

CORRELATION BETWEEN THERMOANALYTICAL CURVES AND TYPES OF PROCESSES*

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The logistic of thermal analysis is similar to that applied, for example, in chemical analysis. In classical chemistry a sample is treated with a reagent and from its consumption, through the law of component balance, we obtain information about the sample composition. During a thermoanalytical experiment we supply heat to the sample and to extract the desired information about the state of the sample we need certain principles which can be found in thermodynamics. First we need to define measurable thermodynamic quantities and to find their dependence on variables which are not necessarily constant during the course of the experiment. Phase transitions taking place within the sample can best be described by a suitable thermodynamic potential as a function of temperature, possibly pressure, electromagnetic field, etc.

The processes under examination can then be classified into first-order and second-order processes. The first-order processes can be further subdivided, according to the equilibrium background of the process, into invariant (one temperature) and variant and combined (temperature interval). It follows that for the theoretical description of a thermal effect it would probably be more correct to use the terms “break” (no inflection), “step” (one inflection), “peak” (two inflections) and “oscillation” (three inflections). We can see that the increasing derivative makes the effect more distinguishable, the oscillation, however, providing no date about the quantitative change during the process. For the evaluation of individual effects we need certain characteristics, such as the temperatures of onset, top and decay for a peak. Quantitative change, however, is proportional to the peak area bounded by the interpolated peak baseline. For TA methods which exhibit no direct proportionality between measured and sought quantities, such as methods associated with the detection of energy changes, it is also very important to investigate the behaviour of the baseline to obtain reliable information about the shape of the effect and the corresponding actual course of the process.

All this was discussed in more detail by Holba in his article “Thermodynamic principles in thermal analysis” [1]. He also proposed that energy conservation

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balance be the basic law of a thermoanalytical experiment. This is conveniently done by writing the flux form of the first law of thermodynamics, $\dot{U} = \dot{Q} - P\dot{V}$, where U , Q , P and V are internal energy, heat exchange, pressure and volume, respectively, and the superposed dot means the time derivative. This may well describe DTA, DSC and/or thermodilatometry, while for the other methods of TA we need to extend the relation by additional work terms, for example:

exchange of volatile component	$\mu\dot{n}$	thermogravimetry, evolved gas analysis and detection
electric and dielectric work	$E\dot{Z}$ and $e\dot{D}$	electric thermal analysis
magnetic work	$H\dot{M}$	magnetic thermal analysis
mechanical work	$F\dot{t}$	thermomechanical analysis
surface work	$r\dot{A}$	surface measurements and possibly emanation thermal analysis

where μ = chemical potential, n = mole number, E = electric potential, Z = electric charge, e = electric field, D = dielectric polarization, H = magnetic field, M = magnetization, F = mechanic field, t = deformation, r = surface tension and A = surface area. For extracting characteristic thermodynamic values we must find response functions which correlate the variables measured by means of thermal analysis with ordinary thermodynamic functions. The kinetic description of the process is rooted in the solution of a set of constitutive equations which express the relationship between the time development of a certain physical property as detected by TA and the instantaneous state of the system. This is conveniently done by expressing the non-dimensional degree of conversion a on the basis of the detected physical property Y , and the instantaneous rate of the process \dot{Y} is then given by their multiple $Y\dot{a}$ (e.g. $n\dot{a}$, $M\dot{a}$ or $t\dot{a}$). By detailed analysis of the condition of TA work terms, we may establish the necessary theoretical correlation between the experimental conditions and the possible non-constancy of externally applied parameters, such as pressure, chemical potential (through partial pressure), heat exchange, mechanical and electromagnetic fields, etc. The concise framework, including the thermodynamics of non-isothermal systems, will be published elsewhere [2].

References

1. P. HOLBA, *Silikáty* 20 (1976) 45.
2. J. ŠESTÁK, Thermodynamic basis for the correct description and interpretation of thermoanalytical experimental (in the course of preparation).