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QUANTITATIVE THERMAL ANALYSIS, VI. INITIAL CONDITIONS OF THE MATHEMATICAL DESCRIPTION OF THERMAL CURVES (GRADIENT THEORY)

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The fundamental concept of the theory of thermal analysis developed in this paper involves the movement of the transformation front in the mass of the sample. Equations are developed for the motion of the transformation front (in the case of invariant processes) for the simplest model of the thermoanalytical cell. For a cylindrical sample, the equation is

$$t = \sqrt{\frac{Hd}{\lambda B}\left(\frac{R^2-r^2}{2} - r^2 \ln \frac{R}{r}\right)}$$

where R is the external radius of the sample, H the thermal effect of the transformation, B the heating rate, D the density, λ the thermal conductivity, r the position of the transformation front, and t time.

The equation is experimentally confirmed by the finding that, as concluded from the equation, the height of the peak is directly proportional to the square root of the rate of sample heating.

The various empirical and semi-empirical approaches to the relationship between the parameters of thermal curves, the properties of the sample being investigated and the experimental conditions allow the use of thermal analysis for the solution of many concrete problems. Frequently, these empirical approaches also permit the development of relatively simply analytical procedures and apparatuses for their implementation. However, in spite of the successes of empiricism, the task of the theoretical description of this relationship continues to be topical.

Numerous attempts at a mathematical description of the course of the differential curve or of its individual elements [1–7] were based on contrasting the heat transfer to the sample investigated with that to an indifferent material. In this approach, the role of the indifferent material was placed at the same level as the role of the sample investigated. This approach, though formally logical, did not, however, allow detection of the motive forces acting in the system of thermophysical processes, or a mathematical description of the causal relationships of the changes observed in the system.

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The unjustified importance of the indifferent material bore the consequence that in the mathematical equations describing the course of the differential record (or rather of its individual elements) parameters characterizing the indifferent material appeared. The growing number of variables required further equations, or increased the number of assumptions and simplifications.

In our opinion, the indifferent material plays essentially only the role of some "value" calculated from the unknown in order to ensure the recording of this unknown in the measure required. It is, of course, desirable in all respects to know this calculated value: in the most favourable case a constant, or at least an accurately known function. The latter is particularly clearly expressed in thermoanalytical instruments (DTA–7), where instead of the signal taken from the indifferent material with a multitude of unknown and varying parameters, a signal with accurately controlled parameters is taken:

$$T_R = BT + T_i$$

where T_R is the signal proportional to the temperature of the indifferent material, in K; B is the heating rate, in K/s; t is time, in s; and T_i is the signal proportional to the initial temperature, in K.

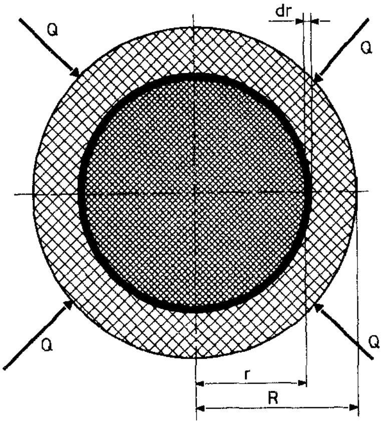

Fig. 1 Motion of the transformation front in the sample

Under such conditions it is particularly obvious that the course of the differential record is defined exclusively by the parameters of the substance investigated, and the task consists in the mathematical description of the phenomena depending on the sample itself.

Let us consider the thermal phenomena taking place in the mass of the sample during the period of the transformation. As a basis we apply the concept of a transformation front motion from the periphery to the centre of the sample, described and experimentally confirmed earlier [6, 8].

To simplify the calculations, some limiting conditions will be introduced: the sample is assumed to be an infinitely long cylinder with radius R; the surface layer of the sample is heated in the linear regime; an invariant process takes place in the sample, not changing its density (e.g. a polymorphic transformation).

Let us consider the state of the sample at some moment t, when the transformation front formed earlier on the surface has shifted towards the interior and has radius r (Fig. 1).

Let us establish the simplest heat balance equation for the infinitely small time interval dt.

The general form of the amount of heat used for the transformation is

$$Q = m \cdot H$$

where m is the mass of substance undergoing transformation during the time $dt(r)$, and H is the specific heat effect of the transformation, in J/g. Also,

$$m = V \cdot d$$

where V is the volume of substance undergoing transformation (m^3) and d is its gravimetric density (g/m^3).

