$$

which differs from Eq. (23) in that here K'_1 is a variable value, since

$$K'_1 = \frac{2\pi l_s \lambda_p}{\ln R_2/R_1} \tag{40}$$

where $R_1 \rightarrow 0$ to the extent that the reaction front approaches the centre of the sample. The limiting situation $R_1 = 0$ and $K'_1 = 0$ will not be realized, for in the final stages of the reaction, to the extent that the mass of the reactant is reduced, the latter will lose the shape of an infinitely long cylinder and will presumably disintegrate into a number of spherical particles. A comparison of Eqs (39) and (28) will lead to the equation

$$K'_1 \Delta T'_1 = K_2 \Delta T_2 \tag{41}$$

where ΔT_1 varies in inverse proportion to the value K'_1 at a given value of the heat flow $K_2 \Delta T_2$; hence, to the extent that the reaction proceeds,

$$\frac{\Delta T'_1}{\Delta T_2} = \frac{K_2}{K'_1} \neq \text{const}; \quad \frac{\Delta T_p}{\Delta T_2} = \frac{K'_1 + K_2}{K'_1} \neq \text{const} \tag{41a}$$

the ratio $\Delta T_p/\Delta T_2$ increases, as reflected by the growing distance between the peaks A and A_2. The value of K'_1 at any moment of the experiment may be found by means of Eq. (41). By jointly solving Eqs (40) and (41) to find R_1 and plotting R_1 *vs.* time, we can find the rate of motion of the reaction front, i.e. the topochemical rate of the reaction.

Let us finally consider the arrangement represented by Fig. 1 V [3]. The sample holder is a small, thin-walled tube, with the dimensions 2 × 6 mm and heat capacity C_1; it is surrounded by a screen with heat capacity C_2. The reduced dimensions of the sample holder and the sample are useful when highly exothermic reactions are being studied, for in such cases problems of homogenization of the temperature of the reaction volume and of self-heating of the system will arise, these usually being solved by dilution of the sample with large amounts of an indifferent substance with high thermal conductivity [5]. This technique, however, has its disadvantages: the increased thermal capacity (inertia) of the sensor, the interaction between the reactant and the diluting substance, and the impeding of gas diffusion; these disadvantages are eliminated in the arrangement shown in the Figure, where the air gap between the screen and the sample holder takes over the role of the diluting substance, and temperature homogenization is ensured by the thermal insulation of the holder and the screen from the heat exchanger and by the reduced dimensions of the holder. Let us write the heat balance for the sample with the holder

$$C_1 \frac{\mathrm{d}T_1}{\mathrm{d}t} + \frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_1(T_2 - T_1) \tag{41b}$$

and for the screen

$$C_2\frac{\mathrm{d}T_2}{\mathrm{d}t} = K_2(T_3-T_2)-K_1(T_2-T_1) \tag{41c}$$

It can readily be understood from Fig. 2 (Part 1) that (with the accuracy of the constant)

$$T_1 = \Phi t+\Delta T_p$$

$$T_2 = \Phi t+\tau_1\Phi+\Delta T_2$$

$$T_3 = \Phi t+\Phi\tau_1+\Phi\tau_2$$

where $\tau_1 = C_1/K_1$ and $\tau_2 = \frac{C_1+C_2}{K_2}$. After introducing these expressions into the equation of the heat balance, we obtain

$$-\mathrm{d}\Delta H\mathrm{d}t = K_1(\Delta T_p-\Delta T_2)+C_1\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t} \tag{42}$$

$$-\frac{\mathrm{d}\Delta H}{\mathrm{d}t} = K_2\Delta T_2+C_1\frac{\mathrm{d}\Delta T_p}{\mathrm{d}t}+C_2\frac{\mathrm{d}\Delta T_2}{\mathrm{d}t} \tag{43}$$

Equations (42) and (43) have a similar structure to that of Eqs (23) and (28). The difference lies in the division of the heat capacity of the sensor into two parts, which are not equal in the general case: the heat capacity of the holder and the heat capacity of the sample, multiplied by the corresponding incremental heating rates. If the sample holder is isothermal, K_1 does not contain the term K_w^{-1}, and $\Delta T_w = 0$. These conditions are satisfied in practice if the holder has thin walls made of a metal with high thermal conductivity. Equation (43) is the general case for Eq. (28), in which the heat capacity of the sensor is divided into unequal parts. The method described may appropriately be termed "the method of split heat capacity", to distinguish it from other possible methods of accounting for non-isothermalness.

