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POLARITY OF THE TRANSFORMATION PROCESSES IN THERMAL MEASURING SYSTEMS

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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 $E = n K + m$ 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:

$$\text{SMS: } \ln \tau = -E(RT) + K \tag{1}$$

$$\text{DMS: } \ln (t_i T) = -E/(RT) + K \tag{2}$$

These equations were established by modelling the eqivalent 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 molecular scission [8]. 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 τ 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:

$$K = \begin{cases} \ln (RC_{\text{inert}}) & \text{in SMS} \\ \ln (ERC_{\text{inert}}/R) & \text{in DMS} \end{cases} \tag{3}$$

where T is a constant of the energetic circuit representing the dissipative coupling of the internal circuit to the boundary condition [2], C_{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 τ 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]

$$\kappa \cong K - \ln |E| \tag{4}$$

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]:

$$E = n\,K + m \tag{5}$$

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

Equations (1) and (2) linearly correlate the response value τ 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*, taking into account that this expresses the resolution power of the external energetic circuit of the measuring system relative to the transformation process defined by (E, K).

It is important in the present work to bear in mind two aspects, namely:

(i) according to the topoenergetic principles and models, it results that (E, K) are not invariable values proper to a certain composite system, but relative to a measuring system; and

(ii) as a function of both the external and internal energetic circuits the parameters (E, K) may result as positive or negative values.

These two aspects result directly from the temporal relativistic principle on which the theory of behaviour of the composite systems is based [2, 9, 10]. In short, this principle refers to the capacitive accumulation of the transforming component in the local reference system (LocRS), which generally differs from the laboratory reference system (LabRS) proper to the inert component. In a previous study [2] the calorimetric systems were analyzed for which the algebraic sign resulting for the activation energy clearly explains this relativistic principle. Hence, for the case in which both fluxes have the same thermodynamic sense (exothermic or endothermic), both reference systems coincide and $E > 0$; if the two fluxes are of opposite sense, $t(\mathrm{LocRS}) = -t(\mathrm{LabRS})$ and the set (t, T, E) changes the algebraic sign by the transformation LocRS → LabRS.

We will call the sense of the energetic flux associated with the transformation component the *polarity* of the transformation process. This concept has a relative meaning, on the one hand relative to the measuring system, and on the other hand relative to the local or laboratory reference system. The question is: on the basis of what values may we define the polarity of a transformation process in a general thermal measuring system?

The answer is the aim of the present work: the crystallization process for a polymer series is considered by using different measuring systems for which the external affine relation [5] may be determined. It has been found that the polarity is characteristic which may be established for a composite system relative to another regarded as standard, by considering the algebraic signs of E or n, but taking into account the other one as being of the same sign. The two compared systems may be tested in the same measuring system or in different ones.

Results and discussion

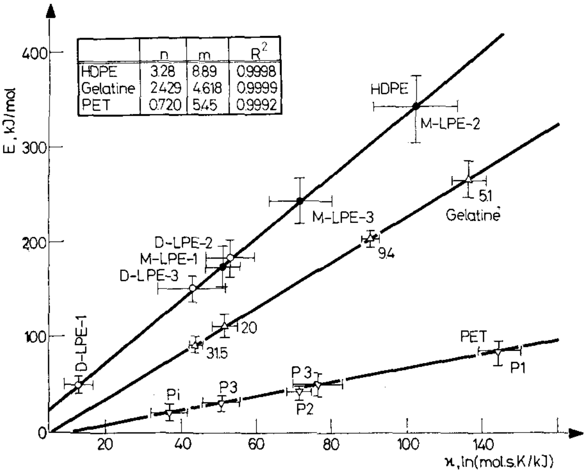
The external affine relation [5] is theoretically justified by the following reasons. The activation energy is defined in both types of measuring system by the Arrhenius dependence of the relaxation period associated with the capacitive accumulation of the transforming component C_{transf}, so that for different amplitudes of this component E varies proportionally with $\ln C_{\mathrm{transf}}$ [2–5]. The amplitude parameters K or κ represent exactly that value, but extrapolated to $T \to \infty$ according to Eqs (1) or (2), respectively, and define the inert component. Thus, the ratio between E and

K according to Eq. (5), expressed by the coefficient n, should be an indication of the polarity of the transformation process; but (E, K) have algebraic sign and the sign of K or κ arbitrarily depends on the units used, so that the significance of n should be taken into account if the compared systems have the same sign in E. This reasoning stands for comparison according to E.