For the considered intermediate state (Fig. 1), one may write

$$V = 2\pi r dr L$$

i.e.

$$Q_1 = 2\pi r dr HLd \tag{1}$$

The amount of heat absorbed by the sample is transferred to it from the exterior. The amount of heat transferred to the sample layer may be described by the equation of heat transfer [7]:

$$Q_2 = \frac{\lambda}{\delta} F_x \Delta T dt \tag{2}$$

where λ is the termal conductivity of the material through which heat transfer takes place ($J\ m^{-1} K^{-1} s^{-1}$), δ is the thickness of the layer (m), and F_x for a cylindrical sample is

$$F_x = \frac{F_{ext} - F_{int}}{\ln \frac{F_{ext}}{F_{int}}} = \frac{2\pi(R-r)L}{\ln \frac{R}{r}} \tag{3}$$

with F_{ext} for the external surface and F_{int} for the internal surface of heat transfer (m^2), ΔT being the temperature difference between the external and internal surfaces.

For the moment of time t

$$\delta = R-r, \text{ and}$$
$$\Delta T = -Bt$$

i.e.

$$Q_2 = \frac{2\pi\lambda BtL(R-r)}{\ln\frac{R}{r}}dt \tag{4}$$

Assuming as a first approach that $Q_1 = Q_2$, one obtains from Eqs (1) and (5)

$$rHd\cdot dr = -\frac{\lambda Bt}{\ln\frac{R}{r}}dt \tag{5}$$

After separation of the variables and integration of Eq. (5), one finally obtains

$$\lambda Bt^2 = Hd\left(\frac{R^2-r^2}{2}-r^2\ln\frac{R}{r}\right) \tag{6}$$

or

$$t = \sqrt{\frac{Hd}{\lambda B}\left(\frac{R^2-r^2}{2}-r^2\ln\frac{R}{r}\right)} \tag{7}$$

In an analogous manner one can obtain the equations for the transformation front motion within a sample mass of any sample shape, e.g. for spheres:

$$t = \sqrt{\frac{Hd}{\lambda B}\left(\frac{R^2}{3}-r^2+\frac{2r^3}{3R}\right)} \tag{7a}$$

for discs:

$$t = \sqrt{\frac{Hd}{\lambda B}(R^2-2Rr+r^2)} \tag{7b}$$

Equation (7) may be considered the first equation obtained on the basis of the novel approach presented in this work to the mathematical description of thermal curves. This novel approach is founded on the concept of the frontal spreading of the transformation and the presence of the temperature gradient in the sample (gradient model). The experimental confirmation of Eq. (7) is undoubtedly of great interest.

On the basis of Eq. (7), one may calculate the relative velocities of transformation front motion, depending on the position of the front between the centre of the sample and its external surface. For this purpose it is convenient to write Eq. (7) in the form

$$t = R\sqrt{\frac{Hd}{\lambda B}}\sqrt{\frac{1-n^2}{2}-n^2\ln\frac{1}{n}} \tag{8}$$

or

$$t = kf(n)$$

where n is defined by the expression $r = n \cdot R$ (Fig. 1).

The plot corresponding to Eq. (8) is presented in Fig. 2. It allows evaluation of the general character of the front radius change *versus* the time interval passed since the moment when the transformation came into existence on the surface of the sample.

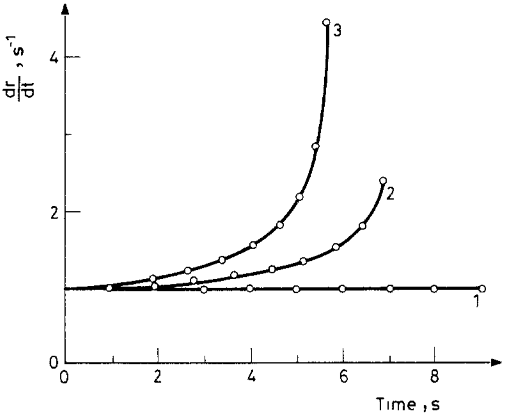

Fig. 2 Velocity of front motion in the sample 1 — for disc-shaped samples; 2 — for cylindrical samples; 3 — for spherical samples

The velocity of front motion within disc-shaped samples is constant (curve 1 in Fig. 2), while in cylindrical (curve 2) and to an even greater extent in spherical (curve 3) samples, the velocity increases with the shift of the transformation front from the periphery towards the centre of the sample.

To check the correctness of Eq. (7) experimentally by measuring the position of the transformation front at various intervals after the beginning of the transformation, as carried out earlier for purely qualitative objectives [6, 8], is obviously pointless, owing to the low accuracy of the results to be expected. Nor will the required accuracy for the experimental confirmation of Eq. (7) be attained by varying the values H, d or λ, since any change in these parameters will affect other parameters, among which the most undefined changes will occur in the thermal conductivity of the sample.

