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QUANTITATIVE THERMAL ANALYSIS
VII. Basic elements of thermal curves in the context of ingradient theory

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Abstract

The supposition of even temperature distribution in the sample mass ('ingradient' approach) led to mathematical expressions describing the basic quantitative elements of thermal curves: the transformation duration, the peak height, the initial and final section peak areas and the total area. The simplest expression is that for the total peak area: $S=(R^2Hd/2k_1)\ln R_1/R$, where R, H, d, k_1 and R_1 are the radius, the specific thermal effect of sample transformation, the gravimetric density and the outer layer encircling the sample, respectively. For the other quantitative elements, the dependences are far more complicated, depending on the duration and variants of the transformation process.

Keywords: heat, heating rate, peak high, peak square, theory, thermal analysis

Introduction

In previous articles, we presented an attempt to give the simplest mathematical description of the basic elements of the differential curve in the context of the 'gradient' theory of thermal analysis, supposing that transformation in a sample does not occur simultaneously in the whole volume, but spreads frontally from the periphery to the centre.

It is interesting to examine another possible approach to the solution of the problem of the mathematical description of DTA curve elements, which assumes that, during the process of transformation, the sample under investigation has the same temperature at all points, and transformation occurs simultaneously in the whole volume: the 'ingradient' approach.

Discussions

Let us imagine a sample with one of the simplest forms for description: an endless cylinder with radius R and thermal parameters d, c and k. This sample is encircled by a heat-insulating layer of material with thermal parameters d_1, c_1 and k_1 (respectively: density, specific heat and coefficient of thermal conductiv-

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ity). The outer surface of the cylinder with radius R is heated strictly according to the linear law. The sample and heat-insulating layer are in ideal heat contact.

In contrast with the gradient theory, the ingradient theory assumes (as a necessary condition of its existence) the availability of a heat-insulating layer between the sample and the surface heated according to the given law. The ingradient theory will then have a more physical justification, the better the heat-insulating properties of this layer. This can be put in terms of mathematics as

$$\frac{R}{k} < \frac{R_1 - R}{k_1}$$

$$ndcR^2 < nd_1c_1(R_1^2 - R^2)$$

The assumptions include neglect the influence of some thermal parameters, and in particular the heat conduction, on the form of the thermal curves.

After some time from the beginning of a linear temperature rise in the outer surface of the heat-insulating layer, a quasi-stationary regime is established in the system. If, at some moment of time, a transformation at constant temperature T_t begins in the sample, then during the whole process the temperature at any point of the sample and on the inner surface of the heat-insulating layer is stable and equal to the temperature of the phase transformation.

After the transformation is over, the stage of levelling begins, during which a quasi-stationary regime is established in the system again. Taking into account the assumptions made, the thermal problem for the transformation stage can be written as follows:

$$\frac{\partial T_1}{\partial t_1} = a_1\left(\frac{\partial^2 T_1}{\partial t^2} + \frac{\partial T_1}{r\partial r}\right) \tag{1}$$

$$T_1|_{t_1=0} = T_o(r)$$

$$T_1|_{r=R} = T_t$$

$$T|_{r=R_1} = Bt$$

where $T_o(r) = T_t + B(r^2 - R^2)/4a_1 - BR^2/2a_1 \ln r/R$, i.e. there is a quasi-stationary temperature distribution in the heat-insulating layer at the moment of transformation.

The substitutions $T=T_1-Bt-T_t$ and $t=t_1-t_o$ convert problem 1 to the problem with zero-order initial condition and canonical boundary conditions:

$$\frac{\partial T}{\partial t} = a_1\left(\frac{\partial^2 T}{\partial r^2} + \frac{\partial T}{r\partial r}\right) \tag{2}$$

$$T|_{t=0} = 0$$

$$T|_{r=R} = -Bt$$

$$T|_{r=R} = 0$$

We note that the magnitude $T|_{r=R}$ (as far as sense is concerned) corresponds to the temperature difference of the sample under investigation and the temperature the sample could have under a quasi-stationary regime of heating.