Differential measuring systems

The differential measuring systems, especially the calorimetric ones, reveal the relative polarity of the fluxes associated with the constitutive components. To establish more exactly the physical meaning of the polarity concept in the framework of the other thermal measuring systems, we will consider the crystallization process for a series of polymers. This choice is suggested by the large number of experimental data capable of being further interpreted by using the topoenergetic principles.

The most simple case of a DMS system is the DTA basic disposition for crystallization from the melt [5]. The sample, initially kept at a temperature above the melting point of the crystalline phase (T_m^0), is subsequently transferred to a crystallization temperature T in the measuring system. thus, the two fluxes are of an exothermic sense and $E > 0$ [2, 5] according to internal affine relation [2]. Figure 1 represents the experimental values for the parameters (E, κ) for three series of polymers: high-density polyethylenes (HDPE) [3, 5], gelatine in aqueous solutions [11] and poly(ethylene terephtalate) (PET) [12]. In each series the mass or amplitude term is different, so that the affine relation [5] can be verified. It results that E,



	n	m	R^2
HDPE	3.28	8.89	0.9998
Gelatine	24.29	46.18	0.9999
PET	0.720	5.45	0.9992

Fig. 1. External affine correlations of the parameters (E, κ) determined in differential calorimetric systems for crystallization from the melt. HDPE: the dry (D—LPE) (○) and medium (M—LPE) (●) samples from references [3, 5]; gelatine in aqueous solutionts from the reference [11] (▽), and PET samples from reference [12] (▽)

Table 1

External affine parameters for thermooxidative process of amorphous phase in HDPE, LDPE and -iPP (Du Pont 990, 10 mg sample, 1 mcal/s.in) [3, 6, 13]

Specimens	n (kJ/mol)/ln (mol.s.K/kJ)	m kJ/mol	R^2
LDPE, HDPE filled with Ketjien EC	0.28 ± 0.05	$-(11 \pm 2)$	0.96
LDPE/Corax L	0.23 ± 0.01	$-(2.650 \pm 0.007)$	0.9993
HDPE/Corax L	0.23 ± 0.01	$-(5.7 \pm 0.24)$	0.998
i-PP/additives	0.23 ± 0.02	$-(2.99 \pm 0.5)$	0.99

$n > 0$, which expresses the fact that the activation energy increases with increase of the inert component.

Let us consider in the same DTA system a transformation process for which the two fluxes are of opposite sign and $E < 0$. An appropriate example recently studied is the thermooxidative process observed for the amorphous phase in high and low (LDPE) density polyethylenes [3, 6, 13], and in isotactic polypropylene (*i-PP*) with different antioxidant additives [13]. Table 1 gives the affine parameters n, m and the correlation coefficient R^2 resulting from linear regression of the (E, κ) values. For such type of processes we have $E < 0$ and $n < 0$. It is important to note that n has the same value for all tested systems against thermooxidative conditions, and this expresses the fact that the considered DSC system (Du Pont 990 apparatus and the overall technique) has the same resolution power for these systems. On the other hand, the m value which represents the activation energy at standard amplitude of the inert component ($\kappa = 0$) decreases in algebraic value with the transformation component, which is consistent with the external affine relation for $n > 0$, no matter what the algebraic sign of the parameters (E, κ). Thus, the polarity in DTA systems as topoenergetic DMS is given exclusively by the algebraic sign of E.

