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Kinetics of chemical reactions and phase transitions at changing temperature: General reconsiderations and a new approach

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An extended analysis is given and a new approach developed on the possibilities to describe in terms of classical kinetic models, developed for isothermal conditions, the kinetics of chemical reactions or processes of phase transition, of structural relaxation and of vitrification in terms of non-isothermal kinetics. The main question investigated is to determine to which extent both the kinetic models involved and the activation energies, determining and limiting the process investigated, can be established by a single cooling or heating run, performed e.g. in a DTA or in a DSC calorimetric device. As a first possibility existing isoconversional methods of non-isothermal analysis are considered and in particular the usually disregarded method of cooling run experimentation, which, it is shown is a necessity and can give excellent results in analyzing processes of melt crystallization and of topochemical reaction kinetics, e.g. when relative activities of nucleants or catalyzers are involved. However, in the framework of isoconversional methods it is impossible to determine both absolute values of activation energies and unambiguously to decide upon possible mechanisms of reactions.

A general method is thus developed, based on Ozawa's concepts, in which the Avrami equation is introduced as a general intermediate algorithm of change, describing both homogeneous reaction kinetics (with power coefficients $n \leq 1$) and topochemical reactions and phase transitions (at $n = 1, 2, 3, 4$). It is shown how analytical and geometrical considerations can be exploited to determine in terms of the employed Avrami algorithm both kinetic models and activation energies in a new and more appropriate generalized Ozawa-type analysis.

The theoretical results obtained are illustrated with examples from nucleation and growth kinetics in polymer melt crystallization, in supersaturated aqueous solutions, in devitrification of glasses and in glass transition and in electrolytical metal deposition at galvanostatic conditions.

Key words: Non-isothermal kinetics, isoconversional analysis, topochemical reactions, Avrami equation, Ozawa method, phase transitions.

1. INTRODUCTION

With the very beginning of thermal analysis, both by DTA and DSC methods, efforts were made to derive approaches, permitting the analysis and determination of both kinetic reaction models and the respective activation energies.

Here first the Kissinger procedure [1], developed end of the 1950-ties, has to be mentioned. In plotting peak reaction temperatures T_{max} *vs.* linear heating rates q, this author calculated activation energies; moreover from the form of the obtained transition rate/temperature curves Kissinger tried to determine the reaction order, i.e. the anticipated reaction model. Kissinger's procedure, described in present-day terms, is analyzed in details in [2] in both its merits and shortcomings. It is essential, that with Kissinger's paper the analysis of non-isothermal reaction kinetics was opened in terms of isoconversional approaches: at the peak, i.e. at the maximum reaction rate temperature, T_{max}, a constant degree of conversion, α, was anticipated or proven to exist.

The isoconversional methods are in principle less informative than methods of analysis, in which the whole course of the non-isothermal transition kinetics is used in order to determine both anticipated models of reaction, of phase transition or change and the corresponding activation energies. The first and very widely used method in this way was indicated by Ozawa beginning of the 1970-ties [3, 4]. It was performed in the framework of the Kolmogorov-Avrami overall crystallization model (see [5, 6 and 7]).

In the present paper an attempt is made to employ and further specify Ozawa's method so as to develop a general approach, applicable to chemical reaction kinetics of any order, to topochemical reactions, to phase transitions and relaxation processes in undercooled melts, in crystalline and amorphous solids, in glasses.

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In developing our approach, we first show, that Avrami equation, derived originally and modified (see [7]) to follow the overall kinetics of crystallization at various phase transitions (in melt crystallization of compact volumes [6], in solid state reactions [8, 9], in the crystallization of finely dispersed materials like glassy semolina or powders [10] brought to micro-dimensions, two-dimensional nucleation, in thin layers [7] etc.) can also be used to describe with sufficient accuracy the kinetics of homogeneous reactions. It is especially shown here, that Avrami dependence can be applied to processes, which according to van't Hoff's classical schemes [11] of homogeneous reactions kinetics are classified as first, second and third order reactions. It is also demonstrated how reaction models, summarized in Garner's book (see [12]), and proposed by authors like Roginskii [13] and Erofeev (see [8]) for solid state decompositions and reaction kinetics can be described with this same dependence. Non-isothermal relaxation kinetics in viscoelastic bodies, i.e. vitrification and devitrification is also analyzed in the present contribution employing Avrami equation. In Section 3 it is shown, that the broad applicability of Avrami equation is determined by the circumstance, that this dependence is the particular case of a very general kinetic relation, following directly from the so called phenomenological equation of the thermodynamics of irreversible processes (see [7]). In this way Avrami form of this general dependence is used here only as a convenient algorithm in describing isothermal reaction kinetics and in transforming it from isothermal to non-isothermal applications

In our treatment, we consider all cases in terms of a non-isothermal variant of the integral form of Avrami equation. A simple procedure to deter-mine the reaction model based essentially on the value of Avrami power index *n* and an unambi-guous procedure to calculate also the corresponding activation energies is derived. It is shown here, that the Avrami power index *n* (originally expected to be *n* = 1, 2, 3, 4, see [6]) can have also non-integer, fractional values, corresponding to physically unexpected and interesting applications.

Thus we continue efforts, initiated by Kissinger [1] and by other authors, like Coats and Redfern [14, 15] in non-isothermal chemical reaction kinetics, and by Henderson [16], Gutzow [17] and Gutzow and Dobreva [18, 19] and Colmenero *et al.* [20] in analyzing processes of overall crystallization and nucleation at increasing or decreasing temperatures (i.e. at increasing supersaturation) in electrolytic phase deposition [17, 18], in polymer crystallization [19, 20] or in glass transitions. This lastly mentioned type of processes, as they are described in [7, 21–23]) can be considered as a non-isothermal kinetic process of structural freezing. Thus we anticipate here in fact not only chemical reaction kinetics, but we are even more interested in structural changes, their relaxation and in phase transition processes, taking place in condensed matter (see also [7, 22, 24, 25]).

The present contribution is organized in the following way:

In Section 2 we summarize basic relations, necessary for our analysis. Then in Section 3 the properties of the Avrami kinetic equation are analyzed in the new general, thermodynamically based form necessary here. It is shown, how this general approach can be used to describe practically any known case of isothermal or non-isothermal change in a new way. This description is done in such a form as to define by the value of Avrami power index *n* the reaction type and by a generalization of Ozawa's procedure – the temperature dependence of the activation energy $U(T)$ in non-isothermal processes. To the possible non-isothermal approaches with Avrami equation are destined Sections 4, 5 and 6. There we employ two isoconversional methods and derive an analytical and geometrical approach to enlarge in Section 7 the classical non-isothermal method of analysis proposed by Ozawa in [3, 4]. In Section 5, the analysis of several examples of reaction kinetics and phase transitions is given in terms of $U(T)$ dependences and considered in order to demonstrate both the possibilities and the limitations of existing and of the newly developed methods. Here we analyze crystallization process in general, chemical reactions and overall crystallization in polymer and simple melts, in glass-forming systems, in aqueous solutions and in electrolytic phase deposition. In Section 6 we describe isoconversional approximations and in Section 7 enlarge Ozawa's method of analysis. In Section 8 we apply the previously formalism developed to the kinetics of non-isothermal glass relaxation, i.e. to glass transitions, vitrification and to glass stabilization. In doing so we use the results and approaches of the kinetic theory of vitrification, initially formulated by Vol'kenstein and Ptizyn [21, 22] and then developed in a generic way by one of the present authors [23–25] on the basis of the thermodynamics of irreversible processes (see [7], [23], [25] and literature cited here in Section 10). In Section 9 a comparison with experimental results is given and lastly, in Section 10 several necessary conclusions are drawn. In Appendixes 1, 2, 3 several mathematical details are discussed.

2. SEVERAL BASIC KINETIC RELATIONS

Since van't Hoff's times the order of a reaction in chemical kinetics is determined by the way rate of change (at isothermal conditions) of the concentration dc_A/dt of one of the components (A, B, C) in the reaction system depends on the sum of the stochiometric coefficients ($a + b + c + \ldots$) in the expression

$$\frac{dC_A}{dt} = K(T)[A]^a [B]^b [C]^c .. \tag{1}$$

Here [A], [B], [C] … indicate the concentrations of the components A, B, C, … in the reaction mixture and $K(T)$ is the temperature dependent reaction constant [11]. In homogeneous reactions (taking place in gaseous or liquid phases) the coefficients a, b, c,…. are as a rule integer numbers. More generally reactions of first, second or third order in chemical kinetics are called chemical or physical changes, following a time dependence of the type

$$\frac{dC}{dt} = K(T)C^m \text{, with } m = 1, 2, 3, \ldots \tag{2}$$

Here C indicates the concentration of any structurally significant unit of the system. The transition of Eqn. (2) to more general formulations is usually done in defining C *via*

$$C = \frac{\xi - \xi_e(T)}{\xi_0 - \xi_e(T)} \tag{3}$$

as the change of a physically significant internal parameter [7, 24, 25] from its momentary value, ξ, to its equilibrium value, $\xi_e(T)$. The initial value of ξ (at time $t = 0$) is indicated in Eqn. (3) with ξ_0. In considering phase transitions or topochemical reaction kinetics the rate of overall conversion (or phase transition), α, is defined *via* the provision

$$\alpha = \frac{V - V_i(T)}{V_0 - V_i(T)} \equiv C, \tag{4}$$

when the notations of Eqns. (2), (3) are considered. Here V_t indicates the momentary value of the volume transformed (e.g. crystallized) at time t at the temperature T, V_0 is the initial and $V_i(T)$ its end value of V in the isothermal crystallization process investigated. This definition of α is particularly used in deriving and employing the Kolmogorov-Avrami equation [6, 7], to be discussed in the following Section 3 in details.

In terms of the still non-reacted, non-changed molar part $(1-\alpha)$ of the reaction participants van't Hoff's equation (2) can be written as

$$d\alpha/dt = K(T)(1-\alpha)F(\alpha) \tag{5}$$

For first, second and third order homogeneous reaction kinetics the reaction model function $F(\alpha)$ in Eqn. (5) has the values

$$F(\alpha) = (1-\alpha)^p, \quad \text{with } p = 0, 1, 2 \tag{6}$$

In considering solid state reactions as a case of heterogeneous, topochemical reaction kinetics, Roginskii and Shultz [13] (see also further similar proposals summarized in [8, 9, 12]) indicated as a realistic general possibility of reaction rate equations these to which $F(\alpha)$ in Eqn. (5) is defined in the form

$$F(\alpha) = \alpha^{2/3} \tag{7}$$

This indicates, that in topochemical reactions not the volume V, but the surface area $S \approx V^{2/3}$of the products formed is reaction determining.

To similar $F(\alpha)$-values in Eqn. (5) leads also Erofeev's topochemical reaction kinetics [8, 9, 26], which he formulated also in terms of the already mentioned Avrami equation. In its integral form, this equation gives the time dependence of α at constant temperature, T, as

$$\alpha = 1-\exp[-K_A(T)t^n] \tag{8}$$

Here, according to Erofeev [8, 9, 26] the value of the integer power index $n = 1, 2, 3, 4$ depends (in analogy with Avrami's initial formulations, see [6, 7]) on the way in which the new interface, S, is formed via nucleation and growth processes in the reacting volume. This same Eqn. (8), as one of us has earlier shown [10, 27], describes also fairly well with values of $n = 1$ to 3 the overall crystallization process in an ensemble of equal spheres of radius R, each one of them crystallizing from the surface to its own volume. This model of crystallization of more or less finely dispersed materials was initially formulated by Mampel [28] in a way, leading to complicated, non-soluble integral dependences. They are, however, as also the results in [10, 27], of particular significance in DTA and DSC thermoanalysis, where usually fine-grained samples have to be investigated. This is one of the possibilities which the Avrami equation gives as a convenient algorithm in reaction kinetics. Further possibilities in this respect are indicated in Section 3.

According to Eqn. (8) the rate of change and conversion is given by

$$\frac{d\alpha}{dt} = nK_A(T)t^{n-1}\exp\left[-K_A(T)t^n\right] =$$

$$= nK_A(T)(1-\alpha)\ t^{n-1} \tag{9a}$$

Thus we arrive at a simple relation, which is of general significance in the following analysis in Section 4: we can write Eqn. (9a) also as

$$\frac{d\alpha}{dt} = n(1-\alpha)[-\ln(1-\alpha)]^{\frac{n-1}{n}}[K_A(T)]^{\frac{1}{n}} =$$

$$= (1-\alpha)F(\alpha)K^*(T) \qquad (9b)$$

Observing that with Eqn. (8) we have $t^{n-1} = [-\ln(1-\alpha)]^{\frac{n-1}{n}} K_A^{2/3}(T)$ we can write Eqn. (9) also in the general form of Eqn. (5) with $K^*(T) = n[K_A(T)]^{1/n}$ and with a reaction model function, which for any power index n in Eqn. (8) is to be written as

$$F(\alpha) \equiv F_n(\alpha) = [-\ln(1-\alpha)]^{\frac{n-1}{n}} \qquad (10)$$

As far as in our notations always the coefficient of conversion has values $0 \leq \alpha \leq 1$, it is evident that for $n = 3$, Eqn. (10) gives by a simple expansion of the logarithm in a good approximation the $F(\alpha)$ value indicated with Eqn. (7) for the Roginskii-Schultz topochemical kinetics. More general and more precise, it can be shown (see [8, 26] and the mathematical procedure described there) that the Avrami Eqn. (8) leads to rate dependences of the type

$$\frac{d\alpha}{dt} = K^*(T)(1-\alpha)^r \alpha^s \qquad (11)$$

They can be also represented in the form of our Eqn. (5), however, with

$$F(\alpha) = F_n^E(\alpha) = (1-\alpha)^{r-1}\alpha^s \qquad (12)$$

and with r and s values, corresponding to concrete n-values [8, 26] in Avrami equation, as this is given on Table 1, taken from [8].