To get an approximate solution of problem 2 which could satisfactorily work for any time of phase transformation, we put the problem in Laplace transforms with a variable t:

$$F\overline{T}-a_1\left(\frac{\partial^2 T}{\partial r^2}+\frac{\partial T}{r\partial r}\right)=0 \tag{3}$$

$$T|_{r=R}=-\frac{B}{F^2}$$

$$T|_{r=R_1}=0$$

With large F values (small time t) Eq. (3) allows asymptotic decomposition, the first member of which is as follows:

$$\overline{T}_\infty=-\frac{R}{F^2}\sqrt{\frac{R}{r}}\mathrm{e}^{-\sqrt{F/a_1}(r\ R)}+\Theta\mathrm{e}^{-\sqrt{F/a_1}(R_1-R)} \tag{4}$$

With small F values, which correspond to a large time t (large thermal transformation effect, low heat speed, etc.), Eq. (3) again allows asymptotic decomposition, the first member of which is a quasi-stationary solution of the problem:

$$\overline{T}_\mathrm{o}=-\frac{B\ln R_1/r}{F^2\ln R/r}+\Theta(F^{-1}) \tag{5}$$

We now construct a function

$$\overline{f}=-\frac{B}{F^2}\left[\sqrt{\frac{R}{r}}\mathrm{e}^{-\sqrt{F/a_1}(r-R)}+\left(\frac{\ln R_1/r}{\ln R/r}-\sqrt{\frac{R}{r}}\right)\mathrm{e}^{-\sqrt{F/a_1}(R_1-R)}\right] \tag{6}$$

Asymptotic decomposition (6) with degree F is equal to Eq. (5). Hence, with a small F the function (Eq. (6)) coincides with the solution of Eq. (2) with accuracy up to $\Theta(\exp[-\sqrt{S}(R_1-R)a_1)]$ close to Eq. (4). Function (6) therefore affords a close solution of Eq. (3) for large and small F values. Taking Eq. (6) as an approximate solution of Eq. (3) and taking the reverse Laplace transform, we obtain an approximate solution of Eq. (2) as

$$T=4Bt\left[\sqrt{\frac{R}{r}}\left(ierfc\frac{r-R}{2\sqrt{ta_1}}+i^2erfc\frac{R_1-R}{2\sqrt{ta_1}}\right)+\frac{\ln R_1/r}{\ln R/r}i^2erfc\frac{R_1-R}{2\sqrt{ta_1}}\right] \tag{7}$$

where i^2erfcZ is a multiple probability integral. The plus sign in the equation corresponds to a differential curve deviation downwards from the zero line on heating (B>0) and upwards on cooling (B<0).

Analysis of the approximate solution (Eq. (7)) and its comparison with the exact solution of Eq. (2) shows that the maximal error of approximation with

$R_1<2R$ does not exceed 3%. The maximal error of heat flow calculations used for phase transformation in the examined sample does not exceed 8%.

The moment at which the transformation stage is over is determined through the equality of the total heat flow obtained for the examined sample after the transformation period and the amount of heat necessary for complete transformation in the sample under investigation:

$$2nRK_1\int_0^{t_1}\frac{\partial T}{\partial r}\Big|_{r=R}\,\mathrm{d}t = nR^2Hd \tag{8}$$

where t_1 is the transformation stage duration, and H is the latent transformation heat.

Equations (7) and (8) give the expression to find the stage duration of the phase transformation:

$$\frac{\pi R^2Hd}{R_1} = 2\pi RB\left\{\frac{t_1^2}{R}\left[\frac{1}{4} - 8\left(1 - \frac{2}{\ln R_1/R}\right)i^4 erfc\frac{R_1 - R}{2\sqrt{t_1a_1}}\right] + \frac{4}{3}\frac{t_1^{3/2}}{\sqrt{\pi a_1}}\right\} \tag{9}$$

The part of the peak area corresponding to the phase (the initial part of the peak area) may be expressed as follows:

$$S_i = \int_0^{t_1} T|_{r=R}\mathrm{d}t = B\frac{t_1^2}{2} \tag{10}$$

Correspondingly, the DTA curve peak height is

$$h = B\mathrm{t}_1 \tag{11}$$

We shall next examine the process of entering the quasi-stationary section after the transformation process in the sample by the DTA curve (levelling stage). For this stage, the heat problem is expressed in the following way:

$$\frac{\partial T}{\partial t} = a_1\left(\frac{\partial^2 T}{\partial r^2} + \frac{\partial T}{r\partial r}\right) \tag{12}$$

$$T|_{t=t_1} = T_1(r)$$

$$\partial T/\partial r|_{r=R} = 0$$

$$T|_{r=R_1} = 0$$

where $T_1(r)$ is the temperature of the heat-insulating wall at the moment when the process of phase transformation is over. In Laplace transforms with a variable in Eq. (12), we have

$$F\overline{T} - T_1(r) = a_1\left(\frac{\partial^2\overline{T}}{\partial r^2} + \frac{\partial\overline{T}}{r\partial r}\right) \tag{13}$$