The dilatometric or densimetric systems also represent topoenergetic DMS frequently used for polymer crystallization in which the sample is subjected to the same stepwise perturbation in temperature as in DTA disposition. Furthermore, the energetic effect associated with the transformation process has an exothermic sense, because the sample volume decreases at constant pressure. In Fig. 2 the values (E, κ) resulting for a series of HDPE fractions dilatometrically crystallized from the melt [3, 14] are given, such that $E, n < 0$. However taking into account Eq. (5), it results that the following transformation

$$(E, n, m) \rightarrow (-E, -n, -m) \tag{6}$$

does not affect the polarity of the transformation process in the considered measuring system. Thus, the situation represented by $E, n < 0$ is identical to $E, n > 0$, and

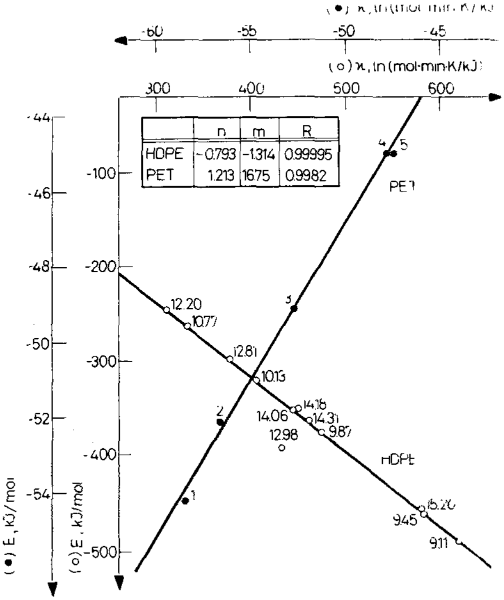


Fig. 2. External affine correlations of the parameters (E, κ) determined in dilatometric measuring system for melt crystallization of HDPE fractions (o) [3, 14]: solid-state crystallization of PET (1) samples with different ingredients: (2) talc, 3 TiO_2, (4) kaolin and (5) SiO_2 (•) [15]

it results that by comparing this dilatometric system with DTA, the crystallization process from the melt for HDPE has the same polarity in both measuring systems.

Let us consider now the case in which the temperature is conversely applied as a stepwise perturbation. This case corresponds to the solid-state crystallization, the sample being initially quenched from the melt to a low temperature at which crystallization is limited and subsequently transferred to an upper crystallization temperature. This temperature perturbation would correspond in the DTA system to different senses of the two energetic fluxes, ($E < 0$, $n > 0$) or ($E > 0$, $n < 0$) respectively, taking into account transformation (6). Figure 2. gives the values of (E, κ) resulting in the dilatometric system for solid-state crystallization by the annealing of PET samples [15]. The dilatometric system does not reveal the flux associated with the inert component, but the energetic effect of crystallization remains exothermic and ($E < 0$, $n > 0$), which is in agreement with the general principle that the time reverse transformation changes the transformation polarity.

Direct measuring systems

The direct measuring systems reveal modifications of the crystalline phase as a result of stepwise perturbation during the crystallization process. Hence, the crystallization appears as a transformation branch [2], separated from an overall pro-

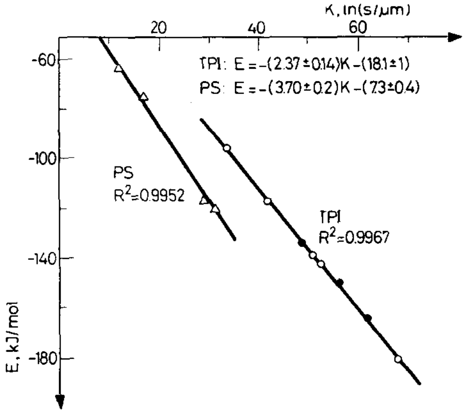


Fig. 3. External affine correlations of the parameters (E, K) for radial crystalline growth from the melt in polystyrene (Δ) and trans -1,4-polyisoprene high ((○) and low (●) melting form) [3, 16].

cess which can be more complex. In polycrystalline and single-crystalline samples the average dimensions $l(t)$ of the crystalline domains increase towards a saturation value l_{eq}. The conversion variation is of SMS type if the crystallization temperature T is below a critical value specific for each composite system, so that the initial rate of radial growth G defines the period $\tau \equiv 1/G$ [3, 4]. In Fig. 3 the values (E, K) determined from these measurements for crystallization from the melt are given for fractions of isotactic polystyrene (*i*-PS) and *trans*-1,4-polyisoprene (TPI) [3, 16]. It results that $E, n < 0$ or $E, n > 0$ according to transformation (6), which shows that the polarity of these crystallization processes is the same as for the similar ones revealed by the above-mentioned DMS.