Table 1. Avrami and Erofeev power indeces in Eqns. (8), (11) and (12).

Avrami power index, n in Eqn. (8)	Erofeev power index			
	Eqn. (11)		Eqn. (12)	
	r	s	$(r–1)$	s
1	1	0	0	0
2	0.774	1/2	–0.226	1/2
3	0.700	2/3	–0.300	2/3
4	0.665	3/4	–0.335	3/4

The essential point, to be mentioned here is, that the kinetic Eqn. (5) is in fact one of the possible forms of a general growth and development dependences (see [29, 30]), determining the rate of change by the present status (here indicated by the value of $(1–\alpha)$) of the system and by an additional correction function, $F(\alpha)$, determined by the concrete model or mechanism of the expected change. This model approach considered initially for isothermal regimes and conditions is to be transformed here to non-isothermal kinetics of reaction and change.

For the particular forms of the $F(\alpha)$-function different integral forms of Eqn. (5) follow. Thus for first, second and third order homogeneous reactions after integration of Eqn. (5) with the indicated values of p in Eqn. (6) and the additional condition $\alpha = 0$ at $t = 0$ it follows

$$\alpha = 1–\exp[–K_A(T)t] \qquad (13)$$

$$\alpha = 1– [1+K(T)t]^{-1} \qquad (14)$$

$$\alpha = 1–[1+2K(T)t^{-1/2}] \qquad (15)$$

Thus for first order reaction kinetics follows directly Avrami Eqn. (8) with $n = 1$.

The integration of the kinetic rate equations of the type (5) with fractional values of the power index, as given by Eqn. (7), leads to mathematically implicit dependences. Thus for $\alpha^{1/2}$ we obtain the complicated expression (see [31] p. 32)

$$\alpha = \left\{1 - \left(1 + \sqrt{\alpha}\right)\exp\left[-K(T)^{1/2}t\right]\right\}^2 \qquad (16)$$

which, as it is obvious from Fig. 1, can be conveniently and with sufficient accuracy approximated by an Avrami-type dependence with $n = 2$. The integration of Eqn. (9) leads directly to the corresponding Avrami Eqn. (8). In Section 3 it is shown, that Eqns. (14), (15) can be also written in the form of the Avrami equation, however, with fractional values of the power index n.

Thus it is turns out, that quite differing kinetic dependences, corresponding to the general kinetic relation Eqn. (5) having various $F(\alpha)$-values, can be represented in their integral form by Avrami equation simply by varying the value of the power index n. In this way seemingly different dependences can be, as discussed in the following Section 3, represented in a relatively uniform way and characterized by a distinct number: the value of the power index n. These properties of Avrami equation give, according to the main idea of the present contribution, also a more easy way to analyze kinetic changes at different mechanisms (i.e. at differing $F(\alpha)$-values in Eqns. (5) and (6)) at non-isothermal conditions, and especially at increasing or decreasing cooling (heating) rates q

$$dT = qdt \qquad (17)$$

taking place with a constant value of q. As far as Eqn. (17) is fulfilled, it is easy to change the argument from time, t, to temperature, T, in both the differential and the integral kinetic dependences, so far introduced above.

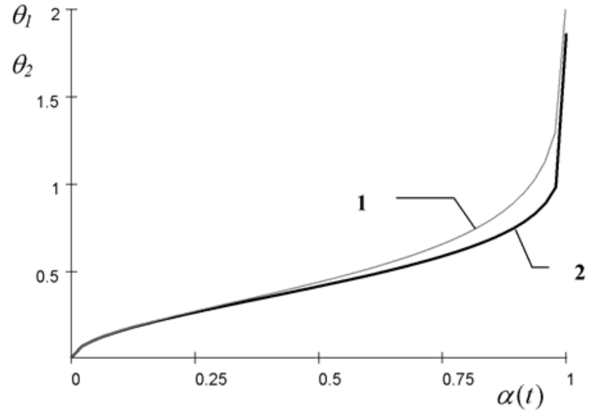

Fig. 1. Approxination of the implicit $\alpha(t)$-dependence, Eqn. (16) with an Avrami-type dependence (Eqn. (8)) with $n = 2$. On the ordinate is plotted $\theta_1 = \frac{t}{\sqrt{K(T)}}$ *vs.* $\alpha(t)$ on the ordinate for Eqn. (16) as (**1**) and $\theta_2 = \frac{t}{\left(\frac{\ln(2)}{K(t)^{1/2}}\right)}$ for Eqn. (8) as (**2**). According to Eqns. (22) and (16) in Section 3, θ_1 and θ_2 are reduced times in respect to the corresponding half transition times, $\tau_{0.5}$, for both dependences.

From a more general point of view Eqn. (5) with the additional specifications, provided by $F(\alpha)$ (Eqns. (6), (7), (12)) is a general form of one of possible equations of steady growth and development [29, 30].

When additional structural specifications are connected with the process investigated, $F(\alpha)$ indicates the way this specifications are transformed, either steadily decreasing the rate of general change (Eqn. (6) or determining a maximum (Eqn. (7)) as seen on Fig. 2. At $F(\alpha) = 1$ as this is for first order kinetics of change we consider unrestricted growth proper, dependent only on the depletion of the concentration of the initial components, $(1-\alpha)$. In Eqns. (7) and (9) the build-up of a new interphase surface determines a maximum value in the $d\alpha/dt$-course. In nucleation and growth processes the nature of both the $F(\alpha)$ and the $K(T)$-functions are determined by the interplay of the activation energies of these two processes (see Section 4).

In describing relaxation processes in glasses (Section 8) we have to discuss cases, when the change of $K(T)$ is dependent on the depletion of the active constituents of the system. Thus there $K(T)$ has in fact the significance of a time dependent resistance, changing with the advancement of the process of structural relaxation [30] and with the alteration of activation energies it causes.

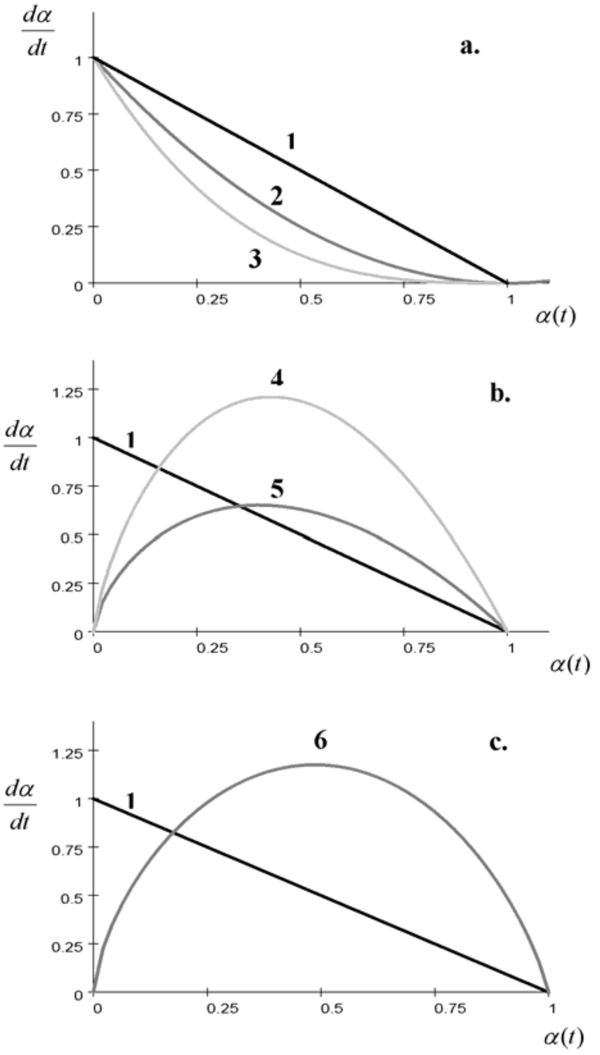

Fig. 2. Rate of transition dependences for various kinetic mechanisms.
a. Homogenous reaction kinetics (Eqns. (5) and (6)). 1 - first order; 2 - second order; 3 - third order reaction;
b. Topochemical reaction mechanisms: 1 - first order; 4, 5 - Roginskii type dependences: according to Eqn. (7) with $\alpha^{2/3}$ and $\alpha^{3/4}$; c. Avrami-type rate dependences, Eqn. (9): 1 - with $F(\alpha) = 1$; 6 - with $n = 3$ and $d\alpha/dt$, according to Eqn. (9).

3. PROPERTIES OF THE AVRAMI EQUATION AS A GENERAL KINETIC DEPENDENCE

The general reaction and crystallization dependence given here as Eqn. (8), usually attributed to Avrami is initially derived by Kolmogorov [5] (for the special case $n = 3$) and than by Avrami [6] more generally in the framework of a crystallization model and as the result of a long history of development of ideas, summarized in [7]. Also on crystallization models are based the already mentioned derivations of Mampel [28] and Gutzow *et al.*

[10] and even Erofeev's applications of this equation to solid state reactions [32], summarized in [8].

There are, however, also other ways of deriving and analyzing Eqn. (8), which we are still denoting here as Avrami dependence, which are based on broader premises. Here first has to be mentioned an attempt by Kazeev [33] to postulate dependences equivalent to Eqn. (8) as following from the theory of physicochemical similarity for reaction kinetics and change, taking place under distinct constraints. In a more recent series of papers by Gutzow *et al.* [30, 34, 35] it was shown, that rate dependences of the type, given here with Eqn.(5) with time dependent $F(\alpha)$-values follow in cases, when the rate of change ($d\alpha/dt$, or $d\xi/dt$, see Eqn. (3)) of the process is determined by a time-changing activation energy $U(T,t)$. In this sense as a result of the analysis in [34, 35] Eqns. (5), (6) having values of the Avrami power index $n < 1$, can be also written as

$$\frac{d\xi}{dt} = \frac{1}{\tau_0(T)} \frac{n}{t^b}(1-\xi) \qquad (18)$$

i.e. as changes, determined by a time dependent relaxation time $\tau^* = \tau_0(T)/t^b$. To Eqn. (18) correspond integral forms of the type

$$(\xi - \xi_0) = (\xi_0 - \xi_{in})\boldsymbol{exp}\left[-\left(\frac{t}{\tau_0^*}\right)^{1-b}\right] \qquad (19)$$

usually referred to as fractional or stretched-exponent relaxation dependences (see the historic background given in [34] and the original publications of R. Kohlrausch [36], F. Kohlrausch, [37] and Boltzmann [38] for this formula). According to these general considerations a value $n > 1$ in Eqn. (8) corresponds to kinetic barriers, $U(T, t)$ decreasing with time, while $n < 1$ suits models with time increasing values of the barrier. In terms of Eqn. (18) the relaxation time $\tau^* = \tau_0 t^b$ gives at $n = 1$, a constant value of the activation energy $U(T,t) = U(T) = U_0 = const$. At $b = 0$ Eqn. (19) thus gives dependences, corresponding to first order reactions and to Maxwell's classical solution of the kinetics of relaxation (see [7, 39])

$$(\xi - \xi_0) = (\xi_0 - \xi_{in})\boldsymbol{exp}\left(-\frac{t}{\tau^{\#}(T)}\right) \qquad (20)$$

According to the initial derivations of Avrami, the power index n in Eqns. (8), (9) has to have only integer values $n \geq 1$ (1 to 4 in three dimensional value growth and $n = 2–3$ for surface growth in thin layers [7], [40], see Table 2). In considering growth of more or less finely dispersed samples according to the already mentioned model considerations and experimental results in [10, 27] also fractional values of n in the range 1 to 1/3 have to be expected in both Eqns. (8) and (9). It becomes thus evident, that with fractional values $n < 1$ of the power index in Avrami Eqn. (8) not only first, second and third order reaction dependences, but also Kohlrausch-type stretched exponent relaxation relations can be described. In fact, the Kohlrausch formula (Eqn. (18)) is a typical case of a second order reaction kinetics dependence. Its integral form (Eqn. (19)) corresponds to the mentioned particular cases of the Avrami dependence with $n < 1$ (usually in glass-forming melts $(1–b) \approx (0.30–0.35)$, i.e. $b = (0.70–0.65) \approx 2/3$, see [7, 22].

Table 2. Avrami power indeces, n in Eqn. (8), see [6, 7] in dependence of mechanism and morphology.

Mechanism of nucleation	Growth morphology	Formula for k_n	n	Author
sporadic	spherical	$\frac{\omega_n}{n} v^3 J$	4	Avrami [6]
athermal	spherical	$\frac{\omega_n}{n} v^3 N^*$	3	Avrami [6]
sporadic	disk-like	$\frac{\omega_n}{n} v^2 hJ$	3	Avrami [6]
athermal	disk-like	$\frac{\omega_n}{n} v^2 hN^*$	2	Avrami [6]
sporadic	needle-like	$\frac{\omega_n}{n} vh^2 J$	2	Avrami [6]
athermal	needle-like	$\frac{\omega_n}{n} vh^2 N^*$	1	Avrami [6]
surface sporadic	Surface growth	$\frac{\omega_n}{n} v^2 J_2$	3	Vetter [40]
surface athermal	surface radial growth	$\frac{\omega_n}{n} v^2 N_2^*$	2	Vetter [40]

In considering the discussion of Avrami Eqn. (8), let us further on observe, that in reduced coordinates $\theta = (t/\tau^{\#})$, where

$$\tau^{\#} = 1/[K_A(T)]^{1/n} \qquad (21)$$

the value $(t/\tau^{\#}) = 1$ determines an iso-conversion constant $\alpha_{iso} = \left(1 - \frac{1}{e}\right)$ = 0.63 for any n-value (Fig. 3). Moreover, because of $-\ln(1-\alpha) \approx 1$ for the same value of α, the product $(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} = F_n(\alpha)$ is also a constant as also evident from Fig. 3. Both properties of the Avrami dependence (Eqn. (8) apply for $n \geq 1$ as well as for $n < 1$ and are essential in analyzing non-isothermal reaction kinetics and change. They define in a natural way the iso-conversional methods of non-isothermal determination of the parameters of Avrami type dependences, discussed here in details in Section 5.