$$\partial\overline{T}/\partial r|_{\mathrm{r=R}} = 0$$

$$\overline{T}|_{\mathrm{r=R_1}} = 0$$

The solution of Eq. (13) may be given as

$$\overline{T} = 2n\int_{\mathrm{R}}^{\mathrm{R_1}}\overline{G}(r, r', F)T_1(r')\mathrm{d}r$$

where

$$\overline{G}(r, r', F) = \begin{cases} u(r)v(r)/2na_1u(R_2) & R \le r \le r' \le R_1 \\ u(r')v(r)/2na_1u(R_2) & R \le r' \le r \le R_1 \end{cases}$$

$$u(r) = K_{\mathrm{o}}\sqrt{\frac{Fr}{a_1}}J_1\sqrt{\frac{FR_1}{a_1}} + J_{\mathrm{o}}\sqrt{\frac{Fr}{a_1}}K_{\mathrm{o}}\sqrt{\frac{FR_1}{a_1}}$$

$$v(\mathrm{r}) = K_{\mathrm{o}}\sqrt{\frac{Fr}{a_1}}J_{\mathrm{o}}\sqrt{\frac{FR_2}{a_1}} - J\sqrt{\frac{Fr}{a_1}}K_{\mathrm{o}}\sqrt{\frac{Fr_2}{a_1}}$$

is the function of Green.

Using limiting theorems for Laplace transforms and the properties of continuous integrals with parameters, we get the peak area value corresponding to the levelling stage. For the final section area of the thermal effect:

$$F_{\mathrm{f}} = \lim\nolimits_{\mathrm{t_2}\to\infty}\int_{\mathrm{t_1}}^{\mathrm{t_2}}T(r, t)|_{\mathrm{r=R}}\,\mathrm{d}t = \lim F\frac{1}{F}\overline{T}(r, F)|_{\mathrm{r=R}} = \lim\nolimits_{\mathrm{F}\to0}\overline{T}|_{\mathrm{r=R}}$$

$$F_{\mathrm{f}} = 2n\lim\int_{\mathrm{R}}^{\mathrm{R_1}}\overline{G}(R, r', F)T_1(r')\,\mathrm{d}r' \tag{14}$$

Performing direct calculations on Eq. (14) and taking into account that with $R<r'<R$, $R_1<2R$ is fulfilled with an error less than 2%:

$$\sqrt{\frac{r'}{R_1}}\ln\frac{r'}{R_1} \approx \frac{r'}{R_1}$$

We get the final expression for the final section area:

$$S_f = B\sqrt{\frac{R}{R_1}}\left\{-\frac{4}{3}\frac{(R_1-R)t_1^{3/2}}{\sqrt{\pi a_1}}+\frac{t_1^2}{2}+\left(\frac{5(R_1-R)t_1}{3a_1}-2t_1^2\right)i^2erfc\frac{R_1-R}{2\sqrt{t_1a_1}}\right\}+ \tag{15}$$

$$+\left\{\frac{(R_1-R)t_1^{3/2}}{3\sqrt{a_1}}ierfc\frac{R_1-R}{2\sqrt{t_1a_1}}\right\}+\frac{Bt_1}{a_1}\left[2R^2\left(\ln\frac{R_1}{R}+1\right)-\frac{R_1^2-R^2}{\ln\frac{R_1}{R}}\right]i^2erfc\frac{R_1-R}{2\sqrt{t_1a_1}}$$

The total peak area is calculated as the sum of the initial and final section areas.

Direct studies of the calculated dependences describing the basic quantitative elements of thermal curves show that the total peak area with an accuracy up to the errors caused by the approximate formulae may be calculated through the expression

$$S=\frac{R^2Hd}{2k_1}\ln\frac{R_1}{R} \tag{16}$$

It should be mentioned that dependence (16) is a linear one and therefore allows generalization in the case of chemical reactions.

The peak height dependence of the phase transformation thermal effect and heating speed is more complicated. First of all, it should be mentioned that the dependence has a different form for large and small transformation durations.

For a transformation of long duration, that is with $t_1a_1/(R_1-R)^2>1$, this dependence will be

$$R=\sqrt{\frac{R^2HBd\ln R_1/r}{k_1}} \tag{17}$$

For a transformation of short duration, that is with $t_1a_1/(R_1-R)^2<1$:

$$h=\frac{1}{4}\sqrt[3]{\frac{9\pi R_1^2d_1}{k_1^2}H^2Bd} \tag{18}$$

Hence, in the context of the ingradient approach, we have a description of the basic quantitative elements of a DTA curve: the phase transformation duration (Eq. (9)), the initial section peak area (Eq. (10)), the final section peak area (Eq. (15)), the total area (Eq. (16)) and the peak height (Eqs (1) and (18)).