

Determination of the Temperature Sensitivity of Kinetic Processes by Temperature Modulated DSC

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In the classical TM-DSC theory the value of the total heat flow is considered as the sum of the reversing heat flow and non-reversing heat flow. The first one is usually interpreted as the heat flow connected with thermal events having the response on the temperature oscillations and containing the information about the heat capacity of the sample. The second one is usually interpreted as the kinetic heat flow because the processes depending only on time and not influenced by temperature oscillations come here [1].

The heat flow of some kinetic processes in the sample depends on time and is independent on temperature. Such processes can be well characterized by reversing and non-reversing heat flows. The rate of other kinetic processes depends on the small temperature changing. The information about such dependence can be received by temperature modulated measurements. For the processes with temperature dependence the values of reversing and non-reversing heat flow are strongly dependent on modulation parameters such as frequency and therefore can not unambiguously characterize the underlying process.

For the process with underlying heat flow $\Phi(T_u, t)$ under the temperature program $T(t)$ with constant heating rate β the value of the first derivative $d\Phi/dt$ contains two parts:

$$\frac{d}{dt} \Phi(T_u(t), t) = \frac{\partial \Phi(T_u, t)}{\partial t} + \frac{\partial \Phi(T_u, t)}{\partial T} \beta$$

The first part $\partial\Phi/\partial t$ is responsible for time dependence of the process, and the second part $\partial\Phi/\partial T$ shows, how sensitive is the process rate to the temperature changing. The current work contains the procedure of separation the total derivative $d\Phi/dt$ of underlying heat flow into these two parts. It is shown that the value $\partial\Phi/\partial T$ is the characteristic of the underlying process and is independent on modulation parameters. This value characterizes the dependence of the rate of underlying process on the small temperature changing and is called here temperature sensitivity of the process. The knowledge of the temperature sensitivity value allows comparing properties of different processes, to find some additional properties e.g. activation energy for chemical reactions [2] and to make correct interpretation of the reversing and non-reversing heat flows.

References

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- [2] A. Toda, T. Arita and M. Hikosaka, J. Therm. Anal. Cal., Vol. 60 (2000) 821-827