An other SMS derived by the same conversion of the average dimensions of crystalline domains may be applied for solid-state crystallization. However, it must be noted that a SMS completely separates the transforming branch so that it would not emphasize the difference between crystallization from the melt or from the solid state, respectively. For verification of this statement we will consider the crystallization of a supercooled solid state by annealing, in which the initial value of average crystalline dimensions l_0 increases directly to l_{eq}. Near T_m^0, l_{eq} increases exponentially against a baseline expressed by the l_0 value, and the period τ may be considered as

$$\tau \equiv R\, C_{transf} \sim \Delta l \tag{7}$$

where $\Delta l \equiv \left(l_{eq}(T) - l_0\right)$ or $\left(l_{eq}(T) - l_{BL}(T)\right)$ if the baseline has a slope different from zero.

Figure 4 gives the values (E, K) determined for HDPE [17, 18], LDPE with CF_3 [19] and CH_3 [20] as side-groups, and PET [21]. It results that the polarity of the crystallization process given by $E, n > 0$ remains the same as for crystallization from the melt.

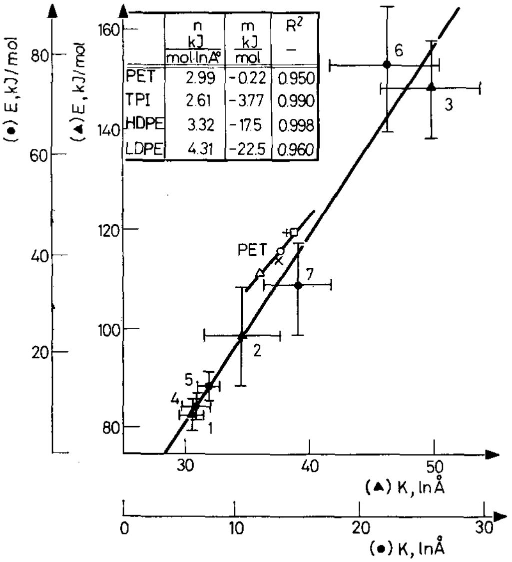


Fig. 4. External affine correlations of the parameters (*E*, *K*) determined by lamellar thickness as measuring system for solid-state crystallization during annealing: lower and left scales HDPE (1) and (2) Hizex 1200 J [17]. (3) Scholex 6150 C [18]: upper and right scales: LDPE with 0.075 (4), 0.071 (5), 0.058 (6) CF_3/C [19], and 0.03 CH_3 (7) [20]; PET samples are taken as from reference [21]

A different case of solid-state crystallization which can be studied by a similar SMS is represented by the grains formed in metallic alloys. We will consider the case of binary alloys of Cr – W, studied in the direct measuring systems of the rate of radial growth *G* and of the self-diffusion coefficients of atomic species of Cr and W, respectively [22]. In Fig. 5*a* and *b* the parameters (*E*, *K*) corresponding to these SMS are given and a revers polarity results against the proper crystallization process considered above, taken into account that:

$$G \sim D_{\mathrm{Cr}} \sim D_{\mathrm{W}} \tag{8}$$

where $D_{\mathrm{Cr,\,W}}$ denotes the self-diffusion coefficient for a given temperature of annealing.