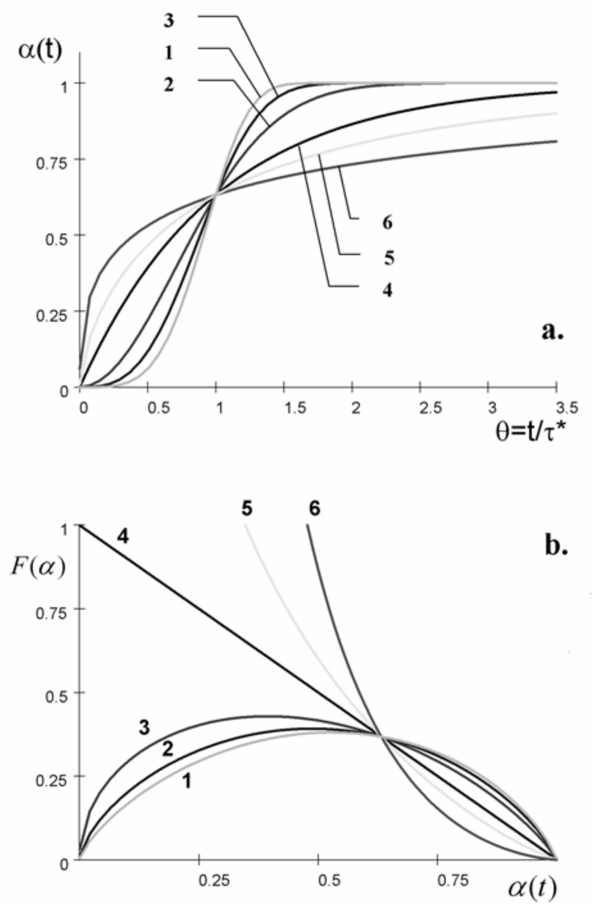

Fig. 3. Properties of the Avrami equation.
a. Avrami curves according to Eqn. (8) in coordinates *α(t) vs*. $\theta = t/\tau^*$, where the time τ^* is given with Eqn. (21). Note that at $\theta = 1$ all curves (for both $n \geq 1$ and for $n < 1$) have the same ordinate, $\alpha = \left(1 - \frac{1}{e}\right) = 0.63$. With 2, 3, 4 are denoted the Avrami power index values of $n > 1$ and with 4, 5, 6, $n = 1$, $n = 2/3$ and $n = 2/5$, respectively;
b. The course of the function $[1 - \alpha(t)]F(\alpha)$ with $F(\alpha)$ given according to Eqn. (10). With numbers are again indicated the n-values in Eqn. (8) as given above. Note that all $F(\alpha)$-curves have at $\alpha = 0.63$ approximately the same value, $\alpha = 1/e$.

An essential parameter to be also used in this connection is the time $\tau_{0.5}$ of half transition (or half conversion) in any process of change investigated: it is the time for α (or any other change coordinate defined with Eqs. (3) or (4)) to become equal to 0.5. Using either Eqn. (8) or Eqn. (13), (14), (15) this time is given by

$$\tau_{0.5} = \ln 2/K(T)^{1/n} \tag{22}$$

according to Eqn. (8) (i.e. also with $\tau_{0.5} = [\ln 2/K(T)]$ for first order reaction kinetics according to Eqn. (13) and with

$$\tau_{0.5} = 1/K(T) \tag{23}$$

and

$$\tau_{0.5} = 3/2.K(T) \tag{24}$$

for second and third order reaction kinetics (see Eqns. (14), (15) respectively).

Further on it is of essence to be mentioned, that the maximal value of the rate of conversion $\left(\frac{d\alpha}{dt}\right)_{\max}$ determined by the Avrami-type equations are given with

$$\frac{d\alpha}{dt}\Big|_{\max} = \left[(n-1)^{n-1}\omega K(T)\right]^{1/n} \exp\left(-\frac{n-1}{n}\right) \tag{25}$$

The time, at which this maximum is reached, is given with

$$\tau_{\max} = \left[\frac{n-1}{K(T)}\right]^{1/n} \tag{26}$$

It is evident, that at $n > 1$ both values correspond at to the inflexion point of the respective $\alpha(t)$-curve, determined by Eqn. (21).

From the $\alpha(t)$ *vs*. $\tau_{0.5}$-representation given on Fig. 4 it is evident that first, second and third order reaction kinetics, originally described by Eqns. (13), (14) and (15) with three seemingly quite differing dependences can be represented with sufficient accuracy by the Avrami Eqn. (8) respectively with $n = 1$, 2/3, 2/5. As seen the coincidence of the corresponding curves goes from $t/\tau_{0.5} = 0$ (i.e. at $\alpha(t) = 0$) through $t/\tau_{0.5} = 1$ to $t \to \infty$. On Fig. 5 the ($d\alpha/dt$)-curves, following with both Eqns. (9) and (25) are also illustrated for both $n \geq 1$ and for $n < 1$.

From Fig. 1 it was also seen that the Roginskii-type dependences Eqns. (6), (7) (for both $F(\alpha) = \alpha^{2/3}$ and $F(\alpha) = \alpha^{1/2}$) are sufficiently well represented with $\alpha(t)$-curves according to Eqn. (8) with $n = 3$ and 2, respectively (c.f. also Fig. 3).

Equations (18) and (19) show moreover, that the mentioned formal resemblance in the $\alpha(t)$-dependence is illustrated by the relative closeness of the respective differential relations – by the course of the $d\alpha/dt$-function in both cases.

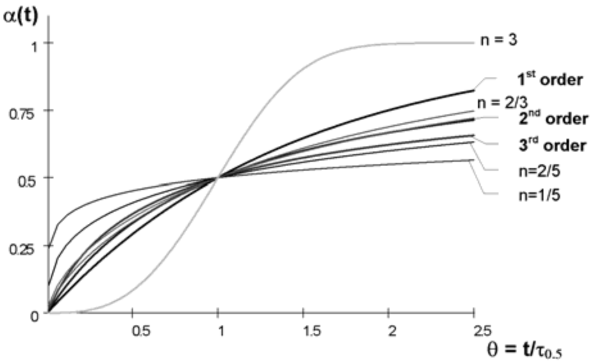

Fig. 4. The specification of first, second and third order reaction kinetics in terms of the Avrami equation, Eqn. (8), as an intermediate algorithm. With bold lines and text are indicated, beginning from below third, second and first order homogeneous reaction kinetics, respectively (c.f. Eqns. (13), (14) and (15)). With thinner lines are indicated the respective Avrami-curves, Eqn. (8) with $n = 1, 2/3, 2/5, 1/5$; on top is drawn the Avrami-curve with $n = 3$. In this way $n = 1, 2/3$ and $2/5$ are chosen to represent the above indicated reaction kinetic curves.

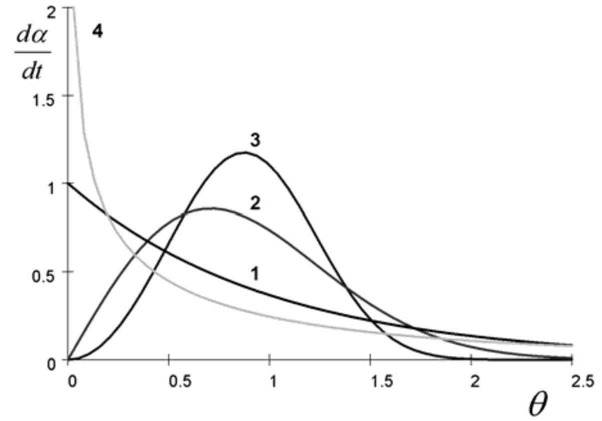

Fig. 5. Transition rate curves $d\alpha/dt$ vs. θ, Eqn. (21), according to first, second and third reaction kinetics, Eqns. (13), (14), (15) expressed as reaction rates, following from the Avrami equation, Eqn. (8), with $n = 1$, 2, 3 and $n = 2/3$. Note first that $n = 1$ is equal with first order kinetics and that for any $n > 1$ a maximum is displayed by the Avrami rate curves. Here are indicated the following rate dependences 1 – $d\alpha/dt = \exp(-\theta)$; 2 - $d\alpha/dt = 2\theta\exp(-\theta^2)$; 3 - $d\alpha/dt = 3x^2\exp(-\theta^3)$; 4 - $d\alpha/dt = 2/3.x^{-1/3}\exp(-x^{2/3})$.

The classical derivation of the Avrami equation in its isothermal formulation treated up to now can be simply made either in terms of the probabilistic models, stemming from Kolmogorov [5, 7], or more appropriate for our further developments via the remarkable notion of the extended volume $Y_n(t)$ and the so called Avrami theorem [6, 7]. According to this theorem, because of the interaction of growing crystallites, we have to write

$$d\alpha(t) = (1-\alpha)d[Y_n(t)] \qquad (27)$$

where $Y_n(t)$ is given in general as

$$Y_n(t) = \int_0^t I(t',T)dt' \left[\int_{t'}^t v(t'',T)dt''\right]^n$$

Thus $Y_n(t)$ is the virtual volume, formed by nucleation and growth, if no interaction should take place between growing crystallites.

Assuming time-constant values of both nucleation rate $I(t,T) \equiv I(T)$ and of growth rate $v(t,T) \equiv v(T)$ the extend volume becomes

$$Y_n(t) = \omega_n I(T) v^{n-1} \int_0^t (t-t')dt' \qquad (28)$$

Here and in Eqns. (25), (29) ω_n is a steric coefficient ($\omega = 4\pi/3$ at spherical drowth). Thus, in a known way of integration ([6, 7, 8], see Eqn. (28) follows directly the Avrami Eqn. (8) and $K_A(T)$ is thus defined *via* nucleation rate $I(T)$ and growth rate $v(T)$ as

$$K_A(T) = \omega I(T)[v(T)]^{n-1} \qquad (29)$$

This approach is used here in order to derive in the next Section 4 more easily the Avrami kinetics also in the non-isothermal case of the nucleation and growth models. We have also to mention, that the usual way to analyze isothermal results in terms of Eqn. (8) by putting the experimental isotherm in $\log[-\log(1-\alpha)]$ *vs.* $\log t$ coordinates and thus to determine both n and $K(T)$ will be also applied in a generalized Ozawa modification to analyze the non-isothermal case in the next Sections.

4. AVRAMI EQUATION AT NON-ISOTHERMAL CONDITIONS

To this point we summarized only results of the isothermal formulation of reaction phenomenology. Now we have to apply these results to the non-isothermal case. In doing so, we have first to specify additionally both the conversion function α, which is now dependent on both time, t, and temperature, T, as $\alpha(T,t)$ and to introduce temperature as a new argument into the formalism derived.

Anticipating in the following with Eqn. (17) only constant rates of temperature change, we have to write in heating run experimentation

$$T = qt + T_{in} \approx qt \qquad (30a)$$

and to employ the right hand side approximation, when the initial temperature, T_{in}, is sufficiently low, when compared with the temperature, T, where the reaction can be actually observed.

In cooling run experimentation, e.g. in melt crystallization at constantly increasing undercooling with Eqn. (17)

$$\Delta T = (T_m - T) \approx qt \qquad (31)$$

Thus, we have to write for the time-dependent increase of the thermodynamic driving force (the supersaturation $\Delta\mu(T)$) of crystallization that

$$\Delta\mu(T) = \Delta S_m qt \qquad (30b)$$

because of

$$\Delta\mu(T) = \Delta S_m \Delta T \qquad (32)$$

The supersaturation is estimated here via the respective melting temperature, T_m, and the entropy of melting, ΔS_m, (see [7] for this approximation and for more precise solutions). In deriving the $\alpha(T,t)$ *vs.* $\alpha(t)_T$ connection (where $\alpha(t) \equiv \alpha$, employed up to now) we have to consider, that in fact the $\alpha(T,t)$ function, because of Eqn. (30), is in fact a composite function of t, i.e. we have to write $\alpha(T,t) = \varphi[f(t)]$. With the $f(t)$ function given by the right hand side of Eqn. (30) and employing the chain rule of differentiation of composite functions (see [31], p. 32) we obtain with Eqn. (17)

$$\frac{d\alpha(T,t)}{dT} = \frac{d\varphi[f(t)]}{df(t)}\frac{df(t)}{dt} = \frac{1}{q}\frac{d\alpha(t)}{dt}\Big|_T \qquad (33)$$

Thus we have specified beside the dT *vs.* dt dependence also the $\alpha(T,t)$ *vs.* $\alpha(t)$ and the $d\alpha(T,t)$ *vs.* $d\alpha(t)$ connections. These connections should make no problem for $q = const.$ in Eqn. (17): in every differential equation such as Eqns. (9), (11), the argument can be directly replaced by another one, linearly connected with the initial argument. Nevertheless, as mentioned in [41] and elsewhere, this simple procedure still gives rise to questions in thermoanalytical literature, and made necessary the derivation indicated with Eqn. (33).

In order to analyze the kinetics of non-isothermal processes of phase transitions and chemical change we have, accounting for the properties of the Avrami equation, two ways open.

First we can use the circumstance, that (Figs. 3 and 4) both isoconversion points ($\alpha = 0.63$ or $\alpha = 0.5$) are reached at the reduced time $\theta = t/\sqrt[n]{K(T)} = 1$ or $\theta = t/\tau_{0.5} = 1$ for any value of the Avrami index n. For $n > 1$ (i.e. for phase change and solid state reaction) this isoconversion value corresponds to the inflexion point of the respective $\alpha(t)$ or $\alpha(T,t)$ dependences and thus also to the respective maximum in the $(d\alpha/dt)$ or $d[\alpha(T,t)/dT)]$-rate relations.