The simplest way to confirm Eq. (7) experimentally is by means of some direct consequence of this equation. For instance, the peak height h_m for an invariant transformation proceeding in a cylindrical sample is described by the equation

$$h_m = R\sqrt{\frac{HdB}{2\lambda}} \tag{9}$$

that is, *the height of the peak of an invariant transformation in a cylindrical sample is equal to the radius of the sample, multiplied by the square root of the product of the density, the specific thermal effect of the transformation and the heating rate divided by twice the thermal conductivity.*

The most convenient procedure to utilize this consequence of Eq. (7) for its confirmation is to make use of the relationship peak height *versus* heating rate, since in this case the constancy of all other conditions can be satisfied for reversible invariant processes with practically ideal accuracy: the sample once placed into the apparatus can be submitted to repeated heating at differing heating rates, without changing any other experimental condition.

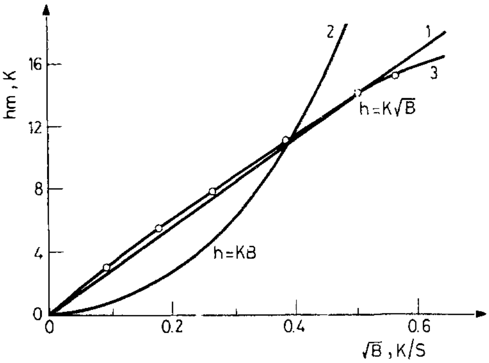

Fig. 3 Peak height *vs.* heating rate 1 — theoretical relationship based on Eq. (9); 2 — theoretical relationship based on the assumption of direct proportionality between peak height and heating rate; 3 — experimental curve

The experiment was performed as described earlier [8]. The sample (potassium perchlorate powder) was placed in a thin-walled glass the tube (internal diam. 3.2 mm). The space between the external surface of the test tube and the wall of the opening in the heating block was filled with metal powder, in order to ensure the condition that the temperature of the external surface of the sample increases linearly even during the time when the phase transformation takes place in the mass of the sample.

Figure 3 presents the relationship peak height *versus* square root of heating rate. If Eq. (9) and consequently Eq. (7) are correct, the experimental data should be located on straight line 1. If the peak height is directly proportional to the heating rate, as is generally accepted in the literature [1, 9], and not to its square root as follows from Eq. (9), the experimental data should be located on curve 2.

The Figure (experimental data: curve 3) fully confirms the correctness of Eq. (9). The slight deviation (which is, in fact, systematic) is obviously related to the inaccuracy of the equation, insofar as it does not take into account the amount of heat used up for heating the external layers of the sample.

All this allows formulation of the relationship found between the peak height and the heating rate in the following rule: The *peak height is directly proportional to the square root of the heating rate.*

The above approach to the mathematical description of thermal curves, notwithstanding the fact that many assumptions are included, appears highly promising.

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Zusammenfassung — Das in dieser Arbeit entwickelte grundlegende Konzept der Theorie der Thermischen Analyse schließt das Fortschreiten der Umwandlungsfront in der Probenmasse in sich ein. Gleichungen zur Beschreibung des Fortschreitens der Umwandlungsfront (im Falle von invarianten Prozessen) werden für das einfachste Modell der thermoanalytischen Zelle abgeleitet. Für eine zylindrische Probe gilt

$$t = \sqrt{\frac{Hd}{\lambda B}\left(\frac{R^2-r^2}{2} - r^2 \ln\frac{R}{r}\right)}$$

worin R den äußeren Radius der Probe, H den die Umwandlung begleitenden thermischen Effekt, B die Aufheizgeschwindigkeit, D die Dichte, λ die Wärmeleitfähigkeit, r die Lage der Umwandlungsfront und t die Zeit bedeuten. Die Gleichung wird durch den experimentellen Befund bestätigt, daß — was auch die Gleichung aussagt — die Höhe des Peaks direkt proportional der Quadratwurzel der Geschwindigkeit der Probenaufheizung ist.

Резюме — В основу развиваемой в работе теории термического анализа положены представления о движении фронта превращения в массе образца. Для простейшей модели термоаналитической ячейки получены уравнения движениа фронта превращения (в случае инвариантного процесса).

Для цилиндрического образца уравнение имеет вид

$$t = \sqrt{\frac{H \cdot d}{\lambda \cdot B}\left(\frac{R^2 - r^2}{2} - r^2 \cdot \ln\frac{R}{r}\right)},$$

где R — наружный радиус образца, H — тепловой еффект превращения, B — скорость нагрева, d — плотность, λ — теплопроводность, r — положение фронта превращения, t — время.

Дана экспериментальная проверка полученного уравнения на основании следствия из него: высота пика прямо-пропорциональна корню квадратному скорости нагрева образца.