Experimental

In the above derivation of the equation for the constant K_2, the heat transfer over the gas gap by convection and radiation has not been taken into account. The share of convection is negligibly small in the technique applied (static atmosphere, central-symmetrical arrangement of the sample holder relative to the heater). The share of radiation, however, must be accounted for by means of the formula

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = 0.227\,\varepsilon S_h\left(\frac{K}{100}\right)^3\Delta T_2 \tag{44}$$

where ε is the degree of blackness of the surface of the sample holder, S_h is its surface and K is the thermodynamic temperature of the experiment.

Heat transfer by radiation is independent of all other modes of heat transfer, and hence Eqs (25) and (44) may be added:

$$K_{2t} = K_2 + K_r = \frac{2\pi l_h \lambda_g}{\ln R_H/R_i} + 0.227\,\varepsilon S_h \left(\frac{K}{100}\right)^3 \tag{45}$$

The coefficient λ_g in Eq. (45) may be expressed as an explicit function of the temperature in the following manner. We use the value of λ for nitrogen from [6] and find the increase $\Delta\lambda$ and the increase of the increase $\Delta(\Delta\lambda)$ over every 100 deg within the interval 0–1000°. The data in Table 1 indicate that $\Delta\lambda = 6.9$ in the interval 0–300° and $\Delta(\Delta\lambda) = -0.614 \pm 0.058$ in the interval 300–1000°. Using these values, for temperatures between zero and 300° we obtain

Table 1 Thermal conductivity of nitrogen *versus* temperature [6]

T, °C	λ, mW/m·deg	$\Delta\lambda$	$-\Delta(\Delta\lambda)$	λ, mW/m·deg calcd. from Eqs (47), (46)
0	24.30			24.3
100	31.50	7.21		31.2
200	38.50	7.00	0.21	38.1
300	44.90	6.40	0.60	45.0
400	50.70	5.80	0.60	50.96
500	55.82	5.12	0.68	55.80
600	60.36	4.54	0.58	60.32
700	64.20	3.84	0.70	64.27
800	67.45	3.25	0.59	67.52
900	70.13	2.68	0.57	70.21
1000	72.33	2.20	0.48	72.27

$$\lambda_{0-300} = 24.3 + 6.9 \cdot 10^{-2}\, T \tag{46}$$

and above 300°

$$\frac{d^2\lambda}{d\left(\frac{T-300}{100}\right)^2} = -0.614 \text{ mW/m}\cdot\text{deg}^3$$

The first integration of this expression yields

$$\frac{d\lambda}{d\left(\frac{T-300}{100}\right)} = -0.614 \cdot 10^{-2}(T-300) + \Delta\lambda_{300-400}$$

where $\Delta\lambda_{300-400} = 6.06 \pm 0.3$ mW/m·deg^2.

The second integration yields

$$\lambda = \lambda_{300} + 6.06 \cdot 10^{-2}(T-300) - 0.307 \cdot 10^{-4}(T-300)^2 \tag{47}$$

The values of λ_g calculated by means of Eqs (46) and (47) are listed in column 5 of Table 1.