It is obvious, recollecting Eqns. (17), (30), (33), that because of the constant value of the cooling/heating rate, q, we can write for the maximal value of the rate of change or conversion

$$\frac{d}{dT}\left[\frac{d\alpha(T,t)}{dt}\right] = \frac{d}{dT}\frac{1}{q}\left(\frac{d\alpha(T,t)}{dT}\right) = 0 \qquad (34)$$

For $n > 1$, this maximum in the $(d\alpha/dt)$ or $[d\alpha(T,t)/dT]$-dependence corresponds to the inflexion point, seen on Figs. 3 and 4. For $n < 1$ the same conversion value $\alpha(t)$ or $\alpha(T,t)$ is also observed when for $n > 1$ the inflection point is reached.

Returning to Eqns.(5) or (9) it thus turns out, than when always the same α-value is reached, the maximum in the $(d\alpha(T,t)/dT)$-dependences is determined for any q value by the maximum of the $K(T)$ *vs.* T dependence *via*

$$nq\frac{d}{dT}\left\{[K(T)]^{1/n}\right\} = 0 \qquad (35)$$

In changing the argument from t to T and integrating the left-hand side of Eqn. (9a) in limits from 0 to α_{max} or from 0 to $\alpha_{0.5}$ according to

$$\int_0^{\alpha_{\max}} \frac{d\alpha}{(1-\alpha)} \cong \frac{n}{q^n}\int_0^{T_{\max}} K(T)T^{n-1}dT \qquad (36a)$$

it turns out, that by using for $\alpha(t)$ an Avrami dependence for any n value the left hand integral in Eqn. (36) has the same constant value for both $\alpha_{\text{inflexion}}$ or $\alpha_{0.5}$.

In this way the maximal value of any theoretically constructed or experimentally obtained $d\alpha(T,t)/dT$ *vs.* T-rate curve is determined by the subintegral function in the right hand integral of Eqn. (36a), i.e. by the course of the $K(T)$ subintegral functions corresponding to the Eqns. (8), (13), (14), (15), (16).

Even more conveniently, using the Avrami-equation (8) is to employ Eqn. (9) in the form (9b); than we have to write

$$\int_0^{\alpha_x} \frac{d\alpha}{(1-\alpha)F(\alpha)} \cong \frac{1}{q}\int_0^{T_{\max}} K(T)^{1/n}dT \qquad (36b)$$

where $F(\alpha)$ is given by Eqn. (10). As far as according to Fig. 3 both α_{in} and $F(\alpha)_{in}$ are constants for any n-value we have at this representation not only a constant value at the right hand side of Eqn. (36b), but the left hand integral is now considerably simplified and determined only by the temperature function of $K(T)$.

In this way the analysis of non-isothermal reaction and transition kinetics according to above so called isoconversional method of analysis is transformed into a problem of the integration of the right hand integrals in Eqn. (36b). At the possible $K(T)$ dependences discussed in the next Section this problem is reduced to a transformation of the respective integrals to two higher transcendent function: to the Integral Exponent function $Ei(Z)$ or to the Gauss Error Function $erf(Z)$ with. The details of this transformation depend on the nature of $K(T)$, i.e. on the temperature function, of the expected kinetic coefficients, as given in Section 5 and in Appendixes 1 and 2.

5. TEMPERATURE DEPENDENCE OF THE KINETIC COEFFICIENTS

Thus we know, that the whole course of the ($d\alpha/dT$)-function at differing cooling or heating runs e.g. in DTA or DSC-arrangements is determined by the temperature function of $K(T)$ or of $K(T)T^{n-1}$ in Eqns. (5, 9) i.e. of the value $K_A(T)$ in the Avrami equation, using the present approach.

In the differing relations, underling above mentioned dependences, the $K^*(T)$ function ($K^*(T) = nK_A(A)^{1/n}$, *etc.*) can be written in general as

$$K^*(T) = K_0 \exp\left[-\frac{U(T)}{RT}\right] \qquad (37)$$

where the particular form of the activation energy function $U(T)$ has to be determined in every case. In homogeneous reaction kinetics an Arrhenian type dependence with $U(T) = U_0 = \text{const}$ is usually assumed [11]. A similar approximation is also made sometimes in most cases of solid state reactions [8, 12]. However in general for topochemical reaction kinetics using appropriate models, based most conveniently on the Avrami theorem (see below Eqns. (41–43) leading to more complicated temperature relations are expected. Thus, $K_A(T)$ depends in such cases on the kinetic and thermodynamic barriers of crystal nucleation $I_0(T)$ and growth rates $v(T)$. In processes of relaxation and vitrification kinetics $U(T)$ in Eqn. (37) is dependent on the concrete mechanism of structural flow and on the change of the ξ-function in Eqn. (3) (see [7, 23, 24, 25] and literature cited there).

In cases of relaxation in glass-forming liquids the $U(T)$-function in Eqn. (37) is determined e.g. by the Vogel-Fulcher-Tammann equation [7] in terms of free volume concepts of liquids flow as

$$U(T) = RT/(T-T_0) \qquad (38)$$

Here $T_0 \approx 0.5T_\text{m}$ is a constant, connected with the respective melting or liquidus temperature, T_m or T_{liq}. In the framework of configurational entropy considerations [7, 42, 43] similar or even more appropriate $U(T)$ – dependences can be derived and used in considering relaxation phenomena in glass-forming melts (see Section 8).

In processes of phase transition the particular structure of Eqn. (29) determines the temperature dependence of $K_A(T)$ according to existing models on nucleation rate and crystal growth kinetics as being defined by both a kinetic barrier of the type given with Eqns. (37), (38) and by second, thermodynamic barrier, determined by the work, $W_c(T)$, necessary to form a crystalline nucleus. According to the classical nucleation theory (see [7, 44, 45]),

$$\frac{W_c(T)}{RT} \approx \frac{W_c^0\Phi}{RT} = \frac{B_0\Phi}{RT\Delta\mu^2(T)} \qquad (39)$$

Here B_0, W_c^0 are determined, according to Gibbs' capillary approximation (see [7, 45]) for a spherical nucleus as

$$B_0 \sim \frac{4}{3}\pi\sigma^3 V_m^2 \qquad (40)$$

by the interphase energy, σ, at the nucleus/ambient phase interface by the molar volume V_m of the crystal and by the thermodynamic driving force, $\Delta\mu(T)$, of the crystallization process. The value of W_c^0 refers to non-catalyzed (homogeneous) nucleation and the factor Φ ($0 \leq \Phi \leq 1$) accounts in heterogeneously induced nucleation for the nucleating activity of foreign nucleation cores [7, 45]. In a good approximation (see [7]) for melt crystallization the value of $\Delta\mu$ is determined by Eqn. (32) *via* undercooling, ΔT, and the respective melting entropy, ΔS_m, of the crystallizing substance.

Thus, the temperature dependence of the dominant factor in Eqn. (29), the rate of nucleation, $I_0(T)$, can be written as

$$I_0(T) \approx const_1 \exp\left[-\frac{U(T)}{RT}\right]\exp\left[-\frac{B_0^{\#}\Phi}{RT\Delta T^2}\right] \qquad (41)$$

where at temperatures $T \approx T_m$ the value of B_0 is to be replaced by $B_0^{\#} = \left(B_0 / \Delta S_m^2 RT_m\right)$.

In considering the Avrami-equation (8) as a particular dependence in describing models of crystal growth (by two-dimensional nucleation, via screw dislocations or by the continuous incorporation of ambient phase molecules on the roughened surface of the crystal (see [7], [44]), the rate of crystal growth in Eqn. (29) has to be written as

$$v(T) \cong const_2 \exp\left[-\frac{U(T)}{RT}\right]\Omega(T) \qquad (42)$$

where Ω(T) depends on the concrete mechanism of growth. It is essential to note , that two-dimensional nucleation growth is of significance only in polymer melt crystallization (see [7,19, 44, 45]) and even there the work of two-dimensional nucleation rate, $W_2(T)$, is considerably lower than $W_c(T)$, $\left[W_2(T)/RT\right] \cong \left[B_2/RT\Delta\mu\right] << W_c^0(T)/RT$

Here W_c^0 indicates, as given with Eqn. (39) the value of the respective work for homogeneous formation of tri-dimensional nuclei (i.e. at $\Phi = 1$) and $W_2(T) \sim \sigma^2 V_m$ is the respective thermodynamic work to form a two-dimensional nuclei at the growing crystal face .

In both growth *via* screw dislocations ($\Omega(T) \sim const_3 \Delta\mu^2(T)$) and at continuous growth ($\Omega(T) \sim const_4 \Delta\mu(T)$) the temperature dependence of $\Omega(T)$) in Eqn. (42) can be neglected when compared with the exponents in Eqns. (41), (42). Thus, it follows that even in polymer melt nucleation (see [7], [44]) with

$$\exp\left(-\frac{W_c^0}{RT\Delta\mu^2(T)}\right)\exp\left(-\frac{W_2}{RT\Delta\mu(T)}\right)^{1/n} \approx$$

$$\approx \exp\left(-\frac{W_c^0}{RT\Delta\mu^2(T)}\left[1+\frac{W_2\Delta\mu(T)}{nW_c^0}\right]\right) \quad (43)$$

it can be taken, that at small undercoolings the temperature dependence of $K_A(T)$ in Eqn. (29) is determined (at medium Φ values) as

$$K_A(T) \approx \omega\ const_0 \exp\left(-\frac{U(T)}{RT}\right)\exp\left(-\frac{W_c\Phi}{RT\Delta\mu^2}\right) \quad (44)$$

i.e. by the thermodynamics and kinetics of the three dimentional nucleation process only.

On the other side, at preexisting populations of very active crystallization cores with $\Phi \approx 0$ (athermal nucleation in Avrami terminology [6]) also the possibility $I_0(T)$ = const has to be considered. This leads to dominant growth determined overall crystallization kinetics (see [7], [27]).

Taking moreover into account that in the vicinity of T_m the value of $W_c(T)$ dramatically increases (at $T \to Tm$, $W_c^0 \to \infty$, $U(T) \to U_0$ = const so that there $W_c(T) >> U(T)$) (see experimental evidence summarized in this respect in [46, 47] for the crystallization of $(NaPO_3)_x$-glasses and of pure H_2O). On the other side at temperatures, approaching on the contrary the glass transition temperature T_g (where usually $T_g \approx 2/3T_m$, see [7]) we have to expect there $W_c(T) << U(T)$. Thus, two possible approximations are to be considered in general as determining the temperature dependence of $K_A(T)$ in melt crystallization:

i.) in the vicinity of melting temperature, T_m:

$$K_A(T) \approx const \exp\left[-\frac{B_0^*\Phi}{\Delta T^2}\right] \quad (45)$$

with $B_0^* = B_0^\# / RT_m$ given with Eqn. (41) and

ii.) at great undercoolings (especially at temperatures in the vicinity of T_g)

$$K_A(T) \approx const \exp\left[-\frac{U_0}{RT}\right] \quad (46)$$

as this is discussed in more details in [46, 47]. It is to be also noted, that in writing Eqn. (46) in fact it is assumed, that the two barriers [$U(T)$ + W_c(T)] in above equations are replaced by a mean constant value, $\overline{U_0}$. The subintegral function in Eqn. (36b) determined by Eqn. (44) or by growth only in athermal nucleation are illustrated on Fig. 6.

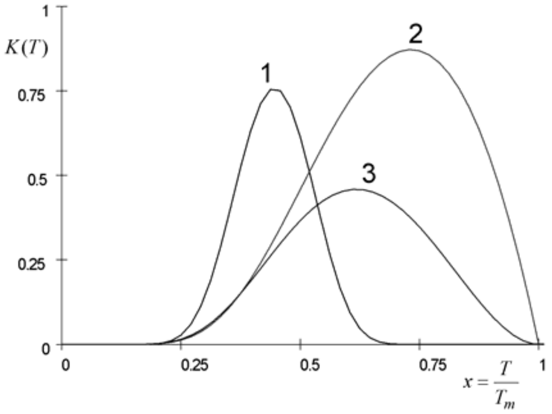

Fig. 6. The form of the subintegral functions in the right-hand integral of Eqn. (36b) at phase transition reactions for different mechanisms of nucleation and growth: 1 – 3D nucleation, according to Eqn. (44); 2 – crystal growth at continuous mechanism of incorporation; 3 – crystal growth at screw dislocations (both with Eqn. (42) and with Ω(T) = (1–x) and with Ω(T) = $(1–x)^2$. The three K(T) curves are drawn with the same kinetic activation energies $U(T) = (2/x)$ and with $A_0 = 10^5$, 50 and 80, respectively. With x is indicated the reduced temperature, $x = T/T_m$.

These two approximations are used in the most often applied method of analysis of non-isothermal crystallization processes given in the next Section, and Eqn. (46) – also for the analysis of all cases of non-isothermal chemical reaction kinetics and especially in polymer crystallization (see [7, 19] and in the crystallization of undercooled aqueous solutions [47]). An interesting case of nucleation, as pointed out in [17, 18], is the electrolytic crystallization of melts on the cathode under galvanostatic conditions. There a steadily increasing overvoltage $\Delta\varepsilon = q_0 t$, determines the supersaturation $\Delta\mu(t)$ and thus a formalism similar to Eqn. (45) has to be applied.

6. ISOCONVERSIONAL APPROXIMATIONS

According to these approximations the integration of the right-hand side of Eqn. (36b) is performed introducing for the subintegral function either Eqn. (45) (as first done in [17, 19, 20] for cooling run crystallization at relatively small under coolings, i.e. when in Eqn. (44) $T \cong T_m$) or – in most cases (beginning with [1, 14–16]) – by using Eqn. (46).