This process is similar to nodule formation in the majority of amorphous polymers [23], for which the calorimetric systems reveal an endothermic flux, and for subsequent "melting" the order-disorder process associated with the paracrystalline morphology also reveals an endothermic effect. For these composite systems an apparent violation of the energy conservation law results, as in the similar case of morphological modifications observed by annealing in chlorinated polyethylenes [10]. These phenomena are explained by the existence of an inductive element in the internal energetic circuit, or more exactly in the coupling between the two com-

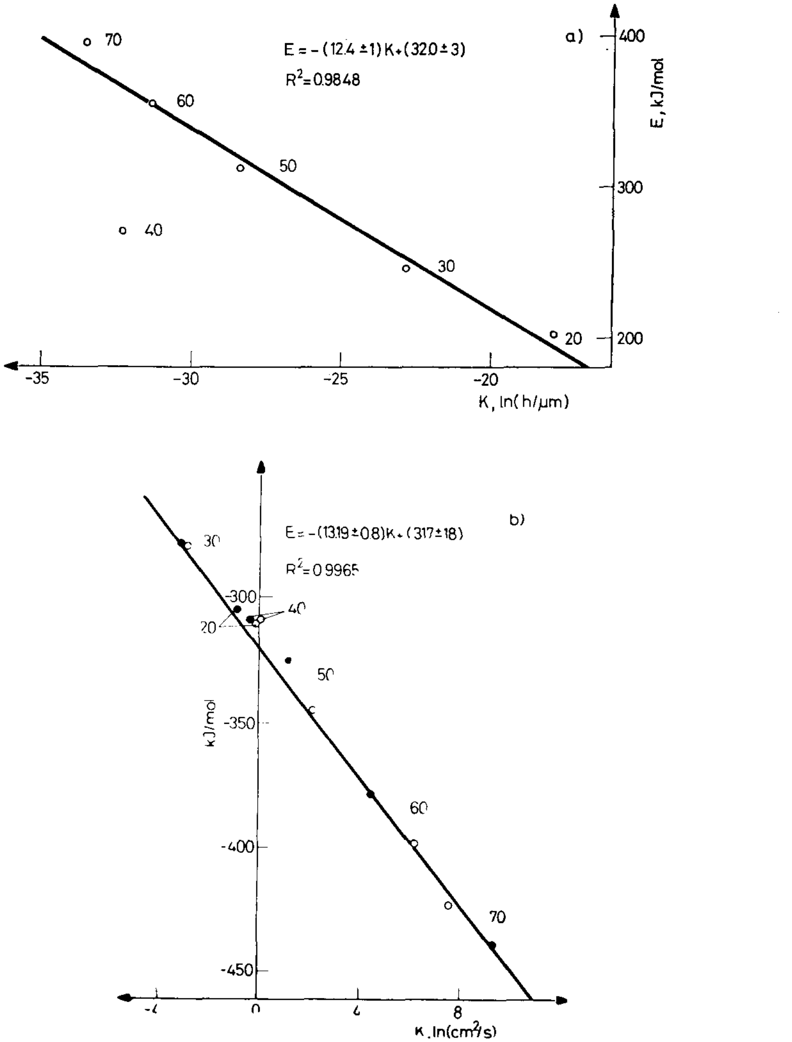


Fig. 5. External affine correlations of the parameters (E, K) determined for the solid-state crystallization of Cr-W alloys by annealing [22]; the associated numbers correspond to the atom percent concentration of W. (a). Radial lamellar growth as measuring system; (b) measuring system of self-diffusion coefficients for W (○) and Cr (●) atoms, respectively

ponents [9, 10], that changes the polarity of the transformation process by the transformation from the LocRS to the LabRS.

Another important result is the fact that the n values for the three SMS are the same, taking into account relationship [8], no matter what the units used.