For the interval between − 170 and 0°, the dependence of λ_g on temperature may be represented by the linear function [7]

$$\lambda_{-170-0} = 9.41 + 8.76 \cdot 10^{-2}(T+170) \tag{48}$$

In Table 2, the values of K_2 and K_r calculated by means of Eq. (45) are listed, together with their sums K_{2t}, and the experimental values of K_{2t} determined by electric calibration utilizing Eq. (2b). In the calculation of K_{2t} with Eq. (45), we used the value $\varepsilon = 1$, and we painted the surface of the 4.4 × 8.0 mm sample holder black. It may be seen that good agreement was found between the theoretical and experimental values for K_{2t}. At low temperatures, heat conduction contributes the major share to K_{2t}, while at high temperatures, from 150° on, radiation becomes predominant.

Table 2 Theoretical and experimental values of the calibration constant for an instrument with insulated sample holder

T, °C	− 140	− 100	− 50	0	50	100	150	200	250	300	420
λ_g, mW/m · °C	11.6	16.0	20.2	24.3	28.0	31.4	34.9	38.4	42.0	44.8	51.8
K_2, mW/deg	0.956	1.18	1.49	1.86	2.0	2.30	2.57	2.82	3.08	3.31	3.83
K_r, mW/deg	0.06	0.165	0.355	0.651	1.10	1.65	2.42	3.36	4.60	6.00	10.6
K_{2t}, mW/deg	1.01	1.34	1.84	2.51	3.10	3.95	5.00	6.18	7.68	9.31	14.44
$K_{2\mathrm{exp}}$, mW/deg	1.28	1.50	2.10	2.70	3.30	4.10	5.00	6.00	7.50	9.60	—

The DTA curve in Fig. 3 illustrates the work of a type III instrument. A benzoic acid sample (mass 18 mg) was melted at a heating rate of 8.0 deg/min in a nitrogen atmosphere. It may be observed from the curve that, after an initial period (119–121°), melting takes place (m.p. 121.9°) at a constant temperature in the case of pure material; in the case of a gradientless sample holder, a constant slope of the descending branch of the peak will correspond to this. In reality, the DTA curve deviates from a straight line. This can be explained by the increase of the internal resistance of the holder owing to the reduced amount of the reactant and to the growing distance between the reaction front and the wall of the holder. If different models of the reaction zone are used, the expected values of K_1 may be calculated and compared with the experimental values to confirm the correctness of the chosen model. In Table 3, the expressions of the constant K_1 are listed for disc-shaped,

Table 3 Expressions for K_1 with different geometries of the reaction zone

Disc	Sphere	Cylinder	Experimental calculation
$\dfrac{1}{K_c^{-1}+\dfrac{\delta}{\lambda_p S_p}}$ ...(3.1)	$\dfrac{1}{K_c^{-1}+\dfrac{R_1^{-1}-R_2^{-1}}{4\pi\lambda_p}}$ ...(3.2)	$\dfrac{1}{K_c^{-1}+\dfrac{\ln R_2/R_1}{2\pi l_s\lambda_p}}$ ...(3.3)	$\dfrac{K_{2t}\Delta T_2+C_2\dfrac{d\Delta T_2}{dt}}{\Delta T_p-\Delta T_2}$ ...(3.4)

spherical and infinite cylindrical reaction zones, as well as an experimental formula obtainable from Eqs (42) and (43). In these formulas, K_c^{-1} is the sum of the contact resistances between the reaction front and the temperature sensor, δ is the thickness of the reaction product layer, S_p is the area of the reaction surface ($S = \pi R^2$, where $R = 2.0$ mm), R_1 is the radius of the reactant, R_2 is the radius of the reactant before the reaction, and λ_p is the thermal conductivity of the reaction products.