With the substitutions $\left(\frac{U_0}{RT}\right) = z$ and $\sqrt{\frac{B_0}{RT^2}} = z$ in both cases (Eqns. (45), (46)) the right hand integrals in Eqn. (36b) are brought (see Appendix 1) to two well known higher transcend-ental functions: the Exponential Integral Function *Ei*(*Z*) and the Gauss Error Function *erf*(*Z*) [48]. Introducing further on [49] the well known asymp-totic expansions of both transcendental functions two simple solutions

$$\log q = const - \frac{U}{nRT} \tag{47}$$

and

$$\log q = const - \frac{B\Phi}{n\Delta T^2} \tag{48}$$

are easily obtained (see [1, 14–16, 19, 49] and Appendix 1). Thus, in coordinates log*q* *vs*. 1/*T*, the value of (U_0/n) can be determined, as first shown by Henderson [16]. In a similar way, as initially demonstrated in [17, 19, 20] for cooling run experiments in nucleation controlled processes with *K*(*T*) according to Eqn. (29) leads to the Gaussian Error Function *erf*(*x*) and solutions (see [49]) of the type of Eqn. (48). This plot as demonstrated by Dobreva *et al.* in a series of publication is especially helpful in determining the nucleating activity Φ of substrates (crystallization cores) or other additives (eventually surfactants [50, 51, 52, 53]) in nucleation kinetics experiments (see Section 9), comparing plain (where $\Phi = 1$) and doped ($\Phi < 1$) melts [44, 53]. Thus especially significant technological problems can be solved [51–53] connected with synthesis of glass ceramics [51, 52] and of polymer materials [16, 53].

Strictly speaking, the right hand integral in Eqn. (36a) can be also brought to simple expressions, containing either the Gauss Error Function (with Eqn. (45), or to the Ei(*Z*)-function (at $n > 1$), and with Eqn. (37) (at $n < 1$) to the Incomplete Gamma Functions $\Gamma(n{-}1, Z)$, as also indicated in Appendix 1.

In Appendix 2 it is also shown, that even integrals, containing $K_A(T)$-subintegral functions of the type determined with Eqn. (44) can be also geometrically estimated with sufficient accuracy.

The main problems as they are discussed also by other well known authors [2, 41, 54] with the isoconversional methods is, however, not integration, but the unknown *n*-value. Only a full analysis of the $\alpha(T)$-curves, as first performed by Ozawa [3, 4] can determine both *n* and U_0 and thus also the type of the kinetic model equation in Eqn. (36) and in $F(\alpha)$ of Eqn. (9).

7. GENERALIZED OZAWA APPROACH

In 1971 Ozawa [3, 4] indicated a remarkable way out of the restrictions of the isoconversional approximations, which we employ here and enlarge to a more general procedure. This enlargement gives both an analytical and a graphical method to determine in one experiment both *n* (i.e. in our Avrami-function approach: the nature of the kinetic reaction model function $F(\alpha)$) and the respective *U*(*T*) – function as real, experimentally accessible temperature dependences. To do this we begin our derivations again with Eqn. (9), using the form, indicated with Eqn. (9a). We have first, to redefine the extended volume $Y_n(t,T)$ employed in Eqn. (28) for constant temperatures in order to satisfy the requirements of Avrami theorem also in the non-isothermal case. For time independent nucleation and growth rates *I*(*T*) and *v*(*T*) we have now to write

$$Y_n(T) = \omega_n \int_0^T I(T)dt'' \left[\int v(T)dt'' \right]^{n-1} = \omega_n \overline{Y_n}(T) \tag{49}$$

where ω_n, *I*, *v* have the same significance as in Eqns. (27–29).

The continuation possible, following Ozawa's idea, is to replace at constant heating/cooling rates in above integrals *via* Eqns. (17) and (30) d*t* and *t* by d*T* and *T*, and thus we obtain directly

$$Y_n(T) = \frac{\omega_n}{q^n}\ \overline{Y_n}(T) = \frac{n\omega_n 1}{q^n} \int_0^T K(T) T^{n-1} dT \tag{50}$$

After integration according to Avrami theorem (c.f. Eqn. (27)) we have now in analogy to Eqn. (36)

and to Ozawa's procedure (see [3]) to write

$$-\log[1-\alpha(T)] = \frac{n}{q^n}\int_0^T K(T)T^{n-1}dT \qquad (51)$$

Here we have to integrate from $\alpha = 0$ to any $\alpha(T)$-value of the $\alpha(T,t)$-dependence, corresponding to the temperature T. In employing again Eqn. (17) we obtain in similarity to the isothermal Avrami process that

$$\lg\{-\lg[1-\alpha(T)]\} =$$

$$= -n\,\mathbf{lg}\,q + \mathbf{lg}\int_0^T K(T)T^{n\ 1}dT + \mathbf{lg}\,\mathbf{lg}\,e \qquad (52)$$

In this way (c.f. Eqn. (50)) only the value of

$$\overline{Y}_n(t) = \int_0^T I(T')dT'\left[\int_0^T v(T'')dT'\right]^{n-1} \qquad (53)$$

can be determined in coordinates $\lg\{-\lg[1-\alpha(T)]\}$ *vs*. $\lg q$ as $\lg Y_n(T)$. The slope of the respective straight line gives only the value of n and after integration of the sublogarithmic function could reveal also the value of $K(T)$.

The direct result of DTA or DSC-measurements is usually obtained in terms of $d\alpha(T,t)/dT$ *vs*. T plots. After a numerical integration we obtain the respective $\alpha(T)$ *vs*. T curves from which we can determine the values of $\alpha(T)$ corresponding to the respective q value, as prescribed by Ozawa in his $\lg\{-\lg[1-\alpha(T)]\}$ *vs*. $\lg q$ coordinates. This is an approach similar to the isothermal Avrami plot. According to the original derivation of Ozawa, it is assumed that a process of overall crystallization kinetics is investigated in terms of Avrami model. Here it becomes evident, that this procedure is applicable to any process, e.g. a chemical reaction, when we can assume that it is described by Avrami Eqn. (8), considered as a general dependence of change.

Now, following Ozawa, we have determined n; however, we have obtained following his method $K(T)$ and $U(T)$ only in the form of a logarithm of a relatively complicated integral, which can be brought approximately to well known transcendental functions (see Appendix 1, 2) in a similar way as done in the isoconversional case (Section 6).

In order to illustrate this task on Fig. 7 is shown the probable course of the subintegral functions and their change in dependence of cooling/heating rates q for various $K(T)$ dependences. On Fig. 8 the graphical way of integration of these dependences mentioned here and in Section 5 is illustrated.

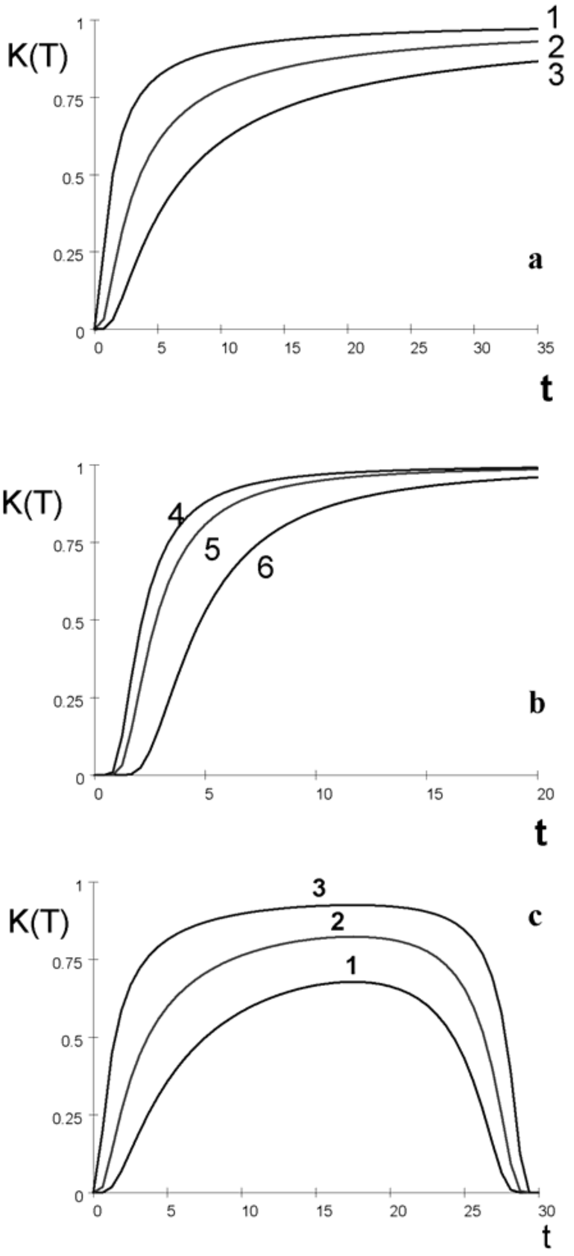

Fig. 7. Influence of cooling/heating rate, q, on the course of the subintegral functions in Eqn. (36b), when the temperature is expressed as $T = qt$, according to Eqn. (30a). a. At an Arrhenian kinetic barrier given with Eqn. (37); b. At a thermodynamic nucleation barrier approximately expressed via Eqn. (45); c. At a nucleation rate dependence, according to Eqn. (44). At picture **a**. the value of q is changed in relative units as $q_{1,2,3} = 1, 2, 5$; **b**. $q_{4,5,6} = 1, 3, 5$; and at **c**. $q_{1,2,3} = 1, 2, 5$. In calculating all three cases in the respective dependences, $U_0/R = 5$, $B/RT_m = 16$, $T_m = 30$, $A_0 = 1$.

A more general approach is, however, possible to determine directly both $U(T)$ and n in the framework of Ozawa's approach.

Suppose we have analyzed, using the already described Ozawa plot, the value of n in Avrami equation: thus we know the kinetic model, underlining the considered non-isothermal $\alpha(T)$-course.

Now we have to determine also the functional dependence and the value of $U(T)$, corresponding to the analyzed model.

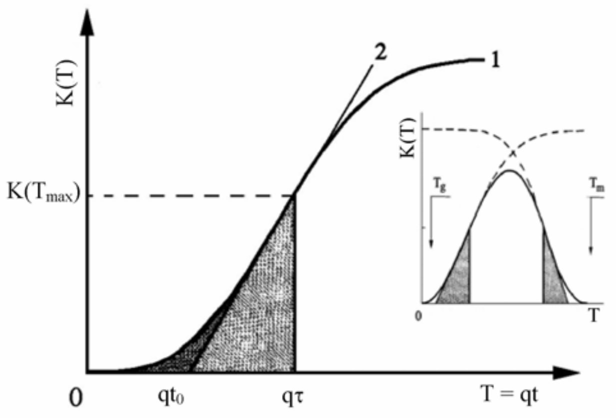

Fig. 8. Geometric interpretation of the determination of the integral, given with the right – hand side of Eqn. (36b). The curve 1, representing the subintegral function *K(T)* at Eqn. (45) with $T = qt$ is approximated by the shaded triangular area of the rectangle. The double shaded area left of the tangent straight line 1 is the part neglected by the approximation of the Gauss Error Function used (see Appendix 2).

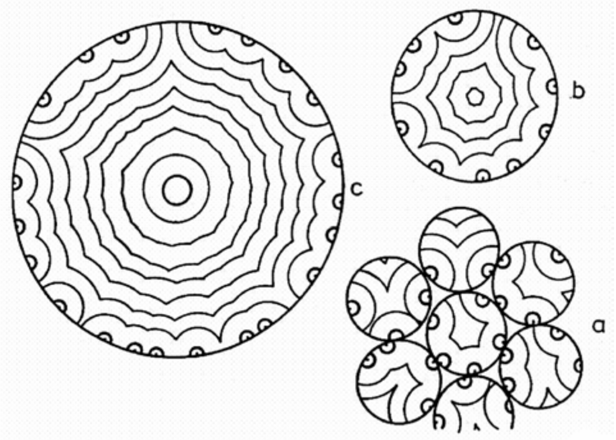

Fig. 9. Effect of mean radius, R_0 on the kinetics of crystallization of samples, constituted of an array of equal spheres (schematically): **a.** At a population of smallest spheres the nucleation event determines to a great extent the crystallization process: Thus, n = 3 in the Avrami equation is expected and found experimentally; **b.** An intermediate case: relatively great spheres allow both nucleation and growth and the formation of a crystallizing front at the end of the process; **c.** The change of the way of crystallization, induced by surface nucleation at relatively great spheres: a crystallization front is formed at the very beginning, proceeding (at a value $n = 1$ in the Avrami index in Eqn. (8)) into the volume of the sphere. For details and subsequent theoretical derivations, see [10].