References

1. Gh. Drăgan, J. Thermal Anal., 9 (1976) 405.
2. Gh. Drăgan, J. Thermal Anal., 15 (1979) 297.
3. Gh. Drăgan, Acta Polymer, 31 (1980) 293.
4. Gh. Drăgan, Rev. Roum. Chim., 24 (1979) 627.
5. Gh. Drăgan, Rev. Roum. Chim., 23 (1978) 629.
6. Gh. Drăgan, V. Dobrescu and N. Goldenberg, J. Polymer Sci., Polymer Phys. Edn., in press.
7. Gh. Drăgan and F. Stoenescu, Rev. Roum. Chim., 24 (1979) 55.
8. I. Negulescu, C. Mihailescu, Gh. Drăgan and Gh. Rusu, Bul. Inst. Polit. Iaşi, 30 (1980) 77.
9. Gh. Drăgan, Rev. Chim., Bucharest, 29 (1978) 214.
10. Gh. Drăgan, J. Polymer Sci., Polymer Symposia, 18 (1978) 141.
11. P. Godard, J. J. Biebuick, M. Daumerie, H. Naveau and J. R. Mercier, J. Polymer Sci., Polymer Phys. Ed., 16 (1978) 1817.
12. A. Dimeo, G. Maglio, E. Martuscelli and R. Palumbo, Polymer, 17 (1976) 802.
13. Gh. Drăgan, Thesis, University of Bucharest, 1980.
14. L. Mandelkern, J. G. Fatou and K. Ohna, J. Polymer Sci., Polymer Lett., 6 (1978) 615.
15. G. Groeninckx, H. Berghmans, N. Overbergh and G. Smets, J. Polymer Sci., Polymer Phys. Ed., 12 (1974) 303.
16. J. H. Magil, Polymer Handbook, (J. Brandrup and E. H. Immergut Eds.), New York, J. Wiley and Sons, 1975, p. III 193.
17. N. Kusumoto, T. Yamamoto and M. Takayanagi, J. Polymer Sci., A 2 (1971) 1173.
18. T. Kajiyama, T. Okada and M. Takayanagi, J. Macromol. Sci. Phys., B9 (1974) 35.
19. I. L. Sanchez, J. P. Colson and R. K. Eby, J. Appl. Phys., 44 (1973) 4332.
20. H. Miyaji and K. Asai, J. Polymer Sci., Polymer Phys. Ed., 15 (1978) 1325.
21. G. Groeninckx, H. Reynaers, H. Berghmans and G. Smets, J. Polymer Sci., Polymer Phys. Ed., 18 (1980) 1311.
22. U. Roll, Thesis von der Universität Stuttgart, 1978.
23. K. Neki and P. H. Geil, J. Macromol. Sci. Phys., B8 (1973) 295.

Zusammenfassung — Das gemäßigte relativistische Prinzip das unlängst für die kalorimetrischen Systeme im Rahmen der Theorie des topoenergetischen Verhaltens der zusammengesetzten Systeme festgelegt worden ist, wird auf allgemeine thermische Meßsysteme ausgedehnt. Ein thermisches Meßsystem wird als ein Meßsystem definiert, in dem die Umwandlung einer Antwortfunktion als Ergebnis einer stufenweisen Temperaturstörung gemessen wird. Der durch verschiedene thermische Meßysteme bestimmte Kristallisationsverlauf wird als eine Serie von Mischungen betrachtet, für welche die Beschaffenheit des Vorganges identisch, jedoch die Amplituden verschieden sind, so daß eine externe Affinitätsbeziehung $E = n K + m$ zwischen der Aktivierungsenergie E und dem Amplitudenausdruck K erfüllt werden kann. Es ergibt sich, daß die Polarität eines Umwandlungsprozesses charakteristisch für das temporale Bezugssystem des betreffenden Meßsystems ist und durch das Zeichen der Parameter E und/oder n ausgedrückt werden kann.

Резюме — Временный релятивистский принцип, установленный недавно для калориметрических систем в рамках теории топознергетического поведения сложных систем, распространен на общие термические измерительные системы. Термическая измерительная система определена как измерительная система в которой превращение функции отклика измеряется как результат ступенчатого возмущения температуры. Процесс кристаллизации, обнаруженный различными термическими измерительными системами, принимается во внимание в ряду соединений, для которых природа процесса идентична, но различается амплитудами. Вследствие этого какое-лилибо внешнее уравнение $E = nK + m$ изменяется между энергией активации и амплитудным членом К. Результатом этого является то, что полярность процесса превращения является характерным свойством временной стандартной системы обсуждаемой измерительной системы и может быть выражено знаком параметров E и (или же) n.