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RELATION OF OBSERVED INITIAL TEMPERATURE OF THERMAL TRANSFORMATION TO SENSITIVITY OF THERMAL ANALYZER

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The relations of the initial temperature of thermal transformation to the sensitivity of thermal analyzer and to kinetic parameters of the studied transformation taking place under non-isothermal conditions are analyzed.

The initial temperature of a transition is one of the most important characteristics in thermal analysis. This temperature can be determined directly from the record on the basis of a noticeable deviation of the thermoanalytical curve from the baseline [1] or can be calculated [2,3] in the case of known kinetic parameters of a studied one-step transformation.

In Logvinenko's monograph [4] it is accepted without an analysis of the phenomenon that the initial temperature of a transformation or thermolysis is the temperature where equal rates of the process are attained, on condition of the sample mass remaining constant. This conclusion is made on the basis that the amplitudes of DTA, DTG, DSC and EGA curves are proportional in each point to the rate of transformation $d\alpha/dt$. Such a treatment of the initial observed temperature of a transformation generally is not quite accurate.

Let us suppose that a process is described by the well-known kinetic equation:

$$d\alpha/dt = A \exp(-E/RT)(1-\alpha)^n \qquad (1)$$

where the designation generally accepted in J.Thermal Anal. and recommended by ICTA is used [5].

Kinetic exponent n at values < 1 characterizes movement of the interphase surface; at $n > 1$, according to [6] it describes diffusion of a volatile product from the depth of a grain to its surface and the subsequent desorption from the outer surface. In ranges of low degrees of transformation ($\alpha_0 < 0.01$) the initial kinetic equation (1) is simplified to

$$(d\alpha/dt)_0 = A \exp(-E/RT) \qquad (2)$$

If we turn now directly to thermobalances, then

$$\frac{d\alpha}{dt} = \frac{1}{\gamma M} \cdot \frac{dm}{dt}$$

where M is the initial sample mass, and γ is the portion of the initial mass volatilizing during heating according to the scheme: $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$. In the range of maximum sensitivity of masses Δm_0, the following holds:

$$K(T_i) = \frac{1}{\gamma M} \left(\frac{dm}{dt} \right)_0 = A \exp(-E/RT_i) \tag{3}$$

where T_i is the observed initial temperature of transformation.

The equation

$$\int_0^{\Delta m_0} dm = \gamma MA \int_0^{T_i} \exp(-E/RT_i)\, dt$$

should be integrated as described earlier [7] in order to obtain an analytical relationship of the sensitivity of balances (Δm_0) to the rate constant of transformation $/K(T_i)/$and the initial temperature of transformation $/T_i/$. After mathematical transformations we obtain:

$$\Delta m = \frac{\gamma MART_i^2}{\beta (E + 2RT_i)} \exp(-E/RT_i) = \frac{\gamma MRT_i^2 K(T_i)}{\beta (E + 2RT_i)} \tag{4}$$

where β is the linear heating rate. The term $2RT_i$ can be excluded from consideration without introducing a considerable error, and the ratio $\gamma MR/\beta = \Omega$ must be kept at a constant level for the series of transformations under consideration. As a result, the following simple relationship is obtained:

$$T_i \cong \sqrt{\frac{\Omega \Delta m_0 E}{K(T_i)}}$$

Consequently, if all the other conditions are identical $/\Omega$, Δm_0 and $K(T_i)/$, then the initial temperature of transformation will be affected by the activation energy of each reaction. It should also be mentioned here that the relation of the initial temperature of transformation T_i to the sensitivity of the thermoanalytical instrument with regard to the scale of the rate of transformation is less definite, i.e. a number of values of $(d\alpha/dt)_i$ for the studied transformation can correspond to a definite value of Δm_0.

For differential thermoanalytical curves in DTA, DSC and EGA (the last one coupled to differential gas chromatographic detectors) the initial temperature of transformation is determined by sensitivity recording of the peak in the form of minimum height h_i, i.e.

$$(\mathrm{d}\alpha/\mathrm{d}t)_i = \frac{1}{S_\Sigma}\left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_i = \frac{h_i}{S_\Sigma} \quad \text{and} \quad h_i = S_\Sigma\,(\mathrm{d}\alpha/\mathrm{d}t)_i$$

where S_Σ is the total area under the peak in mm.s. However, this area can be expressed for DTA and DSC as a ratio $S_\Sigma = QM/\kappa$, and for EGA as $S_\Sigma = \gamma M/\kappa$, where κ is the calibration constant, and Q is the heat of transformation. It is obvious that different values of $K(T_i) = (\mathrm{d}\alpha/\mathrm{d}t)_i$ can correspond to a fixed value of h_i.

Finally, the following conclusion can be drawn: using the observed initial temperature of transformation (determined from the record on the basis of a noticeable deviation of the curve from the baseline) for comparison of the thermokinetic stability of different compounds is not a reliable operation in general, since this temperature also depends on a number of non-kinetic factors which distort its true value (for example, on the adjustment of the recorder sensitivity), and because of the indefiniteness in the initial degree of transformation α_0.

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