From the Ozawa plots, we obtain in $\lg[-[1-\alpha(T)]]$ *vs.* $\lg q$ coordinates beside n also the value (for the temperatures and cooling rates q studied) of a function, which we call the Ozawa function, defined according to Eqns. (50–53) as

$$Oz(T) = \frac{1}{2.3}\,\boldsymbol{lg}\int_0^T (T')^{n-1}K(T')dT' =$$

$$= \boldsymbol{lg}\, n\frac{A_0}{2.3}\int_0^T (T')^{n-1}\,\boldsymbol{exp}\left[\frac{U(T')}{RT'}\right]dT' \qquad (54)$$

Here $U(T)$ stands for any of the already discussed models of activation energies of $K(T)$, given with Eqns. (37–39). Taking the logarithmic derivative from above expression and accounting for the rules of differentiation of definite integrals we have to write

$$\frac{d[Oz(T)]}{dT} = \frac{T^{n-1}K(T)}{\int_0^T T^n K(T')dT} = \frac{T^{n-1}K(T)}{\exp[Oz(T)]} \qquad (55)$$

Thus, we obtain the subintegral function of $Oz(T)$ and $K(T)$ as

$$K(T) = \frac{1}{T^{n-1}}\exp[Oz(T)]\left[\frac{dOz(T)}{dT}\right] \qquad (56)$$

Thus, with Eqn. (37) it follows, that $K(T)$ can be obtained from the Ozawa plot as the product of the antilogarithm of the Ozawa function (Eqn. (54)) and the value of its temperature differential at temperature T (see Appendix 3 and Fig. 14 given there). After taking the logarithm from above expression we determine $U(T)/(RT)$ as

$$-\frac{U(T)}{2.3RT} = Oz(T) + \boldsymbol{lg}\left[\frac{dOz(T)}{dT}\right] + \boldsymbol{lg}\left[\frac{nK_0}{T^n}\right] \qquad (57)$$

Thus, we can analyze the nature of the $K(T)$-function according to anticipated temperature dependences, compatible with the kinetic model function $F(\alpha)$ expected. It is evident, that a standard computer programme connected with the DSC Ozawa plot results can thus directly reveal both the $K(T)$ and the $U(T)$ function. In doing so in a good approximation T^{n-1} in Eqns. (54), (55), (57) can be taken as a constant (e.g. $T^{n-1} = T_m^{n-1}$), when compared with the value of the corresponding exponential functions.

In analyzing cases of phase transition kinetics, e.g. in cooling run experimentation the $U(T)$ dependence as depicted with Eqn. (40) has to be anticipated, while in heating run experimentation Eqn. (37) should prevail as a rule. The above given derivation is graphically illustrated in Appendix 3.

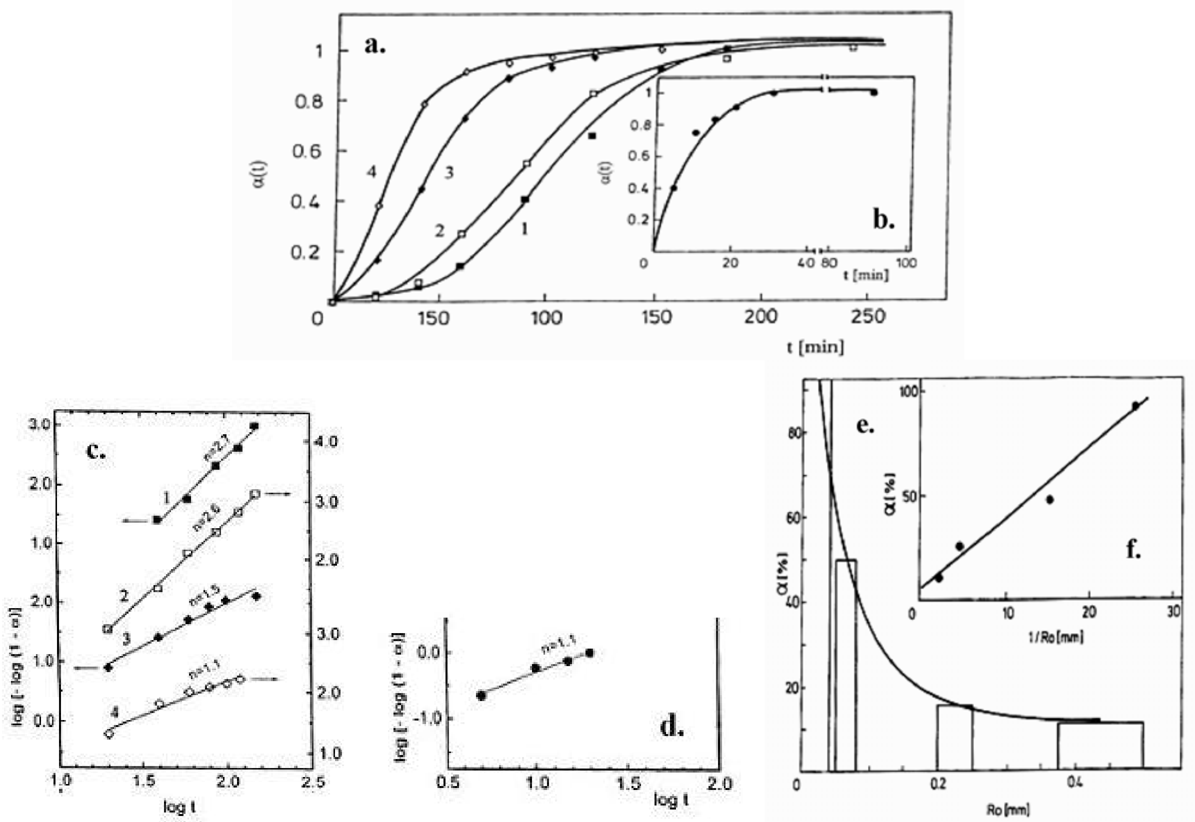

Fig. 10. Experimental verification of the influence of mean radius, R_0 of crystallizing glass semolina samples on the Avrami kinetics. a. Kinetics of overall growth of NaPO$_3$-glass: typical *α(t)*-curves at constant temperature in the temperature range $T = 575$ to 605 K. Curve 1 - $R_0 < 0.04$ mm, $T = 575$ K; curve 2 - $R_0 = 0.05$–0.08 mm, $T = 579$ K; curve 3 - $R_0 = 0.2$–0.25 mm, $T = 598$ K; curve 4 - $R_0 = 0.25$–0.375 mm, $T = 605$ K. b. Kinetics of overall crystallization of diopside glass at 1333 K, $R_0 = 1.25$ mm with $R_0 \approx 1.0$ mm. c., d. The same results in Avrami coordinates lg[–lg(1–α)] *vs*. lg(t) coordinates, giving in dependence of R_0, a change of the Avrami coefficient n from 1 to 3. e. Proof of a reciprocal dependence $n \sim 1/R_0$ for NaPO$_3$ samples, crystallized at 575 K as a function of grain radius, R_0; f. – the same data in coordinates α vs. $1/R_0$. Experimental results from [10] where additionally experimental details are given.

8. KINETICS OF GLASS TRANSITIONS

Long years of investigations have revealed two essential points in the kinetics of glass transition (see [7, 21, 22, 23, 24]):

i) Both isothermal and non isothermal relaxation in glass-forming systems can not be described in terms of Maxwell's linear kinetics (Eqn. (20)), which corresponds to a first order dependence of structural change. This becomes evident in comparing Eqns. (20) and (13) in assuming, that $K(T)$ from Eqn. (13) is the reciprocal of a time independent Maxwellian time of relaxation (i.e. that $[1/K(T)] \equiv \tau^{\#}(T)$). On the contrary, it is well known (see [7, 39]) that only relaxational behaviour of the Kohlrausch-type (Eqns. (18), (19)) with a stretched exponent (ξ–ξ_0)-course satisfy experiment. As far as from such experiments as mentioned the stretched exponent index turns ut to be in the vicinity of (1–b) = 0.33 [7, 22] this gives in terms of Section 3 an indication that the relaxation in glass as a kinetic process is to be considered as of second order (i.e within Eqn. (6) (with $p = 2$) and by Eqn. (14) or with Eqn. (8) with $n = 2/3$). In fact, there were well founded proposals (see [39]) to treat relaxation in glasses according to the so called Adams-Williamson equation:

$$\frac{1}{\xi(T)} - \frac{1}{\xi_0} = \frac{t}{\tau^*(T)} \tag{58}$$

which is only another form of Eqn. (14) obtained from Eqn. (6) with the additional condition, that ξ–ξ_0 at $t = 0$.

ii) In both empirical approximations and kinetic models (see [7, 21, 22]) as well as in the framework of a generic thermodynamic approach (see [7, 23, 24, 25]) it has been shown that the general kinetic condition for glass transition to take place is that

$$\tau^*(T)q\Big|_{T=T_g} \approx const \tag{59}$$

Here $\tau^*(T)$ in the case of Maxwell's relaxation kinetics is given as $\tau^*(T) = [1/K(T)]$ and in more correct contemporary treatments this is according to Eqns. (18), (19) the value of the time dependent time of relaxation

$$\tau^*(T) \cong \frac{\tau_0(T)}{t^b} \qquad (60)$$

With Eqns. (18), (19) the Frenkel-Kobeko-Rainer formula Eqn. (59) indicates, that at every cooling rate a distinct q-dependent part $\xi(T_g)$ of active structural entities ξ is frozen-in to form a glass.

In considering the expected temperature dependence of $\tau_0(T)$ as the reciprocal of the $K(T)$-function (e.g. Eqn. (37)) dependences, similar to the Bartenev-Ritland formula (see [7]) are obtained e.g.

$$\frac{1}{T_g} \cong const_1 - const_2 \log q \qquad (61)$$

where the $const_{1,2}$ both are proportional to the respective activation energy.

A more detailed treatment of the consequences from the Bartenev's formula we have given elsewhere [7] (see also [54–57]. Here we would like only to show the analogy of Eqn. (61) with Eqn. (47), which could be directly written in the way as Eqn. (61). This analogy stems from the fact, that in vitrification it also turns out, that an isotransitional approach can be applied in order to derive Eqn. (61) and to treat vitrification as a non-isothermal relaxation process, in which second order type reactions bring about the freeze – i.e. the fixation of a distinct part of the systems building units into a vitreous state.

9. ILLUSTRATIVE COMPARISON WITH EXPERIMENTAL EVIDENCE

In current literature there is abundant experimental evidence confirming the main ideas and results, developed in the present contribution. Thermal analysis in its various possible forms is of great importance, and according to [58] only in a two years period 2002–2003 there have been well over 6000 citations of this method in articles covered by Web of Science.

Here we would like only to mention several results out of our own laboratory, which according to our feeling may illustrate in a significant way the significance of some of the approaches, developed here.

In a series of experiments, represented here by only two of our publications [10, 27] we investigated the applicability of Avrami-type equations (c.f. Eqn. (8)) to describe the isothermal kinetics of crystallization of simple inorganic glass-forming systems. We developed a model, similar to Mampel's one [28] to analyze in terms of Avrami theorem the dependence of the extended volume $Y_n(t)$ on the dispersity of the samples analyzed. Surface nucleation of every grain of the granulated glass constituting the DTA-samples was assumed and in fact microscopically confirmed. The theoretical analysis per-formed showed, that Avrami power coefficient n has in this case is a function of the mean radius d_0 of the glass semolina employed in every experiment. Thus in variance with the original Avrami model [6, 7], in which an infinitively large volume of the crystallizing sample is assumed, here a distinct dependence $n = f(1/R_0)$ was derived and confirmed experimentally (Fig. 10 and further results in [10]). Witness in this respect are crystallization experiments with both $NaPO_3$-glass semolina and with other inorganic glasses, as this is discussed in details in [10]. In this way, the Avrami power coefficient looses in most cases of DTA and DSC experiments its original significance, when semolina or powder-like samples are analyzed and discussed in terms of Eqn. (8). These experimental evidence summarized in [10, 27] gave one of the starting points of the present analysis.

On the other hand in polymer crystallization [44] in DTA or DSC arrangements, when to a great extent sufficiently large samples are employed so that Avrami model premises are fulfilled, the value of n has to depend in both isothermal and non-isothermal experiments on the interplay of $I(T)$ and $v(T)$ in accordance with Eqn. (29). Moreover, the values of n and $\overline{U}(T)$ determined isothermally and in cooling/heating run experimentation for the same case have to coincide.

Polyethilene terephtalate (PET) is a very convenient crystallization model [44, 50]. We determined in a series of preliminary experiments both the thermodynamic and the kinetic properties of our PET-melts (mainly temperature dependence of specific heats $Cp(T)$ and of viscosity $\eta(T)$ measurements were performed in this respect, see [44] and Fig. 11). In isothermal experiments we determined both n and $\overline{U}(T)$ of our PET-samples (see [19, 50]) and compared them with the $U(T)$ and $W_c(T)$ values, following for these melts from our $Cp(T)$ and $\eta(T)$ measurements. A good coincidence was found in this respect for both PET and several other polymers [19, 53]. Moreover, employing Eqns. (39), (41) we determined the nucleating activity, Φ, of various substrates in both PET [53] and in the already mentioned $NaPO_3$-glass (see [51, 52] and here Fig. 12

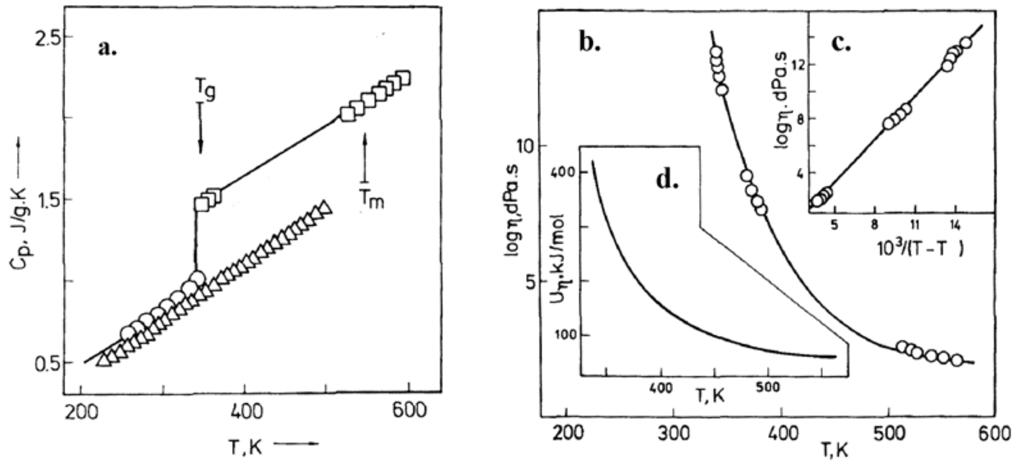

Fig. 11. Crystallization significant properties of polyethylene terephtalate (PET): necessary thermodynamic and kinetic data: specific heats, $C_p(T)$ and viscosity, $\eta(T)$. a. Results of *Cp(T) vs. T* measurements; from there ΔS_m and $\Delta\mu(T)$ were determined. Open squares: *Cp(T)* of undecooled PET melts; open circles: *Cp(T)* of crystallized PET samples; open triangles: *Cp(T)* of crystalline PET samples. b. $\eta(T)$ course of molten PET (open circles: experimental data) according to free volume model Vogel-Fulcher-Tammann formula, Eqn. (38). c. The same data in Vogel-Fulcher-Tammann coordinates, according to Eqn. (38). d. The influence of temperature on *U(T)* of PET, demonstrating the steep decrease of *U(T)* at approaching $T = T_m = 542$ K, where the thermodynamic barrier is more significant [46, 47]. From the η(T) data *U(T)* was determined. Experimental data from [50].

