POLARITY OF THE TRANSFORMATION PROCESSES IN THERMAL MEASURING SYSTEMS

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(Received August 13, 1981)

The temporal relativistic principle, recently established for calorimetric systems in the framework of the theory of the topoenergetic behaviour of composite systems, is extended to general thermal measuring systems. A thermal measuring system is defined as a measuring system in which the conversion of a response function is measured as a result of a stepwise perturbation in temperature. The process of crystallization revealed by different thermal measuring systems is considered for a series of compounds for which the processes are identical in nature, but differ in amplitude, so that an external affine relation $E = nK + m$ is verified between the activation energy $E$ and the amplitude term $K$. It results that the polarity of a transformation process is a characteristic proper to the temporal reference system of the considered measuring system and can be expressed by the signs of the parameters $E$ and/or $n$.

Review of topoenergetic concepts

On the basis of the recently established topoenergetic principles [1, 2], it has been concluded that the behaviour of a composite system in a thermal measuring system is univocally defined by the nature and the amplitude of the revealed transformation process [3]. The two characteristics can be quantitatively determined from the parameters $(E, K)$ which generally define the kinetic equations proper to the direct or single measuring system (SMS) and the differential measuring system (DMS), respectively [4], namely:

\[
\text{SMS: } \ln \tau = -E(\frac{RT}{\tau}) + K
\]

\[
\text{DMS: } \ln (\frac{t}{T}) = -E(\frac{RT}{T}) + K
\]

These equations were established by modelling the equivalent energetic principles, and both impose as the transformation temperature $T$, to be applied by the stepwise boundary condition [2], starting from an initial value at which the process occurs slowly or is completely inhibited. Thus a thermal measuring system can be defined as any kind of energetic circuit in which the time conversion for a physical value can be measured as a result of the stepwise variation of the external temperature. DTA systems represent a particular case recently considered in topoenergetic terms [1 - 6], with a view to determining the behaviour of the processes of crystallization [5], thermooxidation [4, 6], curing-polymerization [7] and degradation by molec-
However, the thermally driven processes may be revealed by the variation of volume (densimetric or dilatometric measurements), mechanical, electric, magnetic or optical characteristics, induced as a result of a boundary condition. The response functions considered may have one of the following types of conversion: (i) SMS: monotonously increasing or decreasing towards a saturation (equilibrium) value for which the maximum rate of conversion occurs at the initial instant, and which defines the period relaxation $\tau$ as the reverse of this rate [4]; (ii) in DMS this maximum conversion rate is delayed at a period $t_i$ from the initial instant. The free terms $K$ associated with the two measuring systems are defined as:

$$K = \begin{cases} \ln \left( \frac{RC_{\text{inert}}}{I} \right) & \text{in SMS} \\ \ln \left( \frac{ERC_{\text{inert}}}{R} \right) & \text{in DMS} \end{cases}$$

where $T$ is a constant of the energetic circuit representing the dissipative coupling of the internal circuit to the boundary condition [2], $C_{\text{inert}}$ is a measure of the inert component in the tested composite system, and $R$ is the gas constant.

It is important to note that this manner of treatment of the behaviour of composite systems in the framework of the thermal measuring systems allows redefinition of the concept of mass [9, 10], taking into account that $K$ is an experimental value which expresses the "mass" of the process or its amplitude. As $\tau$ and $t_i$ values are expressed in arbitrary units, local in the measuring system, the mass of the process also results in these units, the more so as the $K$ value contains the constant $R$. For a DMS, similarly as in a SMS the mass constant may be expressed by [3]

$$\kappa \equiv K - \ln |E|$$

From a mathematical point of view the behaviour of the overall energetic circuit associated with the measuring system given by one of Eqs (1) or (2) is univocally defined by the parameters $(E, K)$. From the physical point of view this condition of univocity corresponds to the definition of the nature and the amplitude of the overall transformation process revealed as thermal behaviour in the measuring system considered. This qualitative and quantitative identification has meaning and is practically possible only by comparing the resulting behaviours for different composite systems in the framework of the same measuring system [3].

For the particular case of a composite system in which the inert to transformation component ratio differs, the kinetic parameters $(E, K)$ also satisfy a linear relationship [4]:

$$E = nK + m$$

In this relation we generally refer to the mass value $K$ (SMS) and $\kappa$ (DMS), respectively.

Equations (1) and (2) linearly correlate the response value $\tau$ or $t_i$ of the composite system with the applied perturbation $T$, and we will call them internal affine relations, considering that they define the behaviour of the internal energetic circuit relative to the measuring system. Eq. (5) may be called an external affine relation,