In Table 4, experimental data are listed for calculating K_1 by means of Formula 3.4 in Table 3 and the theoretical values of K_1 obtained by means of Formulas (3.1) and (3.2) in Table 3, assuming that $K_c^{-1} = 0$; $\lambda_p = 0.171$ W/m·deg, $\varrho = 1.2$ g/cm^3 $R_2 = 1.53$ mm. The radius of the spherical reactant R_1 at the given moment of the reaction (melting) was calculated by means of the formula $R_1 = R_2\sqrt[3]{1-\alpha}$, which can be obtained from the equation

$$\frac{m}{M}=\frac{R_2^3-R_1^3}{R_2^3}=\frac{K_2A_2+C\Delta T_2}{K_2A_{2t}}=\alpha$$

As may be seen from the Table, the experimental K_1 data are several times higher than the values calculated theoretically. This may be explained in the following manner: during melting, the reactant is closer to the holder wall than follows from Formulas (3.1) and (3.2). Actually, the irregular shape of the curve in the vicinity of

Table 4 Experimental and model values of K_1 for the melting process of benzoic acid in an insulated sample holder

$-\Delta T_p$, °C	$-\Delta T_2$, °C	$\dfrac{d\Delta T_2}{dt}$	K_1, $\dfrac{mW}{deg}$	α	R_1	K_1, $\dfrac{mW}{deg}$ (sphere)	K_1, $\dfrac{mW}{deg}$ (disc)
6.35	5.5	0.098	38.9	0.604	1.12	9.0	2.96
7.25	5.7	0.0	22.9	0.707	1.02	6.4	2.53
9.0	6.2	0.041	12.7	0.893	0.726	2.96	2.00
10.1	6.0	−0.095	0.66	1.00	0		1.79

the peak top indicates that solid-phase benzoic acid residues sometimes collide with the wall of the holder in the end-stage of melting; at such moments, the slope of the peak will increase sharply.

For samples with high thermal conductivity (metals), if oxide films are absent from their surface, the peaks corresponding to melting have a well-expressed regular shape: the descending branch is a straight line right to the top of the peak, corresponding to the end-point of the reaction, and therefore the top of the peak is sharp; from the top of the peak, the exponential branch begins; the difference between the measured holder wall temperature and the melting point, i.e. the temperature of the reaction zone, does not exceed 0.5–1.0 deg over the total region of the descending branch. The insulated holder therefore allows us to obtain thermoanalytical curves whose shape depends on the internal resistance of the sample holder in the region temperature sensor—reaction front; a quantitative estimation of this resistance thereby becomes possible, as well as that of its change during the solid-phase reaction.

References

1 Yu. L. Shishkin, J. Thermal Anal., 29 (1984) 105.
2 V. S. Zhukovsky, Fundamentals of Heat Transfer Theory (in Russian), Energiya, Leningrad, 1969.
3 Yu. L. Shishkin, J. Thermal Anal., 29 (1984) 503.
4 L. Reich and S. S. Stivala, Elements of Polymer Degradation, McGraw Hill Book Co., 1971.
5 E. N. Goncharov, G. I. Dratskaya, A. G. Merzhanov and A. S. Shteynberg, Dokl. Akad. Nauk SSSR, 197 (1971) 385.
6 S. S. Kutateladze and V. M. Borishansky, Handbook of Heat Transfer (in Russian), Gosenergoizdat, Moscow–Leningrad, 1959.
7 Handbook of Chemistry and Physics, 59th Ed. The Chemical Rubber Co., Cleveland, 1978–1979.

Zusammenfassung — Volumen- und oberflächenisotherme Meßfühler mit thermischer Gasphasenbarriere werden beschrieben. Bei Verwendung von oberflächenisothermen Meßfühlern kann nach der DTA-Zweipunktsmethode der innere Wärmewiderstand bestimmt werden, wodurch die Aufklärung des Mechanismus (Topochemie) der Reaktion und die Ermittlung genauerer kinetischer Daten über eine neue Spaltwärmekapazitäts-Methode ermöglicht wird.

Резюме — Описаны конструкция и теория объемно-изотермического и поверхностно-изотермического датчиков приборов ДТА с газовым тепловым барьером. Показано, что применение метода 2-х точечного ДТА в случае поверхностно-изотермического датчика позволяет оценить внутреннее термическое сопротивление держателя образца (реакционного объема), знание которого необходимо для выяснения механизма реакции (ее топохимических аспектов) и для более точного определения кинетических констант описанным в работе новым методом расщепленных теплоемкостей.