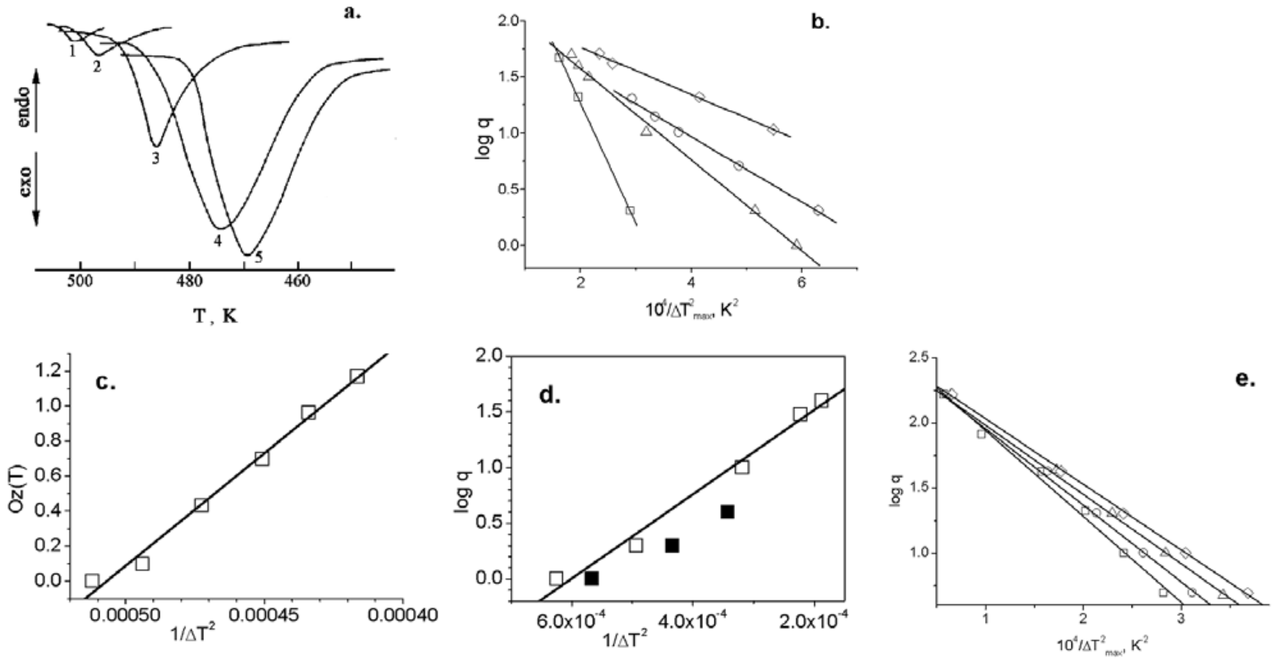

Fig. 12. Experimental evidence on the crystallization of polymer melts.
a. Non-isothermal cooling run curves with a typical crystallization peak of PET at different cooling rates: 1 - 1 K·min^{-1}; 2 - 2 K·min^{-1}; 3 - 10 K·min^{-1}; 4 - 30 K·min^{-1}; 5 - 40 K·min^{-1} (from [19]). b. Non-isothermal crystallization of several polymers in lg*q vs.* $1/\Delta T^2$ coordinates in accordance with Eqn. (48). From above: polyamide; polydeca-methylene tereftalate; polyethylene tereftalate; isotactic polypropylene (from[19]). c. Results from the non-isothermal crystallization kinetics of PET thin films (Ozawa [3]) in coordinates – Ozawa function *Oz(T) vs.* $1/\Delta T^2$. Ozawa function expanded in terms of the Error Function series (see Appendix 1.). Comparison of the results on the crystallization of PET obtained by Dobreva and Gutzow [19], open squares – with the results of Ozawa [3] for the same polymer.
d. The results from non-isothermal crystallization of PET by Dobreva *et al.* [53] and by Ozawa [3], according to the isoconversional approximation formula Eqn. (45). e. The results for the lg*(Oz(T))* – function in coordinates lg(*K*) *vs.* $1/\Delta T^2$ for plain PET. Results for PET doped with active insoluble substrates in coordinates, corresponding to Eqn. (48): top most line – plain PET; second from above – PET nucleated with Al_2O_3 particles; third line – PET nucleated with TiO_2 paricles; fourth line – PET nucleated with ZnO particles. Note the change of Φ from 1 to 0.6.

for the organic polymers). The results thus obtained we used in developing by induced crystallization both glass ceramics (see [7]) and organic polymer–inorganic composite materials [53]. Of more significance for the present analysis was, that in comparing our isothermal results with PET with those obtained by Ozawa [3] with the same object, similar values of both the Avrami coefficient n and of $U(T)$ were found (see Fig. 12).

The isothermal results with one of the crystallization models the $NaPO_3$-glass we employed in performing in 1999 on the "MIR" orbital station experiments on the effect of microgravity conditions on the induced crystallization of the same $NaPO_3$-model glass [46]. In doing so, we used at both cosmic conditions and in the reference experiments in the MUSC Laboratory in Cologne (Germany) non-isothermal simultaneous DTA-analysis of the induced crystallization experiments of the $(NaPO_3)_x$-glass. In both cases a good correspondence between isothermal and non-isothermal conditions was confirmed in the framework of the classical nucleation theory, summarized here in Section 4.

Lastly, we would like also to mention, that in [47] we developed an isoconversion experimental method to follow the non-isothermal crystallization of pure water and of various aqueous solutions in a LINKAM heating (cooling) stage microscope. The obtained results gave, using Eqns. (47), (48) quite similar results in both isothermal and in cooling run experiments. An electrochemical variant of Eqn. (48), in which $\Delta\mu$ was represented by overvoltage $\Delta\varepsilon(t)$ we used in [17, 18] in order to investigate the galvanostatic electrodeposition of Cd on Pt electrodes in $CdSO_4$ electrolytes.

10. CONCLUSIONS

It turns out, that it is possible using as a general algorithm Eqn. (8), corresponding to the Avrami model of overall crystallization kinetics, to describe quantitatively both phase transitions and topochemical reactions and structural changes corresponding to first, second or even third order non-isothermal reaction kinetics. Moreover, even glass transition and the Kohlrausch kinetics of isothermal and non-isothermal relaxation (i.e. kinetics of vitrification and glass stabilization) can be described, using the simple mathematics of the Avrami equation, as an intermediate mathematical algorithm.

It is shown, that the Avrami power index n indicates the nature of the $F(\alpha)$ function in Eqns. (5), (6), which indicates at $n \geq 1$ the kinetics of build up of interfaces in both topochemical reactions and Avrami-like phase transitions. With $n \leq 1$ structural changes, vitrification and homogeneous reactions can be described. This broad applicability of Avrami Eqn. (8) is by no means accidental or purely mathematical. On the contrary, in Section 3 it is shown, that Avrami-like dependences are in fact the particular case of very general relations, describing in a relatively simple way continuous change, taking place either at time – constant (at $n = 1$) values of the activation energy in Avrami-like coefficients

$$K(T) = K_0 \, \boldsymbol{exp}\left[\frac{U(T,t)}{RT}\right]$$

or (at $n > 1$, or $n < 1$) at time dependent, e.g. increasing $U(T, t)$-values.

The broad possibilities of Avrami equation have been already exploited in various applications, e.g. in the already cited ancient monography of Kazeev [33] in describing various metallurgical processes. In recent cosmological literature [59] efforts are summarized to use Avrami equation even as an algorithm, representing the history of the development of the Universe as a whole [59, 60]. In fact, such an analysis, if possible should require a non-isothermal formulation, may be in the form as it is discussed here, or as indicated in [60], accounting for the change of volume V of the Universe as a whole. Various models have been proposed in literature to use Avrami equation for different applications: both in its classical Kolmogorov-Avrami variant in melt crystallization, in Mampel's model for the crystallization of grained more or less finely dispersed solid samples [28], in chemical reaction models [7, 8, 32, 33] with special applications to DTA and DSC analysis [10, 27]. It is a really convenient model and this we hope is demonstrated also in the foregoing analysis. It is pointed out in Sections 3 and 8 that this broad applicability of Avrami-like dependences stems from the circumstance that it is based in fact on non-linear formulations of the phenomenological law of ireversible thermodynamics. Those who are interested in this problem are advised both to classical literature on this subject [61–63] and to the already cited publications [23, 24, 30].

In the present contribution on one side the classical isoconversional models, developed and employed many years ago for both heating [1, 16] and cooling runs [17, 19, 20] experimentation are described and unified and the possibilities and limitations of existing solutions are summarized. Particular attention, however, is given to Ozawa's method [3] of non-isothermal kinetic analysis. An attempt is made these methods to be enlarged and brought to more general applications in both chemical non isothermal kinetics and in non isothermal phase transitions and new analytical and geometrical solutions are proposed in this respect.

Many attempts have been made, beginning with the already cited classical authors, like Kisinger [1] and Coats and Redfern [14] to develop methods of analysis of non-isothermally obtained kinetic results to determine both the nature of the process (in present terms we used here in this respect the $F(\alpha)$-function in the summaric $(1-\alpha)F(\alpha)$-dependence) and the value of the process significant activation energy $U(T)$. In doing so, most researchers prefer to use various variants of trial and error methods as optimization programs, in which out of 30 to 40 different kinetic possibilities to determine the $F(\alpha)$ in a more or less systematic manner as a best fit value [54, 64]. Out of number of recent analyses in this respect we would like to cite the efforts of Vlaev *et al*. [64, 65] and also [66]. In these investigations the most appropriate selection of optimum is attempted, based on possible maximal values of generalized R^2 factors. However, the critical reconsiderations of such efforts, made in [65] shows, that in reality it is very difficult, or even impossible to discern in between such a great variety of kinetic possibilities even in such standard cases as the thermal decomposition of $CaC_2O_2.2H_2O$.

Kissinger tried to resolve the same problem by introducing an analysis of the form ($d\alpha/dt$) dependence. This form, as seen also by one of our mathematical models (Fig. 13), really changes, when the Avrami model with different n-values is used. However, in our opinion too much hope has been invested in such efforts of geometric form analysis of rate dependences. Moreover, beginning with Kissinger [1] and by most further authors, only Arrhenian type kinetic barriers have been considered at changing $F(\alpha)$-function. However, the analysis in Section 5 shows how differing the kinetic barrier can be even for the same $F(\alpha)$-function and that in phase transitions a complicated, non-Arrhenian thermodynamic barrier has to be expected.

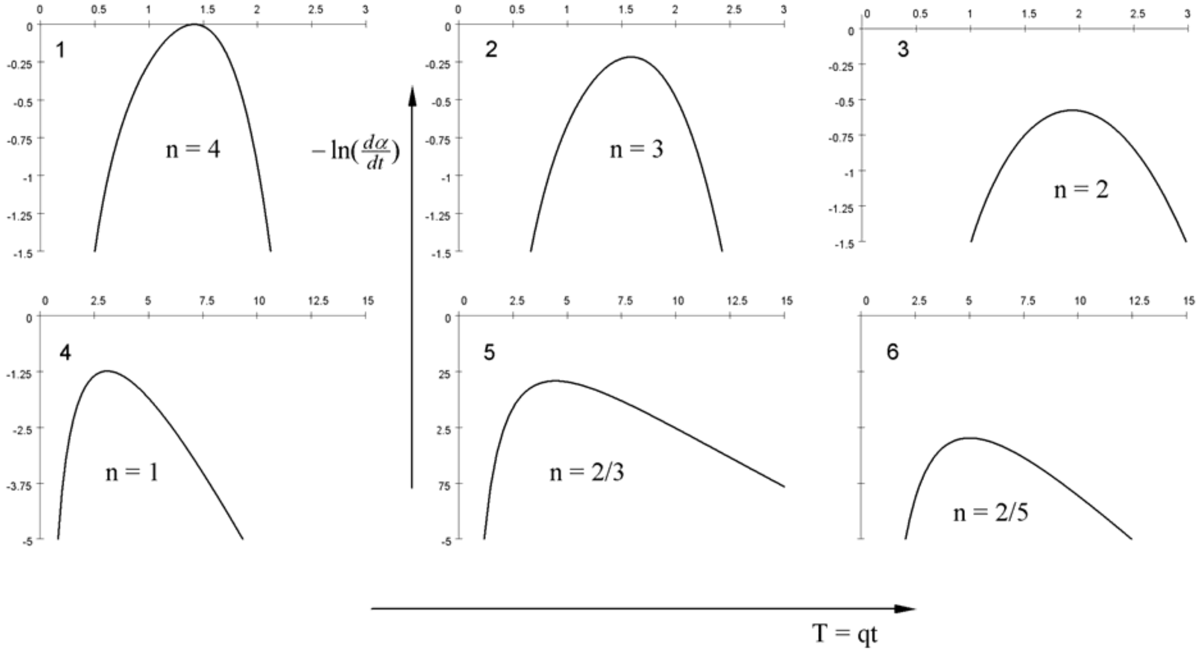

Fig. 13. Influence of the Avrami power index, n, on the form of the $d\alpha/dt$ *vs*. T-curves (in logarithmic scale on the ordinate). In all six cases $\ln\left[\frac{d\alpha}{dt}\right] = \ln nK(T)^{\frac{1}{n}} \exp\left[-K(T)t^n\right]$ is plotted against $T = qt$ for the same value of q, but for n, changing from $n = 4$ through $n = 1$ to $n = 2/5$. Curve 1 is constructed with $n = 4$; curve2 – with $n = 3$; curve 3 – with $n = 2$; curve 4 – with $n = 1$; curve 5 – with $n = 2/3$; curve 6 – with $n = 2/5$. In constructing the figures it was taken that in the expression $K(T) = A_0\, \boldsymbol{exp}(-\frac{U_0}{T})$; $A_0 = 1$; $(\frac{U_0}{T}) = 5$; in all figures the temperature is defined as $T = qt$. Note the change in the appearance of the $\boldsymbol{ln}\left(\frac{d\alpha}{dt}\right)$ *vs*. $\left(\frac{T}{q}\right)$-curves. It is seen that an unambiguous distinction of the curve form from n (as anticipated by Kissinger) is very difficult; nevertheless a change from symmetric curves (at $n > 1$) to asymmetric curves for $n \leq 1$ is clearly observable.

This is why, in terms of present analysis it is assumed, that first a generalization, a standardization of all possible kinetics is necessary in the form of an intermediate Avrami-type equation. Than Ozawa's analysis determines the factor n and thus (out of not more than 10 possibilities $n = 2/5$, 2/3, 1, 2, 3, 4, or fractional values between 1 and 3) the general type of the kinetic process can be determined, independent of the value and nature of the activation energy $U(T)$. The method, described in Section 7 gives after that a method to determine at an already known n the real nature of $U(T)$ out of the analysis of the term we called here the Ozawa number Oz.

In doing this way, both new possibilities and also the necessary limitations are clearer visible.

In this way we hope, that with the present investigation we have indicated an alternative way of thermal analysis, which in its development an application could lead to more distinct results, which can be more straight word obtained.

***Acknowledgements**: We have to thank Prof. Dr. C. Schick and Prof. Dr. J. W. P. Schmelzer both from the University of Rostock, Germany, for a number of fruitful discussions. The financial support of NATO Securirty Through Science Programme, RIG 981956 is gratefully acknowledged.*

APPENDIX 1

With the mentioned substitutions $z = \sqrt{\frac{B_0}{RT^2}}$ for the subintegral functions in Eqn. (36b) we arrive with Eqn. (45) at

$$\frac{\sqrt{B_0}}{q}\int_0^Z \frac{\exp\left(-z^2\right)}{z^2}dz \qquad (a_1)$$

After successive integration in parts it follows

$$\int_0^Z \frac{\exp\left(-z^2\right)}{z^2}dz = \left[\frac{\exp Z^2}{Z^2} - \sqrt{\pi}\,erfc(Z)\right] \qquad (b_1)$$

where $erfc(Z) = 1 - erf(Z)$ and

$$erf(Z) = \frac{2}{\sqrt{\pi}}\int_0^Z \exp\left(-z^2\right)dz \qquad (c_1)$$

is the Gauss Integral form of the Probability function [48].

In a similar way and with the substitution $z = (U_0/RT)$ in the subintegral function (46), Eqn. (36) leads to an expressions of the type

$$\int_0^Z \frac{\exp(-z)}{z^2}dz = \left[\frac{\exp Z^2}{Z^2} - Ei(Z)\right] \qquad (d_1)$$

where

$$Ei(-Z) = \int_Z^\infty \frac{\exp(-z)}{z}dz \qquad (e_1)$$

is the Exponential Integral Function [48].

In employing the already mentioned well known asymptotic expansions of both the Exponential Integral Function

$$E_i(-Z) = \frac{\exp(-Z)}{Z}\left[1 - \frac{1!}{Z} + \frac{2!}{Z^2} - \frac{3!}{Z^3} + \ldots\right] \qquad (f_1)$$

and of Gauss' Error Function $erf(Z)$

$$erfc(Z) = 1 - erf(Z) =$$

$$= \frac{1}{\sqrt{\pi}}\frac{\exp\left(-Z^2\right)}{Z}\left[1 - \frac{1.3.1}{2Z^2} + \frac{1.3.3.1}{\left(2Z^2\right)^2} - \ldots\right] \qquad (g_1)$$

and using only the first members of both expansions Eqns. (47) and (48) are readily obtained. In deriving them *via* Eqn. (36a) $(1/T)$ or $(1/\Delta T_2)$ are neglected when compared with the same arguments in the exponent.

In a similar way also the integrals can be treated, in which (c.f. Eqn. (36a)) expressions of the type $K(T)T^{n-1}$ appear. With the same substitution made to obtain Eqn. (d_1) and integration by parts we arrive e.g. for $n = 2/3$ to the integral

$$\int -\frac{3}{2z^{2/3}}\exp(-z)dz = \frac{2}{3}\Gamma\left(\frac{1}{3}, Z\right) \qquad (h_1)$$

where $\Gamma(n, Z)$ is the so called Incomplete Gamma function [48]. With the asymptotic expansion

$$\Gamma(n, Z) \cong Z^{n-1}\exp(-Z)\left[1 + \frac{n-1}{Z} + \frac{(n-1)(n-2)}{Z^2} + \ldots\right]$$

similar to those indicated with Eqns. (f_1), (g_1) for the already mentioned transcendent functions results, similar to Eqns. (47), (48) can be obtained.

APPENDIX 2

In considering Figs. 7 it is evident, that for all the considered subintegral functions (cf. Eqns. (38), (41), (44–46) the value of the right hand integrals in Eqn. (36) can be approximated with the shade area determined by the rectangular triangle seen on Fig. 8.

$$J(\tau)=\int_0^{\tau}K(t)dt=\frac{1}{q}\int_0^{T_{\max}}K(T)dT=\frac{1}{2}(\tau-t_0)K(\tau) \qquad (a_2)$$

Here with 2 is indicated the subintegral function $K(t)$, and with 1 – the tangent at $qt = q\tau$. It is obvious, that in approximating the unknown integral via Eq.(a2) we have neglected from a geometrical point of view the double shaded area on Fig. 8. For subintegral functions of the discussed exponential type this approximation is quite acceptable. Accounting for the linear T *vs.* t heating/cooling course (cf. Eqn. (17)) the slope of the mentioned tangent straight line is

$$\tan g\alpha=\frac{dK(t)}{dt}=\frac{K(\tau)}{(\tau-t_0)} \qquad (b_2)$$

Thus, it follows that our integral is given simply as

$$J(\tau)=\frac{1}{2q}[K(\tau)]^2\left[\frac{dK(t)}{dt}\right]^{-1} \qquad (c_2)$$

Discussing a cooling run in terms of Eqn. (41) we can write that

$$J(\tau)=\frac{\omega}{2q}constK(\tau)\left[\frac{dW(T)}{dt}\right]^{-1} \qquad (d_2)$$

According to Eqns. (39, 41) $W(T)$ has the structure

$$W(T)=\frac{U(T)}{RT}+\frac{B_0^*}{RT\Delta T^2} \qquad (e_2)$$

In all above expressions $T = qt$ and in the vicinity of melting point $RT \approx RT_m$ in the right hand member of Eqn. (e_2). In this way via Eqns.(c_2), (e_2) the integral $J(\tau)$, necessary for any isoconversional solution and also in the generalized Ozawa solution, discussed in Section 7 can be safely approximated geometrically in the indicated way, e.g. *via* Eqn. (2). With above approximations we have for the discussed case

$$\frac{dW}{dt}=-\left[\frac{U_0}{R}\frac{1}{q_0t^2}+\frac{B_0^*\Phi}{Rq_0^3}\frac{1}{t^4}\right] \qquad (f_2)$$

In this way we may also write

$$J(\tau)=\frac{const}{2q_0}K(\tau)q_0\left[\frac{U_0}{R}\frac{1}{q_0t^2}+\frac{B_0^*\Phi}{Rq_0^3}\frac{1}{t^4}\right] \qquad (g_2)$$

Thus the approximations, obtained analytically in Appendix 1 *via* the Gauss Error Function, follows directly from Eqn. (g_2) at $U(T)/RT = const$. Here, however, approximations are geometrically indicated, which may be used both at heating and cooling run experimentation from both "sides" of the $K(T)$-function, as this shown with both shaded areas of the small insert on Fig. 8.

APPENDIX 3

From the Ozawa plot, constructed out of several cooling rates (when a cooling run experiment is considered) we obtain directly the already discussed Ozawa function (Eq. (54)) in which desired $U(T)$-function is part of the subintegral function and the integral itself is under the logarithmus sign.

We have two way open to determine $U(T)$: first we can follow the analytical procedure given in Appendix 1, i.e. being the subintegral to the Gauss Error Function, expand this transcendent function as discussed there and thus obtain expressions, in which

$$Oz(T)=\frac{U(T)}{RT}+\lg[corrections] \qquad (a_3)$$

where the expression in square brackets depends on the desired accuracy (i.e. on the members used of the asymptotic expansion). The second, geometric approach is more easily performed.

On the construction of Fig. 14 with 1 is indicated the possible temperature course of the Ozawa function Oz(T), given with Eqn. (54). This course is the result of experimental finding, obtained as described from the respective ($d\alpha/dT$) *vs.* T experimental curves after integration.

As far as

$$\frac{d}{dT}\left[\ln\int_0^T K(T)dT\right]=\frac{K(T)}{\int_0^T K(T)dT} \qquad (b_3)$$

we obtain the subintegral function as

$$F(\tau)=\left[\int_0^T K(T)dT\right]\left\{\frac{d}{dT}\ln\left[\int_0^T K(T)dT\right]\right\}$$

as already indicated. Accounting for the experimental course of the possible subintegral functions, we have another already discussed dependence

$$\int_0^T K(T)dT=\exp\left[\ln\int_0^T K(T)dT\right]$$

From Fig. 14 it is evident, that thus the slope

$$\tan g\alpha=\frac{dOz(T)}{dT}=\frac{T_0-T}{Oz(T)}$$

or

$$(T_0 - T) = \frac{d[Oz(T)]}{dT} Oz(T)$$

Thus, it follows that:

$$F(T) \cong \frac{(T_0 - T)}{Oz(T)}$$

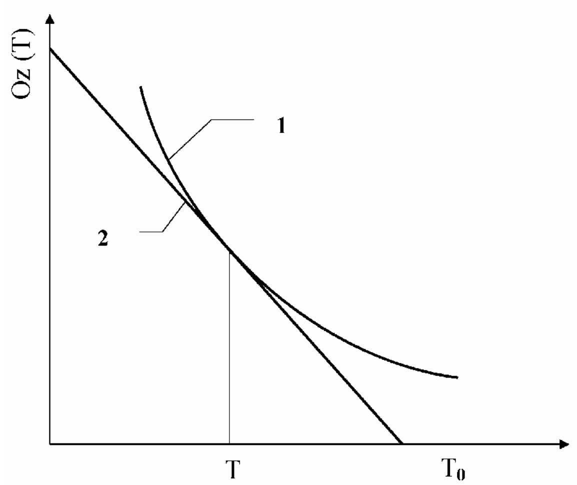

Fig. 14. The graphical determination of the subintegral *K(T)* function from a plot of Ozawa function *Ω(T) vs.* temperature, *T*. Note that according to Eqn. (56), *K(T)* is given directly by the value of $\Omega(T) = (lg\,\alpha)\int_0^T T^{n-1}K(T)dt$ - function (curve 1), multiplied by the slope $\left.\frac{d\Omega(T)}{dT}\right|_T$ of the tangent 2 to the *Ω(T)* curve – 1 at temperature *T*, when $T^{n-1} \approx T_m^{n-1}$.

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КИНЕТИКА НА ХИМИЧНИ РЕАКЦИИ И ФАЗОВИ ПРЕХОДИ ПРИ ИЗМЕНЯЩА СЕ ТЕМПЕРАТУРА: ОСНОВНО ПРЕРАЗГЛЕЖДАНЕ И НОВ ПОДХОД

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(Резюме)

Даден е задълбочен анализ и е развит един нов подход на възможностите за описване на кинетиката на химичните реакции и на процесите на фозообразуване при изотермични условия, също така на процеси на структурна релаксация и на стъклообразуване, от гледна точка на неизотермичната кинетика. Основният проблем на изследване е установяването и на кинетичните модели и на активиращите енергии, определящи и ограничаващи процесите, които се изследват чрез едно единствено измерване при нагряване или охлаждане с ДТА или ДС калориметрия. Една възможност е да се използват съществуващите изоконверсионни методи на неизотермичен анализ и по-специално методът на анализ при охлаждане, който може да даде отлични резултати при процесите на кристализация на стопилки и при топохимичната реакционна кинетика. Въпреки това, в рамките на изоконверсионните методи не е възможно да се определят, както абсолютните стойности на активиращите енергии, така и механизмите на реакциите.

Основният метод се основава на подхода на Озава, където като алгоритъм на промяната се въвежда уравнението на Аврами, описващо, както хомогенна реакционна кинетика със степенни коефициенти $n \leq 1$, така и топохимични реакции и фазови преходи при $n = 1, 2, 3, 4$. Демонстрирано е как аналитични и геометрични подходи могат да се използват при определянето на кинетични модели и активационни енергии, чрез един нов и по-подходящ обобщен метод на Озава.

Получените теоретични резултати са онагледени с примери от кинетиката на зародишообразуване и растеж при кристализацията на полимерни стопилки, при преситени водни разтвори, при девитрификацията на стъкла и при стъклообразуването и електролитното отлагане на метали при галваностатични условия.